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Engineering of Metal Oxide Interfaces for Renewable Energy Applications

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Thesis submitted for the degree of Doctor of Philosophy

July 2014

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I, Anna Iwazuk, certify that this thesis is my own work and I have not obtained a degree in this university or elsewhere on the basis of the work submitted in this thesis.

Anna Iwazuk
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Abstract

Diminishing non-renewable energy resources and planet-wide de-pollution on our planet are among the major problems which mankind faces into the future. To solve these problems, renewable energy sources such as readily available and inexhaustible sunlight will have to be used. Among solar driven process, photocatalysis is a leading approach for energy production, via splitting of water or reduction of CO₂, and for depollution. There are however no readily available photocatalysts that are photocatalytically active under visible light; it is well established that the band gap of the prototypical photocatalyst, titanium dioxide, is the UV region with the consequence that only 4% of sunlight is utilized. For this reason, this PhD project focused on developing new materials, based on titanium dioxide, which can be used in visible light activated photocatalytic hydrogen production and destruction of pollutant molecules. The main goal of this project is to use simulations based on first principles to engineer and understand rationally, materials based on modifying TiO₂ that will have the following properties: (1) a suitable band gap in order to increase the efficiency of visible light absorption, with a gap around 2 – 2.5 eV considered optimum. (2) Although tuning the band gap has been a major driver of research into TiO₂ photocatalysis, the second key aspect in the photocatalytic process is electron and hole separation after photoexcitation, which enable oxidation/reduction reactions necessary to i.e. decompose pollutants. (3) Enhanced activity over unmodified TiO₂. In this thesis I present results on new materials based on modifying TiO₂ with supported metal oxide nanoclusters, from two classes, namely: transition metal oxides (Ti, Ni, Cu) and p-block metal oxides (Sn, Pb, Bi). We find that the deposited metal oxide nanoclusters are stable at rutile and anatase TiO₂ surfaces and present an analysis of changes to the band gap of TiO₂, identifying those modifiers that can change the band gap to the desirable range and the origin of this. Moreover we discuss the electron/hole separation in modified TiO₂ and present a detailed analysis of a model of the photoexcited state of modified TiO₂. We show that upon photo-excitation, electrons and holes are spatially separated which will dramatically improve the photocatalytic properties of designed material. We also compute the excitation energy and relaxation due to electron
and hole localisation. A successful collaboration with experimental researchers in Japan confirms many of the simulation results where the origin of improved visible light photocatalytic activity of oxide nanocluster-modified TiO$_2$ is now well understood. We finally present our results on the activity of nanocluster modified TiO$_2$, with a focus on oxidation catalysis, as well as new results on doping of bulk TiO$_2$ and how doping of TiO$_2$ nanoclusters highlights some effects due to nanostructuring. The work presented in this thesis, creates a road map for the design of materials with desired photocatalytic properties and contributes to better understanding these properties which are of great application in renewable energy utilization.
List of Publications

1. Reactivity of sub 1 nm supported clusters: (TiO$_2$)$_n$ clusters supported on rutile TiO$_2$ (110), A Iwaszuk and M Nolan, Physical Chemistry Chemical Physics, 2011, 13 (11), 4963-4973


5. Photocatalytic activities of tin (IV) oxide surface-modified titanium (IV) dioxide show a strong sensitivity to the TiO$_2$ crystal form, Q Jin, M Fujishima, M Nolan, A Iwaszuk and H Tada, The Journal of Physical Chemistry C, 2012, 116 (23), 12621-12626


13. Working towards a breakthrough on alternative energy, Evening Echo, 16$^{th}$ of July, 2012

My contribution to publications 1 – 12 above was to perform the DFT calculations, analyse results, discussion of the results and their interpretation and to contribute the writing of the papers.
1. Introduction

The explosion in population growth in the last century, along with advances in technology have put immense pressure on our energy supply into the future, with world-wide energy consumption at 13.5TW in 2001[1] and 15TW in 2011 [2]. Energy consumption is forecast to be 27TW in 2050 [3] and 43TW by 2100 [2]. However, our current major energy supply, namely fossil fuels – oil, gas and coal, which provide 80% of our energy [2] – will be able to supply only 25-30TW of this need. It is clear then that within this century we will face an energy crisis, with spiralling prices, falling supply and increased demand [4].

At the same time, the burning of fossil fuels emits carbon dioxide, CO$_2$, into the atmosphere, with 30Gt of carbon emitted in 2008 [5] A 30% increase is predicted by 2020 [6] with a doubling of the 2008 amount by 2050 [7]. The consequence of this is that the atmospheric concentration of CO$_2$ will be 700 ppm by 2100 [7]. It is generally agreed that a concentration of 550 ppm will result in unavoidable climate change and 450 ppm is thought to be the maximum concentration at which some, but not catastrophic, climate change will occur.

Thus, there is a pressing need to develop alternatives to fossil fuels as the primary energy supply, with the following desirable attributes: (1) renewable, (2) carbon emissions free or at least carbon neutral (3) cost effective and (4) deployable world-wide and over large scales. Wind, wave and geothermal energy are deployed throughout the world, but are most suitable for localised energy supply and can be dependent on prevailing conditions. Nuclear energy suffers from a negative perception in many countries and is declining in importance in Europe. Alternative sources of fossil fuels, such as tar sands or shale gas are alleviating in part short term supply issues but will still hit the problem of finite supply and have environmentally questionable extraction methods.

Solar energy, harnessing the power of the sun, is most likely the only large scale world-wide solution to the energy supply squeeze. It is also free and collecting solar energy should also have a low environmental impact. We are already seeing solar being used in a localised sense for hot water heating or power generation in individual houses, while countries that receive substantial sunlight are deploying
large scale solar farms [USA, India, China, Germany, France]. Any excess electricity generated from solar can be stored in so called: grid energy storage e.g. pumped-storage hydroelectricity (PSH), which is then used to supply energy during dark periods.

The hydrogen economy is a leading player in the future deployment of renewable energy. Hydrogen can be used in fuel cells, which are a relatively mature technology. When hydrogen is burned it produces only water and is therefore carbon free. A number of automotive manufacturers are developing fuel cell cars and fuel cell powered buses are in operation [8]. To enhance the roll-out of this technology with maximum likelihood of success, hydrogen production from renewable energy is required. Presently, hydrogen, although being the most abundant element in the universe, is not so abundant on earth and is synthesised from, e.g. methanol. Therefore, a renewable approach to produce hydrogen would be a great benefit for the hydrogen economy.

When we think of solar energy, we usually think of solar panels constructed from silicon. However, there are many other technologies that utilise solar energy. For our work the most relevant technology is that of photocatalysis. Photocatalysis is a process when a photochemical reaction is accelerated due to presence of catalyst. A photocatalyst is a material which is able to absorb light of a wavelength that is determined by its band structure, or energy gap. It is important that the light absorbed be of energy larger than the electronic band gap of the semiconductor photocatalyst which enables the excitation of an electron from the valence to the conduction band. The consequence of this process is creation of an electron-hole, \( e^-/h^+ \), pair. The conduction band electrons can serve as good reductants to reduce \( O_2 \) for production of superoxide radicals \( O_2^- \). The valence band holes can play a role of oxidants reacting with \( H_2O \) or \( OH^- \) adsorbed on the surface for production of hydroxyl radicals (*OH) or hydrogen peroxide (H\(_2\)O\(_2\)). Figure 1.1 shows a schematic of the photocatalytic process.
Semiconductors such as TiO$_2$, ZnO, CdS, ZnS, MoO$_3$ are suitable materials for photocatalysis due to their electronic structure with a filled valence band and an empty conduction band, giving a band gap, together with no continuity of inter-band states that ensures a reasonable charge carrier lifetime. The lifetime is long enough to enable electron/hole diffusion to the catalyst surface to start a redox reaction. The photo-generated electron-hole pairs have the possibility to react with organic or inorganic compounds and also bacterial species for decomposition, which is important in environmental applications. In fact photocatalytically active TiO$_2$ is used in cement for coating buildings to allow for self-cleaning [9].

From the perspective of renewable energy, a key application is photocatalytically driven water splitting to produce hydrogen (H$_2$) (and oxygen (O$_2$)) from water by directly utilizing the energy from solar energy, that is light, using the inexpensive natural resource water as a chemical feedstock. As outlined above, hydrogen is the leading next-generation energy carrier and an ideal fuel for the future. Over the past three decades, photocatalytic water splitting using inexhaustible sunlight
has been studied as a potential method of hydrogen production from renewable resources [10].

Photocatalysts used in water splitting have several strict requirements, including (1) the band gap, which for visible light (wavelengths > 380nm) must be less than 3.0eV, (2) high abundance, (3) non-toxicity and (4) stability. Most semiconductors with suitable band structures for water splitting absorb mostly UV light (which makes up <5% of the solar spectrum) whereas for large scale renewable energy applications it is desirable to absorb visible light so that no external light source is required. At the same time, for indoor applications in, hospital settings, UV photocatalysis can be effective in bacterial removal [11] and it would also be of benefit to not sacrifice the UV activity of a photocatalyst.

While TiO₂ is the most studied example of a photocatalytic material, its band gap of 3.2 eV means that it will only absorb in the UV. Thus, there has been a significant level of activity in developing approaches to narrow the band gap and allow visible light absorption. In general, this has been unfortunately to the exclusion of the fate of the photogenerated electrons and holes, to which we will return below. The solutions to achieve the optimal band gap have included: (1) doping with various metals, (2) non-metals, (3) metal/non-metal co-doping, (4) metal ion implantation, (5) composite semiconductors. Noble metal doping is an efficient strategy to activate TiO₂ in visible-light region mainly because the Fermi level of these metals is lower than that of TiO₂ which results in better transfer of electrons from TiO₂ to the metal particles. Extensive research has also been focused on the transition and rare earth metal ions as dopants for improving the photocatalytic activity of TiO₂ in the visible light region.

There are several successful synthesis methods for modifying TiO₂, including impregnation, deposition-precipitation, sol-gel process, hydrothermal reduction and photo-deposition. However the photocatalytic activities of doped TiO₂ are dependent on the method and dopant content. Non-metal doping is relatively new approach and is of interest due to the fact that anion dopants show a lower formation of recombination centres when compared to metal dopants. A recent, and promising, strategy for the enhancement of visible light utilization is the
incorporation of multiple dopants. It has been demonstrated that co-doped TiO₂ with: P/N, N/W, N/H, Cr/Sb [12-15] resulted in better visible-light photocatalytic activities when compared to single dopant and modelling studies confirm the favourability of co-doping of TiO₂.

Despite the fact that doping has resulted in an improvement of the utilisation of visible light by TiO₂, which should enhance the photocatalytic activity, the major drawback associated with doping is however the increased electron/hole recombination which is caused by impurities levels formed in the band gap of TiO₂. Charge carrier recombination is undesirable, leading to loss of electrons and holes and generating heat. For these reasons, in part, heterostructures which can consist of a rutile-anatase mix, oxide nanoparticle- or small band gap semiconductor quantum dot-modified TiO₂ have also been investigated. The paradigm examples are Degussa P-25, which is a mixture of 70% anatase and 30% rutile, and CdS/CdSe modified TiO₂. The very high catalytic activity of rutile-anatase mixes is reported to be due to efficient electron/ hole separation at anatase/ rutile interface. The quantum dot modified TiO₂ facilitates visible light absorption but requires fast electron transfer to TiO₂ from the quantum dot and the latter is unstable in ambient. Thus, the scientific question of how to modify TiO₂ to induce visible light absorption and reduce charge carrier recombination still has many issues associated with it that need to be investigated and developing an approach to design new photocatalysts is of great need in this field.

This PhD thesis presents a detailed study of a new approach for the development of new photocatalytically active materials based on TiO₂ on the road to developing new solutions to renewable energy generation. The key novelty of our work is that we use first principles simulations based on density functional theory (DFT) to engineer new heterostructures of metal oxide nanoclusters that are supported on TiO₂ surfaces, which we henceforth denote as nanocluster modified TiO₂ to achieve targeted properties such as a reduction in the band gap, charge carrier separation and reactivity. The work presented in this thesis has also been performed in collaboration with the experimental activities of Prof. Hiroaki Tada in Japan.
We present new photocatalyst materials that are heterostructures of TiO$_2$ modified with metal oxide nanoclusters and these structures have smaller band gaps than unmodified TiO$_2$, along with improved charge carrier separation. Our understanding of the band gap change and charge carrier separation permits a rational design approach to develop new photocatalysts based on this idea and has also allowed us to explain some experimental observations. The results of this thesis are a first step in opening up new materials for generating renewable sources of energy and helping to solve the issue of future energy needs. In addition to this, modified TiO$_2$ will find the applications in the areas of: photocatalysis, air purification, cancer therapy, optoelectronics, sensors, organic synthesis, cathodic corrosion protection and self-cleaning antibacterial materials.

To investigate how the band gap can change due to modifications of TiO$_2$ we applied DFT simulations to model structures of metal oxide nanocluster modified TiO$_2$. The utility of DFT simulations in designing new catalysts is well known, e.g. in the work of Norskov and co-workers [16]. We show that this modification of TiO$_2$ permits a reduction in the TiO$_2$ energy gap and provide a detailed understanding of the origin of this effect. A second, and unfortunately neglected, particularly in modelling, aspect of photocatalysis is to assure sufficiently long lifetime of the electron/hole pair to enable a redox reaction. In this regard we present a model of the photoexcited state of surface modified TiO$_2$ to investigate if spatial separation is improved due to TiO$_2$ modification.

Thus, within the problem of developing photocatalytically active materials, the two primary issues that we have investigated are:

- Choice of materials to allow narrowing of the band gap to have light absorption in the visible region; as is well known the band gap of TiO$_2$ lies in the range of 3.0 to 3.2eV (the exact value depends on the crystal form, but it is in the UV region) and it makes the material non active under visible light. In order to improve the light absorption in the visible region it is recommended to reduce the band gap. One aspect of our research is to narrow the band gap of TiO$_2$. The interface between the
supported cluster and the oxide support is considered to be the key in the electronic structure and other properties of the system.

- Achieving separation between the electrons and holes produced after light excitation. Since electrons can reduce for example water to H₂ and holes can oxidise organic molecules the important issue is to design material which promote the separation of electrons and holes after excitation.

To examine the reactivity of our new materials, we identified a reactivity descriptor to predict and understand the chemical reactivity. The rationale for this comes in part from the well-known catalyst systems based on modification of, e.g. Al₂O₃ [17], TiO₂ [18] or CeO₂ [19] with small oxide nanoclusters which are useful in oxidation reactions such as water gas shift (WGS) or alcohol dehydrogenation. The WGS reaction is a reaction in which carbon monoxide reacts with water vapour to form carbon dioxide and hydrogen:

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]

This is very important industrial reaction in providing purified hydrogen for fuel cells and is a potentially interesting means for renewable energy driven hydrogen production (removal and storage of the CO₂ so produced can also been achieved using renewable energy and novel materials). The water gas shift reaction is sensitive to temperature and the best catalysts run at high temperatures or use Pt as a catalyst and thus there are still attempts to find catalysts that can lower the reaction temperature, which is determined by the reactivity of the catalyst to CO oxidation. In addition, using cheaper materials than Pt would bring a significant economic advantage.

For the water gas shift reaction we focused on:

- Finding materials compositions that could lower the temperature of the reaction. To this end, we use the energy needed to form an oxygen vacancy in the catalyst materials in the CO oxidation step: a lower energy cost will lead to a lower reaction temperature.
The final part of this thesis is an analysis of doping of TiO$_2$, where we have considered the effect of doping of TiO$_2$ nanoclusters, which can be compared with bulk doping. However, given a conflicting series of results in the literature and inconsistent application of DFT methods to this important question, we undertook a systematic study of bulk doping of TiO$_2$ using a range of DFT approaches and we also present preliminary results on the effect of doping of TiO$_2$ nanoclusters.

The results presented in this thesis show that modification of TiO$_2$ with metal oxide nanoclusters results in band gap narrowing which shifts the photoactivity of modified material into visible light region. Moreover an enhancement of electron and hole separation after photo-excitation is predicted. The study of reactivity on modified TiO$_2$ indicates enhancement over bare surface TiO$_2$.

The thesis is laid out as follows:

**Chapter 2** presents a review of the pertinent literature, where we highlight the current issues with contemporary photocatalysts. It briefly describes the mechanism of photocatalysis. We also discuss the merits and issues with different approaches for modifying TiO$_2$, such as: doping with metals, non-metals, co-doping, and heterostructuring.

**Chapter 3** presents the background to the computational methods used in the thesis and a description of the set-up of the DFT calculations we have performed.

**Chapter 4** presents an analysis of TiO$_2$ nanocluster modified rutile (110) as a model system for studying modified TiO$_2$. We studied the adsorption of TiO$_2$ nanoclusters on the TiO$_2$ rutile (110) surface as a model of nanocluster modified rutile (110). The clusters adsorb strongly at the surface, creating new bonds between cluster and surface atoms. The electronic structure shows a reduced band gap compared to pure TiO$_2$ which make possible for the material to absorb visible light. We also predict from a density of states analysis electron/hole separation.
The remainder of Chapter 4 presents results of TiO₂ modification with transition metal oxide nanoclusters. We studied nanoclusters of the transition metal oxides NiO and CuO: supported on TiO₂ rutile (110) and anatase (001) surfaces. This work has been carried out together with experimental work performed by Prof. Tada. We found that in NiO/TiO₂ system the band gap for both rutile and anatase is narrowed by up to 0.8eV compare to pristine TiO₂ which pushes the activity in the visible region. For CuOn nanoclusters supported on rutile (110) we found that the change in the band gap of rutile and anatase can be controlled by the coverage of CuO. Our results explain very well the experimental findings.

**Publications:**

1. **Origin of the Visible-Light Response of Nickel(II) Oxide Cluster Surface Modified Titanium(IV) Dioxide, A Iwaszuk, M Nolan, Q Jin, M Fujishima and H Tada,** Journal of Physical Chemistry C 117 (6), 2709-2718

Chapter 5 presents results of TiO₂ modification with p-block metal oxide nanoclusters, namely SnO₂, SnO, PbO₂, PbO and Bi₂O₃. In this chapter, we investigate (1) if the oxidation state of metal in metal oxide nanocluster (Sn²⁺ -v- Sn⁴⁺, Pb²⁺ -v- Pb⁴⁺) can play a role in tuning properties of the new photocatalytic material, (2) the crystal structure sensitivity – rutile (110) versus anatase (001) and (3) the lone-pair effect. We found that nanoclusters of SnO and PbO give very different electronic structure and band gap modifications to SnO₂ and PbO₂. For SnO and PbO nanoclusters, the presence of the lone pair causes a rise in valence band while for SnO₂ and PbO₂ nanoclusters, we found no change in the valence band but the increase of density of states near the conduction band which will intensify the light absorption. For SnO₂ clusters supported on rutile (110) and anatase (001) we explain the experimental findings that the band gap of anatase is unmodified, but that there is some modification of rutile, giving a
dependence on crystal form. For PbO₂, there is no such dependence and we analyse the origin of this.

**Publications:**
1. Photocatalytic activities of tin (IV) oxide surface-modified titanium (IV) dioxide show a strong sensitivity to the TiO₂ crystal form, Q Jin, M Fujishima, M Nolan, A Iwaszuk and H Tada, The Journal of Physical Chemistry C 116 (23), 12621-12626

**Chapter 6** presents our analysis of a model of the photoexcited state of surface modified TiO₂. We analyse the photoexcited state of TiO₂ nanocluster modified rutile (110). We found that there is charge separation upon photoexcitation, with an electron localised on a subsurface Ti atom and the hole is localised on a low coordinated O atom from the nanocluster. For SnO, PbO and Bi₂O₃ nanocluster modified TiO₂, this model shows the effects of the lone pair in these oxides and how the electron and hole localisation can be tuned by metal oxidation state and nanocluster structure.

**Chapter 7** presents a study of the reactivity of TiO₂ nanocluster modified rutile (110). We study oxygen vacancy as a descriptor of the reactivity of modified TiO₂. We find that the most stable oxygen vacancy sites are on supported nanocluster and that formation energies are substantially reduced when compared to unmodified TiO₂. We studied the reaction steps involved in CO oxidation on a representative modified TiO₂ structure. The full catalytic cycle was investigated and indicates a favourable energy at each steps which demonstrates the potential enhancement of the reactivity for oxidation reactions of modified TiO₂ compared to bare titania surfaces.
Chapter 8 presents our work on doped TiO$_2$ with trivalent and tetravalent dopants. We studied doping of bulk rutile with the trivalent dopants Al, In, Ga and doping of bulk rutile and anatase with tetravalent dopants Zr and Ce. The second activity in studying doping is to compare different DFT approaches, namely GGA-DFT, DFT+U and HSE06 (a hybrid DFT functional). We have found that the DFT+U description of doped TiO$_2$ is generally consistent with that from hybrid DFT. However, we have also identified some issues of concern. The first is the quantitative energies involved in oxygen vacancy formation and the second is the dependence of the position of dopant derived states and electron localisation on the precise DFT+U set-up. For nanocluster doping, we studied a doped Ti$_3$O$_6$ nanocluster with Zr and Ce as a representative model system. Together with a project student, we showed a strong dependence of the oxygen vacancy formation energy on the size of TiO$_2$ nanoclusters. Small nanoclusters show enhanced oxygen vacancy formation, however this trend disappears when larger nanoclusters are studied. Finally, for doped Ti$_3$O$_6$ supported on TiO$_2$ rutile (110), the oxygen vacancy formation energy increases when compared to undoped supported nanocluster.

Publications:

Chapter 9 presents a discussion our results, an analysis of complementary experimental work, our conclusions and a discussion of future work.

Figures, numbers and tables are numbered separately in each chapter and references are provided on a chapter-by-chapter basis.
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2. Literature review

2.1. TiO₂-general information

Titanium dioxide is one of the most studied metal oxides with a significant number of publications in both theoretical and experimental studies of this important material. In this review we focus on the bulk and surface structure of rutile and anatase TiO₂, summarising current applications of TiO₂ and the areas where TiO₂ can be utilized in the future. We describe in detail photocatalysis and how TiO₂ has been applied there. We particularly focus on the state of the art in our knowledge of TiO₂ in photocatalysis and what are the gaps that need to be filled in order to design new materials that can functional as visible light active photocatalysts. This review provides the necessary starting point of the thesis work.

The importance of TiO₂ in photocatalysis can be indicated from figure 2.1 which shows the number of papers published according to Web of Knowledge, using the search terms “TiO₂” and “photocat*”. We see that between 1993 and 2012 the number of papers published every year on this topic has grown substantially and continue to grow in 2013. The most obvious jump occurs in the years following Asahi’s 2001 paper on N-doped TiO₂, which really opened up the activity in modifying TiO₂ for visible light activated photocatalysis.
The investigations of crystalline metal oxides surfaces is an important field, motivated by both the fundamental science that can be done and the large range of different applications of metal oxides. In particular, TiO$_2$ presents a broad range of applications which are the driving force to study the properties of TiO$_2$, in addition to it being a prototypical reducible metal oxide. Some examples of applications of TiO$_2$ in which it is used include serving as a gas sensor, rutile is the white pigment in e.g. cosmetic products and paint), protective coating against corrosion, an optical coating, and as a ceramics. In the energy space, TiO$_2$ can be used to produce hydrogen, although there is as yet no readily available TiO$_2$ based catalysts for this, and in producing electrical energy in solar cells, particularly the dye sensitised solar cell [1], TiO$_2$ is also used in heterogeneous catalysis [2].
As a semiconductor, TiO$_2$ is able to change its n-type conductivity due to gas absorption so that it can be used as a gas sensor which could be used to control the air-fuel mixture in automotive engines [4]. Due to its properties in corrosion resistance, and being relatively light and sufficiently strong, and displaying good biocompatibility TiO$_2$ is extensively used in orthopaedic and dental implants [3]. Another important reason for usage in medical device industry is that TiO$_2$ is one of the few biocompatible metals which osseo-integrate, gives direct chemical and physical bonding to a bone without forming a fibrous tissue interface layer.

### 2.2. Bulk and Surface Properties of TiO$_2$

In reviewing the properties of TiO$_2$ in photocatalysis, it is necessary to start with the bulk properties of TiO$_2$. Titanium dioxide is a semiconducting metal oxide with formal oxidation states of Ti$^{4+}$ and O$^{2-}$, although it is generally accepted that TiO$_2$ shows some covalent bonding character. In bulk TiO$_2$, there are three major structural polymorphs: rutile, anatase and brookite. For most researchers, rutile and anatase are of most interest and are used in a wide range of applications. In both structures an octahedral coordination environment is present for Ti, wherein it bonds to six neighbouring oxygen atoms. In this octahedral coordination environment there are two sets of Ti-O bonds: four equatorial and two apical, where the bonds between Ti and O atoms in the apical bond are are the longer [1].

The anatase and rutile structures differ by the details of the interactions between the octahedral chains, figure 2.2. For instance the Ti-Ti distances in anatase are longer than in rutile but the Ti-O distances in anatase are shorter [2]. The crystalline structures of rutile and anatase consist of $[\text{TiO}_6]^{2-}$ octahedra, which share edges and corners in different manners while keeping the overall stoichiometry as TiO$_2$ [4-6]. Even though anatase has more edge sharing octahedra, the interstitial spaces between octahedra are larger which makes rutile denser than anatase (density of anatase is 3.84 g/cm$^3$ and of rutile is 4.26 g/cm$^3$) [7, 8]. Among the various phases of titania reported, anatase shows a better photocatalytic activity and anti-bacterial performance [8-14].
The structural differences between rutile and anatase result in different electronic band structures [19]. For example, the valence band for anatase has a stronger O 2p-Ti 3d character. The other aspect is the role of the ionic and covalent contributions to Ti-O bonds which has been discussed in general for titanium oxides [17].

Figure 2.2 Bulk structure of (a) Anatase, (b) Rutile, (c) Brookite. Ti is indicated by red spheres and oxygen by blue spheres.

Regarding the surfaces, which are where chemistry takes place, the rutile (110) surface is the most stable crystal face for rutile and is widely studied as the prototypical reducible oxide surface in both theory and experiments; indeed, we will use this surface as a support for the oxide nanoclusters throughout this thesis. Despite this, questions regarding the atomic structure and the defect chemistry of this surface still continue to attract our attention. The atomic structure of rutile (110) is shown in figure 2.3

When considering the cleaving of bulk ionic materials, such as TiO₂, to produce different surface orientations, there are three types of surfaces that result, according to the Tasker classification: type I surfaces present neutral cation-anion planes, type 2 surfaces present charged atomic planes, but a repeating group of cation-anion planes is neutral and type 3 surfaces have neither neutral
atomic planes not a repeating group of neutral cation-anion planes. The latter are polar and tend to reconstruct or restructure in some way. For rutile and anatase we have focussed on two surfaces, namely rutile (110) and anatase (001). Both surfaces are type 2 under the Tasker classification and are shown in figure 2.2.

The rutile (110) surface contains two different kinds of titanium atoms in the surface layer. There are coordinatively unsaturated 5-fold coordinated Ti (Ti 5-f) and fully saturated six-fold coordinated Ti (Ti 6-f), which have one additional Ti-O bond into the next sublayer. There are also two types of oxygen atoms: the three-fold coordinated in the main surface plane, (O<sup>ip</sup>) and the two-fold coordinated oxygens that terminate the surface, usually called bridging oxygen (O<sup>br</sup>).

The atomic structure of the anatase (001) surface is also shown in figure 2.3. While (101) surface is considered as being not the most photocatalytically active, we study the anatase (001) surface as an unreconstructed surface, which is reasonable way to describe the anatase (001). Anatase (001) is considered to be the more photocatalytically active surface than (101) [1], so it is of interest to examine modifications to this surface; advances in synthesis techniques allow synthesis of nanostructures that expose this surface. As presented in figure 2.3, the surface is terminated by two-fold coordinated oxygen atoms and in the next layer of oxygen atoms; a three-fold coordination is presented. The outermost Ti atoms in the surface layer are five-fold coordinated. Upon relaxation, the
terminal oxygen atoms relax inwards, while the 3-fold coordinated oxygen relax outwards and the overall surface structure presents a slightly buckled geometry.

Finally, the electronic structure of TiO$_2$ is typical of metal oxides, with the valence band composed primarily of oxygen 2p states; the highest occupied valence band (VB) states are derived from surface terminating oxygen atoms. The empty conduction band states are derived from empty Ti 3d states. In the VB, the electronic density of states usually shows a small Ti contribution. The band gaps of rutile and anatase are \textit{ca.} 3 eV and 3.2 eV, respectively and these are the commonly quoted band gap values for rutile and anatase.

In terms of defect formation, the most well studied point defects are the oxygen vacancy, formed by removing oxygen from the bulk or from the surface layer, and the Ti interstitial, which is an extra Ti atom that lies in an interstitial (vacant) site in the lattice. Rutile (110) turns a light blue colour upon mild heating which is indicative of surface reduction, which can proceed either via O vacancy formation (removal of a bridging oxygen) or Ti interstitial formation. Despite much research on this topic, it still remains one of great interest.

A final point is the modelling of defects in TiO$_2$ using density functional theory (DFT, described in chapter 3). Removing a neutral oxygen vacancy results in two electrons being returned to the lattice and these localise onto two Ti atoms in the structure and give a clear in-gap feature in the UPS spectrum of reduced rutile (110). Standard DFT approximations do not describe this localisation correctly, instead causing the electrons to be delocalised over the entire structure and positioning the defect state at the bottom of the CB. A method beyond standard approximate functionals needs to be used to describe the electron localisation upon formation of oxygen vacancies, which is of course a problem of significant interest and importance in metal oxides in general. Thus, DFT+U and hybrid DFT have been applied in recent years to this problem with some significant success. We highlight this issue here as it is important when we discuss vacancy formation and doping in TiO$_2$ during this thesis.
2.3. TiO₂ and Photocatalysis

The focus of this thesis is in the design of new TiO₂ photocatalyst materials and in this section we discuss briefly the large and growing field (see figure 2.1) of TiO₂ photocatalysis.

In photocatalysis a chemical reaction is accelerated by using a light absorbing catalyst, called a photocatalyst. A photocatalyst absorbs light at certain wavelengths, which depend on its band structure [3]. Absorbing light with an energy that is greater than the band gap of the photocatalyst excites an electron from the occupied valence band to the empty conduction band, which produces electron/hole pair as shown in the schematic in figure 2.4.

The role of the holes (h⁺) is that they are oxidants while the electrons (e⁻) play the role of reductants. Since a semiconductor such as TiO₂ shows no continuation in inter-band states, a suitable lifetime of an electron/hole pair is achieved, such that the electron and hole can diffuse to the surface of catalyst where a redox reaction may be started.

![Figure 2.4 Mechanism of Photocatalysis.](image)

After excitation, the conduction band is partially populated with electrons which reduce O₂ to produce high active superoxide radicals (\(\bullet O_2^-\)) and further reduction will produce reactive singlet oxygen (\(\mathbf{1} O_2\)) [15, 16]. The hole in the valence band
is able to react with H$_2$O or OH$^-$ adsorbed on the surface to produce hydroxyl radicals (•OH), hydrogen peroxide (H$_2$O$_2$) or a protonated superoxide radical (•HOO). Formation of H$_2$O$_2$ is reported to result from the coupling of two •OOH species [17, 18]. The reaction of H$_2$O$_2$ with •OH forms the protonated superoxide radical (•HOO) that functions similarly to •O$_2^-$ [19]. The following are the chemical reactions that are described above from ref [19].

\[
\begin{align*}
\text{TiO}_2 + \text{hv} & \rightarrow e^-_{\text{CB}} + h^+_{\text{VB}} \\
\text{O}_2 + e^-_{\text{CB}} & \rightarrow \cdot\text{O}_2^- \\
\text{O}_2^+ + e^-_{\text{CB}} & \rightarrow \text{O}_2 \\
\text{H}_2\text{O} + h^+_{\text{VB}} & \rightarrow \cdot\text{OH} + \text{H}^+ \\
\cdot\text{O}_2^- + \text{H}^+ & \rightarrow \cdot\text{OOH} \\
\cdot\text{OOH} + \cdot\text{OOH} & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2
\end{align*}
\]

TiO$_2$ has been investigated for over 40 years due to its photoelectric and photochemical properties. The early work of Fujishima and Honda [2] shows that surface defects on TiO$_2$ can be responsible for water decomposition into H$_2$ and O$_2$. Light absorption in TiO$_2$ creates an electron-hole pair that migrates to the catalyst surface and can react with adsorbed water on the surface resulting in formation of radical species. Such species may go into secondary reactions e.g. decomposition of organic molecules, or decomposition of CO$_2$ and H$_2$O. This open large number of applications including VOC (volatile organic compound) decomposition in industry [3], purification of air/water [16], disinfection in hospitals [15], solar cells, organic synthesis, cancer therapy [1, 2].

Titanium dioxide appears to be a perfect photocatalyst due to its low cost, non-toxicity, stability and semiconducting properties, but its relatively large band gap which is 3 - 3.2 eV (depending on the crystal structure) makes TiO$_2$ active only in the UV region, which makes up only 4% of the solar spectrum; the consequence of this is fewer photons that can be absorbed to generate reactive electrons and holes. On the other hand, the peak photon intensity appears in the visible region of the solar spectrum. Thus, in order to develop photocatalyst materials that will function using solar energy, research in this area has focused on inducing visible light absorption in photocatalysts, which is also one of the goals of the research in this thesis.
Since anatase and rutile present differences on the structure their photocatalytic activity may also be different and it is generally accepted that anatase is the more active photocatalyst. The well known Degussa P-25 mixed rutile-anatase material is considered a benchmark photocatalyst, for which the high activity is proposed to originate from the rutile-anatase interface. However, the origin of this activity is still hotly debated. There are also other oxides being considered as new photocatalysts, including WO₃, Fe₂O₃ and ZnO. However, TiO₂ is still the most widely studied photocatalyst [19-22] and the remainder of this review will focus on TiO₂ based photocatalysis.

2.4. Challenges in Modification of TiO₂

An important and widely studied research activity in photocatalysis is modifying TiO₂ in order to allow visible light absorption. The creation of mid-gap electronic states in the band gap, is supposed to reduce the conduction – valence band energy gap of TiO₂ and induce visible light activity [23, 34]. Doping has played the most important role in this regard, since Asahi [23] in 2001 showed that doping of films and powders of TiO₂ with N improved the absorption of visible light and the photocatalytic activity, as monitored by the photodegradation of methylene blue and gaseous acetaldehyde, and the hydrophilicity over unmodified TiO₂ under visible light at a wavelength of 500 nm. Introduction of N into TiO₂ by doping resulted in a reduction of the band gap which was also assessed by first-principles calculations and X-ray photoemission spectroscopy. Doping of TiO₂ with N has maintained a substantial interest since 2001 and very detailed studies have been presented by Di Valentin, Pacchioni, and Selloni in refs [42, 43] where the experimental and modelling results were presented. Further work in this regard has been presented in ref [44-46], where a series of N-doped titania nanoparticles were synthesized and the atomic structure was investigated by EXAFS experiments and compared with DFT calculations at different levels of theory. In ref [45] N-doped nanocrystalline titania microspheres with controlled visible light absorption were obtained by a new route utilizing a heterogeneous hydrolysis of TiCl₄ vapour.
with reactive droplets of aqueous aerosols, followed by instant calcination of the products in a preheated flow reactor. In these references the improved photocatalytic activity was observed. Carbon-doped TiO$_2$ has also been of great interest, and work, using the FIREBALL code, by Wang and Lewis [47] explained the origins of changes in the TiO$_2$ band gap due to doping. C-doped rutile TiO$_2$ (110) surface has been performed by means of periodic density-functional calculations and analysis of the electronic structure confirms the presence of in-gap states that could improve the photocatalytic activity of rutile upon being doped with C [48].

It is interesting to note that despite substitutional metal doping of TiO$_2$ being an obvious approach to modify the band gap, non-metal doping, with N, C, S, Se appears to be more successful in producing visible light active photocatalysts. [46-48, 52].

The significant interest in TiO$_2$ doping has seen almost all the periodic table used to dope TiO$_2$. The most studied dopant candidates are transition metals [27, 52] e.g. anatase particles with sizes below 5 nm were doped at 0.1-0.5 atom % doping levels by the following cations: Fe$^{3+}$, Mo$^{5+}$, Ru$^{3+}$, Os$^{3+}$, Re$^{5+}$, V$^{4+}$ and the activity in the visible region over TiO$_2$ was improved [28]. Doping of TiO$_2$ with Zr and Ce showed promising results where the improved photocatalytic activity was notified [26 – 31]. In ref [29] a mix of rutile and anatase was doped with Ce and a reduction of the band gap was claimed which resulted in an improvement in visible light activity in volatile organic compounds decomposition. Ma et al [33] doped TiO$_2$ with Ce and found that degradation of Rhodamine B and CO oxidation where improved when compared to pure TiO$_2$. The measured X-ray adsorption spectrum and photoluminescence of Ce-doped TiO$_2$ and the red shift in the adsorption edge indicated a reduction of the band gap [26] with increased Ce concentration. Doping of TiO$_2$ with Zr showed some interesting results and Wang [38] studied Zr-doped TiO$_2$ and found that the mixed rutile and anatase phase reached optimum for benzene degradation on UV light. For TiO$_2$ nanotubes doped with Zr the improved photocatalytic activity under UV illumination was also claimed [39]. Another work by Luo [40] where TiO$_2$ was doped by Zr resulted in a shift of the adsorption edge in the lower energy region
and 8% of Zr dopant improved the photocatalytic activity. In contrary to these results Long and English showed, using DFT+U calculations, that there is no band gap change upon Zr doping of TiO$_2$ [41].

Another interesting dopant is Cr$^{3+}$ with which Anpo et al. [51] doped TiO$_2$ by applying magnetron sputtering. This resulted in significant improvement for photoexcitation using sunlight. From the other side Hermann [52] has shown that TiO$_2$ doped with Cr reduced the band but at the same time the photocatalytic activity is killed. There is still some discussion about the effect of doping on the overall photocatalytic activity and this question has not been resolved. We note that simulation and experiment generally demonstrate that although many dopants will indeed reduce the band gap and induce visible light absorption, modelling studies in particular do not go beyond this simple conclusion, usually claiming that the reduced band gap will enhance photocatalytic activity. However, it is clear that the formation of localised in-gap defect states may not be beneficial as these states can trap electrons or holes, acting then as recombination centres and killing activity. Thus, modifications to TiO$_2$ that do not induce recombination need to be considered.

With the previous comments in mind a more recent research activity in band gap modification of TiO$_2$ is so-called co-doping of TiO$_2$ where cation and anion sites are simultaneously doped with a metal and non-metal [52-55]. The idea is that by ensuring charge compensation, e.g. an excess of electrons on the cation (e.g. Mo$^{6+}$) is compensated by a corresponding deficit on the anion (e.g. C$^{4-}$), the localised defect states associated with mono-doping are removed but band gap narrowing is still ensured.

Since N-doped TiO$_2$ is one of the most promising photocatalyst, co-doping with P was introduced to TiO$_2$ in work of English et al. [56] and this work tried to demonstrate that increasing the concentration of P/N dopants leads to significant band gap reduction but with no formation of trap states. Further co-doping pairs were investigated recently in both theoretical and experimental work on (N,W), (N,H) [57,58]; (Cr,Sb) [59] where these materials show significant improvement in photocatalytic efficiency when compared to single doped TiO$_2$ material. The electronic structures of Mg/Ca- and/or Mo/W- (mono- and co-) doped anatase
TiO$_2$ have been investigated via the Heyd–Scuseria–Ernzerhof hybrid functional for exchange-correlation [60-62]. Since the monodoping resulted in only small band gap narrowing introducing impurity bands in so called “forbidden gap,” and this would result in limitation of using new material as efficient photocatalyst active on visible light. The approach with codoping of Mg/Ca and Mo/W serves to passivate the impurity bands, which can harvest visible-light to a greater extent moreover induces appreciable gap narrowing which is the key target in band gap engineering.

While these results appear promising, we must also highlight the complexity of doping where several aspects plays an important role in determining the overall photocatalytic efficiency and they are: (1) dopant concentration, (2) whether the dopant is in the surface or bulk, (3) the dopant oxidation state, (4) light intensity, (5) solubility, (6) stability, (7) finding if doping took place, (8) charge recombination and (8) simulation or experiment methods performances.

In terms of applying DFT to this problem, the important issues include the significant underestimation of the band gap which can lead to incorrect interpretation of DFT results in terms of the positions of dopant states in the band gap and the localisation/delocalisation of charge upon doping. The former would then lead us to conclude, perhaps incorrectly, that a dopant has a certain effect on the band gap (see Chapter 8, where we discuss this point). Having in mind this important issue, the DFT+U approach is a reasonably reliable tool in studying various metal and oxygen oxidation states as well as reduced Ti species. DFT+U generally gives a consistent description of electron/hole localisation, but care must be taken because this method suffers from the problem that the choice of U is empirical and still gives a significant band gap underestimation. The major problem with DFT+U is that parameter U is used for only a single angular momentum of one species so it changes the energy separation between occupied states of the angular momentum for described species while other electronic states are still described by DFT. Since DFT+U presents some issues there is a need to compare either with the experiment or with a more accurate modelling approach. While experimental data are not always available, very often hybrid DFT can work as a reliable benchmark. However hybrid DFT in plane wave
basis set is much more expensive than DFT+U, which creates a significant limitation in terms of the size of the system that can be investigated. Thus, a reasonable solution is comparing of DFT or DFT+U results with experimental data, if available or referring to hybrid DFT results.

Recent research results for TiO$_2$ and other oxides have shown that an alternative approach to doping is fabrication of **heterostructures** which consist of two different metal oxides that are interfaced and this may be a better way to induce visible light absorption and improve the effectiveness of photocatalyst [63-73] than doping. This enhanced activity can be attributed to the presence of the interface between two metal oxides. But there is still a debate regarding the origin of improved photocatalytic activity for the well known mix of anatase and rutile in Degussa P25 [74-78].

Other examples of TiO$_2$ heterostructures with: SnO$_2$, ZrO$_2$, Bi$_2$O$_3$, Fe$_2$O$_3$, Fe$_3$O$_4$, WO$_3$, CeO$_2$, Cu$_2$O, Bi$_2$S$_3$, CdS, CdSe have been studied, with some positive or negative effects on photocatalytic activities [79-89]. Heterostructures of ZnO-TiO$_2$ have been investigated and the formation of such heterostructure resulted in significant charge separation which improves the charge carrier lifetime [90, 91]. The heterostructure also leads to band gap reduction. Recent activity in this field showed that various oxide heterostructures, namely: AgI-BiO [92], Bi$_4$Ti$_3$O$_{12}$-TiO$_2$ [93], BiOBr-ZnFe$_2$O$_4$ [94], BiVO$_4$-WO$_3$ [95] and SnO$_x$-ZnGa$_2$O$_4$ [96] enhanced the photocatalytic activities over pure oxides due to creation of heterostructures and their interfaces; in fact simple mechanical mixtures of the components, which have no interfacial bonds show no enhanced visible light photocatalytic activity. The photoactivity of these heterostructures was induced into visible region which was caused by band gap narrowing and promoting electron and hole separation which improve overall photocatalyst effectiveness.

A further approach that links with the work in this thesis is surface modification of TiO$_2$ with transition metal oxide nanoclusters, which was investigated for Fe$_2$O$_3$ modified TiO$_2$ in 2010 by Libera et al. [97] and Tada et al. [98, 99]. Nanoclusters of Fe$_2$O$_3$ were deposited on TiO$_2$ using atomic layer deposition (ALD) in ref. [98]; ALD is based on the sequential use of a gas phase chemical process. ALD is usually based on two chemicals called precursors which react
with the surface one at a time in sequential and self-limiting manner [100-101]. ALD found great application in industry and experiment in: microelectronics [102], gate oxides [103], DRAM capacitors [104] and transition-metal nitrides [93]. Modifying TiO$_2$ with Fe$_2$O$_3$ nanoclusters induced visible light absorption and the visible light activated photocatalytic degradation of methylene blue was demonstrated. (FeOx)-modified TiO$_2$ was synthesised using the chemisorption-calcination-cycle (CCC) by Tada and co-workers. Figure 2.5 presents the chemisorption calcination cycle where metal complexes adsorbed by strong chemical bonds while the organic part is oxidized by post-heating.

![Diagram of Chemisorption Calcination Cycle](image)

Figure 2.5 Diagram of Chemisorption Calcination Cycle from *Chem. Comm.*, 2011, 47, 8814.

Application of CCC resulted in deposition of highly dispersed metal oxide [92] nanoclusters on the TiO$_2$ surface that are molecular in size [98], rather than being on the order of a few nm. Transmission electron microscopy investigations of CCC synthesised structures have indicated that the FeOx particles adsorbed by the CCC technique have diameters below 1 nm [98, 99]. The heterostructures of (FeOx)/TiO$_2$ system resulted in visible light absorption without any sacrifice in
the UV-light activity which was examined by studying degradation of a dye precursor 2-naphthol. These improved photocatalytic activities were explained by band gap narrowing due to the presence of the (FeOx) clusters shifting the top of the TiO₂ valence band [98]. The reduction of band gap was accompanied by decrease in electron/hole recombination after light absorption by photoluminescence (PL) spectroscopy [98].

ZnGa₂O₄ showed improved visible light absorption examined by the degradation of p-cresol and Mossbauer spectroscopy showed the presence of Sn²⁺ states in the band gap of ZnGa₂O₄ [71]. Since modification with SnO₂ had no effect on the band gap and visible light photocatalytic activity, this raises an interesting question of what is the impact of metal oxidation state in deposited metal oxides. There is still a question of the application of these novel heterostructures in photocatalytic water splitting which is also of general interest.

In terms of DFT simulations, in 2011, a study of some transition metal oxide nanoclusters deposited on rutile (110), that is, Cr₂O₃, CrO₂ and MoO₂ [106] showed that these oxide nanoclusters can induce a band gap reduction over unmodified rutile (110). However, a detailed understanding of these oxide nanoclusters modified TiO₂ systems needs to be undertaken to further develop these interesting ideas.

While the band gap plays an important role in improving the photocatalytic performance of TiO₂, it is necessary to emphasise that the charge carriers produced during light absorption have the same level of importance in determining the photocatalytic activity. Due to light absorption, electrons and holes are produced and they must not recombine (giving out waste heat) otherwise no reaction takes place. So in this case the second important feature of any catalyst is the promotion of charge separation, which limits charge recombination and is monitored by photoluminescence which is explained as a spontaneous emission of radiation from an electronically excited species not in thermal equilibrium with its environment. This technique finds its application in the investigation of recombination mechanism where the return to equilibrium-"recombination," can involve both radiative and nonradiative processes. The amount of photoluminescence and its dependence on the level of photo-
excitation and temperature are directly related to the dominant recombination process. Analysis of photoluminescence helps to understand the underlying physics of the recombination mechanism. Prof. Tada’s work involves a photoluminescence technique and found that in the experiments of refs. [64, 68, 72] a reduced PL intensity is observed for electron-hole recombination in modified anatase and rutile, which, when coupled to improved activity for dye degradation supports the idea that these heterostructures facilitate electron and hole separation, thus reducing the opportunities for charge recombination.

In terms of modelling, excited states are not easily treated in a periodic model of a surface, e.g. with time dependent DFT. However, recently charge separation has been studied using a model of the photoexcited state in which the triplet state is calculated; the triplet state has an unpaired electron and an unpaired hole in the CB and VB respectively. This model was applied for bulk HfO$_2$ [107] and TiO$_2$ surfaces [108, 109]. For bulk anatase and the (101) surface, a localised oxygen hole and a localised Ti$^{3+}$ state were found [108]. Jedidi investigated rutile (110) applying photoexcited model and found a localised Ti$^{3+}$ state [109], but a delocalised oxygen hole state (arising from the DFT approach used). In this research both DFT+U (where U is applied to the Ti 3d and O 2p states) and hybrid DFT result in oxygen hole and Ti$^{3+}$ localisation. In this model, the singlet-triplet excitation energies, and the hole and electron relaxation (trapping) energies can be calculated and this is a useful approach for assessing the effect of surface modification on the energy gap and charge carrier localisation [123].

Since this model shows good promise, we will apply it to study the photoexcited state of modified TiO$_2$ in subsequent chapters to understand if surface modification of TiO$_2$ can improve the separation of charge carriers, and why and where are the holes and electrons localized in modelled heterostructures.

Since these heterostructures will be applied in chemical reactions, we are also interested in the chemical activity of these heterostructures. For example, recently molecular sized Ce$_2$O$_4$/Ce$_2$O$_3$ species supported on TiO$_2$ (110) were studied by Rodriguez et al. as a catalyst in the water gas shift (WGS) reaction [110-112]. The effect of CeO$_x$ deposition is a strong reduction in energy barrier for water dissociation which is known as the rate limiting step in the WGS reaction.
reaction, so that the molecular sized nanocluster enhances the chemical activity of TiO$_2$ in this case. Nanoclusters of (WO$_3$)$_3$ deposited on TiO$_2$ were investigated for catalytic dehydrogenation of propanol [113, 114]. Density functional theory simulations have been presented by Metiu’s group in which Mo, V and Cr, as MO$_3$ nanoclusters [115, 116], were supported on TiO$_2$ and were found to be reactive centres for oxidative dehydrogenation of methanol [115] and oxidation of CO [116]. These findings suggest that molecular sized oxide nanoclusters supported on another oxide may be interesting materials for oxidation reactions.

In examining the potential for activity in oxidation reactions, the oxygen vacancy formation energy which is the energy needed to remove the neutral oxygen atom from the oxide, is found to be effective descriptor in describing the catalytic performance of metal oxides in the CO oxidation reaction [117-119]. According to the Mars van Krevelen mechanism where CO removes oxygen from the catalyst and this oxygen is returned by adsorption of O$_2$ from the atmosphere the main step is the initial removal of oxygen from the catalyst by CO [120]. In this case the pure TiO$_2$ should be considered as poor catalyst with formation energy of oxygen vacancy is relatively high 3.66eV from DFT+U [121, 122]. Any reduction in the oxygen vacancy formation energy will result in enhanced activity towards oxidation and we will explore this in chapter 7 for TiO$_2$ nanoclusters supported on rutile (110).

The state of the art on modifying TiO$_2$ for photocatalysis and oxidation reactions, which is highly significant and growing every year, shows that new concepts are needed to develop effective visible light activated photocatalysts. This review highlights the significant potential for nanocluster modified metal oxide heterostructures but there are several questions that need to be addressed to advance the state of the art:

(1) what is the origin of the band gap change in these new heterostructured and is it similar to or different from classical doping

(2) what is the sensitivity to the TiO$_2$ crystal structure, that is whether rutile or anatase TiO$_2$ is modified,
(3) if the metal oxidation state in deposited metal oxide has any impact on the
modification on TiO$_2$ band gap and on the overall performance of the
photocatalyst,

(4) what role can be played by interesting chemical effects such as the lone-pair
effect in Sn$^{2+}$ on the properties of the new photocatalyst,

(5) the importance of the surface coverage of the modifier in designing the
desired properties of new heterostructures,

(6) how reliable is DFT in terms of band gap assessment and position of new
states due to modification of the TiO$_2$.

The remainder of this thesis is devoted to exploring these questions in a range of
modified TiO$_2$ structures and developing answers to these questions will bring us
closer to a road map for the design of effective visible light activated
photocatalysts.
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3. Method

This chapter contains a description of the theoretical background in electronic structure theory necessary for the calculations presented in the thesis. We also describe in detail our methodology for performing the DFT calculations described in chapters 4 to 8.

3.1. Quantum Mechanics

In computational materials science we need to find the electronic structure and atomic structure of molecules, bulk materials, surfaces and interfaces for a given collection of interacting atoms. The Schrödinger equation (3.1) is the fundamental equation that is used in this task, which is solved in order to obtain the electronic structure of a time independent quantum system.

\[ \hat{H}\psi = E\psi \]

Here \( \hat{H} \) is the Hamiltonian Operator, which acts on the wavefunction \( \psi \) and returns an energy \( E \). The Hamiltonian (is an operator which is the sum of the kinetic and potential energy operators), that acts on \( \Psi(r_1, r_2, \ldots, r_n, R_1, R_2, \ldots, R_i, \ldots, R_n) \) the many-body wavefunction, which is a function of the electronic coordinates, \( r_i \), and the nuclear coordinates, \( R_i \). \( E \) is the energy eigenvalue corresponding to the wavefunction \( \Psi \).
\[
\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \left( \nabla_i^2 \right) - \sum_{i,j} \left( \frac{Z_i e^2}{|r_i - R_i|} \right) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} - \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j e^2}{|R_i - R_j|}
\]

In Eq. (3.2) we show the various terms that make up the Hamiltonian. The first terms describes the kinetic energy of the electrons, with mass \(m_e\). The second term describes the electron-nuclear interaction, with electron and nucleus positions indicated by \(r_i\) and \(R_i\), respectively and \(Z\) is the atomic number of the nucleus. The third term describes the Coulomb interaction between two electrons. The last two terms describe the nuclear kinetic energy and the nuclear-nuclear Coulomb interaction.

The Schrödinger Equation is impossible to solve for a multi-electron system, primarily because of the two-electron Coulomb interaction in Eq. (3.2). To allow for a solution for real systems, the introduction of approximations to the many-body problem is necessary.

### 3.1.1. Born-Oppenheimer Approximation

The Born-Oppenheimer approximation [2] is a simplification of the Schrödinger equation that takes into account the significant difference between the masses of nuclei and electrons. Given this difference, we assume that the motion of the nuclei is significantly slower than for the electrons. In this case the Born-Oppenheimer approximation states that the electrons move in the field of fixed nuclei, and therefore the kinetic energy of nuclei can be omitted and the potential
energy due to nucleus-nucleus repulsion is merely an additive constant. The Hamiltonian equation for the electrons moving in a field of fixed nuclei is now given by:

\[
\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \left( \nabla_i^2 \right) - \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} + V_{\text{ext}}^r (r_i)
\]

In using this approximation, we determine the energy of a collection of electrons in a fixed set of nuclear positions. We can then displace the nuclei and recalculate the energy. Repeating this for different nuclear positions gives an energy surface that describes the electronic energy of a system changes with a change in nuclear geometry, which is the approach used for determining the relaxed geometry of a multi-atom system. However despite the Born-Oppenheimer approximation simplifying the Hamiltonian somewhat, we are still dealing with a multi-electron system.

### 3.1.2. Hartree-Fock approximation

The Schrödinger equation can only be solved exactly for a one-electron system, because there is no electron-electron interaction term for a one-electron system. The central problem in applying the Schrödinger equation to many-electron problems such as molecules is how to account for the two-body electron-electron interaction. Hartree considered a single-electron scheme in which each individual electron moves independently of the other electrons in an orbital \( \phi_i(r_i) \), whose form depends only on the average motion of the other electrons [3]. In essence an electron moves in the potential generated by the presence of the other \((n - 1)\) electrons and the complicated many-body interaction is replaced by a one-electron problem in which electron-electron interactions are treated in an average way. In this scheme, the wavefunction of an \( n \)-body system can be separated into
a product of \( n \) single electron functions (usually called orbitals) that depend only on the coordinates of a single electron,

\[
\Psi(r_1, r_2, \ldots, r_i, r_j, \ldots, r_n) = \varphi^1(r_1)\varphi^2(r_2)\varphi^3(r_3)\ldots\varphi^n(r_n)
\]

(3.4)

where \( \varphi^k(r_i) \) is a single electron function (orbital).

However, the Pauli exclusion principle states that wavefunction must be antisymmetric under exchange of two electron labels,

\[
\Psi(r_1, r_2, \ldots, r_i, r_j, \ldots, r_n) = -\Psi(r_1, r_2, \ldots, r_j, r_i, \ldots, r_n)
\]

(3.5)

In equation (3.5), the labels of electrons \( i \) and \( j \) are exchanged and the wavefunction then goes into its negative under exchange of one electron. Considering all possible permutations leads to the determinant form of the wavefunction

\[
\Psi(r_1, r_2, \ldots, r_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix}
\varphi^1(1) & \varphi^1(2) & \ldots & \varphi^1(n) \\
\varphi^2(1) & \varphi^2(2) & \ldots & \varphi^2(n) \\
\vdots & \vdots & \ddots & \vdots \\
\varphi^n(1) & \varphi^n(2) & \ldots & \varphi^n(n)
\end{vmatrix}
\]

(3.6)

which is a concise way of stating the exclusion principle: If two rows or columns of a determinant are equal, then the wavefunction vanishes. An alternative means of stating the exclusion principle, valid for a single-electron picture is that no two electrons may have the same set of quantum numbers, i.e. allowing for electron spin, only a maximum of two electrons may occupy a single-electron orbital.

The Hamiltonian of equation (3.3) is the sum of one-electron and two-electron operators,

\[
H = \sum_i h_i + \sum_{i\neq j} \frac{1}{r_{ij}}, \text{ where } r_{ij} = |r_i - r_j|.
\]

By considering the matrix elements of the one- and two-electron operators acting on \( \varphi^k(r_i) \),

\[
<\varphi_i|H|\varphi_i>
\]
and $<\varphi, \varphi_j | \frac{1}{r_{12}} | \varphi, \varphi_j>$, we can derive expressions for the resulting integrals over one and two electrons. For the one electron operator:

$$<\varphi_i | h | \varphi_i> = \int d\mathbf{r} \varphi_i^*(\mathbf{r}) h(\mathbf{r}) \varphi_i(\mathbf{r}) \equiv <i | h | i>$$

3.7

where $<i | h | i>$ is a one-electron integral. For the two electron operator:

$$<\varphi_i, \varphi_j | \frac{1}{r_{12}} | \varphi_i, \varphi_j> = \int d\mathbf{r}_1 d\mathbf{r}_2 \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \varphi_j(\mathbf{r}_1) \varphi_i(\mathbf{r}_2) - \int d\mathbf{x}_1 d\mathbf{x}_2 \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \varphi_j(\mathbf{r}_1) \varphi_i(\mathbf{r}_2) \equiv <ij | ij> - <ij | ji>$$

3.8

The term $<ij | ij> - <ij | ji>$ is an antisymmetrised two-electron integral. The total energy can be written

$$E = \sum_i <i | h | i> + \sum_{i<j} <ij | ij> - <ij | ji>$$

3.9

The one-electron term includes the electron kinetic energy and the electron-nucleus interaction. The two-electron integral, $<ij | ij>$, is the classical Coulomb integral and it is termed $J_{ij}$. The second two-electron integral, $<ij | ji>$, is the exchange integral, termed $K_{ij}$. It is a purely quantum mechanical effect arising out of the antisymmetry of the wavefunction, equation (3.9).

By minimising the variational energy, the best set of orbitals can be obtained by solving an eigenvalue equation for each doubly occupied spatial orbital. A molecular orbital, MO, results from the pairing of electrons of opposite spins in identical spatial orbitals. An eigenvalue equation is obtained,

$$f(i)\psi_i(i) = \varepsilon \psi_i(i)$$

3.10
This was derived by Fock and the resulting Fock operator, \( f(i) \), is defined in terms of the single-electron Coulomb and exchange operators as

\[
 f(i) = h(i) + \sum_{k}^{n/2} 2J_k(i) - K_k(i)
\]  

3.11

\( h \) is the one electron term, \( J \) is the two-electron Coulomb interaction term and \( K \) is the two-electron non-local exchange interaction term.

3.1.3. Self-consistent solution of the Hartree-Fock Equations

In this section we describe briefly the self consistent field (SCF) approach to calculate the ground state energy from the Hartree-Fock equations.

To develop a scheme to solve the HF equations, a basis set is introduced, which converts the differential HF equations into a set of algebraic equations. A basis set is a set of fixed functions (atomic orbitals), \( \chi_i \), in terms of which the single electron functions of the determinant wavefunction are written; this is commonly called the linear combination of atomic orbitals (LCAO) approximation. For molecules, the \( \chi_i \) are usually a set of Gaussian functions (of the form \( \chi_i = \exp(-\alpha r_i^2) \)), and the linear expansion for the single electron orbitals, \( \varphi_i(\mathbf{r}) \), in terms of the \( \chi_i \) is

\[
 \varphi_i(\mathbf{r}) = \sum_{\mu} c_{\mu} \chi_\mu
\]  

3.12

The \( c_{\mu} \) are a set of expansion coefficients. With the introduction of the basis set, calculating the HF orbitals reduces to calculating the \( c_{\mu} \). Substituting the linear expansion, (3.12), into the HF eigenvalue equation (3.10) results in the Roothaan equations, which are written in matrix form
where $\mathbf{C}$ is the matrix of expansion coefficients, $\mathbf{\varepsilon}$ is a (diagonal) matrix of energy eigenvalues, $\mathbf{S}$ is the overlap matrix between two atomic orbitals $\chi_\mu(\mathbf{r})$ and $\chi_\nu(\mathbf{r})$, $\langle \chi_\mu | \chi_\nu \rangle$, and $\mathbf{F}$ is the matrix representation of the Fock operator. Matrix elements, $F_{\mu\nu}$ of the Fock matrix are given by

$$F_{\mu\nu} = \langle \mu \mid h \mid \nu \rangle + \frac{1}{2} \sum_k \sum_{\lambda\sigma} C_{\lambda k} C^*_{\sigma k} [\langle \mu\nu \mid \lambda\sigma \rangle - \langle \mu\nu \mid \sigma\lambda \rangle]$$

The operators appear in the Fock matrix as fixed one- and two-electron integrals over the basis functions. Due to the appearance of the MO coefficients on both sides of the eigenvalue equation (the Fock matrix elements depend on the expansion coefficients, which we are trying to determine) iterative calculation of the expansion coefficients is necessary. The procedure for calculation of the energy is called the self-consistent field (SCF) method. In the SCF procedure the single electron moves in an averaged field of the other $(n-1)$ electrons. We start with a set of basis functions, from which the one- and two-electron integrals are calculated. A guess for the elements of the matrix $\mathbf{C}$ is then provided, e.g. from a simpler quantum chemical method, and is used to obtain an averaged field. We solve the HF equations for an electron in this field and obtain a new set of expansion coefficients and the total energy. With these new expansion coefficients as an improved guess, the HF equations are solved again. This procedure is continued until the energy difference between two successive iterations is below a specified tolerance, i.e. self-consistency is achieved. The eigenvalues, forces, energies and stresses are calculated based on converged electron density.
3.1.4. Electron Correlation and Density Functional Theory (DFT)

Since Hartree-Fock is a single electron theory, it is unable to describe the instantaneous two-body electron-electron interactions, which tend to keep electrons apart. The error in the HF calculation as a result of neglecting electronic correlation is the correlation energy, and while it is only a very small fraction of the total energy, for energy differences as well as for the calculation of molecular properties, the correct treatment of electronic correlation is necessary. Most methods for treating electronic correlation use the conceptual idea of exciting electrons into states which are unoccupied in the HF model, known as virtual orbitals. Since virtual orbitals have more nodes, exciting electrons into certain virtual orbitals means the electrons are kept apart from each other, i.e. their motion is correlated.

These methods for including electron correlation give very accurate results for numerous properties. However, they grow very computationally expensive with increased system size. Additionally, one loses the simple physical picture found in single electron formalism. An alternative and more tractable means for handling the correlation problem with only the computational expense of HF theory and retaining the simple one-electron picture is density functional theory (DFT), which is used in thesis calculations.

Density functional theory is the most widely applied method for advanced first principles calculations on materials. DFT applies the electron density as the basic variable rather than the many body interacting electron wave functions that are used in traditional quantum chemical approaches. The electron density determines the probability of finding any of the N electrons within the volume element $d\vec{r}_i^*$ but with arbitrary spin while the other of the N electrons has arbitrary positions and spin in the state represented by $\Psi$. [2]

DFT is built on two theorems, namely the Hohenberg-Kohn theorems. Theorem 1 proposes that if there are $N$ interacting particles within the system and they are moving in an external field $V_{\text{ext}}(r)$, this external field is uniquely determined by the ground state particle density $\rho_0(r)$, up to a constant [4,5]. That is, the
expectation value of any observable (Hamiltonian) for the ground state is the unique functional of the exact ground-state electron density $\rho_0(r)$.

$$\langle \psi | A | \psi \rangle = A[n\rho_0 (r)]$$

3.15

The second Hohenberg-Kohn theorem describes the universal functional for the total energy that it can be defined in terms of density and this is valid for any applied external potential. So if the input density is the real ground state electron density then the functional of the exact ground state energy will have the lowest energy. The total energy is written as a functional of the electron density,

$$E[\rho (r)] = F[\rho (r)] + \int \rho (r) V_{\text{ext}}(r) dr$$

3.16

An approach to solve the Schrödinger Equation for a many electron system was proposed by Kohn-Sham, based on the Hohenberg-Kohn theorems. According to this approach, which is similar to Hartree-Fock, the total energy functional in the external potential $V_{\text{ext}}(r)$ is given by:

$$E[\rho (\vec{r})] = T[\rho (\vec{r})] + \int V_{\text{ext}} (\vec{r}) \rho (\vec{r}) d^3r + E_{\text{ee}}[\rho (\vec{r})]$$

3.17

$$E_{\text{ee}}[\rho (\vec{r})] = \int \int \frac{\rho (\vec{r}) \rho (\vec{\hat{r}})}{|\vec{r} - \vec{\hat{r}}|} d^3r d^3\hat{r} + \hat{E}_{\text{xc}}[\rho (\vec{r})]$$

3.18

Here, the first term is the kinetic energy, the second term is the external potential and the last term includes both classical and non-classical exchange, as indicated in equation (3.18). The exchange-correlation part is what describes the non-classical electron-electron interactions. For solving the Kohn and Sham equations there is an assumption that for the interacting system with the true ground state density, there is a reference non-interacting system with a ground state density
that is the same as the real interacting system. The equation for the reference system is given by:

$$H_{eff} |\psi_i\rangle = [-\sum_i \nabla_i^2 + V_{eff}[\rho(\vec{r})]|\psi_i\rangle = \varepsilon_i|\psi_i\rangle$$

3.19

The kinetic energy of this system is:

$$T_{eff}[\rho(\vec{r})] = \sum_i n_i \varepsilon_i - V_{eff}[\rho(\vec{r})]$$

3.20

The new pseudo kinetic energy takes form of exchange correlation energy functional $E_{xc}[\rho(\vec{r})]$:

$$E_{xc}[\rho(\vec{r})] = T[\rho(\vec{r})] - T_{eff}[\rho(\vec{r})]$$

3.21

We insert the exchange correlation functional into the total energy. After that we derive the total energy of the non-interacting system and this system is in an effective potential with respect to $\rho(\vec{r})$ with conservation of the density, $\int \rho(\vec{r}) d\vec{r} = N$, where $N$ is the total number of electrons.

The Kohn-Sham equations are solved in one-electron Schrödinger like equation, similar to Hartree-Fock, with a potential $V_{eff}$:

$$\left[-\nabla^2 + V_{eff}[\rho(\vec{r})]\right] \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r})$$

3.22

and the final ground state energy is:

$$E_0 = \sum_i n_i \varepsilon_i - \iint \frac{2\rho(\vec{r})}{|r - \vec{r}|} d^3 r - \int \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} d^3 r + E_{xc}[\rho(\vec{r})]$$

3.23

Where $E_{xc}$ is the exchange-correlation potential. If the exact functional of $E_{xc}$ is known then the exact solution of the many electron system can be calculated.
3.1.5. Approximations to the Exchange-Correlation functional

The Kohn-Sham equations, Eq. (3.22), still remain unsolved, as they do not provide any form for the exchange-correlation energy and the exact exchange-correlation functional is unknown, we need to introduce more approximations in order to solve the KS equations and determine the total energy. The major approximations have been the Local Density Approximation (LDA) and the Generalised Gradient Approximations (GGA) and are briefly described.

In LDA, the exchange-correlation energy \( E_{xc} \) is approximated by:

\[
E^{LDA}_{xc} = \int d^3r \varepsilon_{xc}(\rho_0)|\rho_0 \rightarrow \rho(r)|
\]

Where \( \varepsilon_{xc}(\rho_0)|\rho_0 \rightarrow \rho(r) \) is the exchange-correlation energy in a homogeneous electron gas with the density \( \rho_0 = \rho(r) \), i.e., which replaces the local density \( \rho(r) \) of an inhomogeneous system at each point \( r \) by the constant density \( \rho_0 \) of homogeneous electron gas. [3]. The Local spin Density Approximation (LSDA) exchange-correlation functional is calculated using the spin-resolved densities: \( \rho(r) = \rho\uparrow(r) + \rho\downarrow(r) \). The exchange-correlation energy for spin polarised systems is defined as:

\[
E^{LSDA}_{xc}[\rho\uparrow(r),\rho\downarrow(r)] = \int [\rho\uparrow + \rho\downarrow] \varepsilon_{xc}^{\text{hom}}[\rho\uparrow,\rho\downarrow] dr
\]

The density is calculated in the form of a dimension \( r_s \) (this is known as as Wigner-Seitz radius) which is an average orbital of an electron. Common to many approximate functionals, exchange and correlation are treated separately. The exchange energy density deduced by Dirac [6] is calculated from:

\[
\varepsilon_x[\rho] = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{\frac{1}{3}} \rho^{\frac{1}{3}} = -\frac{3}{4} \left( \frac{9}{4\pi^2} \right)^{\frac{1}{3}} \frac{1}{r_s} = -\frac{0.458}{r_s} au
\]
The approximation of the exchange energy is parameterized in Perdew and Zunger's work [7]. Ceperley and Alder [8] parameterized the correlation energy for high density $r_s \geq 1$ and low density $r_s < 1$ by using Monte Carlo methods. In high density conditions $r_s \geq 1$ the kinetic energy is dominant while for low density $r_s < 1$ the electrostatic forces dominates.

The semi-local approximations to DFT, including the local density approximation, the local spin-density approximation, have proven to be very successful in many areas of quantum chemistry and solid-state physics. However, there are important cases, in both fields, where these approximations fail in a qualitative way. Many of these shortcomings can be attributed to the spurious self-interaction of electrons, which is introduced by the semi-local approximations. The self-interaction error, introduced by local and semi-local approximations to density functional theory (DFT), leads to some dramatic failures of DFT, ranging from wrong predictions in chemical reactions to the failure in describing the insulating state in many transition metal oxides, and qualitatively wrong pictures for lanthanide and actinide compounds.

However, despite its usefulness in solids, with relatively homogenous electron densities, the LDA approximation fails in cases where the electron density undergoes rapid changes, such as in molecules, that is for inhomogeneous electron densities. To solve this problem the exchange-correlation energy depends not only on the electron density, but also on the gradient of the electron density:

$$E_{xc} = E_{xc}[\rho(r), \nabla \rho(r)]$$

More sophisticated approaches to the exchange-correlation problem take into account the gradient of the density, $E [ \rho(r), \nabla \rho(r) ]$. This is termed the generalized gradient approximation (GGA) or non-local DFT. Within this endeavor, a number of exchange-correlation functionals have become popular and are well known for the calculation of chemical and physical systems. A popular gradient corrected exchange-correlation functional, which is generally
applied in the study of periodic systems, is the GGA of Perdew and Wang, which is termed PW91 [9, 10].

3.1.6. DFT Corrected for on-site Coulomb Interactions: DFT+U

The failure of the approximate DFT GGA functionals in the situations outlined above can be ascribed to the tendency of approximate \( \text{xc} \) functionals to over-delocalize valence electrons and to over-stabilize metallic ground states due to self-interaction which forces ‘pieces’ of the same electron (described as a charge density associated with it) repel to each other. The over-delocalization which has been described in many papers [11-13], and will be highlighted in in a number of chapters in this thesis, can be attributed to the approximate account of exchange and correlation interactions in the \( \text{xc} \) functional which fails to cancel the electronic self-interaction present in the classical Hartree term. As a consequence of that self-interaction some of the charge density associated with the electron leads to repulsion and, thus an excessive delocalization of the wave function is present. To overcome this problem DFT corrected for on-site Coulomb interactions, so called DFT+U is applied. Here, the strongly correlated electronic states of a system which are typically of d or f orbitals are described using a Hubbard Hartree-Fock-like [14] model while the rest of the valence electrons are treated with the standard approximate DFT functional.

The total energy of a system in DFT+U can be described as:

\[
E_{\text{LDA+U}}[\rho(r)] = E_{\text{LDA}}[\rho(r)] + E_{\text{Hub}}[\{n_{m\alpha}\}] - E_{\text{dc}}[\{n_{\sigma}\}]
\]

Where \( E_{\text{LDA}} \) presents the approximate DFT total energy functional (in this example, LDA) being corrected and \( E_{\text{Hub}} \) is the term that contains the Hubbard Hamiltonian to model correlated states. Due to the additive nature of this correction, it is necessary to eliminate from the (approximate) DFT functional, \( E_{\text{LDA}} \), the part of the interaction energy to be modeled by \( E_{\text{Hub}} \). This is achieved by the subtraction of the so-called “double-counting” (dc) term \( E_{\text{dc}} \) that models
the contribution of correlated electrons to the DFT energy. The second and third terms are seen to depend on the occupation number, \( n \), of the orbital in question.

The DFT+U method is widely used in materials characterized by strongly correlated and/or localized electrons, which includes well known cases such as reduced CeO\(_2\) [15], reduced TiO\(_2\) [16], Fe\(_2\)O\(_3\) [17] and NiO [18]. The main advantage with use of this method is that carries only marginal additional computational cost compared to the standard functionals. DFT+U is applied to improve the evaluation of the band gap of insulators, the description of the structural and magnetic properties of correlated systems, the energetics of electron transfer processes and chemical reactions. It does however suffer from some issues, which we will highlight in later chapters, in particular that properties depend on the value of U chosen, there is no a priori way to chose a value of U for all material properties and only a subset of orbitals can be treated. However, despite these issues, DFT+U have proven to be a useful computational approach to modelling many materials where approximated DFT functionals fail. We use the Dudarev implementation of DFT+U, where an effective \( U^{\text{eff}} \), is defined as \( (U - J) \), and this is used throughout this thesis.

### 3.1.7. Hybrid DFT Functionals

Hybrid DFT is inspired by the idea to introduce a portion of exact exchange from Hartree-Fock theory mixed with exchange and correlation from DFT. The exact exchange energy functional is expressed in terms of the Kohn-Sham orbitals rather than the density, so is termed an implicit density functional. For metal oxides, due to problems in approximate GGA functionals where these functionals do not treat partially filled d and f states, due to self-interaction, hybrid DFT is a suitable and accurate approach for overcoming many of these issues.

The exchange-correlation energy in hybrid DFT can be expressed as a linear combination of Hartree-Fock and DFT exchange plus DFT correlation, where the exchange-correlation functional of choice is used.

\[
E_{xc}^{\text{DFT}} = aE_{x}^{\text{HF}} + (1 - a)E_{x}^{\text{DFT}} + E_{c}^{\text{DFT}}
\]
Although HSE06 has proven to be a rather accurate approach it still has adjustable parameters, namely the exact exchange contribution and the screening length, both of which can be varied to obtain, for example, band gaps that match experiment; the standard values of 25% exchange and a screening length of 0.2 Ångstrom are usually adequate. In a plane wave basis (see next sections) there is a substantial computational cost to evaluate the 2 electron integrals so this makes the cost of a HSE06 calculation significantly greater than a DFT+U calculation and this limits the size of systems that can be approached with hybrid DFT in a plane wave basis.

3.1.8. The Bloch theorem and the plane wave basis set for calculations of solids

For solids we are attempting to treat an essentially infinite system. However, a solid is built up of a periodically repeating crystal and this allows us to model a solid based on a small model of the bulk crystal. The wave function of an electron placed in a periodic potential i.e., that is in a repeating crystal structure means that the effective potential derived in the K-S equations has the periodicity of the crystalline lattice. Bloch’s theorem enables us to write the K-S orbitals, \( \psi^n_k(r) \) as a product of a plane wave \( e^{ikr} \) and a periodic function, \( u^n_k(r) \) that has periodicity of the lattice.

\[
\psi^n_k(r) = u^n_k(r) e^{ikr}
\]

where k is vector in first Brillouin zone and n is a band index. Because the periodicity \( u^n_k(r) \) can be written as a set of plane waves:

\[
u^n_k(r) = \frac{1}{\sqrt{\Omega_{cell}}} \sum_j c^n_j(k) e^{i(k+k_j)r}
\]
Where \( k_j \) is the reciprocal lattice vector, \( \Omega_{cell} \) is the volume of the primitive cell. Due to transferring the K-S orbitals to plane wave basis set, we obtain:

\[
\sum_{j'} H_{j,j(k)} c_{j'}^n(k) = \varepsilon_n(k) c_j^p(k)
\]

Where

\[
H_{j,j}(k) = \frac{\hbar^2}{2m} |k + K_j| \delta_{j,j} + V_{eff}(K_j - K_j)
\]

This term is the matrix element of kinetic energy operator and the plane waves are orthonormalized:

\[
V_{eff}(K_j - K_j) = \int_{\Omega_{cell}} V_{eff}(r) e^{i(k_j - k_j)r}
\]

Where \( k \) and \( K \) are real space wave and reciprocal lattice vectors respectively. The above term is the effective potential. By diagonalization of Hamiltonian we can get discrete set of eigenvalues and corresponding eigenfunctions for all \( n \) band index at each \( k \)-point. The energy eigenvalue looks like,

\[
\varepsilon_n(k) = \varepsilon_n(k + K)
\]

We can choose cut-off vector in reciprocal space, \( K \) as \( K \leq K_{max} \), where \( K_{max} \) is the reciprocal space wave vector corresponding to the energy cut-off.

All-electron calculations are the norm in quantum chemistry with effective core (pseudo) potentials being used only when heavy systems like metals are being treated. For a plane wave basis, pseudopotentials are always used. The reason is that the core wave functions shows rapid oscillations and expansion of these wave functions in a plane wave basis requires many plane waves of high kinetic energy, resulting in an intractable computational problem. The introduction of a
pseudopotential, in which the complex core potentials are replaced by a smooth potential, leads to a reduction in the number of plane waves needed in a total energy calculation, since only the valence region needs to be explicitly considered. Use of the pseudopotential can also be justified by recognising that the physical properties of materials are much less dependent on the core electrons than the valence electrons, and hence explicit treatment of only the valence electrons can be introduced.

In principle, an infinite plane wave basis is required for the expansion of an arbitrary wavefunction within a simulation cell, equation (3.34). However, since the pseudopotential takes care of the high kinetic energy elements (kinetic energy \( \frac{1}{2}|k + G|^2 \)), the plane wave basis is truncated to include only those plane waves with kinetic energy smaller than a given cut-off energy. If pseudopotentials were not used, the higher energy plane waves describing the core would need to be included and the corresponding plane wave cut-off energy would need to be much larger, leading to a correspondingly less tractable problem.

The pseudopotentials of Vanderbilt have been widely used but more recently the projector augmented wave (PAW) approach has been the norm. For the augmented wave methods the wave functions are divided into two parts. The first part of the partial waves are expanded in a within an atom-centred region and second part is expanded near envelope region called: envelope functions. Blöchl [19] developed the PAW general method for all-electron calculations. It is a combination of the features of plane-wave pseudo potential method and linear augmented plane wave (LAPW) method. PAW method uses pseudo-wave-functions \( |\tilde{\psi}_n\rangle \) which are linearly transformed to get one electron wave functions\( |\psi_n\rangle \):

\[
|\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum (|\varphi_i\rangle - |\tilde{\varphi}_i\rangle) \langle \tilde{\varphi}_i | \tilde{\psi}_n \rangle
\]

3.36

The relation is made up on definition of augmentation volume, \( \Omega_R \), where \( R \) is the atomic site, in which the partial waves \( |\varphi_i\rangle \) form a basis of atomic wave functions, where \( \tilde{\varphi}_i \) is are set of projectors on partial waves \( |\tilde{\varphi}_i\rangle \).
The energy is evaluated by integration over electronic states in reciprocal ($\mathbf{k}$) space. Thus, in principle an infinite number of $\mathbf{k}$ points are needed for an evaluation of the total energy. Occupied states at each $\mathbf{k}$ point contribute to the electronic potential, but the wave functions at $\mathbf{k}$ points which are close together are almost identical, so that the wave functions over a region of $\mathbf{k}$ space can be represented by the wave functions at a single $\mathbf{k}$ point. Therefore, only the electronic states at a finite number of $\mathbf{k}$ points are needed. Methods have been developed to approximate the electronic potential by calculating electronic states at special sets of $\mathbf{k}$ points. The values of the integrand are determined at each $\mathbf{k}$ point and are then summed to give the total charge density or energy.

For a bulk system, an $n \times n \times n$ $\mathbf{k}$ point mesh is used, where $n$ is a positive integer. When a surface or surface-adsorbate system is being studied, the periodicity in one direction, e.g. the $z$-direction in figure 3.2, is lost. In order to be able to continue using the periodic boundary conditions, a vacuum layer must be introduced separating the images of the surface/surface-adsorbate in the $z$-direction, so that no spurious interactions between the images are present. The supercell contains the crystal surface (plus adsorbate) and the vacuum region. An $n \times n \times 1$ $\mathbf{k}$ point mesh is then used. In real space, the vacuum direction is usually longer than the lattice vectors in the plane and thus, in reciprocal space a less dense set of $\mathbf{k}$ points is needed in the vacuum direction (e.g. the $z$ direction above). Additionally, the electronic structure along the vacuum direction is not of interest and so only one $\mathbf{k}$ point needs to be used along this direction.
3.2. General Computational Approach

In this thesis we focus on calculations on TiO$_2$ rutile and anatase surfaces modified with metal oxide nanoclusters, as well as presenting results on doping of bulk rutile and anatase. This section describes our general methodology for these calculations. To describe bulk rutile and anatase and the rutile (110) and anatase (001) surfaces used in this thesis, both bare and with the surface modifications with metal oxide nanoclusters, we use density functional theory (DFT) throughout, within a three dimensional periodic model using the VASP5.2 code.

A plane wave basis set describes the valence electronic wave functions and the cut-off energy for the kinetic energy is 396 eV; testing of some structures with larger cut-off energies leads to no significant change in the results presented in this thesis. For the core-valence interaction we apply Blöchl’s projector augmented wave (PAW) approach [19]. For Ti we use 4 valence electrons and for O 6 electrons. Testing a 12 valence electron potential for Ti leads to no significant changes in our results. We further apply a 10 electron valence potential for Ni, for Sn 4 electrons (a test of Sn with 14 valence electrons, including the 4d electrons yields little difference), for Cu 11 electrons, for Bi 5 electrons, for Ce 12 electrons, for Pb 4 electrons and for Zr 4 electrons. We use the Perdew-Wang91 GGA approximation to the exact DFT exchange-correlation functional [20] and Pb PAW potential includes relativistic effects. Hybrid DFT calculations are performed using the HSE06 screened exchange functional with 25 % exact exchange and a screening length of 0.2 / Angstrom.

k-point sampling is performed using the Monkhorst-Pack scheme. For bulk rutile and anatase, sampling is performed with an (4x4x4) sampling grid and for the surfaces; we perform sampling at the Γ-point and with a (2x2x1) sampling grid. A comparison of both sampling grids for the surface calculations showed that they give consistent results.

The Methfessel-Paxton smearing scheme with a smearing parameter of 0.1 eV is used; this smearing parameter allows resolution of the peaks in the electronic density of states. All structures are allowed fully relax in a conjugate gradient
relaxation algorithm, until the forces are less than 0.02 eV/A. No symmetry constraints are applied in the simulation. All calculations are spin polarised with no restrictions on the overall spin. For bulk rutile, a (2x2x3) supercell is used, and for bulk anatase, a (2x 2 x2) supercell is used.

The rutile (110) surface is shown in chapter 2 figure 2.3 (a) and is composed of neutral O-Ti-O tri-layers along the slab with no dipole moment present upon cleaving. It has rows of two-fold coordinated bridging oxygens (denoted Obr) terminating the surface, and in the next layer there are two types of Ti: 6-fold coordinated Ti (Ti6f) and 5-fold coordinated Ti (Ti5f). The anatase (001) surface is shown in figure 2.3 (b) and is terminated by two coordinated oxygen atoms while the oxygen atoms in the surface are three coordinated. The Ti atoms in the surface are 5-fold coordinated.

To describe the electronic states of Ti in TiO2, we have used the DFT+U approach. DFT+U adds a Hubbard U correction for better description of localised, partially occupied transition metal d states, as discussed in a number of papers [21-25]. We applied U = 4.5 eV to the Ti 3d states [21-23], U = 8 eV and J = 1 eV as $U_{\text{eff}} = 7$ eV for Ni [26, 27] (with the effect of the choice of U applied to the Ni 3d states on the electronic properties also examined) and U = 7 eV for Cu [28]. For Sn, the electronic states are consistently described by DFT so no U correction was applied.

3.2.1. Metal oxide clusters supported on rutile TiO2 (110) and anatase (001).

For all calculation of metal oxide nanoclusters supported on the TiO2 surfaces, the free nanoclusters, the bare surfaces and the modified surfaces use the same supercell as the bare TiO2 surface and the same set of technical parameters, which ensures consistency between calculations. To study the adsorbed clusters, the clusters are positioned in a number of configurations at rutile (110) and anatase (001) surfaces and then a full relaxation is performed within a fixed supercell. While DFT calculations are excellent at providing details on the
electronic properties of the type of heterostructures studied in this thesis, screening many different adsorption structures becomes unfeasible for structures of the size considered herein. Therefore, a realistic atomistic potential [29] based model can be used to determine favourable adsorption structures for further refinement with DFT. There is much interest in using the charge equilibration (QEq) scheme of Rappé and Goddard [30, 31] for TiO$_2$ structures, in which the electronegativity of the ions is used to adjust the charge [32] distribution in an adaptive manner. Since the QEq approach gives a good description of the structure in TiO$_2$ compared with DFT [33, 34] and DFT+U [35], the most stable cluster-surface heterostructures found with QEq are a reliable starting point for subsequent relaxation with DFT+U (with DFT for selected comparisons) and the resulting adsorption energy of the nanocluster at TiO$_2$ is computed from:

$$ E_{\text{ads}} = E((\text{MOx})_n-\text{TiO}_2) - \{ E((\text{MOx})_n) + E(\text{TiO}_2) \} $$

3.37

Where $E((\text{MOx})_n-\text{TiO}_2)$ is the total energy of the MOx cluster ($\text{M} = \text{Ti, Sn, Ni, Cu, Pb or Bi}$) supported on the surface, and $E((\text{MOx})_n)$ and $E(\text{TiO}_2)$ are the total energies of the free cluster and the bare surface; in this calculation, a negative adsorption energy signifies that cluster adsorption is stable.

### 3.2.2. Calculation of Models of Excited States

In this thesis we study a model of the photoexcited state by calculating a triplet electronic state, which forces the system to have two unpaired electrons, promoting one electron to the previously empty conduction band, leaving behind a hole in the valence band.

This model of the lowest energy triplet state gives a reasonable description of the photoexcited state; previous studies using this model for photoexcited bulk TiO$_2$ and bare surfaces [37, 38] as well as in bulk HfO$_2$ [39] have indicated the utility of this model. For TiO$_2$, Di Valentin and Selloni [37] and Jedidi et al.[38] have shown that this model produces a localised Ti$^{3+}$ electronic state in bulk anatase
and the (101) surface [37] and in rutile (110) [38] (from hybrid DFT and DFT+U); a localised oxygen hole state was also found with hybrid DFT [37]. In both studies, singlet-triplet excitation energies have been calculated and relaxation (trapping) energies are presented in ref 37.

Figure 3.1 Diagram of the excited electronic state in (TiO$_2$)$_n$/TiO$_2$ system.

A schematic of the valence and conduction band alignments typical of the heterostructure in this thesis is presented in figure 3.2. The top of the valence band comes from the cluster while the conduction band derives from the surface. To describe an excited electronic state of these systems, we recognise that the excited electron is found in the Ti 3d derived conduction band and the hole will be in the O 2p derived valence band as presented in figure 3.2. Therefore, to describe the resulting reduced Ti$^{3+}$ we continue to use DFT+U (U=4.5eV on the Ti 3d states). There is also a need to properly describe the localized hole after excitation and the DFT+U approach is also applied to the O 2p states [40], with U = 5.5eV used for the O 2p states [41].

The following calculations are performed:

- a single point energy of the triplet at the singlet geometry, $E^{\text{unrelaxed}}$.
- a full ionic relaxation in the triplet electronic configuration, $E^{\text{relaxed}}$.

A dipole correction perpendicular to the surface plane is added to the total energies. Within this computational set-up, the following energies are calculated:

(1) The singlet-triplet vertical unrelaxed excitation energy: $E^{\text{vertical}} = E^{\text{singlet}} -$
\( E^{\text{unrelaxed}} \), where the singlet is fully relaxed and the triplet is not relaxed. This should correspond to the simple VB-CB energy gap from the density of states (2) The singlet-triplet vertical excitation energy: \( E^{\text{excite}} = E^{\text{singlet}} - E^{\text{relaxed}} \), where both the singlet and triplet electronic states are fully relaxed. The change in this energy with respect to the bare surface is a further means to determine the effect of the surface modification on the energy gap of TiO\(_2\). (3) The triplet relaxation (or trapping) energy: \( E^{\text{relax}} = E^{\text{relaxed}} - E^{\text{unrelaxed}} \), where the first energy is the fully relaxed triplet and the second energy is the triplet state at the singlet geometry (single point calculation), so that \( E^{\text{relax}} \) is the energy gained when the electron and hole are trapped at their Ti and O sites upon structural relaxation.

The energies (1) – (3) above are presented in a schematic in figure 3.3, that shows the physical origin of these energies.

Figure 3.2 Schematic of the energies calculated in the model photoexcited state.

Using described above model we investigate the localization of the hole and electron after photo-excitation and also calculate the energies related to this phenomena.
References:

4. P. Hohenberg, W. Kohn, Physical Review, 1964,136 (3B), B864


35. http://www.freeware.vasp.de/VASP/optics


4. Transition metal oxide nanoclusters on TiO$_2$

In Chapter 2 we reviewed the important role of transition metal oxides in photocatalysis and discussed the positive and negative points of dopant induced modifications to the properties of TiO$_2$ in particular. We also highlighted the important experimental results from Tada and co-workers in modifying TiO$_2$ with metal oxide nanoclusters, which results in an improvement of both visible and UV photocatalytic activities over pure TiO$_2$. In the experiments Tada et al use chemical-calcination-cycle (CCC) [1-3] and Libera et al used atomic layer deposition (ALD) [4] to achieve highly dispersed deposited nanoclusters. In driving our understanding of these systems, Nolan has studied (FeO)$_x$ modified TiO$_2$ using density functional theory (DFT) simulations and found that such modification cause a reduction in the TiO$_2$ band gap which will activate these heterostructures in the visible region [1]. We have also studied transition metal oxide modified TiO$_2$ in cooperation with Prof. Tada and in this chapter we present our DFT simulations of d-shell metal oxides nanocluster - (TiO$_2$)$_n$(NiO)$_n$, (CuO)$_n$ - supported on TiO$_2$ anatase (001) and rutile (110) to understand in detail how this modification influences the band gap of TiO$_2$ and what are the properties of these new heterostructured photocatalysts. We will show in this and the next chapter that modified TiO$_2$ is a material system that can serve as a new approach in the design of new photocatalysts.

4.1. (TiO$_2$)$_n$ nanoclusters (n=2-30) supported on rutile TiO$_2$ (110)

In this section we present our DFT simulations of TiO$_2$ rutile (110) modified with TiO$_2$ nanoclusters as our model system of TiO$_2$ modified with transition metal oxide nanoclusters. We determine stable adsorption configurations for TiO$_2$ clusters on rutile (110) and study the electronic properties of these structures. We investigate clusters where n = 2, 3, 4, 5, 6, 8, 16, 30 that are supported on the rutile (110) surface; for the biggest cluster the diameter is ca. 1.5 nm which is comparable to cluster sizes found in experiment. We generate representative cluster-surface structures, as described in Chapter 3 where the
clusters are positioned in a number of configurations at rutile (110) and anatase (001) surfaces and then a full relaxation is performed within a fixed supercell. For representative heterostructure we also present the electronic properties of these heterostructures. We find that all clusters adsorb strongly at the surface of TiO₂ rutile (110) with creation of new Ti-O bonds between clusters and surface. The electronic structures show a narrowing of the band gap due to the modification of the surface of TiO₂ which enable activity in the visible region. Moreover the energy band alignments indicate enhancement in charge carrier separation. We conclude that surface modification of TiO₂ is potentially useful approach in tuning photocatalytic properties of the material.

4.1.1.Adsorption structures and geometries

Figure 4.1 presents the atomic structures of the bare rutile TiO₂ (110) surface and the free nanoclusters Ti₂O₄, Ti₃O₆, Ti₄O₈, Ti₅O₁₀, Ti₆O₁₂, Ti₆O₁₆, Ti₉O₃₂, Ti₃₀O₆₀. These clusters are the global energy minima from Monte Carlo sampling and QEq relaxation and subsequent DFT relaxation. Compared to bulk TiO₂, the free nanoclusters show some strong differences in terms of the coordination environment of the Ti and O atoms. In particular, Ti and O atoms have reduced coordination numbers, which is consistent with previous studies [5-8]. Oxygen is 1, 2 or 3 coordinated and there is always a terminal O atom in these nanoclusters. For example, the biggest Ti₃₀O₆₀ cluster has eight terminal O atoms. Looking at the nanoclusters, the Ti₂O₄ cluster presents 3 coordinated Ti atoms and the other nanoclusters have 4 and 5 coordinated Ti atoms. There are no 6 coordinated Ti atoms in the free clusters. The Ti-O distances in the clusters are usually shorter than in the bulk so in the clusters the Ti-O bonds are in the range of 1.7-2.1 Å while for terminal oxygen atoms these distances are even shorter and the range is 1.68-1.78 Å.

For Ti₂O₄, Ti₃O₆, Ti₄O₈ nanoclusters, we compared the structures from two different codes: Turbomole, with the PBE and PW91 exchange-correlation functionals and VASP. For these small clusters after relaxations both methods show the same configurations while the bond lengths differ by only around
0.02Å. These clusters do not show any faceting into surfaces, as distinct from CeO₂ nanoclusters at similar sizes [9]. Moreover SiO₂ nanoclusters show non-bulk structures even up to 2 nm diameter, so that this non-facted structure is typical for oxide nanoclusters with covalent character.

![Figure 4.1 Atomic structure of (a) TiO₂ rutile (110) surface, (b) Ti₃O₄, (c) Ti₅O₆, (d) Ti₈O₁₈, (e) Ti₁₀O₂₀, (f) Ti₁₂O₂₄, (g) Ti₁₆O₃₂, (h) Ti₃₀O₆₀ clusters. The grey spheres are Ti atoms and the red spheres are O atoms; this colour scheme is used in the remainder of the figures.](image)

We also computed Bader Charges [10] on Ti and O atoms in free nanoclusters. All Ti atoms have a Ti⁴⁺ oxidation state, with computed Bader Charges in the range of 1.38 - 1.45 electrons which are typical for fully oxidised Ti⁴⁺. Since O atoms have three different coordination numbers, the Bader charges are able to show these distinctions: their terminal oxygens have the least negative charge of 7.14 electrons, 2-fold coordinated oxygen have charges around 7.30 electrons and 3-fold coordinated oxygen have computed charges around 7.4 electrons. For comparison the bulk rutile computed Ti and O charges are 1.38 and 7.31 electrons while Ti³⁺ species have computed Bader charges of +1.7 electrons.

Figures 4.2 and 4.3 show several stable structures of Ti₂O₄, Ti₅O₆, Ti₆O₈, Ti₅O₁₀, Ti₈O₁₂, Ti₃₀O₆₀ adsorbed on the rutile (110) surface. Within each heterostructure, the structures are denoted with roman numbers and the
adsorption energy is also shown in eV. In general, the results will be shown only for the most stable structures.

For the most stable smaller clusters: Ti$_2$O$_4$, Ti$_3$O$_6$, Ti$_4$O$_8$ supported on TiO$_2$ we have also run ab initio molecular dynamics simulations (for 2 ps, in the NVE ensemble, at a temperature of 500 K) for a wider configuration space sampling. There was a little change to the structures shown in figure 4.2 a) and b) upon relaxing the MD structures. This indicates that these clusters are stable and lower energy structures are not found.

![Figure 4.2 Relaxed adsorption structures in several different configurations and computed adsorption energies for (a) Ti$_2$O$_4$, (b) Ti$_3$O$_6$, (c) Ti$_4$O$_8$, (d) Ti$_5$O$_{10}$ deposited on the TiO$_2$ (110) surface. The roman numerals signify the numbering of the cluster structures. The adsorption energies are given under each structure in eV.](image)

Figure 4.2 Relaxed adsorption structures in several different configurations and computed adsorption energies for (a) Ti$_2$O$_4$, (b) Ti$_3$O$_6$, (c) Ti$_4$O$_8$, (d) Ti$_5$O$_{10}$ deposited on the TiO$_2$ (110) surface. The roman numerals signify the numbering of the cluster structures. The adsorption energies are given under each structure in eV.
The adsorption energies of the most stable nanoclusters on rutile (110) indicate strong adsorption of the nanocluster at the surface. We now consider the possibility of cluster aggregation after the nanoclusters adsorb on the rutile (110) surface, which could take place during e.g. sintering treatments. For this purpose we use the energies for a supported TiO$_2$ nanocluster that is conceptualised as being aggregated from two smaller nanoclusters on the same surface and compare to the situation where these clusters are in the gas phase.

As an example, within the range of structures we have examined, we can compare energies of a supported Ti$_6$O$_{12}$ nanocluster to the energy of two supported Ti$_3$O$_6$ clusters. Our analysis are limited by the fact that we are able to compare energetics of modified rutile TiO$_2$ only for those structures which use
the same rutile (110) surface model. Table 4.1 presents the possible cluster aggregation schemes, which serve to highlight the primary result. We see that free gas phase nanoclusters prefer to aggregate into larger nanoclusters, as evidenced by the stabilisation of the larger cluster. There is however now a different trend when the nanoclusters are anchored at the rutile (110) surface. In this case, the aggregation of the nanoclusters is energetically disfavoured, so that the strong adsorption energy of a nanocluster on the rutile (110) surface will prevent aggregation of the adsorbed nanoclusters to larger structures and isolated nanoclusters will be found at the surface. There are no experiments on TiO$_2$ nanocluster modification of rutile, but the work of Tada et al where modification of rutile and anatase with metal oxide nanoclusters shows isolated metal oxide nanoclusters that do not aggregate to form larger clusters or films even during sintering treatment [1-3].

Table 4.1 Calculated relative energies for aggregation of free TiO$_2$ nanoclusters to larger nanoclusters (left column) and for aggregation of supported TiO$_2$ nanoclusters to larger nanoclusters on TiO$_2$ (right column).

<table>
<thead>
<tr>
<th>Aggregation of Free Nanoclusters</th>
<th>Aggregation of Nanoclusters Supported on TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formation of Ti$<em>8$O$</em>{16}$ from 2 x Ti$_4$O$_8$:</strong></td>
<td></td>
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<tr>
<td>$E(\text{Ti}<em>8\text{O}</em>{16}) = -168.44 \text{ eV}$</td>
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<tr>
<td>$E(2 \times \text{Ti}_4\text{O}_8) = -161.23 \text{ eV}$</td>
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<tr>
<td><strong>Formation of Ti$<em>{16}$O$</em>{32}$ from 2 x Ti$<em>8$O$</em>{16}$</strong></td>
<td></td>
</tr>
<tr>
<td>$E(\text{Ti}<em>{16}\text{O}</em>{32}) = -344.42 \text{ eV}$</td>
<td></td>
</tr>
<tr>
<td>$E(2 \times \text{Ti}<em>8\text{O}</em>{16}) = -336.89 \text{ eV}$</td>
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<tr>
<td><strong>Formation of Ti$<em>{30}$O$</em>{60}$ from Ti$<em>6$O$</em>{12}$+Ti$<em>8$O$</em>{16}$+Ti$<em>{16}$O$</em>{32}$</strong></td>
<td></td>
</tr>
<tr>
<td>$E(\text{Ti}<em>{30}\text{O}</em>{60}) = -647.25 \text{ eV}$</td>
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<tr>
<td>$E(\text{Ti}<em>6\text{O}</em>{12} + \text{Ti}<em>8\text{O}</em>{16} + \text{Ti}<em>{16}\text{O}</em>{32}) = -635.09 \text{ eV}$</td>
<td></td>
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</table>

| **Formation of Ti$_6$O$_{12}$ from 2 isolated Ti$_3$O$_6$ clusters on rutile (110)** |
| $E\{2(\text{Ti}_3\text{O}_6)\text{-rutile (110)}\} = -4482.86 \text{ eV}$ |
| $E\{\text{Ti}_6\text{O}_{12}\text{-rutile (110)}\} + E\{\text{rutile (110)}\} = -4477.51 \text{ eV}$ |

| **Formation of Ti$_{16}$O$_{32}$ from two isolated Ti$_8$O$_{16}$ clusters on rutile (110)** |
| $E\{2(\text{Ti}_8\text{O}_{16})\text{-rutile (110)}\} = -6135.12 \text{ eV}$ |
| $E\{\text{Ti}_{16}\text{O}_{32}\text{-rutile (110)}\} + E\{\text{rutile (110)}\} = -6134.39 \text{ eV}$ |
The details of the geometry involving Ti-O bonds are presented in table 4.2 and we describe the characteristics of the new bonds formed between the nanoclusters and the rutile TiO₂ (110) surface. Figure 4.2 presents several configurations of each of Ti₂O₄, Ti₃O₆, Ti₄O₈, and Ti₅O₁₀ nanoclusters supported rutile (110). There are two Ti atoms coordinated to bridging oxygen atoms of the surface in the Ti₂O₄ nanocluster when supported on rutile (110): one Ti cluster atom makes bonds to two of these oxygen atoms and the second Ti cluster atom makes a bond to one bridging oxygen atom, with Ti–O distances of 2.11 Å, 2.20 Å and 2.22 Å respectively. The cluster Ti atoms also bond with in-plane oxygen, with Ti–O distances between 2.19 Å and 2.22 Å. The terminal oxygen atom that does not bind to the surface while the other terminal oxygen atom binds to Ti from the surface, and has a Ti–O distance of 1.93 Å, and this bond length is consistent with the Ti–O distance in bulk TiO₂.

The Ti₃O₆ nanoclusters adsorbed at the (110) surface have adsorption energies similar in magnitude to other supported clusters. In the most stable adsorption structure of Ti₃O₆ which is indicated as number II, two cluster Ti atoms create bonds with bridging oxygen from the surface. The first Ti bonds to a bridging oxygen atom with Ti–O distance 2.07 Å, while the second Ti bonds with Ti–O distances of 2.04 Å and 2.12 Å. The same Ti also creates an additional bond to in-plane oxygen atom with a Ti–O distance of 2.23 Å. Moreover two oxygen atoms from the cluster make two bonds with 5-fold coordinated Ti from the surface with Ti–O distances of 1.87 Å and 1.94 Å. The two terminal oxygen atoms of the cluster do not bond to the surface and we observe that their Ti–O distances show a small increase to 1.68 Å, similar to the case of Ti₂O₄. The 5-fold coordinated Ti from the surface is pulled up by the oxygen from the cluster and the distance of the surface Ti–O is 2.13 Å.

Three adsorption structures for Ti₄O₈ are shown in figure 4.2 c), for which the structure denoted I is the most stable. The adsorbed cluster is bonded to the surface by three new Ti–O bonds: two Ti from the cluster bond to two bridging oxygen atoms from the surface, with Ti–O distances of 1.96 Å and 2.01 Å. One terminal oxygen from the cluster bonds to surface Ti with an increased Ti–O
distance of 1.76 Å. The second terminal oxygen does not bond with the surface and again shows a small increase in its Ti–O distance to 1.68 Å.

The adsorption energies for four different adsorption configurations of the Ti₅O₁₀ clusters supported on rutile (110) show a strong interaction between the cluster and the surface, lying in the range from -2.95eV to -5.70eV. In all configurations the clusters bond to surface with the creation of new Ti-O bonds. There are adsorption energies within the same range of -3eV for three configurations: I, III and IV. These supported nanoclusters create five new interfacial Ti-O bonds. Configuration II has four bonds and the most favourable cluster adsorption energy. For this configuration, two Ti atoms from the cluster bond to two bridging O atoms from the surface O atoms with Ti-O distances of 2.08 Å and 1.99 Å. Two bonds come from the O atoms from the cluster with two 5 fold Ti atoms from the surface, with Ti-O distances of 1.88 Å and 1.99 Å. When we compare the cluster shape after deposition there is a reduction in the number of terminal oxygen atoms from two in the bare cluster to one after deposition. The most stable configuration has the smallest distortion to the cluster structures. All configurations are characterised with Ti from cluster and O from surface bonds which are in the range of 1.90 Å to 2.28 Å while Ti from surface and O from cluster bonds have distances in the range from 1.89 Å to 2.17 Å.

Figure 4.4 Detailed distances for: (a) Ti₅O₆, (b) Ti₆O₈ supported on TiO₂ rutile (110).

Four configurations for Ti₆O₁₂ supported on TiO₂ rutile (110) are shown in figure 4.3, with the adsorption energies for configurations I and II being the smallest. In These two configurations there is only one Ti-O interfacial bond while
configurations III and IV show more negative adsorption energies, together with a larger number of new Ti-O interfacial bonds. We can observe similar trend for Ti$_8$O$_{16}$ and Ti$_{30}$O$_{60}$ clusters where the smaller number of interfacial bonds result in less negative adsorption energies. The adsorption energies for Ti$_6$O$_{12}$, Ti$_{16}$O$_{32}$ and Ti$_{30}$O$_{60}$ clusters are in the range from -2.72eV for Ti$_6$O$_{12}$ cluster to -6.71eV for the Ti$_{30}$O$_{60}$ cluster and present an effect due to cluster size. The number of new bonds between clusters and surface are: eleven for the most stable configuration of Ti$_8$O$_{16}$, seven for the most stable Ti$_{16}$O$_{32}$ and six for the most stable Ti$_{30}$O$_{60}$ cluster supported on TiO$_2$ rutile (110). For The smaller clusters from Ti$_2$O$_4$ to Ti$_6$O$_{12}$ the bonds between Ti cluster atoms and O from the surface are in the range from 1.92 Å to 2.08 Å while the bigger clusters, Ti$_8$O$_{16}$, Ti$_{16}$O$_{32}$ and Ti$_{30}$O$_{60}$, present Ti cluster to O surface bonds in the range 1.87 Å to 2.12 Å. All clusters O cluster atoms and Ti surface atoms distances are similar ranging from 1.84 Å to 1.99 Å. We also find that Ti-O distances involving the surface Ti interacting with cluster oxygen are shorter than in the Ti-O distances involving cluster Ti interacting with the surface oxygen. It can happen because Ti atoms from the surface are able to reach a 6-fold coordination environment while binding to the cluster, but Ti atoms from the clusters are not always able to reach a 6-fold coordination and the longer Ti-O distances are obtained for some cluster Ti atoms.

In the adsorbed Ti$_6$O$_{12}$ nanocluster, Ti atoms which create bonds to surface oxygen show typical Ti-O bond distances and reach 6-fold coordination. The other clusters present similar binding to the surface, but the nanoclusters are unable to relax their structures and make all Ti atoms 6-fold coordinated. The presence of undercoordinated Ti atoms is a very interesting point in the context of electron and hole localisation and reactivity and we will return to this in Chapter 6, when we present models of the photoexcited state of modified TiO$_2$.

Comparing the geometries of the bare and deposited clusters there is generally not a big change in terms of Ti-O bond distances and the number of terminal oxygen atoms stays the same. However a different situation is found for the Ti$_8$O$_{16}$ cluster where there is a big change in the geometry of the deposited cluster and the number of terminal oxygen atoms is reduced from three in the
bare cluster to zero in deposited one. The bigger Ti$_{16}$O$_{32}$ has an unchanged number of terminal oxygen atoms after relaxation. There are small changes in geometry for the biggest adsorbed Ti$_{30}$O$_{60}$, as a result of cluster-surface interfacial bonding, and a reduction in the number of terminal oxygen atoms from eight in bare cluster to four. We also want to point out that the cluster with the least negative adsorption energy has no change in the number of terminal oxygen atoms while in other clusters, with more favourable adsorption energies, there is always a reduction in the number of terminal oxygen atoms, so that increasing the coordination of terminal oxygen atoms may play an important role in the stability of adsorbed clusters at the TiO$_2$ surface.

A final important point to consider is that of the possibility of water adsorption, in particular given the terminal oxygens present in the adsorbed nanoclusters. These structures could be potentially useful for photocatalytic water splitting to hydrogen. This process would involve adsorption of water at the nanocluster, the water will most likely be adsorbed through the oxygen atom at undercoordinated Ti sites and may well dissociate into H and OH, with adsorption of H at the titanyl oxygen atoms [11]. This may be important for photocatalytic activity and the subsequent oxidation of water. The investigation of this mechanism is of great importance, however it requires a strong collaboration between modelling and experimental work that is outside the scope of this thesis.
Table 4.2 Surface–cluster Ti-O distances, in Å, for: Ti$_5$O$_{10}$, Ti$_6$O$_{12}$, Ti$_8$O$_{16}$, Ti$_{16}$O$_{32}$, Ti$_{30}$O$_{60}$ clusters on TiO$_2$ rutile (110) surface. Ti$^c$ and O$^s$ signify Ti and O from the TiO$_2$ cluster and Ti$^r$ and O$^r$ signify Ti and O from the surface. Also included are Ti-O distances in bulk rutile TiO$_2$.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Ti$^c$-O$^s$</th>
<th>Ti$^r$-O$^r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_2$O$_4$</td>
<td>2.11, 2.20, 2.22, 2.19, 2.22</td>
<td>1.93</td>
</tr>
<tr>
<td>Ti$_3$O$_6$</td>
<td>2.07, 2.04, 2.12</td>
<td>1.87, 1.94</td>
</tr>
<tr>
<td>Ti$_4$O$_8$</td>
<td>1.96, 2.01</td>
<td>1.76</td>
</tr>
<tr>
<td>Ti$<em>5$O$</em>{10}$</td>
<td>2.08, 1.99</td>
<td>1.99, 1.88</td>
</tr>
<tr>
<td>Ti$<em>6$O$</em>{12}$</td>
<td>1.92, 1.92</td>
<td>1.94, 1.91</td>
</tr>
<tr>
<td>Ti$<em>8$O$</em>{16}$</td>
<td>1.90, 2.09, 2.08, 1.95, 1.97, 2.11</td>
<td>1.87, 1.96, 1.91, 1.87, 2.09</td>
</tr>
<tr>
<td>Ti$<em>{16}$O$</em>{32}$</td>
<td>2.12, 2.00, 2.06, 2.08</td>
<td>1.98, 1.85, 1.90</td>
</tr>
<tr>
<td>Ti$<em>{30}$O$</em>{60}$</td>
<td>2.11, 2.18, 2.05, 2.03</td>
<td>1.90, 1.84</td>
</tr>
<tr>
<td>Bulk rutile</td>
<td>1.96, 2.00</td>
<td></td>
</tr>
</tbody>
</table>

4.1.2. Electronic Structure and Band Gap Modification

In determining the effect of modifying rutile (110) with TiO$_2$ nanoclusters, we make use of the projected electronic density of states (PEDOS), where the projection is onto the Ti 3d and O 2p states of the nanocluster and the Ti 3d and O 2p states of the supporting TiO$_2$ surface. The PEDOS plots give the possibility to examine the relative positions of the nanocluster and surface electronic states and thus the effect of surface modification on the band gap of TiO$_2$. It is important to realise that the structures here are not simply TiO$_2$ sensitised with oxide nanoclusters, similar to quantum dot or dye sensitisation, but are instead a structure modification that fundamentally alters the nature of the valence or
conduction band of TiO$_2$, thus changing the band gap. The division of the PEDOS into nanocluster and surface contributions allows us to examine if the valence or conduction band edges are modified by the deposited nanoclusters.

Figure 4.5 presents the PEDOS for most stable structures of Ti$_2$O$_4$, Ti$_3$O$_6$, Ti$_4$O$_8$, Ti$_5$O$_{10}$, Ti$_6$O$_{12}$, Ti$_8$O$_{16}$, Ti$_{16}$O$_{32}$ and Ti$_{30}$O$_{60}$ modified rutile (110). The first piece of information from these plots is that there are no defect states in the band gap, which would arise from formation of reduced Ti$^{3+}$ species after cluster deposition and relaxation, so that all Ti are in a 4+ oxidation state. We have computed the Bader Charges for Ti and O ions in the (110) surface and the supported clusters, which are shown in table 4.3. In this table the O atoms are grouped depending on their coordination number in the nanocluster. For the rutile (110) surface, the Ti charge is around 1.4 electrons which is typical of Ti$^{4+}$. Considering now the nanoclusters, the Bader Charges are as follows. In Ti$_2$O$_4$ the Ti charge is 1.45 electrons, in Ti$_3$O$_6$ the Ti charge is 1.35-1.43 electrons, in Ti$_4$O$_8$ the Ti charge is 1.34-1.40 electrons, in Ti$_5$O$_{10}$ the Ti charge is 1.33 - 1.38 electrons, in Ti$_6$O$_{12}$ the Ti charge is 1.35 - 1.45 electrons, in Ti$_8$O$_{16}$ the Ti charge is 1.33 - 1.39 electrons, in Ti$_{16}$O$_{32}$, the Ti charge is 1.27 - 1.39 electrons and in Ti$_{30}$O$_{60}$ the Ti charge is 1.28 -1.41 electrons. Thus the Ti oxidation state in the nanoclusters is Ti$^{4+}$.

The Bader charges on oxygen show that, similar to the free nanoclusters, there are different charges for 1, 2 and 3-fold coordinated O atoms. For example the Bader Charges for the Ti$_8$O$_{16}$-TiO$_2$ structure are indicative of no terminal O atoms in the cluster. For the other supported nanoclusters we find that the terminal oxygens have Bader charges similar to those computed for terminal oxygen in the free nanoclusters. In Ti$_5$O$_{10}$ a previously terminal oxygen is now 2-fold coordinated due to binding to a surface Ti atom and this is indicated in the change in the Bader charges. There are similar results for oxygens in the other nanoclusters.
Table 4.3 Computed Bader Charges for Ti and O in the heterostructures. The O charges are divided into different groups depending on O coordination.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$Q^\text{Ti}$</th>
<th>$Q^\text{O}\text{1foil}$</th>
<th>$Q^\text{O}\text{2foil}$</th>
<th>$Q^\text{O}\text{3foil}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_2$O$_4$</td>
<td>1.45</td>
<td>7.15</td>
<td>7.28; 7.30</td>
<td>7.39</td>
</tr>
<tr>
<td>Ti$_3$O$_6$</td>
<td>1.35; 1.42; 1.43</td>
<td>7.13; 7.16</td>
<td>7.27; 7.34</td>
<td>7.38; 7.39</td>
</tr>
<tr>
<td>Ti$_4$O$_8$</td>
<td>1.33; 1.38; 1.39; 1.40</td>
<td>7.16</td>
<td>7.23; 7.27; 7.27; 7.30; 7.31</td>
<td>7.35; 7.42</td>
</tr>
<tr>
<td>Ti$<em>5$O$</em>{10}$</td>
<td>1.35; 1.38; 1.39; 1.33; 1.37;</td>
<td>7.14</td>
<td>7.30; 7.27</td>
<td>7.4; 7.34</td>
</tr>
<tr>
<td>Ti$<em>6$O$</em>{12}$</td>
<td>1.45: 1.45; 1.38; 1.35; 1.42</td>
<td>7.11; 7.17; 7.12</td>
<td>7.29; 7.30</td>
<td>7.38; 7.37; 7.35; 7.39</td>
</tr>
<tr>
<td>Ti$<em>8$O$</em>{16}$</td>
<td>1.34; 1.33; 1.39; 1.33; 1.35;</td>
<td>--</td>
<td>7.31; 7.28; 7.26; 7.33</td>
<td>7.32; 7.39</td>
</tr>
<tr>
<td>Ti$<em>{16}$O$</em>{32}$</td>
<td>1.37; 1.34; 1.27; 1.30; 1.38; 1.34; 1.32; 1.36; 1.37; 1.34; 1.35; 1.40;</td>
<td>7.11</td>
<td>7.31; 7.28; 7.29; 7.26; 7.27; 7.28</td>
<td>7.37; 7.38; 7.4; 7.37; 7.41; 7.34; 7.38; 7.35</td>
</tr>
<tr>
<td>Ti$<em>{30}$O$</em>{60}$</td>
<td>1.30 – 1.40</td>
<td>7.13</td>
<td>7.27; 7.28; 7.26; 7.31; 7.27; 7.3</td>
<td>7.38; 7.35; 7.37; 7.38; 7.39; 7.42</td>
</tr>
<tr>
<td>Bulk Rutile</td>
<td>1.40</td>
<td>--</td>
<td>--</td>
<td>7.70</td>
</tr>
</tbody>
</table>

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Turning now to the electronic structure, our aim is to determine the effect which the modifications of the rutile (110) surface by the nanoclusters have on the energy gap of TiO$_2$. This effect may be illustrated by any changes to the composition and position of the valence (VB) and conduction band (CB) due to formation of the interface between the surface and the nanoclusters, which will allow us to determine the effect of nanocluster modification on the energy gap of TiO$_2$. The PEDOS plots in figure 4.5 show the EDOS projected onto the Ti 3d and O 2p electronic states in the rutile (110) surface and the TiO$_2$ nanoclusters. The PEDOS plots show that in all cases of nanocluster modified rutile (110), except for Ti$_8$O$_{16}$, the top of the valence band now comes from the O 2p states in the supported TiO$_2$ nanocluster and the bottom of the conduction band from the Ti 3d states of the TiO$_2$ surface. This means that the surface modification has the effect of both changing the nature of the top of the VB and shifting it to higher energy compared to the unmodified TiO$_2$ surface.
Figure 4.5 Electronic density of states projected (PEDOS) on Ti 3d and O 2p states for a) Ti$_2$O$_4$, b) Ti$_3$O$_6$, c) Ti$_4$O$_8$, d) Ti$_5$O$_{10}$, e) Ti$_6$O$_{12}$, f) Ti$_8$O$_{16}$, g) Ti$_{16}$O$_{32}$, h) Ti$_{30}$O$_{60}$ clusters supported on the rutile (110) surface.
Figure 4.6 Electronic density of states projected (PEDOS) on O 2p states with terminal oxygen (denoted O 2p terminal) and non-terminal oxygen (denoted O 2p non-term) for: (a)Ti$_5$O$_{10}$, (b)Ti$_6$O$_{12}$, (c)Ti$_{16}$O$_{32}$, (d)Ti$_{30}$O$_{60}$ clusters on TiO$_2$ rutile (110) surface.

Given the presence of terminal oxygen in many of the supported nanoclusters, we investigated their contribution to the O 2p PEDOS. Figure 4.6 presents the O 2p EDOS projected onto terminal and non-terminal oxygen from the nanocluster. The PEDOS indicate that the terminal oxygen atoms on the clusters dominate the top of the nanocluster-derived VB states. The lack of terminal oxygen in the
Ti$_8$O$_{16}$ nanoclusters explains why this nanocluster shows no nanocluster derived states lying above the VB edge of the surface.

The modification of rutile TiO$_2$ results in a shift of the VB edge to higher energy compared to the bare surface and the size of this shift depends on the size of the supported nanocluster. While the VB contribution is changed, the bottom of the conduction band comes from the surface Ti 3d states with the nanocluster derived states lying higher in energy. In light of our results we propose that modifying TiO$_2$ rutile (110) with TiO$_2$ nanoclusters will lead to a reduction in the energy gap over bare TiO$_2$.

When looking at DOS we can see that only Ti$_8$O$_{16}$ cluster gives no states in the band gap of the TiO$_2$ surface which results in no change in the bare surface energy gap. It can be in part explained by considering the geometry of the nanocluster, where there is a substantial change in structure after cluster deposition and relaxation. There is a loss of the terminal oxygen atoms and the structure in the deposited cluster is more similar to bulk TiO$_2$ where Ti-O distances in the cluster are 1.85 Å - 2.11 Å.

The presented DOS shows that the simple valence-conduction band energy gap is reduced due to surface modification and this reduction comes from the presence of the electronic states of the deposited nanoclusters. We predict that new heterostructures will improve the photocatalytic activity over unmodified TiO$_2$ and light absorption in the visible region will be possible. For a selection of nanoclusters we also computed the optical (Tauc) gaps, which are 1.55 eV for Ti$_5$O$_{10}$-TiO$_2$, 1.55eV for Ti$_6$O$_{12}$-TiO$_2$ 1.65eV for Ti$_8$O$_{16}$, 1.60 eV for Ti$_{16}$O$_{32}$-TiO$_2$ and 1.45 eV for Ti$_{30}$O$_{60}$-TiO$_2$; for comparison, the bare rutile (110) gap is 1.70eV. Obviously our DFT+U calculations will underestimate the energy gap in unmodified and modified TiO$_2$ but the changes in the energy gap as a result of modification will be reliable.

While modifying the energy gap of TiO$_2$ to induce visible light absorption is undoubtedly an important aspect of developing new photocatalysts, we also need to consider the fate of the electrons and holes that are formed upon photoexcitation and this aspect is generally neglected in studies of TiO$_2$ based
photocatalysts. If we refer again to the PEDOS, the energy level alignments, where the VB (exception of the Ti$_8$O$_{16}$ cluster) is dominated by electronic states from the deposited TiO$_2$ nanoclusters lead us to propose that the separation of the holes and electrons will be improved while compared to bare rutile (110). Di Valentin and Selloni [12] and Jedidi et al [13] have shown in a model of the triplet excited state of bulk TiO$_2$ that upon excitation, a Ti$^{3+}$ and an oxygen hole (O-) are formed after an electron is excited from the VB to the CB and we will return to this point in chapter 6.

In the structures in this chapter, the composition of the VB edge, derived from the TiO$_2$ nanocluster and the CB, derived from the TiO$_2$ surface, will therefore result an improvement in electron and hole separation over bare TiO$_2$. In this case upon excitation the holes will be found on oxygen from the nanocluster while the electrons will be found on Ti atoms of the surface, thus the holes and electrons will be spatially separated and this separation will be larger than on the bare surface. We believe that the terminal oxygen atoms in the cluster will be potential sites for the holes after excitation, while the electrons will be trapped at surface Ti. More detailed analysis of the possible electron/holes locations is in chapter 6. Understanding the fate of electrons and hole is a very important aspect in terms of photocatalysis since enhanced spatial separation will result in longer charge carrier lifetime before any charge recombination can take place and this will improve the overall photocatalytic activity.

From experiments, a useful tool in this regard is PL spectroscopy which probes charge recombination. For TiO$_2$ the PL peak arising from the recombination of electrons and holes is at 540mn for bare TiO$_2$ from work of Tada [1-3, 14] while due to modification with FeOx this peak decreases. Given that the effect of FeOx modification on TiO$_2$ modifies the electronic structure and energy gap in the same was a TiO$_2$ nanocluster modification, it is reasonable to propose that the PL peak arising from charge recombination will be reduced upon modification with TiO$_2$ nanoclusters.
Table 4.4 presents the computed workfunction of a selection of heterostructures with a comparison to unmodified rutile (110) surface. The workfunction is defined as the difference between the Fermi energy of the surface and the vacuum energy. The heterostructures all show a reduction in the workfunction when compared to bare TiO$_2$ and this will facilitate a reduction in the barrier for electron transfer to adsorbed species. This feature could be important for catalysis with metal oxide heterostructures.

Table 4.4 Computed workfunction of the heterostructures from DFT+U.

<table>
<thead>
<tr>
<th>Heterostructure</th>
<th>Workfunction / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ (110)</td>
<td>7.10 eV</td>
</tr>
<tr>
<td>Ti$<em>5$O$</em>{10}$-TiO$_2$</td>
<td>6.83 eV</td>
</tr>
<tr>
<td>Ti$<em>6$O$</em>{12}$-TiO$_2$</td>
<td>6.89 eV</td>
</tr>
<tr>
<td>Ti$<em>8$O$</em>{16}$-TiO$_2$</td>
<td>6.50 eV</td>
</tr>
<tr>
<td>Ti$<em>{16}$O$</em>{32}$-TiO$_2$</td>
<td>5.28 eV</td>
</tr>
<tr>
<td>Ti$<em>{30}$O$</em>{60}$-TiO$_2$</td>
<td>6.25 eV</td>
</tr>
</tbody>
</table>

We present finally, a comparison of the results with DFT, with no +U correction, and DFT+U on the example of TiO$_2$ modified with a Ti$_5$O$_{10}$ nanocluster. Figure 4.7 shows the PEDOS projected onto the Ti 3d states for the Ti$_5$O$_{10}$-TiO$_2$ structure, from surface Ti atoms and nanocluster Ti atoms. While we compare two PEDOS plots, we see that the general description of the change in the VB with nanocluster modification and the unchanging conduction band is described the same with both DFT approaches.
Figure 4.7 Comparison of electronic density of states projected (PEDOS) on Ti 3d states for TiO$_2$ rutile (110) surface and adsorbed Ti$_5$O$_{10}$ cluster (a) DFT results, (b) DFT+U results.

4.1.3. Discussion and conclusions

We investigated the modification of rutile (110) with TiO$_2$ nanoclusters, where $n=2 – 30$; the biggest clusters are up to 1.5 nm diameter, a size achievable in experiments. Modifying the (110) surface results in formation of strong interfacial Ti-O bonds between surface and the clusters. The modification of TiO$_2$ changes the electronic structure such that the valence band edge is pushed upwards in energy which results in a reduction of the band gap over pure TiO$_2$. This arises from the presence of nanocluster derived electronic states and the position of VB edge in the heterostructure depends on the nanocluster size. We predict that this surface modification of TiO$_2$ can lead to an improvement in visible light absorption when compared to unmodified TiO$_2$.

While activity in the visible region is a very important feature for a photocatalyst, the electron and hole separation plays an important role as well. Reduction in non-radiative recombination of electrons and holes can dramatically improve the efficiency of photocatalyst. The heterostructures studied here have energy alignments so that VB edge is dominated by oxygen 2p states from the nanocluster and the conduction band edge is dominated by Ti 3d states from the
surface. As a result, during visible light excitation, the electrons will be found on Ti in the rutile (110) surface and holes on the nanocluster and thus recombination of electrons and holes will be reduced when compared to the bare TiO₂ surface. The potential charge separation facilitates a reduction in charge carrier recombination thus electrons and holes may be used in oxidation and reduction reactions. The importance of this and also the interface between two materials was discussed in several publications [15-22].

We also find that the workfunction in the heterostructure can be reduced by up to 1 eV compared to the bare surface, which should be important for enhanced reactivity.

Our calculations emphasize that the formation of the interface plays an important role in modification of the electronic properties of photocatalyst which can lead to improvement in photocatalytic activity in the visible region together with enhanced electron and hole separation.

Summarizing the results of this section:

- TiO₂ nanoclusters adsorb strongly on the rutile (110) surface, with new interfacial Ti-O bonds and the nanoclusters are thermodynamically stable towards aggregation to larger clusters.
- The electronic structure shows a (nanocluster dependent) reduction in the band gap in the heterostructure over unmodified surface. We postulate that the absorption in the visible region could be possible. However experimental confirmation of this result would be welcome.
- The nature of the VB and CB edges indicates that the valence band edge is derived from the cluster electronic states and the conduction band edge is composed of surface states. The reduction of charge recombination during photoexcitation will facilitate spatial separation of electrons and holes, which will lead to improved photocatalytic activity.
- A reduced workfunction compared to the bare surface can be achieved, which is useful for reactivity in catalysis.
4.2. (NiO)n nanoclusters at rutile (110) and anatase (001)

In ref. [24] Tada and co-workers presented NiO modified TiO₂ and investigated its application as a visible light activated photocatalyst. In collaboration with this work, we investigated the origin of the visible light activity in rutile and anatase surfaces modified with NiO, Ni₂O₂, Ni₃O₃ and Ni₄O₄ nanoclusters allowing us to understand the origin of the experimental findings. The TiO₂ surfaces are anatase (001) and rutile (110) surfaces and we discuss (1) how NiO nanocluster modification of TiO₂ changes the light absorption properties and (2) if there is any sensitivity to TiO₂ crystal form; similar comparisons have been performed for SnO₂- and CuO-modified TiO₂.

4.2.1. Adsorption structures and geometries of NiO Nanocluster modified TiO₂

Figure 4.8 presents the atomic structure of anatase (001) and rutile (110) surfaces modified with NiO, Ni₂O₂, Ni₃O₃, and Ni₄O₄ nanoclusters. These are chosen as representative NiO nanoclusters and we also show the adsorption energies and the numbering of the nanocluster Ni atoms. Figure 4.9 shows the Ni₄O₄ nanocluster adsorbed on a larger surface supercell of rutile (110) to examine any impact due to NiO coverage for a particular nanocluster.
Figure 4.8 Relaxed adsorption structures with adsorption energies given in eV for (a) NiO, (b) Ni$_2$O, (c) Ni$_3$O$_2$, and (d) Ni$_4$O$_4$ clusters on TiO$_2$: anatase (001) and (e) NiO, (f) Ni$_2$O, and (g) Ni$_3$O$_2$:clusters, (h) Ni$_4$O$_4$:clusters on TiO$_2$: rutile (110. The blue spheres are Ni atoms, the gray spheres are Ti atoms, and the red spheres are O atoms. Cluster Ni atoms are numbered.

For all heterostructures we computed the coverage of Ni atoms per unit area and we found that for NiO, Ni$_2$O$_2$, Ni$_3$O$_3$, and Ni$_4$O$_4$ on anatase (001), the coverages are 0.85, 1.70, 2.55, and 3.41 Ni atoms/nm$^2$, while on rutile (110), the corresponding coverages are 0.64, 1.28, 1.92, and 2.56 Ni atoms/nm$^2$. The larger (4x4) rutile (110) surface supercell gives coverage of 1.28 Ni atoms/nm$^2$. On the (2x4) surface supercell of rutile (110), the largest Ni$_4$O$_4$ nanocluster will lead to stronger periodic NiO-NiO interactions compared to the smaller NiO
nanoclusters. These interactions may influence the adsorption structures and affect the electronic properties of modified TiO$_2$ and this is investigated with the larger surface supercell of rutile (110).

![Figure 4.9](image)

**Figure 4.9** Relaxed adsorption structures and adsorption energy in eV for Ni$_4$O$_4$ nanocluster on TiO$_2$ rutile (110) with a (4x4) surface supercell expansion. The colour coding is the same as figure 4.9

The structures for NiO modified anatase and rutile show negative adsorption energies in the range of $-3.18$ to $-6.15$ eV. These energies indicate the strong interaction between the nanocluster and the surface, as well as the high stability of individual NiO nanoclusters adsorbed at both TiO$_2$ surfaces, which, from the analysis in the previous section, prevents aggregation of the nanoclusters into larger structures during post-heating. Detailed geometry information is presented in table 4.5.
Table 4.5 Surface to nanocluster Ni-O bond distances for NiO clusters adsorbed at the TiO$_2$ anatase (001) and rutile (110) surfaces. The numbers in parenthesis are the atom numbers of Ni in each NiO nanocluster in figure 4.8. Ni$_c$, Ni$_s$, O$_c$, O$_s$, and Ti$_k$ indicate atoms in the nanocluster or the surface.

<table>
<thead>
<tr>
<th>Distance / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anatase</strong></td>
</tr>
<tr>
<td>Ni$_c$-O$_s$</td>
</tr>
<tr>
<td>NiO</td>
</tr>
<tr>
<td>Ni$_2$O$_2$</td>
</tr>
<tr>
<td>Ni$_3$O$_3$</td>
</tr>
<tr>
<td>Ni$_4$O$_4$</td>
</tr>
</tbody>
</table>

For NiO nanoclusters deposited on anatase (001), the smallest NiO cluster results in two new bonds with the TiO$_2$ surface with distances of 1.75 and 1.91 Å. It is important to note that an O atom from the anatase surface is pulled out of the surface by Ni from the cluster by 0.26 Å that leads to a distortion of the surface of TiO$_2$ anatase (001); this distortion will be further discussed in later sections and in chapter 5. The same behavior is observed for the Ni$_2$O$_2$ nanocluster supported on anatase (001), where in this case the O atom is pulled out of the surface by 0.17 Å upon bonding to Ni. The number of new bonds in Ni$_2$O$_2$ deposited on TiO$_2$ anatase (001) is three.

The Ni$_3$O$_3$ cluster presents 11 new bonds when deposited on TiO$_2$ anatase (001). There are five bonds between Ni and O atoms, that lie in the range 1.93 – 2.20 Å while oxygen atoms from the cluster bond to Ti surface atoms with two bonds that are 1.90 Å long. The Ni$_4$O$_4$ cluster deposited on TiO$_2$ anatase (001) shows
six new bonds. In this case, the surface O atom is pulled out of the surface by 0.19 Å.

Within the Ni–O nanoclusters, the Ni–O distances are notably shorter compared to bulk NiO, for example, 1.95 Å in Ni₄O₄, compared to 2.10 Å in bulk NiO. Of the NiO nanoclusters adsorbed at anatase (001), the Ni₃O₃ nanocluster forms new intermetallic Ni–Ti bonds, with Ni–Ti distances in the range 2.71 – 2.87 Å, which are consistent with those in the bulk intermetallic NiTi alloy.

At the TiO₂ rutile (110) surface, the smallest NiO cluster bonds to the surface with six new bonds. The Ni atom from the cluster bonds with two bridging O atoms and one surface O atom, and the fourth metal–oxygen bond is from an O cluster atom that bonds to Ti surface atoms. The Ni₃O₃ nanocluster binds to the surface with nine new bonds. Five metal–oxygen bonds are from Ni cluster atoms to surface oxygen, and the last two are from cluster oxygen to surface Ti.

Ni₃O₃ deposition on rutile (110) results in formation of seven new bonds between the cluster and surface. Five bonds are between Ni cluster atoms and surface O atoms with the bond distances from 1.96 to 2.20 Å. The other two bonds come from O cluster atoms and Ti surface atoms, and their distance is 1.89 Å. The Ni₄O₄ cluster bonds to the rutile surface with eight new bonds where three of the cluster Ni atoms create four Ni–O bonds with bridging surface O atoms and one surface O atom, with the shortest distance being 1.96 Å and the longest distance being 2.22 Å. The other two bonds are from cluster O binding with surface Ti.

In each of the structures formed by NiO nanocluster adsorption at rutile (110), surface Ti atoms are pulled out of the surface layer after bonding to cluster oxygen. For the example of NiO adsorbed at rutile (110), this Ti atom is displaced by 0.48 Å. At the (110) surface, we also observe for all structures the formation of new intermetallic Ni–Ti bonds between cluster Ni and surface Ti, with the distances given in Table 4.5. The Ni–Ti distances we observe are consistent with those in the intermetallic NiTi alloy. Since the adsorption energies of NiO nanoclusters on the rutile (110) surface are more negative compared to those on anatase (001) for a given NiO cluster, we suggest that the presence of the new Ni–Ti bonds plays a role in further stabilization of the
heterostructure. The exception is the Ni$_3$O$_3$ nanocluster, where Ni–Ti bonds are formed at both TiO$_2$ surfaces and the adsorption energies at both surfaces are very similar.

4.2.2. Electronic Structure and Band Gap Modification in NiO Nanocluster Modified TiO$_2$

Figure 4.10 shows the electronic density of states (PEDOS) projected onto Ni 3d, Ti 3d and surface and nanocluster O 2p states for the NiO nanoclusters adsorbed on anatase (001) and on rutile (110). Examination of the PEDOS shows that due to the modification of the TiO$_2$ surfaces with NiO, nanocluster derived states are present at the top of the valence bands of the modified structure, which pushes the VB edge to higher energy when compared to the bare TiO$_2$ surface. In the experimental work, the VB-XPS spectroscopy data show that the VB edge moves to higher energy with NiO modification indicating a consistent description of the effect of nanocluster modification of TiO$_2$. We see this shift in the VB edge for modification of rutile and anatase.

Changes to the nature of the conduction band edge do show some dependence on the crystal form of TiO$_2$. For anatase (001) some NiO nanoclusters, for example Ni$_2$O$_2$, lead to the appearance of NiO nanocluster levels near the conduction band minimum. For rutile, the bottom of the conduction band is primarily composed of surface Ti 3d states.
We observe from our DFT calculation results that there is a maximum band gap reduction of 0.8 eV (for Ni$_4$O$_4$ at anatase (001)) from the band gap of pure TiO$_2$ and this is qualitatively comparable to the value determined by the valence band-XPS, in ref [25]; a comparison with experimental work will be presented in chapter 9. In the NiO/TiO$_2$ system since the valence band has been shifted to higher energy, the overall band gap of the composite is thus reduced compared to unmodified TiO$_2$. The consequence of reduced band gap will be induction of visible activity upon light absorption which will improve the overall efficiency of
the photocatalyst. It therefore appears that modifying TiO$_2$ with transition metal oxide nanoclusters, see also ref [26], and pushes the valence band edge to higher energy, which results in a reduction in the band gap. This provides a new approach to engineering the band gap in TiO$_2$.

Figure 4.9 shows the atomic structure of Ni$_4$O$_4$ adsorbed on rutile (110) in a (4x4) surface supercell and figure 4.11 presents the PEDOS. We want to investigate how the change in coverage of this representative NiO nanocluster impacts on the structure and electronic structure of modified rutile (110) surface. First the adsorption energy is -4.50 eV, again indicating a strong interaction between the nanocluster and the surface. When we compare the atomic structures for smaller supercell surface in Fig 4.8 with Ni$_4$O$_4$ modified cluster we can see that the change in coverage results in a different adsorption structure for the nanocluster, as one would expect. In particular the Ni atom that showed no interaction with the surface is now coordinated to nanocluster oxygen that binds to a surface Ti atom. The PEDOS shows that the surface modification with NiO in the bigger surface supercell gives similar results to the smaller surface supercell, where NiO derived states are present at the top of the VB, thus shifting the VB edge to higher energy.
Another factor which can affect the photocatalytic activity of TiO$_2$ is the oxidation state of the metal oxide surface modifier. A Bader charge analysis for the NiO nanoclusters deposited on anatase (001) and rutile (110) gives net charges on Ni that range from 8.7 to 8.9 electrons, which are consistent with an Ni$^{2+}$ oxidation state. For TiO$_2$ we computed net Bader charges of +1.3 electrons which is typical for the Ti$^{4+}$ oxidation state. The oxidation states of Ni and Ti are in agreement with those determined in experiment by XPS [2].

Finally, the nature of the VB and CB states in NiO-modified TiO$_2$ leads us to suggest that the electron and hole separation upon excitation will be enhanced over unmodified TiO$_2$, with holes localising on the NiO nanocluster and electrons on the TiO$_2$ surface. Thus, the charge carriers generated upon photo absorption will be spatially separated, leading to enhanced activity.

While the upwards shift in the VB energy with NiO modification is welcome for inducing visible light activity, there is a trade off in the photocatalytic activity, in that the rise in the VB edge to higher energy reduces the oxidative power of the NiO-TiO$_2$ heterostructure; we will discuss this in chapter 9 when we make a comparison with the experimental results.

4.2.3. Conclusions

We presented in this section the results for (NiO)$_n$ nanoclusters deposited on TiO$_2$ rutile (110) and anatase (001) surfaces. Adsorption of these nanoclusters results in strong energy gains, in the range of $-3.18$ to $-6.15$ eV. A detailed investigation of the geometry shows that in addition to the expected Ni-O interfacial bonds, the rutile (110) surface structure also shows the presence of metallic Ni-Ti bonds which leads to extra stabilization of the nanoclusters on rutile (110) compared with anatase (001). In both surfaces deposited clusters give a narrowing of the TiO$_2$ band gap due to the presence of NiO states at the top of the valence band of TiO$_2$. This has an impact on the photoactivities of the new material where visible light absorption and enhanced charge separation are predicted.
4.3. (CuO)n nanoclusters deposited on TiO₂: Effect of CuO Loading in the Mechanism of Visible-Light Photocatalytic Activity

In this section, we present our DFT results on heterostructures composed of (CuO)n nanocluster-modified rutile and anatase surfaces, using the same surfaces as in Section 4.2. Modification of TiO₂ by Cu²⁺ ion and CuO grafting is a potentially promising approach in regards of surface modification for visible light activation purposes [24-26]. In particular, Irie et al. have shown that Cu²⁺-grafted TiO₂ (Cu²⁺/TiO₂) prepared by the impregnation method has a strong oxidation ability for decomposing 2-propanol under visible-light irradiation [27]. This has been attributed to the formation of a new unoccupied electronic state lying below the TiO₂ conduction band arising from the presence of Cu²⁺ cations with a 3d⁹ electronic configuration; the presence of this electronic state allows for visible light absorption.

In collaboration with Tada and co-workers, we investigated models of this system to study in detail the effect of CuO nanocluster modification of rutile anatase and the CuO loading effects; we recall that Irie et al. do not provide any evidence of their claim that excitation from the TiO₂ VB to empty Cu²⁺ states is the origin of the visible light activity. We will demonstrate that the coverage of CuO nanocluster, here determined by the size of the nanocluster, on the TiO₂ surfaces is a crucial factor in determining the nature of the band edges and hence the mechanism of visible-light-induced photoexcitation.

4.3.1. Adsorption structures and geometries

Figure 4.12 presents the atomic structures of CuO, Cu₂O₂, Cu₄O₄ nanoclusters supported on rutile (110) and anatase (001) surfaces together with the resulting adsorption energies. The adsorption energies show that the CuO nanoclusters adsorb strongly to both TiO₂ surfaces, with the adsorption energies lying in the range from -2.19 to -5.38 eV and new cluster-surface interfacial bonds are created. The coverages of the CuO, Cu₂O₂ and Cu₄O₄ nanoclusters are: 0.64, 1.28 and 2.56 Cu atoms/nm² on rutile and 0.85, 1.70 and 3.41 Cu atoms/nm² on
Table 4.6 presents new surface-cluster Cu-O bond distances for CuO clusters absorbed on TiO$_2$ anatase (001) and rutile (110).

Figure 4.12 Atomic structures and adsorption energies (in eV) of (a) CuO, (b) Cu$_2$O$_2$, (c) Cu$_4$O$_4$ adsorbed on TiO$_2$ rutile (110) and (d) CuO, (e) Cu$_2$O$_2$, (f) Cu$_4$O$_4$ adsorbed on TiO$_2$ anatase (001) surface.

The CuO, Cu$_2$O$_2$ and Cu$_4$O$_4$ clusters supported on rutile (110) create two, five and six bonds between the surface and the nanocluster. For the smallest supported cluster the distance between the Cu atom and a surface 2-fold bridging O atom is 1.79 Å and the O from the nanocluster bonds to a previously 5-fold coordinated Ti surface atom with a Ti-O distance of 1.87 Å. For the Cu$_2$O$_2$ nanocluster three bonds are created between the nanocluster and O surface atoms with distances of 1.99, 2.15 and 1.89 Å. The other two bonds come from cluster O and Ti surface atom bonding with distances of 2.03 Å and 1.81 Å. The adsorption of the biggest Cu$_4$O$_4$ nanocluster resulted in four new cluster Cu to surface O bonds with distances of 1.95, 1.96, 2.21 and 2.19 Å and two bonds between cluster oxygen and surface Ti atom with a distance of 1.91 Å for both bonds. The geometries reveal a substantial distortion of Ti surface atoms that are bonded to cluster oxygen, with a previously 5-fold coordinated surface Ti atom pulled up by 0.29 Å for the smallest CuO nanocluster, 0.34 Å for Cu$_2$O$_2$ and 0.12 Å for the biggest Cu$_4$O$_4$ supported nanocluster.
Table 4.6 New surface-cluster Cu-O bond distances for CuO clusters absorbed on TiO$_2$ anatase (001) and rutile (110). The subscripts are the same as in table 4.5.

<table>
<thead>
<tr>
<th></th>
<th>Distances / Å</th>
<th>Rutile (110)</th>
<th>Anatase (001)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu$_c$-O$_s$(^{(a)})</td>
<td>O$_c$-Ti$_s$(^{(b)})</td>
<td>Cu$_c$-O$_s$(^{(a)})</td>
</tr>
<tr>
<td>CuO</td>
<td>1.79</td>
<td>1.87</td>
<td>CuO</td>
</tr>
<tr>
<td>Cu$_2$O$_2$</td>
<td>1.99; 2.15; 1.89</td>
<td>2.03; 1.81;</td>
<td>Cu$_2$O$_2$</td>
</tr>
<tr>
<td>Cu$_4$O$_4$</td>
<td>1.95; 1.96; 2.21; 2.19</td>
<td>1.91; 1.91;</td>
<td>Cu$_4$O$_4$</td>
</tr>
</tbody>
</table>

(CuO)$_n$ clusters supported on anatase (001) show a similar number of new bonds between the nanocluster and the surface. The smallest CuO cluster bonds to the surface with two new bonds: cluster oxygen bonds to surface Ti with a distance of 1.91 Å and cluster Cu bonds to surface oxygen with a distance of 1.78 Å. The supported Cu$_2$O$_2$ nanocluster bonds to the anatase (001) surface with three new bonds: two bonds between cluster CuO and surface Ti (1.94 Å and 2.08 Å) and one bond, with a distance of 1.79 Å, between cluster Cu and surface O. The adsorption of the biggest Cu$_4$O$_4$ cluster results in two new bonds from cluster oxygen to surface Ti surface atoms, with distances of 1.94 Å and 2.03 Å and an additional three bonds between cluster Cu and surface oxygen with distances of 1.91 Å, 1.91 Å and 1.88 Å. As a result of cluster adsorption on the surface, there are some distortions present. Namely terminal surface oxygens are pulled up by 0.2 Å (for CuO) and 0.13 Å (for Cu$_2$O$_2$) when bonding to Cu from the surface, similar to NiO nanocluster modification, so that this appears to be a general
phenomenon. Moreover surface Ti atoms are also distorted by 0.24 Å, 0.27 Å and 0.20 Å (from the smallest to biggest clusters) when bonding to O from the cluster.

4.3.2. Electronic Structure and Band Gap Modification

The PEDOS plots for CuO clusters supported on rutile (110) and anatase (001) are shown in figure 4.13. These PEDOS plots show some interesting behaviour as the size of the CuO clusters (that is the loading of CuO) adsorbed at both TiO$_2$ surfaces changes.

While the PEDOS of unmodified TiO$_2$ shows an O 2p derived valence band and Ti 3d states making up the conduction band, with a DFT+U valence-conduction band gap of 2.1 eV, CuO-modified TiO$_2$ changes the nature of the band edges. For the Cu$_2$O$_2$ cluster supported on rutile (110), we find an unoccupied Cu$^{2+}$ electronic state lying 1 eV below the TiO$_2$ conduction band edge, which would lead to a reduced band gap over pure TiO$_2$, by virtue of the position of the lowest empty electronic state lying lower in energy compared to unmodified TiO$_2$. Thus, similar to the conclusion of Irie et al [27], visible light absorption will result in the electron being promoted from the filled TiO$_2$ VB to the empty CuO states.
Figure 4.13 Electronic density of states projected (PEDOS) on Cu 3d for (a) CuO, (b) Cu$_2$O$_2$, (c) Cu$_4$O$_4$ adsorbed on TiO$_2$ rutile (110) and (d) CuO, (e) Cu$_2$O$_2$ (f) Cu$_4$O$_4$ adsorbed on TiO$_2$ anatase (001) surface.

However as the CuO nanocluster increases in size (to a Cu$_4$O$_4$ nanocluster) which increases the loading, we find that the VB edge shifts upwards due to the presence of filled CuO-derived states, while the empty CuO state moves to the conduction band of TiO$_2$. While this still results in a reduction in the energy gap over unmodified TiO$_2$, the mechanism for band gap reduction is different. Now the band gap reduction arises from the upwards shift of the VB edge with CuO nanocluster modification, similar to the mechanism discussed for TiO$_2$ and NiO nanocluster modifications of TiO$_2$ and the CB edge will be dominated by the empty Ti 3d states in the TiO$_2$ surface. This mechanism is in contrast to the work of Irie et al and the smaller CuO nanoclusters and highlights the nanocluster size (or loading) dependence of properties related to the electronic structure. Thus,
the nature of the band gap modification of TiO₂ can be tuned by the loading of the CuO nanocluster.

Some similarities are observed when the CuO nanoclusters are supported on anatase (001) but we have also found some differences when compared to modified rutile (110). Examining the PEDOS for CuO clusters supported on anatase (001) surfaces we see that the unoccupied CuO states lie deeper in the energy gap compared to the same nanoclusters adsorbed on rutile (110) and the shift in the valence band is less pronounced than for modified rutile (110), with the empty CuO continuing to lie below the CB edge of anatase (001). Thus a higher CuO loading than possible in these simulations may be required on anatase to modify the mechanism of visible light absorption. The Bader charges confirm the presence of Cu²⁺ cations in the nanoclusters, where for modified rutile (110) and anatase (001) with CuO nanoclusters the net charge of electrons is in the range from 9.83 to 10.09.

The band gap alignment will enhance an electron-hole separation after light absorption and where the electrons and holes localise will depend on the CuO nanocluster coverage. Holes would be localised on the TiO₂ surface while the electrons will be localised on the CuO cluster. These results are in line with work of Irie where empty Cu states are proposed to be present. However consideration of CuO cluster coverage on the rutile (110) surface in particular shows that as the cluster size increases (or the coverage of CuO in terms of ions per unit area increases), there is significant rise in the top of VB, which is up to ca. 0.7 eV for Cu₄O₄-modified rutile (110). Simultaneously the unoccupied Cu(II) states move upwards in energy to reach the conduction band minimum of TiO₂ and in this case unoccupied CuO states lie at TiO conduction band edge, so that holes will localise on the CuO nanocluster and electrons on the TiO₂ surface.

4.3.3. Conclusions

Simulations of TiO₂ modified with CuO nanoclusters show that this modification results in band gap reduction over modified TiO₂, but the change in the valence
or conduction band edges depends strongly on the CuO coverage and the crystal form of TiO$_2$. Thus, for smaller CuO nanoclusters on rutile (110) the density of states plots reveal the appearance of unoccupied Cu 3d levels in the midgap region with no effect on the VB. A larger coverage of CuO, induces CuO derived states at the top of valence band of TiO$_2$, thus reducing the energy gap but changing the mechanism. CuO-modified anatase (001) introduces unoccupied CuO states in the midgap region, with these states lying deeper in the gap compared to rutile (110).

These results are consistent with the experimental work of Tada in chapter 9, but are different from Irie et al., although the general impact of CuO modification of TiO$_2$ should be the same, namely the narrowing of original TiO$_2$ band gap. The experimental results for large coverages of CuO, where the CuO nanoclusters are of 2 – 5nm diameter, shows that the band gap reduces, exclusively as a result of an upwards shift of the VB edge with CuO loading and XPS shows the presence of CuO derived states in the valence band of TiO$_2$. Therefore we postulate as the size of the CuO nanocluster increases, the VB edge continues to shift upwards as a result of the CuO-TiO$_2$ interface interaction and the empty Cu$^{2+}$ electronic state also shifts upwards in energy, rising above the CB edge of TiO$_2$ at some cluster size. Thus, for CuO modified TiO$_2$, there can be two regimes – one in which the empty Cu$^{2+}$ states determine the change in band gap and a second in which the change in VB position due to CuO nanoclusters determines the change in band gap.
References:


5. p-block metal oxides nanocluster modified TiO₂ Photocatalysts

Many oxides from the p-block metals present interesting physical properties and show large number of technological applications. For example SnO nanoparticles are used in rechargeable batteries [1], while Bi₂O₃ is investigated due to its ionic conduction properties [2, 3]. Other applications include optical coatings [4], gas sensors [5] and solid oxide fuel cells [6]. In Sn, Pb and Bi the electronic configurations is such that the outermost ns subshell is filled, which would be 5s and 6s for Sn and Pb. For Bi, the 6s subshell is also filled. Sn and Pb also take a 4+ oxidation state, in which the 5s and 6s subshell is empty.

The presence of this filled ns subshell has an impact on the electronic and atomic structure. For example in SnO, after hybridization the Sn 5s electrons occupy an inert orbital [7] with a projection of the electron density asymmetrically on one side of the Sn atom [8] and this pair of electrons creates the well known sterochemical lone pair. This has an impact on the atomic structure resulting in asymmetric crystal structures for SnO and PbO, as well as in Bi₂O₃ which have been elegantly studied within DFT and experiment by Walsh and Watson and co-workers [9]. An important point is that the valence band edge in SnO and PbO is comprised of states arising from metal and oxygen interactions which allows, e.g. p-type conductivity. In contrast, the valence band edge in SnO₂ and PbO₂ is comprised of O 2p states, typical of metal oxides.

In this chapter we investigate p-block metal oxides SnO/SnO₂, PbO/PbO₂ and Bi₂O₃ supported on the TiO₂ rutile (110) and anatase (001) surfaces to examine: (a) band gap modification of TiO₂ upon surface modification with these metal oxides, (b) if there is any lone pair effect, when comparing Sn²⁺/Sn⁴⁺ and Pb²⁺/Pb⁴⁺ (c) if there is any sensitivity to the crystal form of TiO₂. The results in this chapter show some interesting and strong effects arising from the oxidation state of the metal in the modifying metal oxide and we discuss these in the following sections. Our results suggest a novel concept in photocatalyst materials design – namely exploiting the lone pair in p-block metal oxides to achieve band gap modification in a semiconducting metal oxide.

Please note that Section 5.1 (pp.118-125) is unavailable due to a restriction requested by the author.

CORA Cork Open Research Archive [http://cora.ucc.ie](http://cora.ucc.ie)
5.2. (SnO$_2$)$_n$ nanoclusters supported on TiO$_2$ rutile (110) and anatase (001)

We present in this section our DFT results of SnO$_2$ nanoclusters supported on rutile (110) and anatase (001). We are interested in studying: if the oxidation state of the metal in tin oxide nanoclusters has any impact on the band gap modification of modified TiO$_2$ surfaces and if there is any sensitivity to the TiO$_2$ crystal form. We will then present a comparison of results for SnO and SnO$_2$ modified TiO$_2$.

5.2.1. Adsorption structures and geometries

Figure 5.5 shows the atomic structures of representative SnO$_2$ nanocluster modified TiO$_2$ models, with the SnO$_2$ nanoclusters supported on rutile (110) and anatase (001) surfaces. The adsorption energies for the SnO$_2$ nanoclusters and the atomic structures of the free SnO$_2$ clusters are also shown.

![Figure 5.5 Atomic structure](image)

Figure 5.5 Atomic structure of (a) Sn$_2$O$_4$, (b) Sn$_3$O$_6$, (c) Sn$_4$O$_8$, and (d) Sn$_5$O$_{10}$ clusters adsorbed at the TiO$_2$ rutile (110) surface, (e) SnO$_2$, (f) Sn$_2$O$_4$, (g) Sn$_3$O$_6$ nanoclusters adsorbed at the TiO$_2$ (001) anatase surface, (d, e, f, and g) atomic structures of free Sn$_3$O$_6$, Sn$_4$O$_8$, Sn$_2$O$_4$, and Sn$_5$O$_{10}$ clusters.
While examining the adsorption energies presented on the figure 5.5 we see that adsorption of SnO$_2$ clusters at either TiO$_2$ surface leads to a large gain in energy. For SnO$_2$ nanoclusters supported on rutile (110), the energy gain is in the range from $-4.44$ to $-7.26$ eV and for SnO$_2$ nanoclusters on anatase (001) the energy gain is in the range from $-3.32$ to $-5.29$ eV. We therefore expect that these nanoclusters will remain adsorbed at the TiO$_2$ surfaces and experimental results show that this is indeed the case.

Table 5.2 presents the bond lengths between the SnO$_2$ nanoclusters and the TiO$_2$ rutile (110) and anatase (001) surfaces. For the structures with the most negative adsorption energy, namely Sn$_2$O$_4$ and Sn$_3$O$_{10}$ nanoclusters supported on rutile (110), the nanoclusters bind to the surface with seven and six new bonds, respectively. Sn atoms from these nanoclusters bond to O atoms from the surface with distances in the range 2.01–2.36 Å, and other bonds between O atoms from the cluster and Ti from the surface have distances which are in the range of 1.89–1.98 Å.

The Sn$_3$O$_6$ and Sn$_4$O$_8$ nanoclusters show less negative adsorption energies, with Sn$_3$O$_6$ creating five new bonds after adsorption on rutile (110) and the adsorption of Sn$_4$O$_8$ results in four new bonds. For Sn atoms from the clusters which bond to O atoms from the surface, the Sn-O distances are in the range from 1.97 to 2.17 Å, while the bonds between O atoms from the cluster and Ti atoms from the surface have distances from 1.83 to 2.19 Å.

In terms of any major distortions to the rutile (110) surface, we noticed that for all SnO$_2$-rutile heterostructures there is significant change in the position of of the 5-fold Ti surface atoms that bind to O atoms from the cluster. These atoms are pulled upward or downwards by 0.3–0.6 Å due to bonds with O cluster atoms, however there is no displacement of bridging O atoms from the rutile (110) heterostructures.

For SnO$_2$-anatase heterostructures there are new bonds between the nanoclusters and the anatase (001) surface. The smallest SnO$_2$ nanocluster creates three new bonds. Sn from the nanocluster bonds to oxygen from the surface with distance of 2.17 Å and there are a further two bonds between nanocluster oxygen and Ti
surface atoms with distances of 1.78 and 1.77 Å. The adsorption of the larger Sn$_2$O$_4$ and Sn$_3$O$_6$ nanoclusters at anatase (001) creates five new bonds. Distances between Sn nanocluster atoms and surface oxygen are in the range 1.99 – 2.33 Å, and the Ti–O distances for oxygen in the nanocluster to Ti in the surface are in the range of 1.82 – 1.94 Å. In anatase (001), the adsorption of SnO$_2$ nanoclusters results in two surface oxygen atoms being displaced due to bonding with atoms in the nanocluster. This is in contrast with the rutile (110) surface where there are no distortions to the surface oxygen atoms. However, in rutile (110), surface Ti atoms experience a distortion and displacement when they interact with oxygen in the nanoclusters, which is not the case for the anatase (001) surface. In all heterostructures, Sn atoms are 4- and 5-fold coordinated and O atoms in the clusters are 1-, 2-, and 3-fold coordinated, providing low coordinated sites that will be important for subsequent interaction with molecules.

Table 5.2 New surface-cluster Ti-O bond distances for: SnO$_2$ clusters on TiO$_2$ rutile (110) and anatase (001) surfaces.

<table>
<thead>
<tr>
<th></th>
<th>Rutile</th>
<th>Anatase</th>
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<tbody>
<tr>
<td></td>
<td>$\text{Sn}_n$-$\text{O}_s$ $^{(a)}$</td>
<td>$\text{O}_c$-$\text{Ti}_i$ $^{(b)}$</td>
</tr>
<tr>
<td>Sn$_2$O$_4$</td>
<td>2.31 (Sn1)</td>
<td>1.92</td>
</tr>
<tr>
<td></td>
<td>2.16 (Sn1)</td>
<td>1.98</td>
</tr>
<tr>
<td></td>
<td>2.15 (Sn2)</td>
<td>1.92</td>
</tr>
<tr>
<td></td>
<td>2.36 (Sn2)</td>
<td></td>
</tr>
<tr>
<td>Sn$_3$O$_6$</td>
<td>1.99 (Sn1)</td>
<td>1.95</td>
</tr>
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<td></td>
<td>2.14 (Sn1)</td>
<td>2.17</td>
</tr>
<tr>
<td></td>
<td>1.99</td>
<td></td>
</tr>
<tr>
<td>Sn$_4$O$_8$</td>
<td>2.11 (Sn1)</td>
<td>1.83</td>
</tr>
<tr>
<td></td>
<td>2.05 (Sn3)</td>
<td>2.19</td>
</tr>
<tr>
<td></td>
<td>1.97 (Sn3)</td>
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</tr>
<tr>
<td>Sn$<em>5$O$</em>{10}$</td>
<td>2.01 (Sn1)</td>
<td>1.89</td>
</tr>
</tbody>
</table>

\[distances \text{ Å} \]
2.11 (Sn5) 1.94
2.13 (Sn5) 1.89

5.2.2. Electronic structures and band gap modification

Figure 5.6 presents the PEDOS for Ti 3d and Sn 5s states of SnO₂ nanoclusters supported on the TiO₂ surfaces, and the Bader charges on the Sn nanocluster atoms. We use PEDOS plots in order to investigate changes to the band gap of pure TiO₂ rutile (110) and anatase (001) as a result of nanocluster modification. We have already shown in previous chapters that this analysis gives a reasonable indication of the change in the valence-conduction band energy gap.

On both surfaces Sn always takes 4+ oxidation state which is confirmed in figure 5.6 (h) with Bader charges results and this is also consistent with experiment. From figure 5.6 we notice that for modified rutile (110) there are the unoccupied SnO₂ states lying just below the rutile (110) conduction band. For the Sn₂O₄ and Sn₃O₈ nanoclusters, the empty SnO₂ states lay only 0.2 eV below the CB of TiO₂ while for the Sn₃O₆ and Sn₅O₁₀ nanoclusters, the SnO₂ states show a slightly larger offset from the CB edge of TiO₂. The presence of SnO₂ derived states at rutile (110) conduction band should improve the light absorption; however comparison with FeOₓ-modified TiO₂, for example [12], suggests that there should be no or little reduction in the energy gap of SnO₂-modified TiO₂.

On comparing SnO₂-modified rutile with SnO₂-modified anatase we find that for anatase there are no SnO₂ states found in the band gap. The SnO₂ states lie well below the valence band (VB) and above the conduction band (CB) edges of anatase, so that there will be no reduction in the energy gap of anatase. However this is not necessarily a negative result and it can induce an enhancement of UV activity because electrons can be excited to the empty cluster states under UV light. However, in comparison with rutile this activity should be significantly smaller. In the final conclusions we discuss further this difference between rutile and anatase modified with SnO₂ nanoclusters.
Figure 5.6 Electronic density of states for Ti 3d and Sn 5s for (a) Sn$_2$O$_4$, (b) Sn$_3$O$_6$, (c) Sn$_4$O$_8$, and (d) Sn$_5$O$_{10}$ modified TiO$_2$ rutile and (e) SnO$_2$, (f) Sn$_2$O$_4$, (g) Sn$_3$O$_6$ modified TiO$_2$ anatase (001), (h) Bader charges on cluster Sn atoms.
5.3. PbO and PbO$_2$ nanoclusters Supported on TiO$_2$ Surfaces – the role of the oxidation state of the metal

In this section we present our results of the modification of TiO$_2$ rutile (110) and anatase (001) with PbO and PbO$_2$ nanoclusters, continuing our investigations of p-block metal oxides. We want to examine if lead oxides supported on TiO$_2$ will impact the band gap of bare TiO$_2$ surface and if the oxidation state of Pb has any impact on TiO$_2$ band gap properties (which was quite apparent comparing SnO and SnO$_2$) and make a comparison between the lone pair effects in PbO and SnO, which are stronger for SnO than PbO.

5.3.1. Adsorption structures and geometries

In figure 5.7 we present the relaxed atomic structures of PbO nanoclusters, PbO, Pb$_2$O$_2$, Pb$_4$O$_4$, and PbO$_2$ nanoclusters, Pb$_2$O$_4$, Pb$_3$O$_6$, Pb$_4$O$_8$, supported on the model rutile (110) surface and the adsorption energies for each structures. From figure 5.7 we see that all clusters adsorb strongly at the surface with adsorption energies in the range from -2.81 eV to -7.16 eV. Moreover all heterostructures create new interfacial metal-oxygen bonds. Table 5.3 presents the details of the new metal-oxygen bonds between the nanoclusters and the rutile (110) surface.

The adsorption of the smallest PbO nanocluster supported on rutile (110) results in three new bonds. Pb in the nanocluster bonds to two surface oxygen with Pb-O distances of 2.25 Å and 2.45 Å while the third bond between oxygen from the nanocluster and Ti in the surface is 1.80 Å. The Pb$_2$O$_2$ nanocluster adsorbed on rutile (110) creates seven new bonds and five of them are between Pb atoms and surface oxygen with the Pb-O distances in the range from 2.26 Å to 2.61 Å. The last two bonds between O cluster atoms and Ti surface atoms have Ti-O distances of 1.78 Å and 1.9 2Å. For the biggest Pb$_4$O$_4$ nanocluster, adsorption on rutile (110) results in five new bonds: three bonds between Pb in the nanocluster and surface oxygen, with Pb-O distances of 2.31 Å, 2.45 Å and 2.55 Å. The remaining two bonds from oxygen in the nanocluster and Ti in the surface have Ti-O distances of 1.89 Å.
For the PbO₂ nanoclusters adsorbed on rutile (110) there are also new interfacial bonds formed. For Pb₂O₄ and Pb₃O₆ nanoclusters, adsorption on rutile (110) gives seven new bonds: four bonds from Pb nanocluster atoms and O surface atoms, with Pb-O distances in the range from 2.29 Å to 2.52 Å and three bonds from nanocluster oxygen and surface Ti atoms with Ti-O distances in the range 1.85 Å - 1.99Å. The largest number of new bonds is found upon adsorption of the Pb₄O₈ nanocluster, with five new bonds between Pb atoms in the nanocluster and oxygen in the surface with Pb-O distances in the range from 2.15 Å to 2.65 Å and four other bonds from oxygen in the nanocluster and Ti atoms in the surface, with Ti-O distances from 1.82 Å to 2.06 Å.

While comparing the Pb-O distances in the clusters with those in the bulk we can see that for nanoclusters Pb-O are from 2.25 Å to 2.55 Å while the bulk Pb-O distance from the literature is 2.35 Å in litharge and 2.63 Å in rocksalt [16] structures. We also observe in all new structures significant displacements of Ti atoms in the surface that are pulled out of the surface layer when they bond to oxygen from the nanocluster. These displacements are 0.74 Å for the smallest PbO nanocluster to 0.91 Å for the biggest Pb₄O₈ nanocluster.

![Figure 5.7 Relaxed adsorption structures with adsorption energies given in eV for (a)PbO, (b)Pb₂O₂, (c)Pb₄O₄, (d)Pb₂O₄, (e)Pb₃O₆ and (f) Pb₄O₈ nanoclusters supported on TiO₂ rutile (110).](image)

![Table 5.3 New surface-cluster Pb-O bond distances for (PbO)n and (PbO₂)n nanoclusters absorbed on TiO₂ rutile (110).](table)
Distances / Å

<table>
<thead>
<tr>
<th></th>
<th>( \text{Pb}_{c} - \text{O}_s^{(a)} )</th>
<th>( \text{O}_c - \text{Ti}_s^{(b)} )</th>
<th>( \text{Pb}_{c} - \text{O}_s^{(a)} )</th>
<th>( \text{O}_c - \text{Ti}_s^{(b)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{PbO} )</td>
<td>2.25; 2.45</td>
<td>1.80</td>
<td>2.29; 2.52; 2.48; 2.29</td>
<td>1.96; 1.99; 1.96</td>
</tr>
<tr>
<td>( \text{Pb}_2\text{O}_2 )</td>
<td>2.52; 2.60; 2.56; 2.61, 2.26</td>
<td>1.93; 1.78</td>
<td>2.44; 2.30; 2.44; 2.30</td>
<td>1.91; 1.99; 1.85</td>
</tr>
<tr>
<td>( \text{Pb}_4\text{O}_4 )</td>
<td>2.31; 2.45; 2.55</td>
<td>1.89; 1.88</td>
<td>2.15; 2.23; 2.65; 2.39; 2.33</td>
<td>1.91; 2.02; 1.82; 2.06</td>
</tr>
</tbody>
</table>

[a] Pb from the cluster \( (\text{Pb}_c) \) and O from the surface \( (\text{O}_s) \) [b] O from the cluster \( (\text{O}_c) \) and Ti from the surface \( (\text{Ti}_s) \)

5.3.2. Electronic structures and band gap modification

In figure 5.8 we present the electronic density of states (PEDOS) projected onto the Pb 6s and O 2p states of the supported PbO and PbO\(_2\) nanoclusters and the Ti 3d and O 2p states of the rutile (110) surface. We use PEDOS plots to investigate the band gap changes as a result of modifications to the valence and conduction band edges due to adsorption of the lead oxide nanoclusters.
Figure 5.8 Electronic density of states projected (PEDOS) onto Pb 6s, O 2p states of the PbO and PbO₂ clusters and Ti3d, O 2p states of the rutile (110) surface.

The PEDOS shows that the smallest PbO nanocluster has no impact on TiO₂ rutile (110) band gap and there are no new states in the band gap. However Pb₂O₂ nanocluster modification of rutile (110) results in the presence of cluster derived Pb and O states at the top of the VB. For the biggest (PbO)₄ nanocluster, there is the obvious appearance of PbO derived electronic states above the VB edge of TiO₂. The introduction of these PbO derived electronic states gives a reduction in the energy gap of TiO₂ without changing the position of the conduction band edge. In the resulting structure, the valence band edge lies higher in energy which will result in a reduction of the original TiO₂ band gap. This VB edge shift grows together with nanocluster size and for the biggest investigated Pb₄O₄ nanocluster supported on TiO₂ we obtain an indicative VB shift of 1eV compared to original TiO₂ band gap, which would result in visible light absorption.

In comparison to this, if we consider the PbO₂ nanoclusters, there is no change at all in the region of the valence band of TiO₂ for all PbO₂ supported nanoclusters. We find new electronic states derived from the empty Pb 6s states lying in the energy gap, well below the conduction band edge of TiO₂. This is different to
other systems we have studied but may still be a positive modification, since the presence of these states can reduce the energy gap over bare TiO$_2$, since Pb 6s states can function as states into which an electron from the (unmodified) TiO$_2$ valence band can be excited. However with the empty Pb states lying ca. 0.9 eV above valence band edge, this does suggest that DFT energy gap underestimation is important here, so that we can only state that the PEDOS in this case is a reasonable indicator that PbO$_2$ modification of TiO$_2$ does lead to a reduction in the energy gap.

Comparing the PEDOS plots for PbO and PbO$_2$ nanoclusters supported on rutile (110) we conclude that in both cases the reduction of the original TiO$_2$ band gap will occur which should lead to induction of visible light absorption and electron/hole separation (since the VB and CB edges have different origins) and due to different changes in the VB and CB edges with PbO or PbO$_2$, the mechanism of the band gap reduction will be different. This can be explained that since after excitation of PbO-TiO$_2$, the electron will be found in the surface and the hole on the nanocluster, while for PbO$_2$-TiO$_2$, the electron will be found on the PbO$_2$ nanocluster and the hole on the rutile surface, giving different mechanisms for electron-hole separation after photoexcitation.

We also investigated Bader charges on Pb and for PbO-TiO$_2$ nanoclusters are +1.20 electrons and in the PbO$_2$ nanoclusters, we computed Pb charges around +0.58 electrons.

### 5.3.3. PbO and PbO$_2$ nanoclusters on anatase (001)

Figure 5.9 presents the atomic structures of representative PbO and PbO$_2$ nanoclusters supported on the TiO$_2$ anatase (001) surface. The purpose of this investigation is to examine if the different crystal of TiO$_2$ can impact the properties after metal oxide cluster deposition, in a similar fashion of modification with SnO$_2$. Comparing to figure 5.8 we can see that the adsorption energies are similar to modified rutile (110) surfaces with a similar number of new interfacial bonds between the nanoclusters and the surface. We show the detailed metal-oxygen distances in table 5.4. After comparison with modified
rutile (110), we conclude that the metal-oxygen distances between nanoclusters and surface atoms are similar to those for modified rutile.

![Relaxed adsorption structures](image1)

Figure 5.9 Relaxed adsorption structures with adsorption energies given in eV for (a)Pb$_2$O$_2$, (b)Pb$_2$O$_4$ clusters on TiO$_2$ anatase (001).

<table>
<thead>
<tr>
<th>Distances / Å</th>
<th>Pb$_c$-O$_s$ (a)</th>
<th>O$_c$-Ti$_s$ (b)</th>
<th>Pb$_c$-O$_s$ (a)</th>
<th>O$_c$-Ti$_s$ (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$_2$O$_2$</td>
<td>2.45; 2.45; 2.45; 2.44</td>
<td>1.92; 1.92</td>
<td>Pb$_2$O$_4$</td>
<td>2.11</td>
</tr>
</tbody>
</table>

[a] Pb from the cluster (Pb$_c$) and O from the surface (O$_s$) [b] O from the cluster (O$_c$) and Ti from the surface (Ti$_s$).

In figure 5.10 we present the PEDOS projected onto the Pb 6s and O 2p states of the nanocluster and the surface and Ti 3d and O 2p states of anatase (001) after modification with PbO and PbO$_2$ nanoclusters. When comparing to modified rutile (110), we can see the same trends: the PbO nanocluster introduces new states at the top of the valence band of anatase (001), while the PbO$_2$ nanocluster results in new states below the original conduction band of anatase (001). Thus,
for PbO and PbO$_2$ nanocluster modified TiO$_2$ we find no crystal structure sensitivity. In contrast, we showed in Section 5.2 that modifying rutile or anatase with tin oxide, SnO$_2$, nanoclusters results in a strong crystal sensitivity. For SnO$_2$ nanocluster modified TiO$_2$, a positive effect on the visible light photocatalytic activity was only seen for rutile$^{31}$ while anatase modification gave no changes in anatase band gap. This difference can be explained that for SnO$_2$ and PbO$_2$ modifications since the PbO$_2$ energy states lie lower in energy than the SnO$_2$ energy states and will create new electronic states in the original energy gaps of both TiO$_2$ surfaces. There is no obvious difference between rutile and anatase modified SnO or PbO.

![Figure 5.10](image)

Figure 5.10 The electronic density of states projected (PEDOS) onto Pb 6s of the PbO and PbO$_2$ clusters and Ti 3d of the anatase (001) surface.

5.3.4. Discussion on Rutile and Anatase TiO$_2$ Modified with PbO, PbO$_2$, SnO and SnO$_2$ Nanoclusters

In the first two sections of this chapter, we investigated (a) band gap changes in TiO$_2$ upon modification with tin and lead oxide nanoclusters, (b) the importance of the lone pair and metal oxidation state in tin and lead oxides and (c) the crystal sensitivity.
We found that SnO modification of TiO$_2$ anatase (001) and rutile (110) resulted in a band gap reduction due to the lone-pair present in the SnO nanoclusters. Moreover a comparison of anatase (001) and rutile (110) surfaces shows no crystal structure sensitivity. We propose that due to this reduction the material activity will move to the visible region and present valence-conduction band setup will improve electron/hole separation. These results show a novel approach for band gap reduction and charge separation by using the presence of lone-pair in nanoclusters of SnO that lie at the top of the valence band, rather than the highly localised O 2p states in other oxides.

We also studied the modification of TiO$_2$ rutile (110) and anatase (001) with SnO$_2$ nanoclusters. Here the surface modification of rutile TiO$_2$ leads to a great increase in its UV light activity, with no significant visible light activity. In contrast, for modified anatase (001) there is no effect, with no change to the TiO$_2$ energy gap or the nature of the VB and CB edges. Our DFT simulations reveal the origin of these significant differences. The PEDOS plots for rutile (110) modified with SnO$_2$ nanoclusters result in presence of SnO$_2$ states at the conduction band edge which increases light absorption and enhances charge separation. In contrast, for anatase, SnO$_2$ states lie above the TiO$_2$ CB which will only slightly improve UV light absorption. Our results are consistent with the experiment.

We have examined modification TiO$_2$ rutile (110) and anatase (001) surfaces with PbO and PbO$_2$ nanoclusters in a similar fashion to SnO and SnO$_2$. Our results show that due to modification of rutile (110) and anatase (001) surfaces with PbO and PbO$_2$ nanoclusters the band gap of TiO$_2$ is predicted to be reduced when compared to unmodified TiO$_2$, with visible light activity predicted. However the mechanism of band gap reduction and charge separation highlights some interesting effects due to the two Pb oxidation states.

The results of PbO nanoclusters supported on rutile (110) and anatase (001) gives a reduction in the TiO$_2$ band gap due to the introduction of electronic states from the nanoclusters above the TiO$_2$ valence band edge. While PbO$_2$ nanocluster
modification also gives a reduction of the TiO$_2$ band gap, it presents a striking difference in terms of the mechanism of band gap reduction and the nature of the valence and conduction band edges. Here new, empty PbO$_2$ states are found below the CB edge of TiO$_2$ (somewhat similar to CuO modified TiO$_2$) so that excitation is to the empty PbO$_2$ electronic states.

In light of these results we postulate that the oxidation state of the metal in the modifying oxide nanocluster can play an important role in tuning the properties of photocatalyst. For the lone pair effect, we found that for SnO-modified TiO$_2$, a strong effect on the energy gap is present and the valence band edge which derived from the Sn-6s-O2p interaction in the nanocluster is shifted upwards. For PbO, the shift of the TiO$_2$ band gap is due to the presence of Pb-6s-O-2p derived states from the PbO nanocluster pushing up the valence band edge. However the photoexcited states calculations suggest that the effect of the lone-pair is smaller compared to SnO-modified TiO$_2$, since the hole formed after photoexcitation is now also localised on oxygen in the nanocluster. Comparison with bulk indicates that the weakening of the lone pair effect is similar to bulk SnO and PbO [17] see chapter 6. We compared the properties of PbO and PbO$_2$-modified rutile (110) and anatase (001) for any crystal structure sensitivity which we found for SnO/SnO$_2$ modified anatase, we conclude that there is no sensitivity to crystal structure for lead oxide modified TiO$_2$. 
5.4. Bi$_2$O$_3$ nanoclusters supported on rutile (110) – the role of the Bi$^{3+}$ stereochemical lone pair

In this section we present our results from first principles simulations of Bi$_2$O$_3$ nanoclusters supported on the rutile (110) surface. Our DFT results show that the band gap of rutile can be reduced by modification with Bi$_2$O$_3$ nanoclusters, but the lone-pair effect arising from Bi$^{3+}$ is minimal, which is consistent with the weaker lone pair effect in bulk Bi$_2$O$_3$, compared with bulk SnO.

5.4.1. Adsorption structures and geometries

In figure 5.11 we present representative relaxed atomic structures of representative Bi$_2$O$_3$ nanoclusters supported on rutile (110) and their adsorption energies. The Bi$_2$O$_3$ and Bi$_4$O$_6$ nanoclusters adsorb strongly at the rutile (110) surface with large adsorption energies of -5.76 eV and -5.18 eV. The adsorption of nanoclusters results in creation of new interfacial metal-oxygen bonds. The magnitude of these energies indicates that the nanoclusters will not aggregate into large particles or films [Chapter 4.1]. The details of the new metal-oxygen bonds between the nanoclusters and the surface are presented in table 5.5.

![Image of adsorption structures](image)

Figure 5.11 Relaxed adsorption structures with adsorption energies given in eV for (a)Bi$_2$O$_3$, (b)Bi$_4$O$_6$ clusters on TiO$_2$ rutile (110).
For the smaller Bi$_2$O$_3$ nanocluster, there are three new bonds between oxygen from the cluster and Ti from the surface, with O-Ti distances of 1.91 Å to 2.10 Å. For the larger Bi$_4$O$_6$ nanocluster adsorbs at rutile (110) surface creating five new bonds: There are two bonds from Bi atoms bridging surface oxygen, with Bi-O distances of 2.17 Å and the other three new bonds are between cluster oxygen and previously 5-fold coordinated Ti surface atoms, with Ti-O distances in the range of 1.83 Å to 2.05 Å. In the bulk Bi$_2$O$_3$ the Bi-O distances are in the range of 2.19 Å to 2.59 Å and are longer than Bi-O distances of nanoclusters. This arises from the lower coordination of Bi in the nanoclusters compared to bulk.

Table 5.5 New surface-cluster Bi-O bond distances for Bi$_2$O$_3$ clusters absorbed on TiO$_2$ rutile (110).

<table>
<thead>
<tr>
<th>Distances / Å</th>
<th>Bi$_2$-Os$^a$</th>
<th>O$_c$-Ti$_s$$^b$</th>
<th>Bi$_4$-Os$^a$</th>
<th>O$_c$-Ti$_s$$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$O$_3$</td>
<td>1.93; 2.10; 1.91</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi$_4$O$_6$</td>
<td>2.17; 2.17</td>
<td>1.91; 2.05; 1.83</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[a] Bi from the cluster (Bi$_c$) and O from the surface (O$_s$) [b] O from the cluster (O$_c$) and Ti from the surface (Ti$_s$).

5.4.2. Electronic structure and band gap modification

Figure 5.12 shows the electronic density of states (PEDOS) projected onto Bi 6s and O 2p states of the Bi$_2$O$_3$ nanoclusters and Ti 3d and O 2p states of the modified rutile (110) surface. We use PEDOS plots in order to investigate any band gap changes due to adsorption of the Bi$_2$O$_3$ nanoclusters on rutile (110).

For the smaller Bi$_2$O$_3$ nanocluster supported on rutile (110) we see that modification with Bi$_2$O$_3$ makes no change in the energy gap of TiO$_2$, since the Bi
6s and Bi-derived O 2p states lie below the VB edge of TiO₂ and would therefore we do not expect any modification in the energy gap. We compare the VB-CB gap in unmodified and Bi₂O₃-modified TiO₂ and we find that it is unchanged at 2.1 eV in both cases.

For the larger Bi₄O₆ nanocluster we find that modification of TiO₂ introduces new states derived from Bi₂O₃ into the band gap of rutile (110). The new states are from the Bi 6s-O2p interaction in the nanocluster and the PEDOS also indicates a Bi 6s-O 2p interaction involving surface oxygen. The energy of the valence band is pushed to higher energy by these states which are found above the valence band edge of TiO₂ rutile (110) and this will impact the original TiO₂ band gap by reducing it, while leaving the conduction band edge unmodified. Reduction of TiO₂ band gap may cause visible light absorption upon photoexcitation although we estimate this reduction in the energy gap may not be sufficient to allow visible light absorption.

![Figure 5.12 Electronic density of states projected (PEDOS) onto Bi 6s, Ti 3d and O2p (from the nanoclusters and the surface) states for (a) Bi₂O₃, (b) Bi₄O₆ clusters supported on TiO₂ rutile (110) surface.](image)

We analysed the composition of the valence and conduction band in Bi₄O₆ modified rutile. The valence band comes from Bi 6s and O 2p due to the Bi 6s
lone pair affect while the conduction band edge is derived from Ti 3d states from surface of TiO₂. Therefore we propose that the valence-conduction band composition will enhance electron/hole separation after photoexcitation and improve the effectiveness of this proposed photocatalyst compared to unmodified TiO₂. Results of (Bi₂O₃) nanoclusters supported on rutile (110) are similar to other metal oxide nanoclusters supported on rutile (110) such as SnO, NiO and FeO, as discussed in the literature.

5.4.3. Discussion and Conclusions

In this chapter we have presented the results of a first principles analysis of modification of TiO₂ rutile (110) and anatase with nanoclusters of p-block metal oxides, namely tin, lead and bismuth oxides. The purpose of these simulations is to investigate changes in the band gap and the nature of the valence and conduction band edges of modified TiO₂ compared to unmodified TiO₂. In addition, we have been able to investigate interesting question such as the importance of the lone-pair effect in Sn, Pb and Bi as a new means to modify the electronic properties of TiO₂, both light absorption and charge carrier separation. Finally, the question of the effect of the crystal form of TiO₂ was also investigated by comparing rutile and anatase modified with oxide nanoclusters.

We find that SnO and PbO modified rutile and anatase, in which the metals have a filled 5s and 6s subshell, will push the valence band edge to higher energy which will lead to a band gap reduction. The lone pair in SnO and PbO is key to this modification and results in predicted electron and hole separation upon excitation (this will be further examined in the next chapter). Significant upwards shifts of the VB edge that will induce visible light absorption are predicted. Rutile modified with Bi₂O₃ also appears to be promising, in that there is a band gap reduction. However, the weaker lone pair effect in Bi³⁺, compared with Sn²⁺ and Pb²⁺ means that this change in the energy gap is not so large, probably not larger enough to induce visible light absorption.
A different scenario is present when we compare SnO$_2$ and PbO$_2$ modified rutile and anatase. Experimentally, SnO$_2$ modified rutile and anatase behaves differently and show different photocatalytic activities. Our simulations are able to show that SnO$_2$ modified anatase has no change to the VB or CB positions and thus the band gap while SnO$_2$ modified rutile shows some change to the CB edge, which will induce a higher level of photocatalytic activity since charge separation will be predicted. PbO$_2$ modified rutile and anatase on the other hand show no effects arising from the crystal form of TiO$_2$. The results in this chapter are very promising in showing the potential to use different p-block metal oxides to tune the properties of new photocatalyst materials, not just TiO$_2$. 
References:


6. Modelling Photoexcitation in Metal Oxide Nanocluster Modified TiO$_2$ Surfaces

6.1. Modelling Charge Separation after Light Excitation in TiO$_2$ Modified with TiO$_2$ Nanoclusters

In previous chapters we analysed models of TiO$_2$ surfaces modified with metal oxide nanoclusters and focussed on the structures of these systems and their electronic properties, in particular the electronic density of states to obtain information of how surface modification affects the light absorption properties. We have also used the EDOS to conclude the likely location of the electrons and holes that form after photoexcitation. In this chapter, we will examine a model of the photo-excited state of metal oxides nanoclusters supported on rutile (110) and anatase (001) surfaces, using the structures obtained in the previous chapters. We will show that that this modification will indeed result in a band gap reduction over unmodified TiO$_2$ and focus on the nature of the photo-excited state and charge separation.

While experiments of surface modified TiO$_2$ with nanoclusters [1-3] generally show visible light absorption and improved photoactivity, we still need to understand the origin of these findings. The former is well explained by data from valence band XPS [4] and our modelling results [2,5-7] and section 4.5, both showing a rise in the valance band edge or a small downwards shift in the CB edge.

The improved activity is attributed to reduced recombination of electrons and holes that are formed after photoexcitation. Experimentally, this is usually characterised by photoluminescence [8], in which the structure is excited and emission from charge carrier recombination is monitored at specific energies characteristic of particular defects, such as oxygen vacancies. A reduction in the PL intensity of modified TiO$_2$ signifies a reduction in a particular charge recombination event, when compared with bare TiO$_2$ [8]. In the experiments of references [1-2, 4, 5] a reduced PL intensity is observed for electron-hole recombination in modified anatase and rutile, which, when coupled to improved
activity for dye degradation supports the idea that these heterostructures facilitate electron and hole separation, thus reducing the opportunities for charge recombination.

From our DFT simulations in chapters 4 and 5, we proposed that the composition of the valence and conduction band edges gives a good indication of the location of excited electrons and holes after excitation. In particular, in most cases, the electrons and holes would be expected to localised onto the TiO$_2$ surface and the nanocluster. This separation of electrons and holes would reduce charge recombination – electrons in the surface and holes in the cluster will be spatially separated compared with electrons and hole on an unmodified TiO$_2$ surface (with a similar analysis for the case where the electrons would localise onto the nanocluster and holes onto the surface). For this study we have chosen to use a physically reasonable model for the excited state which involves generating a triplet electronic state and by construction will have an unpaired electron and an unpaired hole, which will localise onto particular sites, thus giving a model of electron and hole localisation and separation upon photoexcitation. This model appears to be a useful model system to study photoexcited metal oxides as shown in a number of papers on TiO$_2$ and HfO$_2$ [9-11].

The triplet electronic state results in an electron being promoted to the conduction band and a hole is present in the valence band. With this model we can compute the vertical singlet-triplet energy (corresponding to the VB-CB difference), the relaxed singlet-triplet energy (loosely thought of as an excitation energy) and the triplet relaxation energy (that is the energy gain when the electron and hole localise). In this chapter, we will examine this energetics for our heterostructures and compare to unmodified rutile and anatase TiO$_2$ and also the nature and location of the electron and hole formed after excitation, which allows us to draw some conclusions regarding charge separation in these structures.
6.1.1. Energetics, Geometry and Electronic structure of the Photoexcited State of TiO2 Modified with TiO2 Nanoclusters

In this section, we focus on the energetics of the excited state and the geometry and electronic properties and the relationship to photocatalytic properties of TiO2 nanocluster modified rutile TiO2 (110). The vertical and singlet-triplet excitation energies and relaxation energies for TiO2 nanocluster modified TiO2 and the bare rutile (110) surface are presented in table 6.1.

The computed DFT+U excitation energy, $E_{\text{excite}}$, for the bare rutile (110) surface within our DFT+U set up is 1.70 eV, which when compared with the energy gap between the valence and conduction bands of 2.1 eV, indicates that this energy is smaller than the simple VB and CB energy eigenvalue difference from the ground state calculation. In refs [9] and [11], it was also found that the excitation energies for anatase (101) and rutile (110) surfaces, which were obtained with different DFT approaches, are also smaller than the simple VB-CB band gap difference within the same DFT set-up. This difference arises from the fact that the VB-CB energy difference takes no account of relaxation in the excited state and we find that calculating the energy difference between the singlet ground state and the unrelaxed triplet state, $E_{\text{vertical}}$, yields an energy very close to the VB-CB energy difference. When one takes account of relaxations in the structure after forming the excited state, then this lowers the total energy of the excited state, thus making the value of $E_{\text{excite}}$ smaller.

As seen in table 6.1 this energy change, is the relaxation energy, $E_{\text{relax}}$, and is 0.52 eV for bare rutile (110). Comparing unmodified rutile (110) with a representative selection of TiO2 nanocluster modified rutile (110) structures, a smaller excitation energy is obtained for modified TiO2, so that we can predict that the absorption edge of these heterostructures will be shifted to smaller energies, this shift is large enough to potentially result in visible light absorption.

We note that the absolute energies in table 6.1 reflect the underestimation of the energy gap with DFT+U and therefore in our discussion of the vertical and excitation energies, the key point is the trends in these numbers. We can refer our results to figures from ref [10] where hybrid B3-LYP DFT was applied for
calculation of excitation energy for anatase (101) and gave 3.25eV, while the same DFT+U set-up as in our calculations for rutile (110) resulted in an energy 1.7 eV [6], where in both cases, that is hybrid DFT and DFT+U, these energies are smaller than TiO₂ valence-conduction energy gap.

It is also important to note that the values of the relaxation energy for the heterostructures are notably larger than at the bare (110) rutile surface. This indicates a substantial stabilisation of the excited state upon relaxation which impacts on the value of the excitation energy compared to the vertical excitation energy. The upshot of this is that we predict that light absorption in the visible region will occur.

Table 6.1 Excitation, relaxation and vertical energies for the triplet states of Ti₃O₆⁻, Ti₄O₈⁻, Ti₅O₁₀⁻TiO₂ rutile (110) and the same energies for bare TiO₂ rutile (110) surface.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$E^{\text{excite}}$ / eV</th>
<th>$E^{\text{relax}}$ / eV</th>
<th>$E^{\text{vertical}}$ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutile TiO₂ (110)</td>
<td>1.70</td>
<td>0.52</td>
<td>2.25</td>
</tr>
<tr>
<td>Ti₃O₆-TiO₂</td>
<td>0.25</td>
<td>1.37</td>
<td>1.62</td>
</tr>
<tr>
<td>Ti₄O₈-TiO₂</td>
<td>0.71</td>
<td>1.24</td>
<td>1.95</td>
</tr>
<tr>
<td>Ti₅O₁₀-TiO₂</td>
<td>0.59</td>
<td>1.49</td>
<td>2.08</td>
</tr>
</tbody>
</table>

To understand the trends in the relaxation energy, we examine the location of the photogenerated electrons and holes and the geometry around these sites. To examine the location of the photogenerated electron and hole in the heterostructures figure 6.1 presents the excess spin density plots for the relaxed triplet states. The spin density is plotted to show the location of the electron and hole after relaxation. Recall from Chapter 5, that the EDOS plots indicate that holes will be found on the TiO₂ nanocluster and electrons on the rutile (110) surface. Upon examining the spin density in each structure, we find that the
excited electron is localised on a subsurface Ti atom of the rutile (110) surface in all heterostructures. With a computed Bader charge of 1.6 electrons and a spin magnetization of 0.9 electrons, this is assigned as a Ti$^{3+}$ species. Localisation of a Ti$^{3+}$ species is common in TiO$_2$ with point defects such as oxygen vacancies [12-14] and this species was also found at the bare rutile (110) and anatase (001) surfaces upon photoexcitation [12-14].

The valence band hole is localised on a single terminal O atom of the cluster, having a net Bader charge of 6.7 electrons and a spin magnetisation of 0.8 electrons, characteristic of a localised O 2p derived hole state [2, 7]. We see that, importantly for potential photocatalyst activity, the electron and hole are separated onto the TiO$_2$ substrate and the nanocluster, so that heterostructure formation encourages charge carrier separation after excitation. We propose then that this will reduce electron and hole recombination, thus increasing photocatalytic activity and reducing the intensity of the photoluminescence associated with recombination. By contrast on the bare rutile (110) surface and anatase (101), the electron and hole are much closer.

We also note that the hole preferentially localises on the lowest coordinated oxygen atom in the nanocluster, namely a terminal oxygen, or a two-fold coordinated oxygen. The appearance of such oxygen sites in metal oxide nanoclusters can be of benefit for photocatalysis, as these will then be sites for hole localisation and can also be reactive to incoming molecules, which will be important for the activity of these structures.
The local geometry (Ti-O distances) around the holes and electrons is also presented in figure 6.1 and shows that hole localisation is coupled with local distortion to the geometry. An elongation of the Ti-O bonds of 0.3 Å involving the localised oxygen hole species when compared to singlet ground state is found. This elongation is typical of the geometry around a localised oxygen hole. Around the reduced Ti$^{3+}$ site, the local Ti-O distances are also elongated, this time by 0.1 Å - 0.13 Å when compared to the singlet ground state geometries. This coupling of charge localisation and distortions to Ti-O distance around the localised charge site is characteristic of species such as Ti$^{3+}$ and O$^-$, e.g. refs. [11, 15-20].

We present in figure 6.2 the PEDOS projected onto Ti 3d states in the surface and O 2p states in the clusters. There are now two new states in the TiO$_2$ band gap which come from (1) the localised Ti$^{3+}$ state, found at 0.6eV (Ti$_3$O$_6$-TiO$_2$),
1 eV (Ti$_4$O$_8$-TiO$_2$) and 0.9 eV (Ti$_3$O$_{10}$) above the valence band edge; (2) an empty O 2p state associated with the localised oxygen hole located 1.7 eV (Ti$_3$O$_6$-TiO$_2$), 1.8 eV (Ti$_4$O$_8$-TiO$_2$) and 2.0 eV (Ti$_5$O$_{10}$) above the valence band edge.

Figure 6.2 Ti 3d (from the surface) and O 2p (from the nanocluster) PEDOS for the relaxed triplet excited states for (a) Ti$_3$O$_6$, (b) Ti$_4$O$_8$, (c) Ti$_5$O$_{10}$ modified TiO$_2$.

6.1.2. Discussion and conclusions

Our calculations confirm that after light excitation the photogenerated electron and hole will be separated so that the hole will be found at an oxygen atom in the nanocluster while the electron will be found at a subsurface Ti site in the rutile (110) surface. This can be compared with bare rutile and anatase, where the electron and hole neighbour each other, so that the presence of the nanocluster leads to a spatial separation of charge, which will positively impact the photocatalytic efficiency of the heterostructure because the charge carrier recombination, that wastes electrons and holes, will be reduced. The structure of the nanocluster and localisation of the hole onto terminal oxygen in the nanocluster allows for strong relaxations, which leads to a large relaxation.
energy and hence a notable shift in the computed excitation energy in the heterostructure.

6.2. Modelling Photoexcitation in SnO-Modified Anatase

In this section we investigate a photo-excited model of anatase (001) modified with an Sn₄O₄ nanocluster, which is a continuation of the work in chapter [5.1]. There we showed that due to the modification with SnO nanoclusters, the original band gap of anatase is reduced which will induce light absorption in the visible region and the composition of the valence and conduction bands suggests charge separation upon photoexcitation. In this section, we investigate the nature of the photoexcited state and if the lone-pair on Sn has any impact on the electron and hole localisation in this novel heterostructure.

6.2.1. Energetics, Geometry and Electronic structure of the Photoexcited State

Referring to PEDOS plots of figures 5.3 and 5.4 in section [5.1] we already found that the valence-conduction band of TiO₂ is strongly modified as a result of modifying anatase (001) with SnO nanoclusters so that the top of the valence band is dominated by SnO derived states arising from the Sn²⁺ stereochemical lone pair, while the surface Ti 3d states dominate the bottom of the CB. We postulate that this alignment of valence and conduction band edges improves separation of electrons and holes upon photoexcitation and electrons will be localized on the surface while holes will be localised on the nanocluster, possibly spread over Sn-O bond. Table 6.2 shows the excitation, relaxation and vertical energies for the photoexcited state in Sn₄O₄ modified anatase as a representative example of SnO-modified anatase, using the previously defined excitation, vertical and relaxation energies.
Table 6.2 Excitation and relaxation energies for the triplet excited state in SnO-modified TiO$_2$ in eV. Also shown are the same energies for the bare anatase (001) surface.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$E^{\text{excite}}$ / eV</th>
<th>$E^{\text{relax}}$ / eV</th>
<th>$E^{\text{vertical}}$ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO-TiO$_2$</td>
<td>0.50</td>
<td>0.96</td>
<td>1.46</td>
</tr>
<tr>
<td>Anatase TiO$_2$ (001)</td>
<td>1.11</td>
<td>1.26</td>
<td>2.37</td>
</tr>
</tbody>
</table>

We compute vertical excitation energy for bare anatase (001) of 2.37 eV, which is larger than rutile (110). Interestingly, this is not the case with the singlet-triplet excitation energy where the anatase (001) excitation energy is 1.11 eV and is smaller than for rutile (110). We explain this with different relaxation patterns, which for anatase (001) give relaxation energy of 1.26 eV and for rutile (110) the relaxation is much smaller 0.52 eV [6], so that this anatase surface undergoes rather strong relaxations. The vertical singlet-triplet energy Sn$_4$O$_4$-modified anatase (001) is 1.46 eV which is notably smaller than for pure anatase (001) and consistent with the conclusions derived from the EDOS plots in chapter 5.

Moreover the relaxed singlet-triplet relaxed excitation energy is 0.5 eV which is much smaller when compared to the bare anatase (001) surface. We understand that these energies are underestimated by DFT issues however these results indicate that TiO$_2$ modification with SnO nanocluster will impact positively on the absorption properties by inducing the absorption of visible light.

However to improve the efficiency of photocatalyst the second very important aspect is the location of the electron and hole produced after photoexcitation. We determined the position of the electron and holes which are produced after photoexcitation by using the excess spin density. Figure 6.3 (b) presents the excess spin density for bare anatase (001) and we see that the hole is localized on a two-fold coordinated surface oxygen atom, while the electron is found on a subsurface Ti site. Localized hole $O^-$ and electron Ti$^{3+}$ are positioned close to
each other which has potential for charge recombination; similar to the anatase (101) surface in reference [8].

Figure 6.3 Computed excess spin density (isosurface values of 0.03 electrons/Å³) and local geometry around the hole and electron sites in (a) Sn₄O₄-TiO₂ anatase (001) and (b) the unmodified anatase (001) surface from the relaxed triplet excited state model.

In figure 6.3 (a) we present the spin density for the triplet state of the Sn₄O₄-anatase (001) heterostructure. We found that an electron is localized on a Ti site in the surface layer of anatase (001), giving a Ti³⁺ species. To confirm this further, we compute the Bader charge, which is 1.68 electrons and the spin magnetisation is 0.97 electrons. The Bader charge of the Ti⁴⁺ cation is 1.27 electrons and it carries zero spin magnetisation. Moreover together with the electron localisation there is an elongation of ca 0.1 Å in the local Ti-O bonds around the reduced Ti site which is typical for for Ti³⁺-O distances.

For the valence band hole, the spin density plot shows that the hole is localized on two Sn-O bonds from the Sn₄O₄ nanocluster; we were not able to break the
symmetry around the Sn-O bonds and localise the hole onto a single Sn-O bond. The character if the valence band hole can also be determined from the analysis of the valence band edge (Chapter 5), which we found to be composed of Sn^{2+}-sp and O 2p states, which form the well-known lone-pair in Sn^{2+}. Thus an analysis of the nature of the VB and CB edges can indeed be useful to determine the character of the photogenerated electrons and holes.

The computed Bader charges on the Sn atoms carrying the VB hole are +1.67 and +1.65 electrons. These are different from those for Sn^{2+} (which we computed as 1.84 electrons) and for Sn^{4+} (which we computed as 0.2 electrons). We therefore assign a 3+ oxidation state to these Sn ions, consistent with their having an electronic hole.

### 6.2.2. Discussion and conclusions

In this chapter we investigated the photoexcited model for SnO nanocluster deposited on anatase (001) and we found that the localisation of the hole is strong and the position of electron and hole indicate that the charge separation will be enhanced compared to bare anatase (001). Due to charge separation upon photoexcitation a reduction in charge recombination will be achieved. We also noticed that the geometry around the hole is different when compared to singlet state structure. Overall the improvement of spatial charge carrier separation will impact in positive way the photocatalytic properties.

The experimental work on ZnGa$_2$O$_4$ [21] where material was modified with SnO and SnO$_2$, with the oxidation state of Sn controlled by different precursors, shows that only modification with SnO nanoclusters results in a reduction of the band gap and enhanced photocatalytic activity, but modification with SnO$_2$ does not change the band gap. Our analysis in this chapter and in chapter 5 provides important insights into this difference – namely that the lone pair in SnO results in a band gap reduction, which is not present with SnO$_2$. 

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6.3. PbO and PbO$_2$ nanoclusters supported on TiO$_2$ - the role of the oxidation state in mechanism of photoexcitation

In this section, we investigate the photo-excited model state of PbO and PbO$_2$ nanoclusters supported on TiO$_2$ rutile (110).

6.3.1. Energetics, Geometry and Electronic structure of the Photoexcited State

In Chapter 5 we presented an analysis of rutile (110) and anatase (001) modified with PbO and PbO$_2$ nanoclusters and we found that, similar to Sn, the oxidation state taken by the metal has a profound effect on the nature of the valence and conduction band edges and the energy band alignments. For PbO nanoclusters supported on rutile (110) and anatase (001), the top of the valence band derives from PbO nanocluster states while the bottom of conduction band is dominated by Ti 3d states of TiO$_2$, which is similar to SnO modified TiO$_2$ and arises from lone pair in Pb$^{2+}$. In contrast, for supported PbO$_2$ nanoclusters the top of the valence band is derived from Ti 3d states while the conduction band edge in the heterostructure is derived from empty PbO$_2$ states, which arises from the empty Pb 6s states in a Pb$^{4+}$ oxidation state, similar to SnO$_2$ modified TiO$_2$.

In both cases the EDOS indicates a band gap reduction over unmodified TiO$_2$ and we also use the energy level alignments in the EDOS to predict electron and hole separation improvement upon photoexcitation. However we propose that the mechanism of electron and hole localisation will be different in each case, so that the locations of hole and electrons will depend on oxidation state.

Figure 6.4 presents a schematic diagram indicating the proposed location of electrons and holes upon photoexcitation for both PbO- and PbO$_2$- rutile (110) heterostructures. Looking at this figure, we propose that photoexcitation in PbO-TiO$_2$ structure will result in the electron populating the conduction band which is from the TiO$_2$ surface, leaving the hole at the top of the PbO derived valence band. By contrast, the PbO$_2$–rutile (110) heterostructure will show a different
location of the electron and hole: the electron will be found in conduction band states derived from empty Pb-O electronic states, while the hole should be localised on TiO$_2$ valence band derived states.

![Schematic diagram](image)

Figure 6.4 Schematic diagram for indication of electron/hole localisation. h$^+$ and e$^-$ indicate the electron and hole formed after photoexcitation.

For further investigation and to demonstrate how changing the Pb oxidation state, which can be achieved by changing the Pb precursor in a synthesis, can lead to two different mechanisms of electron/hole separation we model the photoexcited state. In table 6.3 we present the vertical, excitation and relaxation energies for bare rutile (110) and representative Pb$_3$O$_4$-rutile and Pb$_2$O$_4$-rutile heterostructures as an example of each Pb oxidation state.

For the Pb$_2$O$_4$ modified surface the computed excitation energy is close to 0 eV due to the close proximity of the empty Pb 6s states to the valence band (see figure 5.8). The energy gap is underestimated with approximate DFT functionals, so that in this case we emphasize that DFT functional plays an important role and it is necessary to be aware of these issues.
Table 6.3 Excitation and relaxation energies for the triplet excited state in PbO-modified TiO$_2$ in eV. Also shown are the same energies for the bare rutile (110) surface.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$E^{\text{excite}}$ / eV</th>
<th>$E^{\text{relax}}$ / eV</th>
<th>$E^{\text{vertical}}$ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutile TiO$_2$ (110)</td>
<td>1.69</td>
<td>0.52</td>
<td>2.21</td>
</tr>
<tr>
<td>Pb$_4$O$_4$ rutile 110</td>
<td>0.92</td>
<td>0.96</td>
<td>1.88</td>
</tr>
</tbody>
</table>

For PbO-modified rutile (110), the vertical singlet-triplet energy shows a reduction over unmodified TiO$_2$, confirming the simple DOS analysis. The computer relaxed singlet-triplet energy is reduced by 0.7 eV over unmodified rutile (110), so that we predict PbO modified rutile TiO$_2$ will indeed show a red shift of light absorption into the visible region.

In terms of the relaxation energy, this is larger for PbO-modified rutile (110) and this is caused by large gain in energy when the nanocluster strongly relaxes around the localised electrons and hole, compared to the relaxations in the unmodified (110) surface.

Figure 6.5 Spin density and geometry of the photoexcited state in representative structures of (a) PbO and (b) PbO$_2$-modified rutile (110).
In figure 6.5 we present the spin density of the relaxed photoexcited state for the (PbO)$_4$ and Pb$_2$O$_4$ nanoclusters supported on rutile (110). The Pb$_4$O$_4$ nanocluster supported on rutile (110) has the electron localised on a subsurface Ti site that is assigned as a Ti$^{3+}$ site - the computed Bader charge is +1.66 electrons and spin magnetisation is 0.9 electrons. This localisation of electron gives an elongation of nearest Ti-O bonds of ca. 0.1 Å which is typical for Ti-O bonds with a Ti$^{3+}$ cation.

We found that the hole is localised on O from the PbO nanocluster with a computed Bader charge of +7.11 electrons and a computed spin magnetisation of +0.76 electrons. The Pb ions are in their 2+ oxidation state, with a computed Bader charge of 2.01. In comparison with the case of SnO nanoclusters supported on TiO$_2$, we found that the hole is spread over Sn-O bonds, but Pb states make very little contribution to the valence band hole, indicative of a weaker lone pair effect in PbO. This trend is consistent with the bulk materials (PbO, SnO) where the strength of the lone pair effect diminishes as one goes down the group 14 column from Sn to Pb [20].

For the sake of comparison, we took into consideration the photoexcited state of Pb$_2$O$_4$-modified rutile (110), even though the excitation energies showed the issues discussed above. After photoexcitation the empty Pb states in the energy gap are occupied and the excited electron is distributed over an O-Pb-O moiety in the nanocluster. In this case Pb is characterised as a Pb$^{3+}$ ion with Bader charge of +1.49 electrons while Pb$^{4+}$ Bader charge is of +0.58 electrons. The Bader charges of the oxygen atoms that partly carry the excited electron are +7.3, +7.6 electrons and the computed spin magnetisations are 0.57 and 0.23 electrons gives the indication that the electron is spread over O-Pb-O unit. We found also that this gives an elongation of the cluster Pb-O bonds of ca. 0.3 Å.

For the hole we found that is localised bridging oxygen from the surface, with a computed Bader charge of +6.74 electrons and a spin magnetisation of 0.77 electrons, together with an elongation of the nearest Ti-O bonds that involve this oxygen of 0.1 Å.
6.3.2. Discussion and conclusions

In this section, we presented an investigation of photoexcited states of PbO- and PbO$_2$- modified TiO$_2$. In chapter 5 we showed that in both nanocluster modification, a reduction in the band gap of TiO$_2$ is predicted, but the valence-conduction set-up is different in each case, which will result in different electron/hole locations. In this section, we show explicitly that for PbO nanocluster modified rutile (110) the hole is found on the nanocluster and the electron on a single Ti$^{3+}$ in subsurface of the rutile (110) surface. Contrary to that, the PbO$_2$-TiO$_2$ photoexcited state will also show electron-hole separation enhancement but with different locations of the hole and electron: the hole is localised on a bridging O atom from the surface while the electron is associated with an O-Pb-O structure in the PbO$_2$ nanocluster. We conclude that the oxidation state plays an important role in tuning of the photocatalytic properties of metal oxides. We also found that the lone-pair effect when compared to SnO- rutile (110) is smaller which is similar to the weakening of the lone pair effect in bulk SnO and PbO [20].

6.4. Photoexcited model of Bi$_2$O$_3$ nanoclusters supported on rutile (110)

In this section we present an analysis of photoexcited state of TiO$_2$ modified with Bi$_2$O$_3$ nanoclusters; similarly to Sn$^{2+}$ and Pb$^{2+}$ the Bi$^{3+}$ species has a stereochemically active lone pair [20].
6.4.1. Energetics, Geometry and Electronic structure of the Photoexcited State

Table 6.4 presents the excitation and relaxation energies and shows that modification of rutile (110) with Bi$_4$O$_6$ leads to smaller excitation energy than unmodified rutile (110). This result is also consistent with the simple DOS analysis. The relaxation energies also show larger values in the nanocluster compared to the bare surface, which, similar to previous results, arises from the ability of the nanocluster to undergo larger relaxations than the surface.

In figure 6.6 we present the computed excess spin density for the example of a Bi$_4$O$_6$ nanocluster supported on rutile (110). The spin density is useful to determine the positions of the electron and hole and their localisation. The results for Bi$_4$O$_6$-modified rutile (110) show that the electron is localised on a surface Ti site which is assigned to be a reduced Ti$^{3+}$ species and this is further confirmed by a calculated Bader charge of 1.67 electrons and a spin magnetisation of 0.9 electrons. Together with the charge localisation there is strong elongation in the Ti-O distances by 0.1 Å, typical of the elongation of Ti-O distances around a Ti$^{3+}$ polaron. The electronic hole is localised on a 2-fold coordinated oxygen atom in the nanocluster, with a computed Bader charge of 6.7 electrons and a spin magnetisation of 0.73 electrons. The Bi-O distances around this oxygen are longer by 0.1 Å. We also found a slight spreading of the hole onto a second O atom from the cluster, which has a small change in the Bader charge from 7.30 for O$^{2-}$ in the lattice to 7.09 and a small spin magnetisation of 0.14 electrons.

Table 6.4 Excitation and relaxation energies (in eV) in Bi$_4$O$_6$-modified TiO$_2$. Also shown are the same energies for the bare rutile (110) surface.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$E^{\text{excite}}$ / eV</th>
<th>$E^{\text{relax}}$ / eV</th>
<th>$E^{\text{vertical}}$ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_4$O$_6$-TiO$_2$</td>
<td>1.20</td>
<td>0.83</td>
<td>2.03</td>
</tr>
<tr>
<td>Rutile (110)</td>
<td>1.69</td>
<td>0.52</td>
<td>2.21</td>
</tr>
</tbody>
</table>
In figure 6.6 we see that $\text{Bi}^{3+}$ contribution to the electronic hole is not present despite there being Bi 6s electronic states at the valence band edge. We conclude that there is a weaker lone-pair effect on $\text{Bi}_2\text{O}_3$ when compared to $\text{SnO}$ or $\text{PbO}$, with $\text{SnO}$ displaying the strongest lone pair effect out of these oxides [20].
6.5. Photocatalytic properties of metal oxides supported on TiO$_2$ based on photoexcited model - conclusions

We presented photoexcited models of TiO$_2$, SnO, PbO/PbO$_2$ and Bi$_2$O$_3$ nanoclusters deposited on the TiO$_2$ rutile (110) surfaces in this chapter. In all heterostructures we found that nanocluster deposition leads to reduction of both the simple vertical singlet-triplet excitation energy, similar to the simple valence-conduction band energy gap, compared to unmodified TiO$_2$. The relaxed singlet-triplet excitation energy is also notably reduced over unmodified TiO$_2$ for SnO, PbO and PbO$_2$ modified TiO$_2$. Thus, these modifications of TiO$_2$ will cause a shift into visible light activity upon photoexcitation. Bi$_2$O$_3$-modified rutile may lead to a small red shift in light absorption, but not to the same extent as the other modifiers.

Moreover we found that due surface modification, the photogenerated electron and hole are spatially separated, which gives better charge separation and reduced charge recombination. This is particularly striking for SnO modified TiO$_2$. For PbO and PbO$_2$ nanoclusters supported on TiO$_2$ the mechanism of band gap reduction is different depending on the oxidation state of the leads and this leads to different localisation of the photogenerated hole and electron.

An interesting aspect of this study is the lone-pair effect in those oxides, which is also related to the oxidation state in tin and lead oxides. We found that for SnO, the lone pair effect dominates in modifying the valance band edge and gives a very different effect on TiO$_2$ compared to SnO$_2$, with no lone pair. For PbO, the lone pair effect is present, but is less strong than in SnO-modified TiO$_2$. Finally, the weakest lone pair effect is found in Bi$_2$O$_3$ modified TiO$_2$.

Thus both the band gap, and light absorption, and the electron and hole localisation can be tuned by the choice of the oxidation state of the modifying metal oxide which provides a novel approach for tuning the band gap and excited state properties of photocatalysts based on metal oxides.
References:


7. Probing the Reactivity of Modified TiO$_2$.

7.1. Probing Reactivity of Modified TiO$_2$ through Oxygen Vacancy Formation

In this chapter we probe the reactivity of TiO$_2$ modified with TiO$_2$ nanoclusters, using the oxygen vacancy formation energies as our descriptor. For oxidative reactions, such as CO oxidation to CO$_2$, a common descriptor to understand the ability of a metal oxide to catalyse this reaction is the oxygen vacancy formation energy of the metal oxide, ref [1-3] i.e. the energy needed to remove a neutral oxygen atom from the oxide. This is a good descriptor since the CO oxidation reaction generally follows a Mars van Krevelen mechanism, [4] in which CO removes oxygen from the catalyst and the oxygen is returned by adsorption of O$_2$ from the atmosphere (or NO$_x$, which is reduced). The key step is the initial removal of oxygen from the catalyst by the CO molecule and hence using the oxygen vacancy formation energy as a descriptor is reasonable. A small vacancy formation energy means that a lower reaction temperature would be required for the reaction. Conversely, one does not want to make this energy so small that the healing of the vacancy by oxygen will not take place. Thus, there is a balance between the ease of oxygen vacancy formation and the healing of the vacancy during the redox reaction.

In this regard, undoped TiO$_2$ should not be a very good oxidation catalyst since the formation energy of an oxygen vacancy in the (110) surface from DFT+U is 3.66 eV. [3] Metiu and co-workers have examined how this energy can be reduced by substitutional doping of metal atoms at Ti sites in rutile (110). It is possible that small clusters of TiO$_2$ will show more favourable oxygen vacancy formation energies, as it is generally the case that small clusters are more reactive than their bulk counterpart; this has been discussed extensively for ceria nanoclusters in recent years.[5]

In this chapter, we examine the possibility that our new structures formed from rutile (110) modified with TiO$_2$ nanoclusters could be useful in oxidation reactions in which the key reaction step is the initial removal of oxygen. We
examine firstly the energetics of oxygen vacancy formation and we find that the most stable oxygen vacancy sites on the cluster show formation energies that are significantly lower than in bulk TiO$_2$ suggesting that these systems could be useful in oxidation reactions. We present an analysis of the structure, electronic structure and the sites for Ti reduction. In Section 7.2 we study the oxidation of CO to CO$_2$ at a representative example structure, namely rutile (110) modified with the Ti$_3$O$_6$ nanocluster, paying particular attention to the energetics involved in each step of the sequence: CO interaction, CO$_2$ removal, O$_2$ interaction, CO interaction and CO$_2$ formation.

7.1.1. Formation energies and geometries of nanocluster modified TiO$_2$ with oxygen vacancies

To investigate if the reactivity of rutile (110) modified by supported TiO$_2$ nanoclusters is enhanced when compared to unmodified TiO$_2$, we study the formation of oxygen vacancies in different sites in both the supported clusters and the rutile (110) support. Figure 7.1 shows the atomic structure of rutile (110) modified with the TiO$_2$ nanoclusters Ti$_2$O$_4$, Ti$_3$O$_6$, Ti$_4$O$_8$ and Ti$_5$O$_{10}$. We also show the numbering of the oxygen vacancy sites considered in each case. Recall from chapter 5.1 that the supported nanoclusters present a number of oxygen sites with singly coordinated (titanyl) oxygen as well as the more familiar 2 and 3-fold coordinated oxygen. There are also oxygen sites that are shared between the nanocluster and the surface. While choosing the oxygen sites to examine, we took into consideration coordination, position of the oxygen and if the oxygen is from the surface or from the cluster. The results below for vacancy formation energies show that oxygen vacancy formation is generally more favourable in the TiO$_2$ clusters than in bulk TiO$_2$ or on the bare (110) surface, where computed formation energies are 4.2 eV and 3.66 eV, respectively [6-8]. The numerical results for the oxygen vacancy formation energies are shown in table 7.1.
Figure 7.1 Labeling of the oxygen vacancy sites for rutile (110) modified with (a) Ti$_2$O$_4$, (b) Ti$_3$O$_6$, (c) Ti$_4$O$_8$, (d) Ti$_5$O$_{10}$ nanoclusters.
Table 7.1 Oxygen vacancy formation energies, $E^{\text{Ovac}}$, for adsorbed TiO$_2$ clusters from DFT+U. The most stable vacancy site is highlighted for each supported cluster.

<table>
<thead>
<tr>
<th>Structure</th>
<th>O Vacancy Site</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_2$O$_4$-TiO$_2$</td>
<td>$E^{\text{Ovac}}$ / eV</td>
<td>2.87</td>
<td>3.09</td>
<td>3.03</td>
<td>3.08</td>
<td>3.97</td>
<td>2.54</td>
</tr>
<tr>
<td>Ti$_3$O$_6$-TiO$_2$</td>
<td>$E^{\text{Ovac}}$ / eV</td>
<td>1.53</td>
<td>0.60</td>
<td>2.48</td>
<td>0.55</td>
<td>3.93</td>
<td>0.54</td>
</tr>
<tr>
<td>Ti$_4$O$_8$-TiO$_2$</td>
<td>$E^{\text{Ovac}}$ / eV</td>
<td>2.13</td>
<td>2.14</td>
<td>---</td>
<td>2.99</td>
<td>1.70</td>
<td>0.57</td>
</tr>
<tr>
<td>Ti$<em>5$O$</em>{10}$-TiO$_2$</td>
<td>$E^{\text{Ovac}}$ / eV</td>
<td>1.95</td>
<td>1.95</td>
<td>2.14</td>
<td>3.04</td>
<td>3.04</td>
<td>3.38</td>
</tr>
</tbody>
</table>

For the Ti$_2$O$_4$ cluster, the most stable oxygen vacancy structure has the lowest formation energy, at 2.54 eV and the atomic structure of this vacancy site is shown in Fig. 7.2 (a). The remaining TiO$_2$ nanoclusters show formation energies that are significantly smaller, in the range from 0.54– 1.95eV, showing a strong dependence on the size of the nanocluster and on the nature of the oxygen removed.

In Ti$_2$O$_4$, the most stable oxygen vacancy site is the terminal oxygen from the nanocluster. Interfacial oxygen atoms show larger formation energies (vacancy sites 1 and 2) and the highest energy cost is for oxygen atoms from the surface (vacancy site 5). One way to understand an origin of these vacancy formation energies is to examine the structures upon relaxation after vacancy formation. In the Ti$_2$O$_4$ cluster, the structure in Fig. 7.2 (a) is not substantially different to that
from the oxidised cluster, so that the structural relaxations after vacancy formation are relatively small. Fig. 7.3 shows the Ti–O distances and the cluster Ti atom neighbouring the oxygen vacancy site shows the largest change in geometry upon vacancy formation. It is well known that geometry relaxation in the presence of oxygen vacancy defects is key for the final distribution of electrons released by the vacancy and the resulting energetics [9].

Figure 7.2 (b) shows the most stable oxygen vacancy structure for the example of Ti$_3$O$_6$-TiO$_2$ with the oxygen vacancy site indicated with a ‘V’. Upon relaxation, this structure changes to an interesting mirror symmetric structure, which can form by removing an oxygen atom from sites 2, 4 and 6 (see figure 7.1 (b)) and results from oxygen 2 moving downwards to fill sites 4 or 6; when oxygen 2 is removed, the same relaxed structures is found. In the relaxed structure, additional Ti-O bonds between the nanocluster and the surface are created which stabilizes the vacancy structure. The symmetry can be clearly seen in the Ti-O distances in the nanocluster and between the nanocluster and the surface. The relaxed structures from OV2 and OV4 are shown on the figure 7.4. The mirror symmetry in the resulting reduced cluster is apparent from Fig. 7.2 (b) and 7.3 (b). Comparing the oxidized cluster and reduced cluster, we observe that two Ti atoms from the reduced cluster create more bonds with the surface with Ti–O distances 2.02 Å (shortest), and 2.22 Å (longest). The reduced cluster has only one terminal O atom with a Ti-O distance of 1.69 Å; the second terminal oxygen in Ti$_3$O$_6$-TiO$_2$was oxygen site 2. There is the same number of 2 coordinated O atoms with the distances 1.77 Å (shortest), and 1.99 Å (longest) and 3 coordinated O atoms with distances 1.77 Å (shortest), and 2.16 Å (longest).

For Ti$_4$O$_8$-TiO$_2$, the formation of the vacancy also leads to structural relaxations in the cluster and the formation of additional Ti–O bonds between the cluster and the surface, again contributing to enhanced stability of the reduced cluster at the surface and the small vacancy formation energy. We see that oxygen vacancy sites O1 and O2 have very similar vacancy formation energies, but the structures, shown in the appendix, Fig. 7.1, are rather different. The similarity in the oxygen vacancy formation energies is most likely co-incidental. The most stable reduced Ti$_4$O$_7$ cluster creates six Ti–O bonds to the surface, while the oxidized cluster
creates only three bonds. Two Ti atoms from the reduced cluster bond to four bridging O atoms from the surface with Ti–O distances 2.00 Å (shortest), and 2.28 Å (longest) where the Ti from the oxidized cluster bonds to the surface bridging O atom with only two bonds with distances 1.96 Å and 2.01 Å. In both clusters we can find one terminal O atom with Ti–O distance 1.70 Å for the reduced cluster and 1.66 Å for oxidized cluster.

Figure 7.2 (d) presents the most stable reduced Ti$_5$O$_9$-TiO$_2$ structure where the nanocluster has four bonds with the surface: there are two bridging oxygen atoms from the surface which bond Ti atoms from the nanocluster with the 1.90 Å and 1.94 Å and the distances between O atoms from the nanocluster and Ti surface 5-fold coordinated atoms are 1.97 Å and 2.05Å. Within the nanocluster, there are no terminal titanyl oxygen atoms, with 2-fold coordinated oxygen atoms showing typical Ti-O distances for such atoms. The most stable oxygen vacancy site is site O1, which is a terminal oxygen atom. A second site O2 is originally two-coordinated oxygen and upon relaxation oxygen O1 moves to fill this site, so that sites O1 and O2 produce the same structure, hence giving the same formation energies in table 7.1.

Figure 7.2 The most stable oxygen vacancy site in the (a) Ti$_2$O$_4$-TiO$_2$, (b) Ti$_5$O$_8$-TiO$_2$, (c) Ti$_4$O$_8$-TiO$_2$ and (d) Ti$_5$O$_{10}$-TiO$_2$ nanocluster modified rutile (110) surface. The vacancy site is indicated with a “V”
Figure 7.3 Geometry data for the most stable oxygen vacancy structures for (a) Ti$_2$O$_4$, (b) Ti$_3$O$_6$ (c) Ti$_4$O$_8$ and (d) Ti$_5$O$_{10}$ nanoclusters modified rutile (110).
Figure 7.4 Relaxed atomic structures for oxygen vacancy sites 2 and 4 in reduced Ti$_3$O$_6$ supported on TiO$_2$. (a): site 2, (b): site 4.


Figure 7.5 shows the spin density for the most stable oxygen vacancy in the Ti$_2$O$_4$, Ti$_3$O$_6$, Ti$_4$O$_8$, and Ti$_5$O$_{10}$ nanocluster modified rutile (110) structures. The spin density is the difference between the up spin and down spin electron density and allows us to examine the destination of the two electrons released by the neutral oxygen vacancy. On Ti$_2$O$_4$-TiO$_2$ and Ti$_4$O$_8$-TiO$_2$, one electron is found in a subsurface Ti site and the second electron is found on a Ti atom from the cluster, indicating that cluster Ti atoms can be reduced. The corresponding Bader charges on these Ti are 1.7 and 1.8 electrons, consistent with formation of Ti$^{3+}$ ions. Examining Ti$_3$O$_6$- and Ti$_5$O$_{10}$-modified TiO$_2$ we find that two electrons released by the oxygen vacancy are localized on the rutile TiO$_2$ surface, indicating that these Ti atoms are reduced from Ti$^{4+}$ to Ti$^{3+}$. In all cases DFT+U approach localizes the electrons on two Ti$^{3+}$ sites.
Figure 7.5 Spin density for the most stable oxygen vacancy in (a) Ti$_2$O$_4$-TiO$_2$, (b) Ti$_3$O$_6$-TiO$_2$, (c) Ti$_4$O$_8$-TiO$_2$ and (d) Ti$_5$O$_{10}$-TiO$_2$ nanocluster modified rutile (110).

The corresponding PEDOS is shown in Fig. 7.6 for the most stable oxygen vacancy in each of the structures considered. For each cluster, the PEDOS shows the introduction of electronic states in the band gap after the oxygen vacancy forms. The origin of the gap state depends on the particular cluster structure, but its appearance is indicative of formation of reduced Ti$^{3+}$, [6-8] consistent with the spin density plots. For Ti$_2$O$_4$ and Ti$_4$O$_8$, one peak in the gap state has its origin in
Ti from the nanocluster, which is the peak nearest to the valence band edge. The second peak has its origin in Ti from the supporting rutile (110) surface, which lies deeper in the gap, at an offset of around 0.8 eV from the top of the VB. The two peaks in the energy gap are quite distinct and are separated by ca. 0.7 eV. The Ti$_3$O$_6$ cluster with a vacancy behaves rather differently—its gap state is made up of contributions from two Ti$^{3+}$ ions in the support oxide, as shown in Fig. 9.5 (c). These are two distinctly different Ti$^{3+}$ species, as can be seen from the spin density plot, and hence they show up as two different peaks in the PEDOS. The highly symmetric structure of the defective Ti$_3$O$_6$ cluster prevents a Ti atom of the cluster being reduced, as this would break the symmetry and therefore only surface Ti can be reduced.

For Ti$_3$O$_{10}$-TiO$_2$ in the most stable oxygen vacancy site, the PEDOS is similar to that of Ti$_3$O$_6$-TiO$_2$, in that the two states in the energy gap arise from the two reduced surface Ti atoms.

Figure 7.6 PEDOS projected onto Ti 3d states for the oxygen vacancy in the supported TiO$_2$ clusters. (a) Ti$_2$O$_4$, (b),(c) Ti$_3$O$_6$, (d) Ti$_4$O$_8$. For Ti$_3$O$_6$, we show in part (c) the PEDOS projected onto the two surface Ti ions carrying the spin...
density from Fig. 9.5, as their PEDOS is swamped by the contributions from the remaining Ti of the TiO₂ support.

7.2. An Examination of CO Oxidation on TiO₂ Nanocluster Modified TiO₂ Structures

In this section, given the relatively favourable oxygen vacancy formation energies that we have computed for TiO₂ nanocluster modified TiO₂, we examine the possibility of these structures being useful for a prototypical oxidation reaction, namely the oxidation of CO to CO₂ following the Mars-van Krevelen mechanism. In this mechanism the oxygen required to form CO₂ from CO is supplied by the oxide catalyst, which is replenished in turn by oxygen from another source such as NO₂ which is reduced, or from atmospheric O₂ and we take the latter as our oxygen source in this investigation.

Thus we present a study using Ti₃O₆- modified TiO₂ as model catalyst structures in which we examine the following reactions

(i) Interaction of CO with the stoichiometric Ti₃O₆-TiO₂ structure

(ii) Removal of CO₂ and formation of an oxygen vacancy

(iii) Interaction of O₂ with the oxygen vacancy and the possibility of superoxide or peroxide formation

(iv) Interaction of CO with the structure in reaction (iii) and formation of a second CO₂ molecule.

The overall reaction is therefore: 2CO + O₂ → 2CO₂.

Figure 7.7 show the energy pathway and intermediate structures for steps (i) – (iv) above for the Ti₃O₆-TiO₂ structure, where we have considered the initial CO adsorption event at two different oxygen sites in the nanocluster.
Figure 7.7 Energy pathway and intermediate structures for CO oxidation at the Ti$_3$O$_6$-TiO$_2$ structure, starting from two possible CO adsorption sites in the nanocluster.

We start from two possible CO adsorption sites, O3 and O6 in the nanocluster, both of which show favourable energies for oxygen vacancy formation and in both sites the O atom in question a low coordinated oxygen.

After the interaction of site O3 with CO, the adsorption energy is negative namely -1.09 eV, which indicates a reasonably favourable interaction between the CO and the oxide; in contrast, no such interaction occurs on the bare rutile (110) surface. In this structure, CO binds to the terminal O atom from the nanocluster, forming a bound CO$_2$-like species. The bond length between terminal O atom from the nanocluster and C atom is 1.19 Å while the distance between C–O atoms directly bonded to terminal oxygen has the distance of 1.16 Å which are typical of the bond distances between C and O atoms in CO$_2$. The Ti-O distance to the original titanyl oxygen is elongated to 2.22 Å, showing a weakening of this bond in the oxide as the CO$_2$ molecule forms. Thus, there is no formation of carbonate species upon CO adsorption at this oxygen site. The
second step is the removal of CO₂ which results in oxygen vacancy formation. The energy gain upon removal of CO₂ is 0.25 eV which suggests that formation of CO₂ from CO in this case is favourable.

The next step is the step where O₂ is added (e.g. from the atmosphere) and this results in a further energy gain of 0.2 eV, giving an overall energy gain of 1.54 eV. The O₂ molecules adsorbs at the vacancy site that was created from oxidation of CO and the distances between the two oxygen atoms is 1.29 Å which corresponds to a superoxide species, that is O₂⁻, which forms by transfer of one electron from the oxide, (which had two Ti³⁺ species after formation of CO₂), to the O₂ molecule and leaving behind one Ti³⁺ in the nanocluster; formation of superoxide in this step is well known in other oxides, e.g. CeO₂ [10].

However, comparison with the energy profile in figure 9.8 for initial CO adsorption at site O₆ indicates that this pathway is not as favourable, with the primary difference arising from the less favourable adsorption of O₂ in this pathway. Therefore, we do not pursue any further reactions along this pathway.

We investigated the interaction of CO with oxygen from site 6, O₆, which is also a terminal oxygen atom. The interaction of this oxygen with a CO molecules results in an energy gain of -1.78 eV, with CO bonding to the terminal O atom. The distance between this oxygen from the nanocluster and carbon is 1.19 Å and the distance between carbon and oxygen from the CO is 1.16 Å. Similar to site O₃, a CO₂-like species is formed directly by interaction of reactive oxygen with the CO molecule. The next step is the removal of CO₂, which has a small energy cost of 0.19 eV, which is more than compensated by the energy gain in forming the CO₂ from CO and lattice oxygen and would be easily overcome at typical catalytic temperatures.

The next step is the addition of O₂ to the structure with an oxygen vacancy, which results in a significant energy gain of 1.42 eV, which is much larger than the pathway followed starting at the O₃ site in the oxide. Examining the structures for O₂ adsorption in each case, we see that in the O₃ pathway, the O₂ binds to a single Ti site in Ti₃O₆, whereas in the O₆ pathway, O₂ binds around the original oxygen vacancy site. The bond length between O atoms in adsorbed
O$_2$ is 1.42 Å, which is consistent with peroxide, O$_2^{2-}$ formation. When we examine the electronic structure, we indeed see formation of a peroxide species with two electrons transferred from the TiO$_2$ structure to the O$_2$. This is in contrast to the O$_3$ pathway. The Ti-O distances to O$_2$ are 1.94 Å.

The addition of the second CO molecule gives an energy gain of -3.88 eV and CO interacts with TiO$_2$ to form a carbonate species, which has a C-O distance of 1.21 Å (from the original CO molecule) and two further C-O distances of 1.36 Å and 1.37 Å, involving oxygen from the nanocluster. The energy cost to remove the final CO$_2$ from this system is 0.82 eV, which would be surmountable.

### 7.3. Conclusions

In this chapter, we have presented a DFT+U investigation of the reactivity of heterostructures of TiO$_2$ nanoclusters supported on TiO$_2$ rutile (110) by investigating two important aspects. The first is the process of oxygen vacancy formation, which is a useful descriptor of the reactivity of a metal oxide towards oxidation and the second process is to follow the reactions involved in CO oxidation over a representative nanocluster-modified TiO$_2$ structure.

We find that the most stable oxygen vacancy sites are on the supported nanocluster, which for the particular nanoclusters presented in section 9.1. always show reduced formation energies compared to unmodified TiO$_2$, which would indicate that these structures could be potentially useful in redox catalysis and providing an alternative to the well known VO$_x$-modified TiO$_2$ system. Other work on the formation energies of oxygen vacancies in larger supported TiO$_2$ nanoclusters also shows a reduction in the vacancy formation energy over unmodified TiO$_2$. In particular, the Ti$_3$O$_6$-modified rutile structure shows very low oxygen vacancy formation energies.

The fate of the two electrons released by the neutral oxygen vacancy shows some dependence on the precise nanocluster that modifies the rutile surface. The Ti$_2$O$_4$-TiO$_2$ and Ti$_4$O$_8$-TiO$_2$ structures show localisation (facilitated by using a DFT+U
approach) of the electrons onto two Ti sites – one Ti site is in the rutile surface and the second Ti site lies on the nanocluster. The localisation of the electron on the Ti nanocluster is such that the electron is found on a low coordinated Ti site, while the second electron can localise onto a surface 5-fold coordinated Ti atom or a subsurface Ti atom. Localisation of electrons arising from bridging oxygen vacancy in the rutile (110) surface is generally found to be in the subsurface sites, but the surface 5-fold coordinated Ti site is also a favourable site for electron localisation.

In contrast, the Ti$_3$O$_6$-TiO$_2$ and Ti$_5$O$_{10}$-TiO$_2$ nanoclusters show electron localisation onto Ti atoms in the rutile (110) surface. In both cases, the electrons prefer to localise onto two surface 5-fold coordinated Ti sites rather than onto the nanocluster. For Ti$_3$O$_6$-TiO$_2$, this arises quite simply from analysis of the structure: the most favourable oxygen vacancy sites each generate the same final structure which is mirror symmetric. Localising an electron onto one Ti site in the structure will break the symmetry and hence the electrons localise onto Ti sites in the surface. For Ti$_5$O$_{10}$-TiO$_2$, the plan view of the most stable oxygen vacancy structure also shows mirror plane symmetry and, again, localisation of an electron on a Ti site in the nanocluster will break the symmetry.

Taking a representative Ti$_3$O$_6$-TiO$_2$ structure, we have examined the interaction with CO and oxidation to CO$_2$, following the full catalytic cycle that produces two CO$_2$ molecules from two CO and an O$_2$ molecule. The two reaction sites for the initial CO oxidation show a gain in energy upon formation of a bound CO$_2$ species by abstraction of oxygen from the nanocluster (which takes place at two of the most stable vacancy sites). The difference between these pathways appears to be found in the interaction of O$_2$ with the oxygen vacancy formed after release of CO$_2$: for the O3 pathway, this interaction does not lead to any significant energy gain and formation of a superoxide species (O$_2^-$) is predicted. On the other hand, the interaction of O$_2$ with the oxygen vacancy in the O6 pathway leads to a substantial energy gain and formation of peroxide. The subsequent interaction with CO results in another large energy gain and formation of a surface bound carbonate.
The results in this chapter thus show that rutile (110) modified with TiO$_2$ nanoclusters produces a material system that we predict to show enhanced reactivity for oxidation reactions over un-modified TiO$_2$ and may be useful for the CO oxidation reaction or water gas shift.
References:

8. Doping of TiO₂ Bulk, Surfaces and Nanoclusters

In this chapter we discuss our work on doping of TiO₂ with metal cations, specifically the trivalent dopants Al, In and Ga and tetravalent dopants Ce and Zr in bulk, surfaces and nanoclusters. The motivation for undertaking this work was that we originally planned to examine the doping of supported TiO₂ nanoclusters to examine the effect of nanocluster doping compared to bulk and how this doping may impact the properties of supported nanoclusters compared to undoped supported nanoclusters. However, our survey of the literature on the topic of TiO₂ doping showed a range of different approaches and conclusions and lead us to undertake our own examination of doping of bulk TiO₂ in order to have a consistent set of bulk calculations with which to compare nanocluster doping. A further outcome of this activity is that it allowed a comparison of different calculation methods, specifically standard approximate DFT functionals, the DFT+U correction and the hybrid DFT HSE06 screened exchange functional.

To recap, the role of the dopant is to introduce new electronic states into the energy gap of TiO₂, which should lead to a reduction of the valence band and this should improve the visible light absorption properties of TiO₂. However the band gap reduction is only the one of the aspects which needs to be considered for photocatalyst design; the second important feature is charge carrier separation and their lifetimes. Contrary to this requirement there is also in some situations a need reduce the photocatalytic activity of TiO₂, which is applied in pigment in white paint [1, 2] and for which photocatalytic activity is undesirable. For this purpose Al is added which as a trivalent dopant has one fewer electron than Ti⁴⁺. The effect of doping with Al³⁺ is the formation of an oxygen hole, i.e. the well known O⁺ polaron state. There is another charge compensation mechanism which occurs by oxygen vacancy formation where one oxygen vacancy is formed for two Al³⁺ dopants, giving the following defect reactions (in Kroger-Vink notation)

\[ \text{Al}_2\text{O}_3 \rightarrow 2(\text{AlTi}^{1+} + \text{O}^{-}) \]  

8.1
There have been experimental studies of Al doping into TiO$_2$ [1, 2] and modelling works in this subject using density functional theory [3-5]. For instance Stashans et al [5] showed with Hartree–Fock (HF) that Al doping of TiO$_2$ produces an oxygen hole polaron. Density functional theory (DFT) with local exchange – correlation functionals is widely applied to study TiO$_2$. However it suffers with significant band gap underestimation and a generally incorrect description of defect states in oxides [6-8]. DFT issues play an important role not when applied to TiO$_2$ doping but method is also questioned in the field of metal oxides in general. Moreover there are other systems where DFT method gave incorrect description such as reduced cerium dioxide [9, 10] and there is a pressing need to assess the reliability of widely used DFT methods.

Doping of TiO$_2$ with Ce and Zr shows some potential in design of photocatalytic material [11-14]. Ce-doped TiO$_2$ (mixture of rutile and anatase) resulted of improved visible light activity which was assessed against volatile organic compounds and it was claimed that the band gap of Ce-TiO$_2$ was reduced [13]. Nanotubes of TiO$_2$ were doped with Zr and UV activity was improved over undoped TiO$_2$ [15]. Luo [16] prepared the Zr-doped TiO$_2$ photocatalyst and claimed that the absorption edge of the doped material was shifted to the lower energy region. With 8% Zr doping, improved photocatalytic activity was found. Lippens et al. [17] characterized Zr-doped TiO$_2$ nanopowders with EXAFS and DFT. No indication of formation of defect states or a change in band gap was found. Long and English [18] showed, using DFT+U calculations, that there is no band gap change upon Zr doping of TiO$_2$.

Since DFT presents obvious issues with doping of TiO$_2$ study there is a need to try more reliable method to describe the systems of interest. We took into consideration DFT corrected for on-site Coulomb interactions, DFT+U [19–22], in which a Hubbard U term is added to the DFT energy expression to
describe localized electronic states. DFT+U is still not a perfect solution due
to the fact that method presents empirical part of U parameter which has an
influence on material properties [23] and underestimation of the band gap is
also present. Despite this DFT+U is still used as pragmatic approach for the
study metal oxides having the computational cost of a standard DFT
calculation. Recently Hybrid DFT in a plane wave basis set [24] was applied
to study defects in metal oxides and resulted with the proper estimation of the
band gap and defect properties for the metal oxides Cu2O [25] and ZnO [26].
While hybrid DFT has two parameters which are the HF exchange
contribution and the screening length, in most cases, they can be considered
universal and used with values of 25% for exchange and 0.2 / Å for the
screening length [27]. The drawback of hybrid DFT in a plane wave basis is
the significant computational cost compared to standard DFT which requires
long calculation times for systems of interest to us – around 80 times longer
than DFT+U for the systems in this chapter.

In this chapter we investigate the following doped systems:

(1) the formation of an oxygen hole polaron and charge compensation upon
doping with Al3+, Ga3+ and In3+ using DFT, DFT+U and the screened
exchange HSE06 implementation of Hybrid DFT in order to assess the
reliability of DFT methods. We found that DFT gives a completely incorrect
description of the oxygen hole polaron defect while corrections such as
DFT+U and Hybrid DFT do lead to polaron formation. We also investigate
the energetics of oxygen vacancy compensation and highlight some issues
with approximate DFT approaches in this regard that are worthy of further
study.

(2) Ce and Zr doped into bulk rutile and anatase TiO2, and oxygen vacancy
formation in Ce and Zr-doped rutile, using DFT+U and hybrid DFT. The
stability of the dopant in TiO2 and the effect of doping on the oxygen vacancy
formation process were assessed by both methods and they gave qualitatively
similar results. However the band gap underestimation of undoped and doped
TiO2 is shown to strongly impact on the position of the defect states in
doping, with a notable dependence on the precise DFT+U set-up that is used and in addition, the description of oxygen vacancy formation in doped TiO$_2$. In particular, our results indicate that the DFT+U description of these properties and any quantitative statements from DFT+U results must be carefully done.

(3) Finally, we present the first studies of doping of free and supported TiO$_2$ nanoclusters, with the aim to examine how nanocluster doping may differ compared to bulk or surface doping. While we do present initial results here, and make some comparisons to bulk doping, our investigations are not complete and further work on this topic will certainly be of great interest.
8.1. Doping with 3+ dopants: Al, Ga, In on bulk rutile TiO$_2$

8.1.1. Atomic structure of doped bulk rutile TiO$_2$

The bulk rutile unit cell, in a (2x2x3) supercell expansion is presented in figure 8.1 with the position of the dopant atom indicated by the blue sphere; in all figures in this chapter, Ti is represented by the grey spheres and oxygen by the red spheres.

Figure 8.1 The bulk rutile (2 x 2 x 3) supercell. In this figure Ti is the grey sphere, oxygen is the red sphere and the dopant is generically indicated by a bulk sphere.

Figure 8.2 (a) – (i) presents the local atomic geometry and selected structural data around the dopant site for Al (figures 8.2(a)–(c)), Ga (figures 8.2(d)–(f)) and In (figures 8.2(g)–(i)). Figure 8.3 (a) – (f) shows the local geometry around the polaron site. These figures show results for the three DFT approaches considered (DFT, DFT+U and HSE06).

From the geometry data, we see that there are two general solutions in terms of geometry and electronic structure. There is symmetric solution in which dopant-O distances are equal and little or no geometry distortion is present, in the sense
that the four equatorial dopant-O distances are equal and the two apical dopant-O distances are equal, but different to the equatorial dopant-O distances. In the asymmetric solution notable geometrical distortions around the dopant are present so that the distances between dopant and O atom are no longer symmetric.

Applying DFT to trivalent-doped rutile results in only the symmetric solution being stable while for DFT+U and hybrid DFT both solutions are possible and have been found. However the DFT+U and hybrid DFT approaches always result in the asymmetric solutions being more stable by around 0.4 eV, so the symmetric solutions in these cases will not be discussed further.
For the symmetric DFT solution the equatorial and apical Ti-O distances are dependent on the dopant ionic radius, so that the shortest dopant–O distances 1.92 Å and 1.96 Å are found with Al]$^{3+}$ (the smallest ionic radius cation) and the longest distances are found with the In]$^{3+}$ dopant, being 2.15 Å and 2.12 Å (the largest ionic radius cation). Al]$^{3+}$ and Ga]$^{3+}$ have a similar ionic radius to Ti]$^{4+}$ so that incorporation of these dopants should be favourable. The precise geometry from the DFT+U solution depends on the dopant, with In]$^{3+}$ showing different behaviour to Al]$^{3+}$ and Ga]$^{3+}$. The pair of equatorial dopant–O distances and the four apical dopant–O distances shows a small degree of symmetry breaking, consistent with the dopant ionic radius. For In dopant the equatorial In–O distances are similar but the apical In–O distances result in a distortion, with In–O distances of 2.16 Å and 2.08 Å, compared to 2.00 Å in undoped rutile.

According to these results we can distinguish two types of distortion: one is around the dopant and the second is around the polaron. The former depend on the dopant ionic radius and the first indication is the distortion between dopant and O atoms where the Ti-O and dopant-O distances depend on the dopant ionic radius and for In (with the largest ionic radius) the distances between In and O atom are the longest. The second distortion is where the polaron is centred near the dopant. We also find this for In, where the In-O distances are consistent with an elongated bond between In and a (localised) oxygen polaron, [19-22]. These particular distortions are not found for Al and Ga dopants. Where hybrid DFT and DFT+U give similar distances around the dopants (figures 8.2 and 8.3 for In) this helps to build confidence in the DFT+U description of these systems. Examining figure 8.3 which presents cation–O distances in the vicinity of the polaron site we find that the geometry is consistent with the presence of a localised oxygen polaron [19-22]. In contrast to In, here the dopant is not bound directly to the polaron oxygen for Al and Ga. The polaron is in a next-nearest neighbour position relative to the dopant. Thus in figure 8.3 we do not show the Al and Ga sites, but do show the In site.

For Al, there is one equatorial Ti–O distance of 2.15 Å (DFT + U) and 2.14 Å (HSE06), with a correspondingly shorter equatorial Ti–O distance of 1.85 Å (DFT+U) and 1.84 Å (HSE06) to the other oxygen. For Ga doping there are
similar Ti-O distances consistent with the polaron and with DFT+U and HSE06 this Ti-O distance is 2.14 Å while the corresponding shorter Ti-O distance is 1.85 Å in DFT+U and 1.88 Å with HSE06.

Figure 8.3 Structure around the polaron for (a) Al DFT + U, (b) Al HSE06, (c) Ga DFT + U, (d) Ga HSE06, (e) In DFT + U, (f) In HSE06.

We find further that DFT+U and HSE can predict the polaron site on different oxygen atoms. To investigate the energetics of different solutions for polaron-dopant distributions we have used, for the example of Ga doping, the DFT+U structure as an input to HSE06 and also the HSE06 structure as an input to DFT+U. Using hybrid DFT on the DFT+U solution results in the dopant-polaron
distribution being degenerate with the original DFT+U solution. Starting from
the hybrid DFT polaron distribution, the same dopant-polaron distribution with
DFT+U lays 22 meV higher in energy. This is of course a rather small energy
difference so that both dopant-polaron distributions are accessible in a real
sample. These findings are similar to CeO$_2$ [10, 19] where there are number of
stable polaron solutions which lie close in the energy. This small energy
difference between different solutions, explains experimental findings in similar
systems where an averaging over energetically accessible defect configurations
would be observed, as has been discussed recently for TiO$_2$ [28].

8.1.2. **Electronic Structure of trivalent doped Rutile TiO$_2$**

Figures 8.4 to 8.6 present the electronic density of states (EDOS) projected onto
the O 2p states for Al doped TiO$_2$, Ga doped TiO$_2$ and In doped TiO$_2$, from the
three DFT methods. The EDOS are used to examine the localization of the
oxygen hole (polaron) state due to doping of Al, Ga and In. As the insets we
present the excess spin density (defined as the difference between the spin-up
electron density and the spin-down electron density). We applied spin density to
investigate the position of the oxygen hole.
Figure 8.4 EDOS plots for Al doped bulk TiO$_2$. The inset shows the spin density. (a) DFT, (b) DFT+U, (c) Hybrid DFT.
Figure 8.5 EDOS plots for Ga doped bulk TiO$_2$. The inset shows the spin density. (a) DFT, (b) DFT+U, (c) Hybrid DFT.
Figure 8.6 EDOS plots for In doped bulk TiO$_2$. The inset shows the spin
density. (a) DFT, (b) DFT+U, (c) Hybrid DFT.
The DFT solution delocalizes the oxygen hole over all oxygens in the structure for each dopant; contrary to this with DFT + U and HSE06, the hole is primarily localized on one oxygen ion near the dopant. With this result we see that DFT+U approach used for doped systems gives the consistent description of the polaron formation, compared to HSE06 which is considered as a more complete method for the description of polaronic systems [24-25; 27-28]. In terms of EDOS DFT+U and hybrid DFT are quite similar for the doped systems investigated here.

Examining the EDOS, the DFT solution gives no states in the band gap which is consistent with the delocalization of the oxygen hole. Instead the hole state is found at the top of the VB, and this was found for other oxides with these oxygen hole polarons [29-33].

A different solution for the electronic structure is found for DFT+U and hybrid DFT where a defect state is clearly present in the TiO₂ band gap. This defect state arises from the localized oxygen hole state shown in the accompanying spin density plot for each dopant. It needs to be pointed out that the precise position of the defects which are in the band gap of TiO₂ is dependent on the DFT approach used, and we present in table 8.2 the offsets of the polaron state from the valence and conduction band edges. The DFT+U prediction is that the offset of the polaron state from the VB to within 0.35 eV of the hybrid DFT offset, with both methods placing the polaron state well inside the band gap of the oxide. However the offset to the CB states shows large differences where DFT+U predicts offset no larger than 0.65 eV, but hybrid DFT predicts much larger offsets. These differences are result of underestimated band gap from DFT+U, while these issues should be resolved by hybrid DFT. The offsets of the defect state to the VB are well described with DFT + U since U is applied to the O 2p states and the defect states come from O 2p-derived VB state. The value of U was determined by determining the position of the polaron state relative to the VB of in Li-doped MgO [30] and can be also found in the experimental data [34]. The issues with incorrect band gap and the offset of the defect state to the CB while DFT+U is applied can be explained by the fact that U has no effect on the CB states, which derive from Ti 3d orbitals. While the use of the +U correction on Ti could be
undertaken, this will introduce two +U corrections in one calculation which will have its own issues [35]. Moreover our expectation is that hybrid DFT solution gives the correct description and is used to check the DFT+U solution. Finally, if we consider the effect of U in the DFT + U calculation, then we have shown in [31], that a smaller value of U on O 2p states moves the defect state away from the CB, but correspondingly reduces the offset to the VB edge, and leads to increased delocalization of the oxygen hole. A larger value of U on O 2p states would move the defect state closer the CB. Thus, we can highlight a key issue with DFT + U, namely that since the correct band gap cannot be obtained, then the position of defect states relative to both the valence and conduction bands cannot be obtained. Despite this, DFT + U provides a useful approach for doped systems such as considered herein.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Al $E^{VB}$/ eV</th>
<th>Ga $E^{CB}$/ eV</th>
<th>In $E^{VB}$/ eV</th>
<th>Ga $E^{CB}$/ eV</th>
<th>Al $E^{VB}$/ eV</th>
<th>Ga $E^{CB}$/ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT+U</td>
<td>1.30</td>
<td>0.45</td>
<td>1.25</td>
<td>0.45</td>
<td>1.05</td>
<td>0.65</td>
</tr>
<tr>
<td>Hybrid DFT</td>
<td>1.65</td>
<td>1.55</td>
<td>1.55</td>
<td>1.65</td>
<td>1.25</td>
<td>1.95</td>
</tr>
</tbody>
</table>

**8.1.3. Energetics of oxygen vacancy compensation**

We study charge compensation of the trivalent dopants due to oxygen vacancy formation which takes the form of the following configuration: the defect formed by two dopants and an oxygen vacancy. Each dopant introduces one oxygen hole as a result of its lower oxidation state than Ti and the neutral oxygen vacancy acts to donate two electrons that fill these holes. In this section we determine the most favourable dopant-dopant configurations for each dopant and then the most
favourable dopant-vacancy configurations for each dopant. All calculations are carried out with our DFT+U set-up and the most favourable DFT+U structures are further examined for energetics with hybrid DFT.

Figure 8.7 presents for each dopant the four configurations we have considered for a dopant pair, with different distances between the dopants. We find that the least stable dopant-dopant distribution after relaxation is less stable than the most stable dopant pair structure by no more than 0.5 eV for all dopants. In this case, such a small energy difference shows that in a real system a distribution of dopant pair configurations for all dopants will be present, depending on temperature and processing conditions. To examine this effect briefly, we show for Al and In dopants only the most stable dopant pair configuration, while for Ga doping we present results for charge compensation for two dopant pair configurations. For the typical dopant pair configuration these results can be treated as the representative. We determined the most stable site for a compensating oxygen vacancy, with the oxygen vacancy sites shown in figure 8.8. The most stable dopant-dopant configurations, from which the oxygen vacancy is formed, are as follows: the Al–Al distance is 2.97 Å, the Ga–Ga distance is 2.97 Å (we also consider a Ga-Ga distance of 5.55 Å) and the In–In distance is 3.60 Å.
In Table 8.2 we present the formation energies of the compensating oxygen vacancy in each dopant-pair structure from DFT + U. The key finding is that the resulting formation energies are negative, or at least very small and positive. The configurations with negative vacancy formation energies indicate spontaneous charge compensation via oxygen vacancy formation. However, since these calculations are at 0K this means that the very low cost of forming the compensating oxygen vacancy according to the DFT+U results in the other dopant–vacancy configurations indicates that under typical experimental conditions, dopant compensation through oxygen vacancy will occur. These results suggest that finding a signature of an oxygen hole polaron in trivalent doped bulk rutile will not be expected.

The experimental studies show clearly that that Al doping is always compensated by oxygen vacancy formation [17, 18], while for Ga and In doping, the present
results also indicate that charge compensation will occur if these dopants are present.

For further validation of the DFT+U findings, we computed the oxygen vacancy formation energy of the most stable vacancy compensated structure with HSE06. The formation energies are as follows: $-0.85$ eV (Al), $-1.31$ eV (Ga) and $-1.21$ eV (In). Although hybrid DFT is more favourable towards oxygen vacancy compensation than DFT + U (which has also been examined for doped CeO$_2$ [37]), nonetheless the results of the DFT + U calculation are consistent with the hybrid DFT description and provide reasonable confidence in using DFT + U for these systems. The question of the difference between the quantitative DFT+U and hybrid DFT results is one of general interest, but is outside the scope of this thesis. However, we do suggest that when possible, a check on DFT + U results with hybrid DFT would always be recommended for increased confidence.

![Figure 8.8 Oxygen vacancy positions for (a) Al, (b) Ga (with a Ga–Ga distance of 5.55Å), (c) In.](image)
Table 8.2 Formation energies ($E_{\text{Ovac}}$ (eV)) of compensating oxygen vacancies for Al, Ga and In doped TiO$_2$. All results are from the DFT + U method.

a: Ga-Ga distance of 5.55 Å
b: Ga-Ga distance of 2.97 Å

<table>
<thead>
<tr>
<th>O vacancy site</th>
<th>Al</th>
<th>Ga$^a$</th>
<th>Ga$^b$</th>
<th>In</th>
</tr>
</thead>
<tbody>
<tr>
<td>OV1</td>
<td>0.27</td>
<td>0.05</td>
<td>-0.25</td>
<td>0.14</td>
</tr>
<tr>
<td>OV2</td>
<td>0.45</td>
<td>0.13</td>
<td>-0.27</td>
<td>0.32</td>
</tr>
<tr>
<td>OV3</td>
<td>0.75</td>
<td>0.38</td>
<td>0.22</td>
<td>0.12</td>
</tr>
<tr>
<td>OV4</td>
<td>0.75</td>
<td>0.18</td>
<td>-0.50</td>
<td>0.23</td>
</tr>
<tr>
<td>OV5</td>
<td>0.46</td>
<td>0.47</td>
<td>-0.50</td>
<td>-0.31</td>
</tr>
</tbody>
</table>
8.2. Doping with 4+ dopants: Ce, Zr

Doping of TiO$_2$ with Ce and Zr shows potential in the design of photocatalytic materials [11-13, 38]. Ce-doped TiO$_2$ (composed of a mixture of rutile and anatase) resulted in improved visible light activity which was assessed against volatile organic compounds and it was claimed that the band gap of Ce-TiO$_2$ was reduced [13]. Nanotubes of TiO$_2$ were doped with Zr and UV activity was improved over undoped TiO$_2$ [15]. Luo [16] prepared Zr-doped TiO$_2$ photocatalysts and claimed that the absorption edge of the doped material was shifted to the lower energy region. With 8% Zr doping, improved photocatalytic activity was found. Lippens et al. [17] characterized Zr-doped TiO$_2$ nanopowders with EXAFS and DFT. No indication of formation of defect states or a change in band gap was found. Long and English [18] showed, using DFT+U calculations, that there is no band gap change upon Zr doping of TiO$_2$.

In this section we study Ce and Zr doped into bulk rutile and anatase TiO$_2$, as well as oxygen vacancy formation in doped rutile, using DFT+U and the screened exchange HSE06 implementation of hybrid DFT. The stability of the dopant in TiO$_2$ and the effect of doping on the oxygen vacancy formation energy were assessed by both methods and they gave qualitatively similar results. However the underestimation of the band gap of doped TiO$_2$ with DFT+U is in contrast to hybrid DFT and plays an important role in interpreting results. The incorrect band gap resulting from DFT+U is crucial in determining the position of the defect states after doping and oxygen vacancy formation and description of these properties needs to be carefully considered. Thus care must be taken in making any quantitative statements from DFT+U results.

In figure 8.1, we showed the general structure of bulk rutile with a dopant on the Ti site and in figure 8.9 we show the general structure of bulk anatase with a dopant (brown colour) on the Ti site.
Table 8.3 presents the energy associated with substituting the dopant for Ti in bulk rutile and anatase. We find that for TiO$_2$ rutile and anatase and both the DFT+U and HSE06 approaches the incorporation energies are negative, favouring dopant incorporation. Comparison of two DFT methods used shows that HSE06 predicts dopant incorporation to be less favourable than with DFT+U, but the differences are relatively small and Ce doping of rutile is always more favorable than Zr doping. For bulk anatase the results are different: (1) the relative stability of Ce and Zr as dopants depends on the calculation method used, (2) the difference between the DFT+U and HSE06 energies is larger than for rutile.

Table 8.3 Formation Energy for Doping Bulk Rutile and Anatase TiO$_2$ with Ce and Zr.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>$E^{dope}$/eV rutile TiO$_2$</th>
<th>$E^{dope}$/eV anatase TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>-1.21 eV DFT+U</td>
<td>-1.44 eV DFT+U</td>
</tr>
<tr>
<td>Zr</td>
<td>-0.25 eV DFT+U</td>
<td>-0.57 eV DFT+U</td>
</tr>
</tbody>
</table>

Figure 8.9 Atomic structure of bulk anatase TiO$_2$, showing the dopant site. Ti is gray, oxygen red, and the dopant brown.
Figure 8.10 shows the geometry around the dopant site in bulk rutile from DFT+U and HSE06. For Ce doping, the Ce-O distances are longer than in undoped TiO$_2$ and this trend the same for, DFT+U and HSE06. For Zr, all Zr-O distances are equal at 2.06 Å with DFT+U while with HSE06 the Zr-O distances are 2.07 Å and 2.08 Å. These differences between dopants can be explained by the ionic radii of the dopants: Ce$^{4+}$ has an ionic radius of 1.06 Å and Zr$^{4+}$ an ionic radius of 0.72 Å, while the ionic radius of Ti$^{4+}$ is 0.52 Å, so that both dopants should have longer cation-O distances than Ti and those for Ce are longer than for Zr. A similar result for the Zr-O distances in Zr-doped TiO$_2$ have been reported by Lippens et al [17] where Zr-O distances are longer than Ti-O distances. Comparison of the two DFT methods shows that HSE06 gives dopant-O distances no longer than 0.02 Å compared with DFT+U.
The relaxed atomic structures for anatase doped with Zr and Ce are presented in figure 8.11 and we see that the cation-oxygen distances are longer than in undoped TiO$_2$ and differences in cation-O distances between DFT+U and HSE06 are no larger than 0.03 Å, which suggests that DFT+U can be considered as reliable for describing geometry. The Ce-O distances are always longer than the Zr-O distances, similar to bulk rutile.

However the electronic structure of Zr and Ce doped TiO$_2$ brings to light some deficiencies in applying the DFT+U approach. DFT+U presents an issue with the band gap, which is underestimated from the underlying approximate DFT exchange correlation functional and its precise value shows a strong dependence on the choice of U. In order to recover the correct value of the band gap, we can go to larger values of U [42, 43]; however, this choice of U tends to degrade the description of other important properties and should not be recommended. Hybrid DFT has been shown to give a better description of the band gap in metal oxides, both undoped and doped [43]. However despite many works showing the importance of using DFT+U or hybrid DFT for metal oxides and with some
successful examples, there is still a substantial usage of standard approximate
DFT exchange-correlation functionals (without any corrections) to study doping
of TiO$_2$. To examine this point, figures 8.12 and 8.13 show the Ti 3d and dopant
(Ce 4f and Zr 5d) projected electronic density of states (PEDOS) from DFT+U
(U = 4.5 eV on Ti and 0 = eV on Ce) and HSE06; for doped bulk rutile in figure
8.12 and doped bulk anatase in figure 8.13 There are no reduced Ti species or
reduced species originating from the dopant since the electronic structure shows
no electronic states in the band gap. Thus Ti atoms and the dopants have +4
oxidation states which is also confirmed by Bader Charge analysis, where Ti in
rutile has a charge of +1.32 electrons, Ce a charge of +2.27 electrons, and Zr a
charge of +2.57 electrons from DFT+U. With HSE06, the charge on Ti is +1.41
electrons, +2.50 electrons on Ce, and +2.74 electrons on Zr. For anatase similar
Bader charges are found and are typical of 4+ oxidation states for Ti, Ce, and Zr.

In the PEDOS of doped TiO$_2$, the Zr 5d states are positioned well above the TiO$_2$
conduction band edge with little interaction with the host electronic states, and
the band gap is unchanged over undoped TiO$_2$ which is found for doped rutile
and anatase and from both DFT methods. This is consistent with a number of
papers in the literature [15-17, 16, 40].

For bulk rutile doped with Ce, DFT+U with U = 4.5 eV on Ti and U = 0 eV on
Ce, predicts that the Ce 4f states are positioned below the bottom of the TiO$_2$
conduction band, giving a small reduction in the energy gap of 0.1 eV. For
anatase the band gap shows no change and the Ce4f states and the bottom of the
conduction band lie at the same energy. This difference arises from the larger
energy gap in anatase compared to rutile.

The DFT+U prediction of a band gap which is slightly decreased in Ce-doped
rutile is consistent with ref [41]. Contrary to this result, the PEDOS from the
HSE06 calculation of Ce-doped rutile and anatase shows no band gap change due
to doping. For both rutile and anatase, the Ce 4f states appear above the CB edge
of TiO$_2$. While looking closely to PEDOS we found that the Ce 4f peak is
narrower with HSE06 than with DFT+U, indicating that there is less interaction
between the Ce 4f states and the Ti 3d states from the HSE06 description compared with DFT+U.

However we must remember that the PEDOS presented in figures 18.12 and 8.13 are for a particular DFT+U set-up and to examine the impact of the precise DFT+U setup on the position of the dopant and TiO$_2$ electronic states, we have performed DFT+U calculations with the following combinations:

(i) $U = 4.5$ eV on Ti 3d and $U = 5$ eV on Ce 4f,

(ii) $U = 3$ eV on Ti 3d and $U = 0$ eV on Ce 4f,

(iii) $U = 3$ eV on Ti 3d and $U = 5$ eV on Ce 4f.

We choose $U = 3$ eV on Ti 3d since this DFT+U set-up has been investigated in the literature [42, 43] and $U = 5$ eV on the Ce 4f states is a well-used value of $U$ for this species [43]. These DFT+U set-ups allow us to examine how the positions of the Ti and Ce energy states can be modified by the DFT+U set-up, with comparison to the HSE06 results available.

Figure 8.14 presents plots of the PEDOS for the Ti 3d and Ce 4f states and shows a significant dependence on the DFT+U setup used. If we compare $U = 5$ eV and $U = 0$ eV on the Ce 4f states (with $U = 4.5$ eV on Ti), we find that for $U = 5$ eV the position of the Ce 4f and the Ti 3d conduction band states is consistent with the HSE06 result. If however, $U = 0$ eV on the Ce 4f states, then the precise value of $U$ on the Ti 3d states does not influence the position of the electronic states and Ce 4f states remain below the TiO$_2$ CB. Thus the description of the potential change in the band gap using DFT+U depends significantly on the choice of DFT+U setup, and caution must be urged in attempting such analyses without reference to more accurate calculations or high quality experimental data.
Figure 8.12 PEDOS for doped bulk rutile TiO$_2$. (a) Ce-doped DFT+U (U=0eV on Ce, 4.5eV on Ti), (b) Zr-doped DFT+U, (c) Ce-doped HSE06, (d) Zr-doped HSE06.
Figure 8.13 PEDOS for doped bulk anatase TiO$_2$. (a) Ce-doped DFT+U, U ($U = 0$ eV on Ce, $4.5$ eV on Ti), (b) Zr-doped DFT+U, (c) Ce-doped HSE06, (d) Zr-doped HSE06.
Figure 8.14 PEDOS for Ce doped bulk rutile with different combinations of $+U$ correction applied to Ti and Ce.
8.2.1. Zr and Ce doping of the rutile TiO$_2$ (110) surface

Figures 8.15 and 8.16 present the atomic structure of the rutile (110) surface doped with Zr and Ce in their most stable lattice site, i.e., a 5-fold coordinated surface Ti site. We have used a (2x2) surface supercell (figure 8.15) with DFT+U and HSE06 and a (2x4) surface supercell with DFT+U, figure 8.16. For the (2x4) supercell only the DFT+U results are shown since this surface supercell is too large to be treated with hybrid DFT in a plane wave basis at present.

Figure 8.15 Structure of Ce and Zr doped into the (2x2) surface supercell of the (110) rutile surface. (a) Ce DFT+U, (b) Ce HSE06, (c) Zr DFT+U, and (d) Zr HSE06. The gray spheres are Ti, the red spheres O, the white spheres Ce, and the blue spheres Zr.
Figure 8.16 Structure of Ce and Zr doped into the (2x4) surface supercell of the (110) rutile surface. (a), (b) DFT+U Ce, (c),(d) DFT+U Zr. The grey spheres are Ti, the red spheres are O, the white sphere is Ce and the blue sphere is Zr.

The energy for dopant incorporation is negative for both surfaces which mean that dopant incorporation is favoured. The energy for substitution of Zr dopant from DFT+U calculation is similar for both supercells - for the (2x2) surface supercell it is 0.7 eV while for the (2x4) surface supercell, it is 0.8 eV. The energies for Ce dopant incorporation show a dependence on dopant concentration. HSE06 calculation for the (2x2) surface supercell gives an incorporation energy of 1.70 eV for Zr and 1.90 eV for Ce. We can conclude that for both DFT approaches the incorporation of both dopants into the rutile (110) surface is favourable. With Zr doping of the rutile (110) surface a small distortion in the local geometry is present, together with an elongation of the dopant-O bonds, which is presented in table 8.4.
Table 8.4 Dopant-O distances (in Å) in Ce and Zr doped rutile TiO2 (110) surface from DFT+U and HSE06.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Dopant-O distance /Å (110) (2x2)</th>
<th>Dopant-O distance /Å (110) (2x4)</th>
<th>Dopant-O distance/Å (110) (2x2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DFT+U</td>
<td>DFT+U</td>
<td>HSE06</td>
</tr>
<tr>
<td>Ce</td>
<td>2.14 (x2), 2.15 (x2)</td>
<td>2.11 (x1), 2.12 (x3)</td>
<td>2.16 (x4)</td>
</tr>
<tr>
<td></td>
<td>2.51 (to subsurface)</td>
<td>2.47 (to subsurface)</td>
<td>2.45 (to subsurface)</td>
</tr>
<tr>
<td>Zr</td>
<td>2.05 (x4)</td>
<td>2.07 (x4)</td>
<td>2.06 (x4)</td>
</tr>
<tr>
<td></td>
<td>1.98 (to subsurface)</td>
<td>1.97 (to subsurface)</td>
<td>1.97 (to subsurface)</td>
</tr>
</tbody>
</table>

There is additionally a small Zr displacement of 0.06 Å out of the surface plane. Distortions to the atomic structure around the site of the dopant are obvious when the rutile (110) surface is doped with Ce. For both surface supercells, Ce is pushed out of its surface lattice site, which is connected with its larger ionic radius and the free surface allowing motion of this species. The displacement perpendicular to the surface is 0.80 Å in the (2x2) surface supercell (with both DFT methods) and 0.75 Å in the (2x4) surface supercell. The subsurface oxygen experience strong distortions, which is caused by the displacement of the Ce atom. A plan view of both surfaces also shows that the local structure around the dopant is distorted, with in-plane oxygen atoms displaced away from their lattice sites, and the nearest bridging oxygen atoms also moving.

Figure 8.17 presents the Ti and dopant PEDOS for Zr and Ce doping of the TiO2 (110) (2x2) surface supercell from DFT+U (U = 4.5 eV on Ti and 0 eV on Ce) and HSE06; the PEDOS for the (2x4) surface supercell with DFT+U is very similar to the smaller surface supercell with the same DFT+U setup. For both DFT approaches there are no electronic states in the band gap of TiO2 and Zr is in its +4 oxidation states; which is also confirmed by computed Bader charges of +2.50 and +2.63 electrons with DFT+U and HSE06 for Zr. For Ce, the Bader charges are +2.37 and +2.44 electrons with DFT+U and HSE06. For Zr dopant incorporated into TiO2 there is no change in the band gap of TiO2, with the unoccupied Zr states positioned well above the CB of TiO2.
The position of the Ce 4f state depends on the DFT method applied. In Figure 8.17 we present the PEDOS from DFT+U with $U = 4.5$ eV on Ti and $U = 0$ eV on Ce) and this predicts a strong reduction in the band gap of TiO$_2$ surface. However HSE06 positions the Ce 4f states around the conduction band edge essentially at the same energy as the Ti 3d conduction band states. Thus, in a real sample made up of nanocrystals and where surfaces dominate, it is possible that the precise effect of Ce doping and any band gap change will depend on the exact details of structure, processing, experimental conditions, etc., all of which could be the origin of apparent disagreements between some experimental studies.

8.2.2. Oxygen Vacancy Formation in Doped Rutile TiO$_2$

In order to investigate the reactivity of doped TiO$_2$ we study the oxygen vacancy formation energy. We removed one oxygen atom from different sites in the doped structures and computed the oxygen vacancy formation energy and table
8.5 presents the energies for the most stable oxygen vacancy site in undoped and doped bulk rutile TiO$_2$ and the (110) surface from DFT+U and HSE06 are shown. While comparing the bulk and the surface it is shown that the oxygen formation energy is lower for the surface. Comparison of the surfaces shows that the (2x4) surface supercell has a smaller oxygen vacancy formation which can be explained by the smaller vacancy concentration.

A comparison of the DFT approaches shows that HSE06 results in larger oxygen vacancy formation energy than DFT+U. However we use the typical U set up from the literature, so we have to be aware that the precise energy in a DFT+U calculation strongly depends on the value of U. The comparison of Ce and Zr dopants shows that for the bulk material, Zr doping increases the oxygen vacancy formation energy, while Ce doping lowers the oxygen vacancy formation energy, but that reduction is not significant.

The fact that Ce doping lowers of the oxygen formation energy can be explained that facile reduction of Ce from Ce$^{4+}$ to Ce$^{3+}$ takes place (see next section) upon formation of an oxygen vacancy and the Ce$^{4+}$ ion has a larger ionic radius compared to Ti$^{4+}$, which would distort to the local atomic structure around Ce and usually results in a lower oxygen vacancy formation. The example of Zr doping suggests that despite the fact the structure around the dopant is distorted compared to TiO$_2$ this is not a guarantee that it will be easier to remove an oxygen atom. Moreover the fact that Zr is not reducible is important as well. In the (110) surface the dopants reduce the oxygen vacancy formation energy while compared to undoped TiO$_2$. 


Table 8.5 Oxygen Vacancy Formation Energies for the Most Stable Oxygen Vacancy Site in Bulk Rutile TiO₂ and the Two Rutile (110) Surface Supercells from DFT+U and HSE06.

<table>
<thead>
<tr>
<th>dopant</th>
<th>bulk rutile TiO₂</th>
<th>TiO₂ rutile (110) (2x2)</th>
<th>TiO₂ rutile (110) (2x4)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E&lt;sup&gt;Ovac&lt;/sup&gt;/eV DFT+U</td>
<td>E&lt;sup&gt;Ovac&lt;/sup&gt;/eV HSE06</td>
<td>E&lt;sup&gt;Ovac&lt;/sup&gt;/eV DFT+U</td>
</tr>
<tr>
<td>None</td>
<td>4.97</td>
<td>4.32</td>
<td>3.68</td>
</tr>
<tr>
<td>Zr</td>
<td>5.19</td>
<td>4.76</td>
<td>3.48</td>
</tr>
<tr>
<td>Ce</td>
<td>4.06</td>
<td>3.93</td>
<td>2.38</td>
</tr>
</tbody>
</table>

Figure 8.18 presents the atomic structure and excess spin density of the relaxed structures for oxygen vacancy formation in doped bulk rutile. The DFT+U and HSE06 comparison of Ce-O distances in the most stable oxygen vacancy structure shows significantly longer Ce-O distances from HSE06 compared to DFT+U and for both DFT methods, the Ce-O distances are longer than in undoped TiO₂. While comparing Ce-O distances where O vacancy is not present they are similar as shown in table 8.4.

From both DFT methods, Ce is a neighbour to the O vacancy site and coordinates to four neighbouring oxygen atoms and does not bond to the fifth oxygen atom. The most stable oxygen vacancy site is an oxygen that was originally shared by the dopant and Ti.

The distortions around the dopant and the vacancy are much smaller for Zr doping and there is one short Zr-O distance and four Zr-O distances that are essentially uniform. After removing an oxygen from Zr doped bulk rutile, the two electrons are distributed over Ti ions near the dopant, with no reduction of the dopant. The DFT+U result is to localize one electron on a Ti ion (that is not a
direct neighbour to the vacancy site), with a computed spin magnetization of 0.90 electrons and a Bader charge of +1.66, so that this is assigned as a Ti$^{3+}$ ion. The second electron is shared by two partially reduced Ti ions, where each Ti has a spin magnetization of 0.37 electrons. The HSE06 result is different, where there are two fully reduced Ti$^{3+}$ ions, with computed spin magnetizations of 0.75 and 0.77 electrons and Bader charges of +1.53 and +1.52 electrons. These reduced Ti ions are not neighbours to the vacancy site.

For Ce doped rutile with an oxygen vacancy, the DFT+U result gives one electron on a Ti that neighbours the vacancy site, with a computed spin magnetization of 0.97 electrons and a Bader charge of +1.72 electrons which is again consistent with formation of a Ti$^{3+}$ species. Contrary to Zr doping, the second electron is shared by Ce and a neighbouring Ti with spin magnetizations of 0.41 (Ce) and 0.34 (Ti), suggesting partial reduction of Ce and a second Ti in DFT+U, instead of full localization on two ions.
Figure 8.18 Atomic structure and excess spin density for the most stable oxygen vacancy structure with Ce and Zr doping in bulk rutile TiO$_2$. (a) Ce DFT+U, ($U = 0$ eV on Ce, 4.5 eV on Ti), (b) Ce HSE06, (c) Zr DFT+U, and (d) Zr HSE06. The orange color indicates the spin density isosurface; Ce is white; and Zr is blue. V indicates the vacancy site.
The HSE06 result is again different compared to DFT+U where the two electrons released by formation of the oxygen vacancy are found on the Ce species and on one Ti ion, with computed spin magnetizations of 0.93 and 0.84 electrons and Bader charges of 2.19 electrons and 1.58 electrons, respectively. This gives a Ce$^{3+}$ and a Ti$^{3+}$ ion, which are separated due to the repulsion that arises between two metal 3+ cations. We showed in table 8.4 that due to Ce doping there is a significant elongation in the Ce-O distances over the non-defective bulk that is typical of a fully localized Ce$^{3+}$ ion from HSE06, rather than the partially localized reduced Ce ion found with DFT+U that results in shorter Ce-O distances.

We explored in more detail the different solutions from DFT+U and HSE06 by using the DFT+U and HSE06 solutions as inputs to the other DFT approach to investigate if there are multiple solutions for the distribution of the electrons after oxygen vacancy formation [25, 28]. The results are presented in table 8.7 and show that using the DFT+U solution as a starting point for the HSE06 relaxation gives a solution that is less stable than the original solution by ca. 0.3 eV. For a relaxation with DFT+U starting from the HSE06 solution, the final solution is less stable by 0.60 eV. We can conclude that the precise distribution of the electrons that result from oxygen vacancy formation depends sensitively on the DFT approach and starting structure.
Table 8.6 Oxygen Vacancy Formation Energies (in eV) in Bulk Rutile from DFT+U and HSE06 under different input structures.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Zr</th>
<th>Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>Most stable $E^{\text{Ovac}}_{\text{eV}}$ with DFT+U</td>
<td>5.19</td>
<td>4.06</td>
</tr>
<tr>
<td>Most stable $E^{\text{Ovac}}_{\text{eV}}$ with HSE06</td>
<td>4.76</td>
<td>3.93</td>
</tr>
<tr>
<td>$E^{\text{Ovac}}_{\text{eV}}$ with DFT+U from HSE06</td>
<td>5.77</td>
<td>4.56</td>
</tr>
<tr>
<td>$E^{\text{Ovac}}_{\text{eV}}$ with HSE06 from DFT+U</td>
<td>5.07</td>
<td>4.30</td>
</tr>
</tbody>
</table>

Table 8.7 Effect of combinations of U applied to Ti and Ce on the oxygen vacancy formation energy in bulk rutile TiO$_2$.

<table>
<thead>
<tr>
<th>U on Ti</th>
<th>U on Ce</th>
<th>$E^{\text{vac}}_{\text{eV}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5 eV</td>
<td>0 eV</td>
<td>4.06</td>
</tr>
<tr>
<td>3 eV</td>
<td>0 eV</td>
<td>4.19</td>
</tr>
<tr>
<td>4.5 eV</td>
<td>5 eV</td>
<td>3.42</td>
</tr>
<tr>
<td>3 eV</td>
<td>5 eV</td>
<td>3.48</td>
</tr>
</tbody>
</table>
Figure 8.19 Excess spin density plots for oxygen vacancy in bulk rutile doped with Ce with different \( +U \) combinations on Ti and Ce.

In table 8.7 and figure 8.19 we show how the precise choice of \( U \) parameters on Ti and Ce can affect the oxygen vacancy formation energy. The energetics and the localization of the electrons from oxygen removal can depend on the DFT+U approach taken. It is important to emphasize that DFT+U approach with different \( +U \) set always results in reduction of the formation energy of the oxygen vacancy compared with undoped TiO\(_2\) and the formation of reduced Ce and Ti species.

This issue is quite general and work published recently has shown with reducible metal oxides that here can be solutions within a few tenths of an electron volt of the most stable solution from a given method [28, 44-45]. In ref [28], Camellone et al. used Car-Parrinello molecular dynamics to show that the distribution of Ti\(^{3+}\) in the reduced rutile TiO\(_2\) (110) surface with a bridging oxygen vacancy changes over time — the system samples energetically accessible distributions of reduced Ti\(^{3+}\) species. Chretien and Metiu [43] and Deskins et al.[44] have shown the Ti\(^{3+}\) species that result from oxygen vacancy formation can be distributed in many ways that lie close in energy. In ref. [45] it is discussed that adsorption of Au on the ceria (111) surface can result in different solutions for the oxidation state of Au, which is extremely sensitive to the method and starting structure used. Meredig et al. have demonstrated a controlled DFT+U approach to obtaining the most stable solution to a particular system within DFT+U and showed for an oxygen vacancy in the CeO\(_2\) (111) surface that different solutions with respect to orbital occupations can give energy differences up to 0.25 eV.
Other examples [38, 46] shows that for oxygen vacancies in ceria there can be multiple, energetically similar solutions.

In figure 8.19 we presented the structure which is the lowest energy structure, while other solutions can be higher in energy by 0.1-0.6 eV and this further emphasises the existence of multiple, low energy minima solutions to the problem of oxygen vacancy formation.

In figure 8.20 we present the PEDOS projected on Ti and the dopant in doped bulk rutile to further highlight differences between DFT+U and HSE06. DFT+U approach for both dopants result in two Ti 3d peaks in the band gap. However the localization of the peaks is different and the peak nearest the VB comes from the fully reduced Ti$^{3+}$ while the partially reduced Ti ions are the source of the peaks close to the CB. For Ce doping, the DFT+U approach shows a peak for partially reduced Ce$^{3+}$ in the same position as the peak of the partially reduced Ti ion. For Zr doping with DFT+U, there are no states associated with the dopant. In terms
of HSE06 solution for Zr dopant there is one broad peak that is made up of the
two reduced Ti ions in the structure; their peak positions are slightly different,
due to the different environment experienced by each Ti$^{3+}$ ion.

For Ce doping there are two peaks, where one comes from Ce$^{3+}$ and the second
from Ti$^{3+}$ and they lie at the same position in the band gap. The reduced Ti and
Ce are shown as peaks in PEDOS and are consistent with the spin density plots
presented in figure 8.20.

For doping of the (110) surface, figures 8.21 and 8.22 present the atomic
structures of Ce and Zr doped rutile (110) in the (2x2) surface supercell. Table
8.8 presents dopant-O distances for the most stable oxygen vacancy site where
bridging oxygen atom neighbouring the dopant, as shown in Figure 8.19. For Ce
dopant both approaches give similar description where the reduced symmetry in
the surface has a strong impact on the local structure around the dopant. Ce
dopant breaks the bond to the subsurface oxygen directly under it and makes a
new bond to a neighbouring bridging oxygen atom. The distances are similar to
both approaches and for DFT+U is 2.55 Å while for HSE06 is 2.65 Å. The Ce-O
distances are significantly longer over non-doped surface which is consistent
with formation of reduced Ce$^{3+}$. 
Figure 8.21 Atomic structure and excess spin density for an oxygen vacancy in the Ce-doped (110) rutile surface. (a) Oxygen vacancy in the Ce-doped (2x2) surface, (b) spin density with DFT+U, and (c) spin density with HSE06.

Figure 8.22 Atomic structure and excess spin density for an oxygen vacancy in the Zr-doped (110) rutile surface. (a) Oxygen vacancy in the Zr-doped (2x2) surface, (b) spin density with DFT+U, and (c) spin density with HSE06.
Table 8.8  Dopant-O Distances (in Å) in the Ce- and Zr-Doped Rutile TiO$_2$ (110) Surface with the Most Stable Oxygen Vacancy.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Dopant-O distance/Å</th>
<th>Dopant-O distance/Å</th>
<th>Dopant-O distance/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(110)(2x2) DFT+U</td>
<td>(110)(2x2) HSE06</td>
<td>(110)(2x4) DFT+U</td>
</tr>
<tr>
<td>Ce</td>
<td>2.24(x2), 2.34, 2.38, 2.55 (to bridging O)</td>
<td>2.21, 2.22, 2.33, 2.34, 2.65 (to bridging O)</td>
<td>2.25(x2), 2.38(x2), 2.56 (to bridging O)</td>
</tr>
<tr>
<td>Zr</td>
<td>2.04(x2), 2.09(x2), 1.94 (to subsurface O)</td>
<td>2.06(x2), 2.08(x2), 1.93 (to subsurface O)</td>
<td>2.04(x2), 2.09(x2), 1.96 (to subsurface O)</td>
</tr>
</tbody>
</table>

In the surfaces doped with Ce, an oxygen vacancy always results in formation of two reduced cations, namely, Ce$^{3+}$ and Ti$^{3+}$. For the smaller supercell both approaches both predict that a 6-fold coordinated Ti neighbouring the vacancy site is reduced to Ti$^{3+}$. The DFT+U result for the larger surface supercell, figure 8.23, is different to the smaller supercell. This surface model shows creation of subsurface Ti$^{3+}$ which is well-known for this particular surface supercell [28, 43, 44]. The elongation of Ce-O distances due to oxygen vacancy formation is consistent with the formation of localised Ce$^{3+}$.

Doping with Zr dopant in smaller surface supercell with DFT+U and HSE06 gives the reduction of a surface 6-fold Ti and a subsurface Ti, while for the larger surface cell, it is two subsurface Ti atoms that are reduced. This fact explains negligible distortion around Zr due to oxygen vacancy formation where only Ti ions which are away from the dopant site become Ti$^{3+}$. The Zr is not reducible so we have not found any stable solutions in which Zr is reduced.
Figure 8.23 Atomic structure and excess spin density for an oxygen vacancy in (a) Ce and (b) Zr doped (110) rutile (2x4) surface from DFT+U.

Figure 8.24 PEDOS for an oxygen vacancy with Ce and Zr doping in the (110) TiO$_2$ surface. (a) (2x2) Ce HSE06 , (b) (2x2) Zr HSE06 , (c) (2x2) Ce DFT+U, (d) (2x2) Zr DFT+U.

Figure 8.24 shows the PEDOS for the doped (110) surfaces with an oxygen vacancy. The DOS shown are projected onto the dopant 4f and 5d states for Ce.
and Zr and the Ti 3d states, and the PEDOS for both surface supercells are similar. Doping with Ce results with two peaks one due to reduced Ti $^{3+}$ and the other due to reduced Ce $^{3+}$. Both peaks lie at different energies in the band gap. The positions of the defect states are comparable within DFT+U and HSE06 where for HSE06 the defect states are well inside the gap, with Ti $^{3+}$ found closer to the conduction band than Ce $^{3+}$. While DFT+U give the same ordering of the peaks, both are positioned quite close to the valence band, particularly for Ce $^{3+}$. With Zr doping, the only peaks found arise from Ti $^{3+}$, and again similarities and differences between the DFT+U and HSE06 results are apparent.

8.3. Zr and Ce Doping in free and Supported TiO$_2$ Nanoclusters

We consider the Ti$_3$O$_6$ doped with Ce and Zr as an example of a TiO$_2$ nanocluster and examine how doping of a free nanocluster and a nanocluster supported on rutile (110) compared with bulk TiO$_2$ doping with Ce and Zr. These initial results provide a first examination of how nanostructuring may impact on the effect of doping of TiO$_2$. Subsequent work has been performed by Ms. A. Lucid [46] on other free TiO$_2$ nanoclusters doped with Ce and Zr and reference to this work will be made during this discussion.

For doping of a Ti$_3$O$_6$ nanocluster the three Ti sites were substituted with Ce and Zr, using the DFT+U approach applied for bulk doping (U = 4.5 eV on Ti and U = 0 eV on Ce) to determine the most stable dopant site. Figure 8.25 presents the atomic structure of undoped Ti$_3$O$_6$ and the most stable doping sites for Ce and Zr. For both dopants the most stable dopant site is at the same position in which the dopant is 3-fold coordinated which is the highest coordination number for Ti in this nanocluster. In the work on doping of larger Ti$_8$O$_{16}$ and Ti$_{16}$O$_{32}$ nanoclusters with Ce and Zr, it was found that the most stable dopant site for Zr is that where Zr can take a 5-fold coordinated cation site, while for Ce a 4-fold coordinated site is the most stable. Thus, we can see some effects due to nanostructuring in terms of dopant sites. We attribute these finds to the following. Zr has a similar ionic radius to Ti, so will strive to maximise its coordination number when it substitutes onto a Ti site. On the other hand, Ce has
a much larger ionic radius than Ti and in a nanocluster will take a cation site that facilitates structural distortions that stabilise the final structure, even if Ce usually prefers to take a high coordination number. Thus, one can see a balance between stable coordination number of a cation and the ability of the host lattice to distort so as to accommodate the foreign cation.

The Ti-O, Zr-O and Ce-O distances presented in figure 8.25 show typical cation-O bonds for the different cations present. The Ti-O distances are shorter than in bulk rutile or anatase due to the lower Ti coordination, while the elongation with Zr doping is similar to bulk and for Ce doping, the strong elongation in the cation-O distances is consistent with the ionic radius of the dopant.

Table 8.9 The oxygen vacancy formation energies for undoped Ti$_3$O$_6$ and for doped nanocluster with Ce and Zr.

<table>
<thead>
<tr>
<th>Ti$_3$O$_6$ nanocluster</th>
<th>E$^{O_{vac}}$/eV</th>
<th>E$^{O_{vac}}$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>2.31</td>
<td></td>
</tr>
<tr>
<td>Dopant</td>
<td>Ce</td>
<td>Zr</td>
</tr>
<tr>
<td>O vacancy site</td>
<td>E$^{O_{vac}}$/eV</td>
<td>E$^{O_{vac}}$/eV</td>
</tr>
<tr>
<td>O vac 1</td>
<td>+3.01</td>
<td>+0.71</td>
</tr>
<tr>
<td>O vac 2</td>
<td>+3.73</td>
<td>+2.23</td>
</tr>
<tr>
<td>O vac 3</td>
<td>+2.93</td>
<td>+0.76</td>
</tr>
<tr>
<td>O vac 4</td>
<td>+1.97</td>
<td>+2.83</td>
</tr>
<tr>
<td>O vac 5</td>
<td>-0.91</td>
<td>+2.76</td>
</tr>
<tr>
<td>O vac 6</td>
<td>-0.90</td>
<td>+2.94</td>
</tr>
</tbody>
</table>

Figure 8.25 Atomic structure and cation-O distances in the free Ti$_3$O$_6$ nanocluster (a): un-doped, (b): Ce-doped and (c) Zr-doped.
Table 8.9 presents the computed oxygen vacancy formation energies for undoped Ti$_3$O$_6$ and for doped nanocluster with Ce and Zr. The vacancy formation energy for the most stable vacancy site with Ce doping is +1.97 eV and for Zr the formation energy is +0.71 eV. In both cases the oxygen vacancy formation energies for the doped nanocluster are smaller than for the undoped nanocluster which is computed to be +2.31 eV; all oxygen vacancy formation energies are smaller than in bulk TiO$_2$, either undoped or doped with Ce and Zr. This indicates that a Ti$_3$O$_6$ nanocluster and doping of this cluster can improve the reactivity compared to bulk TiO$_2$. The reduction in the oxygen vacancy formation energy with doping is similar is broad terms to the bulk material, with the nanocluster doping showing enhanced reactivity by Zr doping, rather than by Ce doping.

However for the larger nanoclusters (Ti$_8$O$_{16}$ and Ti$_{16}$O$_{32}$ from Ms. Lucid work) the effect of doping on the vacancy formation energies now reveals strong cluster size dependence. The vacancy formation energies for Zr and Ce doped Ti$_8$O$_{16}$ are larger than for undoped Ti$_8$O$_{16}$, but these are still reduced over the bulk TiO$_2$ situation. For the Ti$_{16}$O$_{32}$ nanocluster, with diameter of 1.5 nm, doped with Zr, the vacancy formation energy is 1.74 eV while for the same undoped nanocluster, the vacancy formation energy is 1.63 eV. So for the largest nanocluster that has been investigated to date, Zr doping has only a negligible impact on the reactivity of the system. However, again, the formation energies in the nanocluster are reduced when compared with bulk TiO$_2$, so that nanostructuring may be a useful approach to enhanced activity of TiO$_2$. Further work remains to be performed on this topic, but the present results provide first insights into this interesting topic.

Figures 8.26 and 8.27 present the atomic structure around the most stable oxygen vacancy site in doped Ti$_3$O$_6$ nanoclusters, originally with composition CeTi$_2$O$_6$ and ZrTi$_2$O$_6$, respectively. For Ce doped Ti$_3$O$_6$ the most stable vacancy site is in the neighbourhood of the dopant while for Zr doped Ti$_3$O$_6$ the most stable vacancy sites are the two terminal oxygen atoms, with similar formation energies.
Table 8.10 presents the oxygen vacancy formation energies in supported Ti$_3$O$_6$-TiO$_2$, with the most stable oxygen vacancy formation energy for the undoped structure being +0.54 eV (as discussed in Chapter 7). Comparing this result with the energies in Table 7.2, we see that undoped Ti$_3$O$_6$ is more reactive when supported on the rutile (110) surface, as measured by the oxygen vacancy formation energy.
Table 8.10 The oxygen vacancy formation energies for the undoped and Ze, Ce doped Ti$_3$O$_6$-TiO$_2$

<table>
<thead>
<tr>
<th>Undoped</th>
<th>E$_{Ovac}$/eV</th>
<th>+0.54</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dopant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O vacancy site</td>
<td>E$_{Ovac}$/eV</td>
<td>E$_{Ovac}$/eV</td>
</tr>
<tr>
<td>O vac 1</td>
<td>+1.56</td>
<td>+1.94</td>
</tr>
<tr>
<td>O vac 2</td>
<td>+0.80</td>
<td>+1.07</td>
</tr>
<tr>
<td>O vac 3</td>
<td>+1.88</td>
<td>+3.01</td>
</tr>
<tr>
<td>O vac 4</td>
<td>+4.57</td>
<td>+5.32</td>
</tr>
<tr>
<td>O vac 5</td>
<td>+2.83</td>
<td>+3.52</td>
</tr>
<tr>
<td>O vac 6</td>
<td>+1.74</td>
<td>+2.16</td>
</tr>
</tbody>
</table>

However, Ce doping gives formation energy of the most stable site of +0.80 eV, which is larger than on the undoped Ti$_3$O$_6$-TiO$_2$ structure, but smaller than in the unsupported nanocluster. Zr doping of the supported nanocluster has an oxygen vacancy formation energy of +1.07 eV in the most stable site, which is again larger than the undoped supported nanocluster, but smaller than in the unsupported Ti$_3$O$_6$ nanocluster. In all cases, the most stable oxygen vacancy site is the same, oxygen site 2 (Figure 7.2 in reactivity chapter), showing that doping will not change the nature of the most reactive oxygen site.

Figure 8.28 presents the atomic structure and cation-O distances in undoped and Ce, Zr doped Ti$_3$O$_6$-TiO$_2$ with no oxygen vacancy. The geometry around the dopant compared to the undoped structure shows an elongation of the dopant-O bonds over the Ti-O distances, which is again particularly strong for the Ce doped structures, with Ce-O distances longer by 0.30 Å, which is again connected with the ionic radii of the dopant compared to Ti.
8.4.1. Discussion and conclusions

Given the extensive interest in doped TiO$_2$ for photocatalytic applications and our own interest in doping of TiO$_2$ nanoclusters (both free and supported on rutile (110)), as well as the vast literature on applying DFT to doped TiO$_2$, it was nonetheless somewhat unexpected to find that the literature was not so clear on the effect of dopants on the electronic properties and stable structures (e.g. charge compensating dopants) of doped TiO$_2$.

Before studying doped TiO$_2$ nanoclusters, we therefore undertook an extensive study of doping of bulk rutile and anatase and the rutile (110) surface with different dopants. We examined bulk rutile doping with trivalent dopants (Al, Ga, In) and bulk rutile and anatase and rutile (110) with tetravalent dopants (Ce, Zr). In addition, given the well known problems with using standard DFT exchange-correlation functionals to describe doping of oxides, we undertook each of these investigations with three DFT approaches: DFT with a GGA functional, DFT+U (with a variety of DFT+U setups, described in section 8.2.2) and hybrid DFT (in the form of screened exchange HSE06 functional).

DFT+U is often used for modelling of reduced cations in metal oxides such as TiO$_2$ and CeO$_2$, where the addition of the Hubbard U parameter recovers a
localized description of reduced cation states and has been applied to oxygen hole polarons that result from lower valent doping [38]. Despite the significant usage of DFT+U, it still creates some issues over its band gap underestimation and the dependence of properties on the precise DFT+U set-up. In this case comparison either with experiment which many DFT+U studies do, or with a more accurate modelling approach is required. However since reliable experimental results are not always available, hybrid DFT often serves as an excellent benchmark for DFT+U modelling. To date hybrid DFT in a plane wave basis set is significantly more expensive than DFT+U, limiting the size of the system to which it can be applied. Our intention in this investigation is testing DFT+U against a well-studied implementation of hybrid DFT for tractable systems, and if it provides a consistent description of the system under examination, then we can use it for larger-scale simulations. Based in these calculations we are able to assess the performance of DFT+U and point some on the strengths and weaknesses.

Taking first the trivalent dopants, the standard GGA-DFT approach is further confirmed to give an incorrect description of the nature of the oxygen hole formed upon trivalent doping of bulk rutile. The hole is delocalised and there are no structural distortions expected from a localised polaron state. However, we find that both DFT+U (with $U = 7$ eV on the O 2p states) and hybrid DFT give a solution with a localized oxygen hole and a distorted structure around the dopant site that are typical of an oxygen hole polaron. The extent of the local structural distortion, that is, the elongation of the metal-oxygen distances, is proportional to the ionic radius of the dopant. For DFT+U and hybrid DFT the density of states results in a localized feature in the band gap characteristic of the oxygen hole. However, while the DFT + U offset to the valence band is consistent with the hybrid DFT offset, the band gap underestimation in DFT +U means that the offset to the conduction band is too small and thus DFT+U will not result in correct offsets of the defect state to both the VB and the CB.

Oxygen vacancy compensation calculations show that from DFT+U and hybrid DFT, oxygen vacancy compensation of these dopants will occur. However, an important issue here is that the hybrid DFT energies are significantly more
negative than the DFT+U energies (for the present DFT+U set-up, which is a robust and typical DFT+U set-up in such calculations). This difference has also been seen in divalent doped ceria [38]. This difference in computed energies, which is a general issue, is interesting when one wishes to examine deeper differences between DFT approaches in describing reducible metal oxides and has been discussed in a recent review [49]. However, it is important to note that the qualitative findings regarding the energetics of oxygen vacancy compensation are the same from DFT+U and HSE06, giving some confidence in using the former approach.

We studied Ce and Zr doping of rutile and anatase bulk TiO$_2$ and the rutile (110) surface, using DFT+U ($U = 4.5$ eV on Ti 3d states, but see section 8.2), and HSE06 DFT. We conclude that both simulation approaches result in many similar qualitative results like: favourable incorporation of the dopants, reduced oxygen vacancy formation energies with Ce doping, and larger oxygen vacancy formation energies for Zr doping. However, the quantitative comparison between DFT+U and HSE06 result highlights some issues with DFT+U.

One such difference is a notable difference in computed oxygen vacancy formation energies, which could be important in assessing the stability of defect structures. In our investigations where the oxygen vacancy results in formation of reduced cations, HSE06 stabilizes the bulk oxygen vacancy compared to DFT+U. In terms of the TiO$_2$ rutile (110) surface the HSE06 oxygen vacancy formation energy is larger than the DFT+U formation energy. Since this is associated not only with strong dependence on $U$, other factors that can influence this difference include the error in the binding energy of O$_2$ with DFT [47] and the improved description of electronic states with HSE06. We may assume that these differences between DFT+U and HSE06 may not be so important, as long as the two methods are consistent, nevertheless it is important should always to be aware that an assessment of errors in the DFT+U energies, e.g., by comparison to a more accurate approach, needs to be undertaken.

Second, while investigating the electronic structure of doped material the DFT+U band gap from the present setup is too small. This issue may be resolved
by application of the large U value (ca. 8-10eV) [48] such values of U impact negatively on other properties.

Table 8.11 Offsets (in eV) from the valence and conduction bands of the Ce$^{4+}$ state in Ce doped bulk rutile TiO$_2$ and of the Ce$^{3+}$ and Ti$^{3+}$ states in Ce doped bulk rutile TiO$_2$ with an oxygen vacancy. A positive sign of the offset from the VB means that the state is found above the VB, while relative to the CB, a negative sign means that the state is found below the CB and a positive sign that the state is found above the CB.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Offset from VB DFT+U</th>
<th>Offset from VB HSE06</th>
<th>Offset from CB DFT+U</th>
<th>Offset from CB HSE06</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce doped bulk TiO$_2$</td>
<td>Ce 4f: +2.1 eV</td>
<td>Ce 4f: +3.6 eV</td>
<td>Ce 4f: -0.1 eV</td>
<td>Ce 4f: +0.5 eV</td>
</tr>
<tr>
<td>Ce doped bulk TiO$<em>2$$</em>{x}$</td>
<td>Ce 4f: +2 eV</td>
<td>Ce 4f: +2.2 eV</td>
<td>Ce 4f: -0.3 eV</td>
<td>Ce 4f: -1.1 eV</td>
</tr>
<tr>
<td></td>
<td>Ti 3d: +1.1 eV$^a$, 2eV$^b$</td>
<td>Ti 3d: +2.2 eV</td>
<td>Ti 3d: -1.6 eV$^a$, -0.3 eV$^b$</td>
<td>Ti 3d: -1.1 eV</td>
</tr>
</tbody>
</table>

$^a$: the fully localised Ti$^{3+}$

$^b$: the partially localised Ti$^{3+}$

In Table 8.11 we present the position of the Ce 4f states in doped bulk rutile and in the (110) surface and the position of the reduced Ti$^{3+}$ and Ce$^{3+}$ states after oxygen vacancy formation in Ce-doped bulk TiO$_2$ and in the (110) surface. The strongest consistency within DFT+U and HSE06 takes place in the position of the defect states relative to the conduction band. In Ce-doped TiO$_2$, with no oxygen vacancies, the Ce 4f states are very close to the conduction band. DFT+U predicts them to lie lower than the oxide conduction band, while HSE06 predicts the Ce 4f states to lie above the CB in bulk and at the CB edge in the (110) surface. However during experiment the oxide is usually a film or in nanoparticle form, rather than the bulk structures in the present investigations so the observed small red shift of the absorption edge may come from structure itself and we have examined this aspect as well, with the doped rutile (110) surface presenting a different position for the Ce4f states relative to the Ti 3d CB compared to bulk doping.

Since DFT+U presents significant issue with band gap underestimation the precise position of the dopant states in a DFT+U calculation will depend on the
value of U used and to which species it is applied. To better illustrate this problem, we applied U to the Ti 3d states, raising the empty Ti 3d states to higher energy, but if we also apply U = 5 eV to the Ce 4f states, then these move higher in energy and lie above the Ti 3d conduction band. In light of this problem we need to take extreme care in making quantitative statements about the position of dopant states from DFT+U calculations without making reference to higher quality calculations or experimental data.

The oxygen vacancy calculation results also shade the light on the differences with respect to the distribution of the two electrons released upon removal of oxygen, with DFT+U spreading the two electrons over three cations and HSE06 is fully localizing the electrons on two cations. Again this difference plays an important role in the comparison between DFT+U and HSE06 approaches. The presented results in table 8.11 show that the biggest difference between HSE06 and the present DFT+U setup is in the position of the Ti$^{3+}$ state relative to the valence band, with a smaller error for the offset to the conduction band. The similar trend is found for the Ti$^{3+}$ species in the oxygen-deficient (110) surface. We found that the offset to the conduction band is better with applied value of U than is the offset to the valence band which can be explained that Ti$^{3+}$ states come from the Ti 3d derived conduction band. However resolving the issue with DFT+U could be choosing the U value which would give the exact same result as HSE06 but this would then introduce a large error in the conduction band offset. Thus DFT+U approach would always give different band gap alignments because it is not possible to obtain a position for the gap state that is consistent with HSE06.

Finally, from our initial examination of doping of a Ti$_3$O$_6$ nanocluster with Ce and Zr, along with some work on other doped TiO$_2$ nanoclusters, there is a strong dependence of the oxygen vacancy formation energy on the size of the TiO$_2$ nanocluster, with the smallest nanoclusters showing enhanced oxygen vacancy formation upon Ce doping, but this disappears with larger nanoclusters. Supporting a doped Ti$_3$O$_6$ nanocluster on the rutile (110) surface leads to a small increase in the oxygen vacancy formation compared to the undoped supported nanocluster.
References:


46. A. Lucid; Doping Metal Oxides Nanostructures: Elucidating Differences to Bulk Doping


9. Experimental methods and connection to experiment, Conclusions and Future Work

9.1. Relation to experiment

First principles simulations play an ever growing and important role in predicting the properties of new structures and materials compositions, as demonstrated and discussed in detail in the previous chapters of this thesis. However while we can obtain a reliable picture of the changes due to modification of the parent material, there are still some issues with DFT simulations, and therefore a comparison of DFT results with experiment serves to provide more confidence in the computed results. With the development of the chemisorption-calcination cycle (CCC) approach by Tada and co-workers to modify TiO₂ with metal oxide nanoclusters, a direct comparison of theoretical and experimental results is now possible and indeed in a series of papers, we have shown the consistency between experiment and simulation [1-5].

In our cooperation with Prof. Tada and his research team, we have investigated a number of metal oxide nanocluster modified TiO₂ systems using DFT and experiment. The preparation of the experimental samples is based on the CCC technique, in which the metal complexes are adsorbed via strong chemical bonds while the organic part is oxidized by post-heating [3]. After this synthesis process, molecular sized metal oxide nanoclusters are formed in a highly dispersed state on TiO₂ surfaces [3]. It is important that the modifying oxide be present in this state and not as a film or large particle. In the latter case the oxide nanoparticle would function as a sensitizer instead of a modifier. In the following we discuss the relationship between our DFT results and those from the experiments.
9.2. NiO Modified TiO₂ Rutile and Anatase

Heterostructures of NiO nanocluster on P-25 (which is a mixture of rutile and anatase = 4/1 w/w) were formed using CCC technique. The samples were characterized by high resolution transmission electron microscopy (HRTEM) presented in figure 10.1 which shows highly dispersed NiO clusters that are smaller than ~2nm adsorbed at TiO₂ surfaces. VB-XPS analysis was performed, with the results shown in figure 9.2 and the XPS data show clearly that the top of the valence band rises with an increase in the loading of NiO.

Figure 9.1 HRTEM images of NiO Nanocluster modified TiO₂. (A) \( \Gamma = 0 \); (B) \( \Gamma = 0.014 \); (C) \( \Gamma = 0.47 \); (D) \( \Gamma = 0.83 \).

Figure 9.2 (A) VB-XPS Results for NiO loaded P/25, \( \Gamma = 0.0018, 0.014, 0.16, 0.32, 0.39, 0.47, 0.7, 0.83 \), (B) magnified VB-XPS near the VB maximum.
Figure 9.3 (A) Optical absorption plot for NiO loaded P/25. (B) Tauc plot.

The optical absorption data are shown in figure 9.3, where 9.3 (A) shows the plot of Kubelka-Munk function against wavelength and the shift of the absorption edge to longer wavelength with increased NiO loading is clear. Figure 9.3 (B) shows a Tauc plot of the same data to determine the optical gap. The optical gap shifts to lower energy with an increase in NiO loading.

The effect of the band gap narrowing on photocatalytic activity was also examined through studying the degradation of 2-Napthol and p-cresol degradation which followed the first order rate under irradiation of UV and visible light. However the visible light activity shows an optimum loading, which is achieved at $\Gamma = 0.47$ whereby the visible light activity is $\sim 2.8$ times of P-25 activity.
Figure 9.4 Visible-light (A) and UV-light (B) activities of NiO/P-25 for 2-naphthol (red circles) and p-cresol (blue circles) degradations.

To understand the experimental findings, our DFT simulations show that NiO clusters interact strongly with TiO₂ surface by formation of interfacial Ni-O-Ti bonds at both rutile (110) and anatase (001) surfaces. In addition, there are new intermetallic Ni-Ti bonds formed. Due to the interaction of NiO and TiO₂ NiO derived Ni 3d and O 2p states appear at the top of the valance band and this pushes the valence band higher in energy compared to unmodified TiO₂, which will shift the absorption to lower energy and induce light absorption in the visible region. Examining the density of states, we see that visible light excitation of NiO nanocluster modified-TiO₂ will result in electron transfer to the CB of TiO₂, leaving a VB hole which will be localised on the NiO nanocluster. This improves electron and hole separation which is important for the photocatalytic activity and leads to improved performance in UV and visible light activity. The photoexcited holes are utilized for oxidation of 2-NAP and p-cresol, while the
electrons will be used in the reduction of O\textsubscript{2} to superoxide. The finding of an optimum activity of 2-NAP and p-cresol degradation arises from the rise of the VB in energy with NiO loading. Initially, the NiO loading induces visible light absorption, which enhances the photocatalytic activity, but at higher loadings, the VB edge shifts high enough in energy that the oxidative power of the photogenerated holes is reduced, as discussed in ref [4].

**9.3. CuO Nanocluster Modified TiO\textsubscript{2}**

CuO clusters were formed on P-25 Degussa the CCC approach in a highly dispersed state, where Cu(acac)\textsubscript{2} was used as precursor. Figure 10.6 presents the UV-visible absorption spectra of CuO/P-25 samples. There is a band gap narrowing present, with the absorption tail at 400-500nm at a loading of $\Gamma$=0.32. A weak d-d transition typical for Cu\textsuperscript{2+} ions appears at 700-800nm which is in contrast with work of Hashimoto [6] where Cu\textsuperscript{2+}/TiO\textsubscript{2} were prepared by ion impregnation. For CuO/modified TiO\textsubscript{2} the band gap shows a narrowing from 3.1eV at $\Gamma$=0 to 2.9eV at $\Gamma$=2.1. The oxidation state was studied by XPS and confirmed as +2 for copper.
To study the photocatalytic activity 2-napthol and p-cresol were used as model water pollutants. For both pollutants the photocatalytic degradation followed the first-order rate law under UV and visible light illumination. CuO-modified TiO$_2$ shows strongly enhanced activity for the degradation of these model pollutants in figure 9.7, particularly under visible illumination. Similar to other modified TiO$_2$ structures, there is a peak in the activity of pollutant degradation with CuO loading, with the plot in figure 9.7 showing a volcano-like shape.
Figure 9.6 Plots of the rate constants for the degradations of 2-naphthol (A) and p-cresol (B) under irradiation of visible-light and UV-light as a function of $I$.

From the DFT simulations, we found that the smallest CuO nanoclusters ($\text{CuO}_n$, where $n=1$, supported on rutile and anatase gives rise to an unoccupied Cu 3d level in the band gap arising from the unoccupied Cu 3d state in Cu$^{2+}$. At the same time, the top of the valence band of TiO$_2$ is only slightly affected. However in larger CuO nanoclusters, which would be equivalent to higher CuO coverage, a significant upwards shifts in the position of the valence band of TiO$_2$ is found which is consistent with the experiments. It therefore appears there are two possible mechanisms for visible light absorption in this system and this depends on the size or loading of the CuO nanocluster.

As the photocatalytic activity depends on the ability to enhance the electron/hole separation, we predicted that charge carrier recombination will be reduced due to surface modification. The PL (photoluminescence spectroscopy) spectra were obtained for CuO/P-25. When compared to P-25 the PL intensity significantly
decreases and disappears at $\Gamma > 1.08$ thus signifying that charge carrier recombination is significantly reduced.

Figure 9.7 PL spectra of CuO/P-25 with varying $\Gamma$ at 77 K: excitation wavelength = 320 nm.

9.4. SnO$_2$ modified TiO$_2$ Rutile and Anatase

For the formation of SnO$_2$ nanoclusters on rutile and anatase, as an example of a p-block metal oxide modifier, [Sn(acac)$_2$]Cl$_2$ was used as a precursor, and this work allowed differences between the rutile and anatase TiO$_2$ crystal forms to be studied. Transmission electron microscopy (TEM) was used to examine the surface of rutile and anatase and no particles were found after post-heating of the complex-adsorbed TiO$_2$, which is taken as evidence that molecular sized nanoclusters are formed. The oxidation state of Sn in SnO$_2$ was confirmed to be 4+ using X-ray photoelectron spectroscopy. Boppana showed that the oxidation state of tin in SnO$_x$ modified ZnGa$_2$O$_4$ is controlled simply by changing the precursor to have the desired Sn oxidation state [7].
The optical properties of SnO$_2$ nanocluster modified TiO$_2$ were examined by UV-vis absorption and the spectra are shown in figure 9.8. There are immediately apparent differences in the optical properties when comparing rutile and anatase TiO$_2$ modified with SnO$_2$. For anatase, there is no spectral change due to surface modification with SnO$_2$: the absorption edge is invariant with SnO$_2$ loading and the absorption intensity is also essentially unchanged, see figure 9.9 (a).

For SnO$_2$-modified rutile, the absorption intensity clearly increases at short wavelength, while the absorption edge is invariant. This indicates some enhancement of light absorption and is in contrast to anatase.

The photocatalytic degradation of 2-NAP, and acetaldehyde, which is a model air pollutant, was undertaken. Under UV irradiation there is a significant increase in the rate of degradation of 2-NAP and acetaldehyde for SnO$_2$-modified rutile (red points in figure 9.9 (A)), but this effect is only very small for SnO$_2$ deposited on anatase and disappears under low SnO$_2$ loading. Under visible light irradiation, SnO$_2$-anatase shows no activity, while rutile does show an increase in visible light activity, the effect of SnO$_2$ on the visible light photocatalytic activity is still rather small.
Comparison with the DFT simulations gives the necessary insights to understand these differences. Firstly, there is no band gap change predicted as a result of modification of anatase with SnO$_2$, as the electronic states from SnO$_2$ lie too far below the VB and above the CB edges of anatase to modify the band gap. The presence of empty SnO$_2$ above the CB can enhance UV activity if electrons can be promoted to those states, as this would enhance charge separation.

For rutile we found unoccupied SnO$_2$ states lying just below the rutile conduction band, which can enhance light absorption around the UV region, but not necessarily increase visible light absorption. This enhanced UV absorption can be explained by the fact that due to the proximity of the SnO$_2$ states to the TiO$_2$ CB (and these states are nearer the TiO$_2$ than are the SnO$_2$ in modified anatase) the electrons can be excited to the SnO$_2$ states with slightly lower energy radiation which can improve photocatalytic activities. These cluster levels will further improve UV light activity due to an enhancement in charge separation.
9.5. Conclusions and future work

The function of a photocatalyst is to absorb light energy which produces electrons and holes that can be utilized in redox reactions, either directly or by transfer to another active species. TiO$_2$ is a leading candidate as a practical photocatalyst due to its non-toxicity, abundance and relatively low cost. However, TiO$_2$ suffers because its band gap does not allow unmodified TiO$_2$ to absorb light in the visible region. In this thesis we have focused on modifying TiO$_2$ with metal oxide nanoclusters in order to design new materials that will serve as new photocatalysts that are active under visible light illumination, which will allow them to be used with solar energy, for example.

We examined different nanocluster modifications of rutile and anatase TiO$_2$ to try to derive some general ideas for nanocluster modification of semiconducting metal oxides for visible light photocatalysis. This included modification with TiO$_2$ nanoclusters, transition metal oxide nanoclusters, p-block metal oxides and an examination of the effect of metal oxidation state, TiO$_2$ crystal form and nanocluster size. The nature of the photoexcited state was studied, giving important insights for the question of charge carrier separation and photocatalytic activity. Since these materials would be used in chemical reactions, we examined the reactivity of TiO$_2$ nanocluster modified TiO$_2$ for a prototypical oxidation reaction, namely CO oxidation. Finally, since bulk doping is widely studied as a means to modify TiO$_2$, we present some studies benchmarking bulk doping of TiO$_2$ with different DFT approaches and initial results on doping of TiO$_2$ nanoclusters, making comparison to bulk doping.

The modification of TiO$_2$ with TiO$_2$ nanoclusters from sub-nm to 1.5 nm diameters allowed us to investigate (1) what is the impact on TiO$_2$ band gap after surface modification, (2) if the size of nanoclusters can play a role in tuning properties of modified TiO$_2$ and (3) the fate of excited electrons and hole. The adsorption energies upon deposition of the nanoclusters are large and negative which indicates that the formation of interfacial Ti-O bonds drives the thermodynamic stability of these structures. The creation of the interface between the nanoclusters and TiO$_2$ surface modifies the electronic structure of
TiO$_2$ and reduces its band gap. Moreover the nature of the valence and conduction bands indicates that spatial separation of charge after photoexcitation will be enhanced over unmodified TiO$_2$. In terms of the effect of nanocluster size, the extent of band gap narrowing is strongly dependent on the size of the nanocluster, suggesting a means to tune the photocatalytic activity.

Models of NiO nanoclusters supported on rutile (110) and anatase (001) surfaces were also studied. The modification of TiO$_2$ with NiO nanoclusters can result in a reduction of the band gap by up to 0.8 eV. Given the errors associated with DFT and DFT+U, the qualitative agreement with the experimental shift in the absorption edge and the 0.8 eV shift in the VB edge from XPS [8] is rather encouraging. The deposition of NiO nanoclusters on P-25, resulted in a reduction of the original band gap of TiO$_2$. The photocatalytic activity in the visible region is predicted to be enhanced, which was confirmed by the degradation of 2-NAP over NiO-modified TiO$_2$. The deposition of CuO nanoclusters on rutile and anatase surfaces results in a reduction in the band gap, consistent with experiment. However our detailed examination of the electronic structure of CuO-modified TiO$_2$ material reveals that the size of the CuO nanoclusters (the loading at the surface in the experiments) plays an important role. For the smallest nanoclusters we find an unoccupied Cu$^{2+}$ 3d electronic state lying 1 eV below the TiO$_2$ conduction band edge, which is similar to the interpretation of Irie et al in their studies of Cu$^{2+}$-modified TiO$_2$ – the absorption of visible light will excite an electron from the VB to the empty Cu$^{2+}$ state in the band gap. On the other hand, with larger CuO nanoclusters, the valence band edge shifts upwards due to the presence of CuO-derived states and the empty Cu$^{2+}$ states move towards the conduction band of TiO$_2$ so that the band alignments now indicate excitation of an electron from CuO to the empty Ti 3d states of the surface.

The next series of metal oxides was the p-block metal oxides SnO/SnO$_2$ and PbO/PbO$_2$. We investigated in detail two important aspects of these systems. (1) the influence of the Sn$^{2+}$ and Pb$^{2+}$ lone pair and (2) to investigate if there is any sensitivity to the TiO$_2$ crystal form. The third question that we tried to answer is if the oxidation state of the metal in the metal oxide nanocluster is important in modifying the band gap of TiO$_2$. SnO nanoclusters supported on both rutile and
anatase TiO$_2$ surfaces result in a reduction of the original band gap of TiO$_2$.
Moreover these findings are consistent with previous experimental and theoretical work for [9,10]. The DFT simulations show a band gap reduction rising from an upwards shift of valence band edge, leaving the conduction band un-changed.

In contrast, while SnO$_2$ nanoclusters adsorb strongly at rutile and anatase surfaces, there is a significant difference arising from the Sn oxidation state. As discussed in Sec 9.4, SnO$_2$ modification of anatase does not change the band gap of anatase and there is no improvement in the photocatalytic activity of anatase TiO$_2$. For rutile TiO$_2$, SnO$_2$ does modify somewhat the light absorption around the absorption edge, with new SnO$_2$ derived states present around the rutile CB edge. This does result in an enhancement of the visible light photocatalytic activity over unmodified rutile.

Comparison between the effect of SnO and SnO$_2$ nanocluster modification of TiO$_2$ shows clearly that the oxidation state plays an important role in tuning photocatalytic properties of modified TiO$_2$. The electronic structure in this section shows a novel way for band gap reduction due to the lone-pair present in SnO. This result sheds new light on the possibility of exploiting the different electronic features of the metal in deposited metal oxide for tuning the photocatalytic properties.

To further study the oxidation state effect in p-block metal oxides, we examined modification of TiO$_2$ with PbO and PbO$_2$ nanoclusters. The modification of both TiO$_2$ rutile (110) and anatase (001) results in reduction of the band gap for both lead oxide oxidation states, so we conclude that there is no sensitivity to the form of TiO$_2$. Based on our DFT simulation results we postulate that for PbO and PbO$_2$ nanoclusters supported on TiO$_2$ the visible light activity will be induced. The most interesting result is that the electronic structure suggests different mechanisms for band gap reduction and charge separation. For PbO supported on TiO$_2$ the lone pair states from PbO nanoclusters are introduced at the top of the valence band of TiO$_2$, while the modification with PbO$_2$ nanoclusters results in new states below the original conduction band of TiO$_2$. Thus, PbO promotes
excitation of electrons from the PbO valence band, while PbO₂ promotes excitation of electrons from the TiO₂ valence band. In light of these results we postulate that the oxidation state can have important role in tuning the properties on the photocatalyst. With PbO nanoclusters the presence of the Pb 6s-O-2p derived lone pair pushes up the valence band edge. However, the lone pair effect is smaller when compared to SnO modified TiO₂. Comparison with the bulk materials shows a similar trend, where the lone-pair is weaker in PbO compared to SnO [11].

As a final investigation in exploiting the lone-pair effect metal oxides, we studied Bi₂O₃ nanoclusters supported on rutile (110). Our DFT simulations suggest that the band gap reduction of TiO₂ for Bi₂O₃ nanoclusters is not promoted by the lone pair in Bi₂O₃, but is instead similar to the mechanism outlined for supported transition metal oxide nanoclusters discussed above. The electronic structure shows the introduction of the new states of Bi 6s-O-2p at the top of the valence band of TiO₂ and conduction band is left unmodified. The reduction of the band gap may cause visible light absorption. The investigation of any lone-pair effect shows no notable influence of the lone pair, which is consistent with the weaker Bi³⁺ lone pair, compared with SnO [6].

We thus propose some overall concepts important for inducing band gap reduction in TiO₂ based on modification with metal oxide nanoclusters

(1) Small, well dispersed metal oxide nanoclusters

(2) Formation of metal-oxygen-metal interfacial bonds, and metal-metal bonds where possible

(3) Oxides with band gaps similar to TiO₂ are advantageous towards band gap reduction

(4) Oxides with conduction bands derived from empty d-states

(5) The lone pair in Sn²⁺ and Pb²⁺ can be used to shift the valence band to higher energy.
A second and very important aspect in designing efficient photocatalysts is the fate of the photoexcited electrons and holes, which are used in the photochemistry of these materials. Of great importance is that charge separation be enhanced over unmodified TiO$_2$ to increase the lifetime of electrons and holes and reduce the probability of charge recombination. While we face a challenge to develop a material that promotes the separation of holes and electrons during photoexcitation, this key problem remains generally neglected in modelling studies.

To address this situation, we have investigated a model of the photoexcited state of our modified TiO$_2$ structures, which was discussed in chapter 6. The simple density of states analysis predicts that the localisation of the photogenerated electrons and holes is driven by the nature of the valence and conduction bands and we examined this idea in our models of the photoexcited state.

We have examined the localisation of photogenerated electrons and holes in representative Ti$_3$O$_6$, Ti$_4$O$_8$ and Ti$_5$O$_{10}$ nanoclusters on rutile (110) surface, SnO nanocluster on anatase (001) and PbO$_2$ and PbO nanoclusters deposited on rutile (110) and Bi$_2$O$_3$ supported on rutile (110). For all these structures we found that deposition of nanocluster on TiO$_2$ result in a decrease of the singlet-triplet excitation energy, entirely consistent with the DOS analysis. The composition of modified TiO$_2$ determines the details of changes to the VB or CB with surface modification.

For TiO$_2$ nanoclusters, Sn$_4$O$_4$, PbO and Bi$_2$O$_3$ nanoclusters supported on TiO$_2$ the excitation, relaxation and vertical energies were analysed. For modified TiO$_2$ the excitation energies are notably smaller than for bare surface which confirms the shift to smaller excitation energies, potentially into the visible energy region, that was discussed from the density of states. Importantly we also investigated the location of the photogenerated electrons and holes. For TiO$_2$ nanoclusters supported on TiO$_2$ the excited electron is localised on a subsurface Ti atom of rutile (110) while the hole is found on a low coordinated oxygen atom in the nanocluster. As a consequence of this charge carrier separation will be improved.
over bare TiO$_2$. The ability of the hole to localise onto a low coordinated oxygen site is important in determining the localisation of the photogenerated hole.

For SnO nanocluster supported on TiO$_2$ the electron and hole separation is also found; however as a result of the Sn-O lone pair, the hole is distributed over Sn-O bonds. For PbO and PbO$_2$ nanoclusters supported on TiO$_2$, the oxidation state of Pb plays a determining role. In PbO supported on TiO$_2$ the electron is again found on a subsurface Ti site while the hole is localised on oxygen atom from the PbO nanocluster, which arises from the weaker lone-pair in PbO compared to SnO. PbO$_2$ nanocluster modified TiO$_2$ shows a different electron and hole localisation. The excited electron is distributed over the PbO$_2$ nanocluster and the hole is found on localised 2-fold coordinated bridging oxygen from the rutile (110) surface. In both PbO and PbO$_2$, a reduction of the band gap is present; however the differing localisation of the electron and hole suggest different photoexcitation mechanisms.

We have examined the reactivity of TiO$_2$ nanocluster modified TiO$_2$, considering the possibility for these structures to be applied in oxidation reactions such as CO oxidation to CO$_2$. For such reactions we employ the oxygen vacancy formation energy as a descriptor to understand the the potential catalytic activity of the oxide [13-15]. The unmodified rutile (110) surface has a rather high oxygen vacancy formation energy, which is +3.6 eV and we can compare this number to nanocluster modified TiO$_2$. For a series of TiO$_2$ nanocluster modified TiO$_2$ structures the vacancy formation energies are much smaller, for example 0.54 eV for Ti$_3$O$_6$ modified TiO$_2$, indicating that these structures will be more reactive than unmodified TiO$_2$. We examined the possibility of a Ti$_3$O$_6$-TiO$_2$ structure to be used for a simple oxidation reaction, that is the oxidation of CO to CO$_2$ following the Mars van Krevelen mechanism. We investigated the following reactions (i) interaction of CO with the stoichiometric Ti$_3$O$_6$-TiO$_2$ structure, (ii) removal of CO$_2$ and formation of an oxygen vacancy, (iii) interaction of O$_2$ with the oxygen vacancy and the possibility of superoxide or peroxide formation, (iv) interaction of CO with the structure in reaction (v) and formation of a second CO$_2$ molecule.
We found that most of the reaction steps in this set of reactions are favourable so that overall, the oxidation of CO to CO₂ is favourable. This suggests that the reactivity of modified TiO₂ for oxidation reactions is enhanced over un-modified TiO₂ which can be utilized in CO oxidation reaction or water gas shift.

Finally, we studied doping of bulk TiO₂. These investigations arose since we proposed to study doped TiO₂ nanoclusters and compare their doping to bulk doping. However, the literature on this topic was not satisfactory, so we undertook a study of doping of TiO₂ with trivalent and tetravalent dopants, while at the same time examining the applicability of different DFT approaches. The latter is important as a local GGA exchange-correlation functional can present significant issues when applied to doping of TiO₂. Thus, we compared GGA-DFT, DFT+U and hybrid DFT (using the HSE06 screened exchange functional).

For trivalent dopants we investigated the formation of an oxygen hole polaron and oxygen vacancy charge compensation upon doping with Al³⁺, Ga³⁺ and In³⁺ using DFT, DFT+U and HSE06. We confirmed that standard GGA-DFT approach gives an incorrect description of the oxygen hole formed in trivalent doping of bulk TiO₂: the hole is delocalised and there is no distortion around the localised polaron state. The DFT+U and hybrid DFT approaches result in formation of a localised polaron state together with local distortions around the polaron. A quantitative comparison of the electronic structure and the formation of compensating oxygen vacancies highlights some issues with DFT+U namely: the underestimation of TiO₂ band gap, giving incorrect offsets of the defect state to both valence and conduction band and the notable difference in the magnitude of the oxygen vacancy formation energies compared to the HSE06 approach. However, the issues with the computed energies are already known [13, 14], and the qualitative similarities bring some confidence in using DFT+U. However if possible, there should be screened experimental results should be compared in order to assess DFT+U results.

For Zr and Ce doping of TiO₂ with DFT+U and HSE06. The major issue is the description of the electronic structure of Ce-doped TiO₂ with DFT+U, taking the HSE06 result as a benchmark. The position of the Ce derived 4f state depends
sensitively on the DFT+U set-up, which means that one must take care in deciding of a dopant induced state is really present or not. The oxygen vacancy formation energy is reduced for Ce doping, while for Zr doping the vacancy formation energy is larger compared to undoped TiO$_2$. In addition, the location of electrons released by oxygen vacancy formation can depend on the DFT+U set up.

The initial results for doping TiO$_2$ nanoclusters with Ce and Zr shows strong dependence of the oxygen vacancy formation on the size of the TiO$_2$ nanocluster size. We also find that the oxygen vacancy formation with Ce as the dopant is no longer more favourable over undoped nanoclusters for larger nanoclusters. When we consider a doped Ti$_3$O$_6$ nanocluster supported on the rutile (110) surface, the oxygen vacancy formation energy shows a small increase when compared to undoped supported nanocluster. Further work on doped TiO$_2$ nanoclusters will be of interest to establish the effect of nanocluster size on the reactivity.

The results presented in this thesis demonstrate clearly that a DFT simulation approach can be used to design, in a rational fashion, new photocatalyst materials based on a novel approach of modifying TiO$_2$ (or any semiconducting metal oxide) surfaces with nanoclusters of metal oxides. We have shown that this modification will generally result in the upwards shift of the valence band due to new nanocluster derived electronic states. In some cases, it is the conduction band edge that is shifted or there is little or no effect arising from the modification. These scenarios are well understood.

We have shown that the photoexcited electrons and holes will localised onto low coordinated metal or oxygen sites and that the location of the electrons and holes can be predicted from an analysis of the density of states. The localisation of charge carriers will lead to improved charge separation.

Comparison with experimental results, where these have been undertaken, confirms the results of the DFT analysis, giving further confidence in this design approach. This gives further confidence in this design approach. Thus, this thesis has demonstrated a novel approach for designing, in a rational fashion, new photocatalyst materials based on modifying TiO$_2$ with nanoclusters of metal
oxides, where visible light absorption and enhanced charge carrier separation can be induced. The structures we have considered are composed of non-toxic, earth abundant elements, with no need for precious metals or rare earths or materials that are unstable under, say, water splitting conditions. This opens up a new avenue to developing and deploying TiO$_2$ as a visible light active photocatalyst.

Further work that can be undertaken in this area includes

- an analysis of other metal oxide nanocluster modifiers, such as CoO$_x$, MnO$_x$, VO$_x$, and investigating the properties of these new heterostructures.
- a dynamics approach to study the lifetime of photogenerated electrons and holes, such as developed by the groups of Coker or Prezdiho, would allow the lifetime and stability of the excited electron and hole to be examined. This would allow conclusions regarding the effect of surface modification on the lifetime of charge carriers to be drawn. These can be compared with experimental results.
- Given that this work has shown the potential for surface modified TiO$_2$ photocatalysts, the possibility exists to investigate these new photocatalyst materials for the initial stages in the photoreduction of CO$_2$ (for, e.g. CH$_4$ production) or water oxidation. This activity, while very important, lies outside the scope of this thesis.
- Further work on the effect of nanocluster doping would be interesting.
- Finally, one could extend this novel concept to other semiconducting metal oxide photocatalysts, such as Fe$_2$O$_3$, which suffers from electron-hole recombination. This issue could be alleviated by a surface modification approach.
References:


