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Origin of the Visible-Light Response of Nickel(II) Oxide Cluster Surface Modified Titanium(IV) Dioxide

Anna Iwaszuk,† Michael Nolan,*,‡ Qiliang Jin,‡ Musashi Fujishima,‡ and Hiroaki Tada*†

Tyndall National Institute, University College Cork, Lee Maltings, Prospect Row, Cork, Ireland
Department of Applied Chemistry, School of Science and Engineering, Kinki University, 3-4-1, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan

Supporting Information

ABSTRACT: A number of NiO clusters have been formed on TiO2 (anatase/rutile = 4/1 w/w, P-25, Degussa) in a highly dispersed state (NiO/TiO2) by the chemisorption—calcination cycle technique. The NiO/TiO2 causes high visible-light activities for the degradations of 2-naphthol and p-cresol exceeding those of FeO2/TiO2 (Tada et al. Angew. Chem., Int. Ed. 2011, 50, 3501–3505). The main purpose of this study is to clarify the origin of an electronic level by the density functional simulation for NiO, Ni2O2, and Ni4O4 clusters supported on TiO2 chloride (110) and anatase (001) surfaces. The clusters adsorb strongly on both rutile and anatase with adsorption energies ranging from −3.18 to −6.15 eV, creating new interfacial bonds between the clusters and both surfaces. On rutile, intermetallic Ni—Ti bonds facilitate stronger binding compared with anatase. The electronic structure shows that the top of the valence bands (VBs) of rutile and anatase arises from electronic states on the NiO cluster. On the other hand, the conduction band of rutile is from the Ti 3d states, whereas NiO cluster levels are generated near the conduction band minimum of anatase. This is in contrast to the SnO2/rutile TiO2 system, where the density of states near the conduction band minimum increases with the VB unmodified. In the NiO/TiO2 system, the band gaps of both rutile and anatase are narrowed by up to 0.8 eV compared with pristine TiO2, which pushes the photocatalytic activity into the visible region. In view of the calculated electronic structure, we have attributed the enhanced photocatalytic activity both to the charge separation due to the excitation from the NiO cluster levels and the strong binding of NiO clusters to both rutile and anatase with Ti bonds facilitating charge transfer.

1. INTRODUCTION

One of the biggest challenges for our energy security is to be independent of fossil fuels, and the development of suitable photocatalysts may help in solar energy harvesting. TiO2 has gathered much attention because it is relatively cheap, readily available, stable, and nontoxic. Since TiO2 absorbs only in the ultraviolet region, there have been many attempts to modify it in such a way that it will also absorb visible light.1,2 A popular approach for material modification over many years has been substitutional cation or anion doping at titanium or oxygen sites.3–19 In 2001, Asahi et al. demonstrated that N-doping of TiO2 results in visible light absorption,3 and there has been much work since devoted to examining doping as a means to shifting the band gap of TiO2 from the UV to the visible. N-doped TiO2 continues to be of great interest and has been studied in depth by Di Valentino, Pacchioni, and Selloni in refs 4 and S, while there have been recent experimental and modeling reports on this prototype of doped TiO2.6,7 Carbon-doped TiO2 has also been of great interest,8–11 while Wang and Lewis have used the FIREBALL code to study doping of TiO2.12,13 and obtained results that were used to explain the band gap changes in doped TiO2. Finally, other studies of doped TiO2 in refs 14–19 serve to highlight the range of dopants that have been studied.

It has been highlighted that there are practical questions associated with doping of TiO2, including solubility, stability, determining that doping has actually taken place, and charge recombination.20,21 Herrmann has shown that Cr-doping of TiO2, which does reduce the band gap, will in fact have a detrimental effect on the photocatalytic activity.22 With this in mind, there have been many efforts to find alternative ways to shift the band gap of TiO2 in order to make it more efficient in terms of visible-light absorption and reducing charge recombination. This includes modification with metal particles, such as gold,23 modification with quantum dots, for example, CdS24 (which, although displaying an initially high photocatalytic efficiency, does subsequently degrade as a result of CdS oxidation), and heterostructures of graphene and TiO2.24 Recent studies have demonstrated that oxide—oxide heterostructures composed of nanoscale metal oxide clusters on TiO2 can drastically improve the photocatalytic properties.
modified to pure TiO$_2$. Modification of TiO$_2$ with metal oxide nanoclusters has been investigated by Libera et al. and Tada et al. Libera et al. used the atomic layer deposition technique to deposit Fe$_2$O$_3$ nanoclusters on TiO$_2$ and found visible-light absorption and efficient photocatalytic degradation of methylene blue. Tada et al. synthesized FeO$_2$-modified TiO$_2$ using the chemisorption—calcination cycle (CCC) that deposits highly dispersed metal oxide nanoclusters on the TiO$_2$ surface at a molecular scale. The FeO$_2$/TiO$_2$ structure shows improved visible-light activity and also good UV-light activity. These features came from band gap narrowing and were explained by the presence of the FeO$_2$ clusters that are responsible for shifting the valence band (VB) maximum of TiO$_2$. Further, with SnO$_2$-modified TiO$_2$, striking differences between the light absorption properties and the visible-light photocatalytic activity of modified rutile and anatase TiO$_2$ were observed and rationalized with first-principles simulations. Other examples of heterostructures have included BiOBr–ZnFe$_2$O$_4$, BiVO$_4$–WO$_3$, SnO$_2$–ZnGa$_2$O$_4$, and AgI–BiO$_2$, displaying improved photocatalytic activity compared to the pure oxides or simple physical mixtures, highlighting the important role of the interface. Further, the Ni$^{2+}$ surface modification of rutile TiO$_2$ by the impregnation method was reported to enhance both the UV- and visible-light activities, whereas the effect is much smaller than that by the Fe$^{2+}$ surface modification. Recently, we have shown that the surface modification of TiO$_2$ with extremely small NiO clusters by the CCC technique (NiO/TiO$_2$) causes a high visible-light activity concomitantly with the UV-light activity increased for the decomposition of 2-naphthol. However, the origin of the visible-light response is not fully understood and needs further investigation to facilitate the development of this exciting approach to developing photocatalytic materials.

On the other hand, to understand the origin of the experimental findings, density functional theory (DFT) simulations are of great help. Iwaszuk and Nolan have shown that that subnanometer diameter (TiO$_2$) clusters, with $n = 2−4$, adsorbed on the rutile TiO$_2$(110) surface, can reduce the band gap compared to pure TiO$_2$ (although that work was also focused on examining the reactivity of these heterostructures). The presence of Ti 3d states of the cluster above the Fermi level leads to the formation of additional Ti metallic bonds that are not possible at the anatase (001) surface. The electronic structure shows that the band gap is narrowed and the energy band alignments will give electron and hole separation after light excitation.

2. METHODOLOGY

2.1. Photocatalyst Synthesis. The NiO/P-25 was prepared by the CCC technique. After P-25 (1 g) had been added to 100 mL of a Ni(acac)$_2$(H$_2$O)$_2$ solution (solvent, ethanol/n-hexane = 3:17 v/v), they were allowed to stand for 24 h at 298 K. The Ni(acac)$_2$(H$_2$O)$_2$ concentration was changed ranging from 1 × 10$^{-3}$ to 1 × 10$^{-3}$ M. The resulting samples were washed repeatedly with the solvent for the physiosorbed complexes to be removed and dried, followed by heating in air at 773 K for 1 h. The complex adsorption and the subsequent heating were repeated to increase the Ni loading amount. The loading amount was shown by the amount of Ni$^{2+}$ loaded on the unit surface area of P-25 ($\Gamma$, ions nm$^{-2}$).

2.2. Photocatalyst Characterization. High-resolution transmission electron microscopy (HRTEM) observation and X-ray energy dispersive spectroscopic measurements were performed using a JEOL JEM-3000F and a Gatan imaging filter at an applied voltage of 300 or 297 kV. UV–visible diffuse reflectance spectra of NiO/TiO$_2$ were recorded on a Hitachi U-4000 spectrophotometer. The spectra were converted to the absorption reflectance spectra by using the Kubelka–Munk function. X-ray photoelectron spectroscopic (XPS) measurements were performed using a Kratos Axis Nova X-ray photoelectron spectrometer with a monochromated Al Kα X-ray source ($h\nu = 1486.6$ eV) operated at 15 kV and 10 mA. The takeoff angle was 90°, and multiplex spectra were obtained for Ni 2p, O 1s, and Ti 2p photopeaks. All the binding energies were referenced with respect to the C 1s at 284.6 eV. The photoluminescence spectra were measured with an excitation wavelength of 320 nm at 77 K using a JASCO FP-6000 spectrophotometer.

2.3. Photocatalytic Reactions. A 50 mL amount of 1.0 × 10$^{-5}$ M 2-naphthol solution (solvent, acetonitrile/water = 1:99 v/v) or 5.0 × 10$^{-4}$ M p-cresol solution (solvent, water) was placed in a double-jacket-type reaction cell made of borosilicate glass, and then, P-25 (Degussa) or NiO/P-25 particles (0.1 g) were added. The reaction cell was irradiated with a Xe lamp (Wacom XRD-501SW) through a band-pass filter (33U, SIGMA KOKI CO., Ltd.) superposed on FTO-coated glass (two pieces of FTO glass for 2-naphthol and a piece of FTO glass for p-cresol) transmitting only the 330–400 nm range for the UV-light photocatalytic activity evaluation and a high-pass filter (L-42, Toshiba) to cut off UV light for the visible-light-induced activity test. The irradiation conditions are as follows: for 2-naphthol UV light, 330 < $\lambda$ < 400 nm, $I_{320-400 \text{ nm}} = 0.18$ mW cm$^{-2}$, and visible light, $\lambda > 400$ nm, $I_{420-485 \text{ nm}} = 1.0$ mW cm$^{-2}$; for p-cresol UV light, 330 < $\lambda$ < 400 nm, $I_{320-400 \text{ nm}} = 2.18$ mW cm$^{-2}$, and visible light, $\lambda > 400$ nm, $I_{420-485 \text{ nm}} = 2.0$ mW cm$^{-2}$. A 3 mL amount of the solution was sampled every 15 min, and the absorbance at $\lambda = 224$ nm was measured using a 1A absorption detector.

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252 nanocluster supported on the surface and
248 relaxed. The adsorption energy was computed from the
247 The clusters were deposited on both TiO\textsubscript{2} surfaces and fully
246 more reliable, is our primary focus.
243 still an underestimation of band gap remains, and this depends
242 gives a reasonable description of transition metal d states, but
241 found here for the electronic structure. The DFT+
239 literature, for example, refs 51
238
236 states of NiO are known to be poorly described with
235 applied the +
234 electronic states of d or f shells is well known.46
231 For the calculations we use the DFT+
229 cells and technical parameters for the free nanoclusters are the
228 representative molecular-sized NiO nanoclusters. The super-
227 with composition NiO, Ni\textsubscript{2}O\textsubscript{2}, Ni\textsubscript{3}O\textsubscript{3}, and Ni\textsubscript{4}O\textsubscript{4} are studied as
226 more widely separated NiO nanoclusters. NiO nanoclusters
225 images, thus reducing the periodic interactions and modeling
224 surface supercell giving a bigger distance between periodic NiO
223 with periodic images on the resulting properties, with the larger
222 studied to examine the e
221 nanocluster considered, a (4 \times 4)
219 to have isolated NiO nanoclusters, we employed a (2 \times 4)
218 known for TiO\textsubscript{2} being the subject of ongoing studies. In order
215 photocatalytically active anatase surface.44,45 We consider the
212 We use models of rutile (110) and anatase (001), since (110) is
210 surface model of anatase is terminated by 2-fold coordinated
209 and 5-fold coordinated Ti atoms. The (unreconstructed) (001)
208 bridging oxygen atoms, and the next sublayer consists of 6-fold
207 The rutile (110) surface is terminated by 2-fold coordinated
206 used for k-point sampling with a (2 \times 2 \times 1) sampling grid.
205 Perdew
204 exchange-correlation functional is the approximation of
203 and 10 for Ni, within the PAW approximation, and the
200 models with the VASP code. 40 The valence electrons are
199 anatase (001) surfaces, we use three-dimensional periodic slab
198
196 250 mm (NEOS); mobile phase = water
194 determined by high-performance liquid chromatography
193 tration of 2-naphthol. The
192 spectrometer (UV-1800, Shimadzu) to determine the concen-
191 tration of 2-naphthol. The p-cresol concentration was
190 determined by high-performance liquid chromatography
189 (SPD-6A, Shimadzu; column = Fluorix INW425 4.6 mm ×
188 250 mm (NEOS); mobile phase = water–ethanol (3.7 v/v); λ
187 = 277 nm).
2.4. DFT Simulation. For modeling TiO\textsubscript{2} rutile (110) and
199 anatase (001) surfaces, we use three-dimensional periodic slab
200 models with the VASP code.40 The valence electrons are
201 described by a plane wave basis set, and the cutoff for kinetic
200 energy is 396 eV. The valence electrons are 4 for Ti, 6 for O,
203 and 10 for Ni, within the PAW approximation, and the
202 exchange-correlation functional is the approximation of
201 Perdew–Wang (PW91).41,42 The Monkhorst–Pack scheme is
200 used for k-point sampling with a (2 \times 2 \times 1) sampling grid.
207 The rutile (110) surface is terminated by 2-fold coordinated
206 bridging oxygen atoms, and the next sublayer consists of 6-fold
205 and 5-fold coordinated Ti atoms. The (unreconstructed) (001)
204 surface model of anatase is terminated by 2-fold coordinated
203 oxygen and has 5-fold coordinated Ti ions in the next sublayer.
202 We use models of rutile (110) and anatase (001), since (110) is
201 by far the most stable surface of rutile and is well studied,43
202 while for anatase, (001) is of great interest as the most
201 photocatalytically active anatase surface.44,45 We consider the
200 rutile and anatase surfaces in their perfect, stoichiometric form,
200 with consideration of the OH-terminated surfaces that are well
200 known for TiO\textsubscript{2} being the subject of ongoing studies. In order
200 to have isolated NiO nanoclusters, we employed a (2 \times 4)
200 surface supercell for each TiO\textsubscript{2} surface; for the largest NiO
200 nanocluster considered, a (4 \times 4) rutile (110) surface was also
200 studied to examine the effect of the interaction of NiO clusters
200 with periodic images on the resulting properties, with the larger
200 surface supercell giving a bigger distance between periodic NiO
200 images, thus reducing the periodic interactions and modeling
200 more widely separated NiO nanoclusters. NiO nanoclusters
200 with composition NiO, Ni\textsubscript{2}O\textsubscript{2}, Ni\textsubscript{3}O\textsubscript{3}, and Ni\textsubscript{4}O\textsubscript{4} are studied as
200 representative molecular-sized NiO nanoclusters. The super-
200 cells and technical parameters for the free nanoclusters are the
200 same as the extended surfaces.
201 For the calculations we use the DFT+U approach46,47 where
202 we applied U = 4.5 eV on the Ti 3d states. The need to
203 introduce the U parameter in order to describe properly
202 electronic states of d or f shells is well known.36–50 We also
201 applied the +U correction for Ni in NiO, since the electronic
200 states of NiO are known to be poorly described with
200 DFT,50,51–53 for Ni, we apply U = 8 eV and J = 1 eV (giving
200 U – J = 7 eV), generally consistent with values from the
200 literature, for example, refs 51–53; a check with other values of
200 U, namely, (U – J) = 5 and 6 eV, gives similar results to those
200 found here for the electronic structure. The DFT+U approach
200 gives a reasonable description of transition metal d states, but
200 still an underestimation of band gap remains, and this depends
200 on the precise DFT+U setup. With this in mind, the change in
200 the band gap of TiO\textsubscript{2} upon modification with NiO, which is
200 more reliable, is our primary focus.
200 The clusters were deposited on both TiO\textsubscript{2} surfaces and fully
200 relaxed. The adsorption energy was computed from the
200 following:
\[
E^{\text{ads}} = E(\text{NiO}_n - \text{TiO}_2) - \{E(\text{NiO}_n) + E(\text{TiO}_2)\}
\]
(1)
251 where \(E(\text{NiO}_n - \text{TiO}_2)\) is the total energy of the NiO
252 nanocluster supported on the surface and \(E(\text{NiO}_n)\) and
\(E(\text{TiO}_2)\) are the total energies of the free cluster and the bare
253 surface, respectively. A negative adsorption energy signifies that
254 the cluster adsorption is stable.

3. RESULTS

The point of effective surface modification of TiO\textsubscript{2} with metal
255 oxide clusters is the dispersion state and the strict control of the
257 loading amount.30 The Ni(acac)\textsubscript{2}(H\textsubscript{2}O\textsubscript{2}) complex is chem-
258 isorbed on P-25 via the partial ligand exchange between the
259 acac ligand and the acidic surface Ti–OH group to yield NiO
260 clusters by postheating.37 Figure 1 shows HRTEM micrographs
261 of NiO/TiO\textsubscript{2} with varying Ni loading amount \(\Gamma\) (ions nm\textsuperscript{-2}).262 Highly dispersed NiO clusters smaller than ~2 nm are observed
263 on the surface of P-25. The strong chemisorption of the complex on the
264 TiO\textsubscript{2} surface (DFT results) prevents aggregation of the small NiO clusters into larger structures
266 during the subsequent heating, thus yielding extremely small
267 adsorbed NiO clusters.
268 2-Naphthol and p-cresol were used as model water
269 pollutants. 2-Naphthol, a starting material of azo-dyes, has no
270 absorption at \(\lambda > 330\ \text{nm}\).54 Both the degradations of 2-
271 naphthol and p-cresol apparently followed the first-order rate
272 law under irradiation of UV light and visible light, and the
273 activity was evaluated by the pseudo-first-order rate constant \((k_f)\).
274 Figure 2A (red circles) shows visible-light activity for the
275 2-naphthol degradation as a function of \(\Gamma\). The surface
276 modification with NiO clusters endows P-25 with visible-light
277 activity, whereas pristine P-25 has only low activity. The visible-
278 light activity drastically increases with increasing \(\Gamma\), passing
279 through a maximum at \(\Gamma \sim 0.32\). The maximum activities of
280 several metal oxide surface modified P-25 are on the order of
281 NiO > FeO \textsubscript{2} > SnO\textsubscript{2} > none under the same reaction
282 conditions, and the value of NiO/P25 reaches approximately
283 twice that of the FeO/P-25 system (Table S1, Supporting
284 Information).30 Figure 2B (red circles) shows UV-light activity
285 for the 2-naphthol degradation as a function of \(\Gamma\). The UV-light
286 activity further increases by the surface modification with the

![Figure 1. HRTEM images of NiO/P-25: (A) \(\Gamma = 0\); (B) \(\Gamma = 0.014\); (C) \(\Gamma = 0.47\); (D) \(\Gamma = 0.83\).](image-url)
NiO clusters. The loading at $\Gamma = 0.47$ affords a maximum activity, which is $\sim 2.8$ times the activity of P-25. The maximum activities of several metal oxide surface modified P-25 are on the order of FeO$_x$ > NiO > SnO$_2$ > none (Table S1, Supporting Information). We have recently reviewed the difference in the surface modification effect between FeO$_x$ and SnO$_2$ clusters. On the other hand, p-cresol widely used as a sterilizer and disinfectant has no absorption at $\lambda > 330$ nm. As shown in Figure 2A,B (blue circles), similar trends are also observed for the degradation of p-cresol, while the enhancement effect is somewhat smaller as compared to that for the 2-naphthol degradation.

The effect of the surface modification of P-25 with varying amounts of NiO clusters on the optical property was studied. Ni-doped TiO$_2$ prepared by the solid-state reaction of TiO$_2$ with NiO has a broad and weak absorption around 450 nm due to the d–d transition, while the intrinsic absorption edge is invariant. Chemical doping of Cr and N ions into TiO$_2$ yields similar weak shoulders in the visible region due to the formation of localized impurity levels within the band gap.

Figure 3A shows UV–visible absorption spectra of NiO/P-25 with varying $\Gamma$: $F(R_{\infty})$ is the Kubelka–Munk function. In contrast to the spectra of Ni-doped TiO$_2$, band gap narrowing occurs for NiO/P-25, whereas the d–d transition band grows at $\Gamma > 0.47$. Figure 3B shows plots of $[F(R_{\infty})h\nu]^{1/2}$ versus $h\nu$ for NiO/P-25. The indirect band gap determined from the extrapolation of the tangent to the abscissa decreases from 3.1 eV at $\Gamma = 0$ to 2.6 eV at $\Gamma = 0.83$. A similar spectral feature is observed for Cr- and N-doped TiO$_2$ prepared by physical techniques such as ion implantation and magnetron sputtering. Also, the VB-XPS was measured for NiO/P-25 with varying $\Gamma$.

As shown in Figure 4A, the emission from the VB extends from 2 to 9 eV for every sample. Figure 4B magnifies the energy region near the VB maximum. The top of the VB rises with an increase in $\Gamma$. The magnitude of the change reaches approximately 0.5 eV at $\Gamma = 0.83$, which is comparable with the decrement in the band gap with the surface modification. Consequently, the visible-light absorption of TiO$_2$ by the surface modification with the NiO clusters stems from the rise in the top of the VB.

To understand the effect of the surface modification with the NiO clusters at an electronic level, DFT simulations were performed for model systems consisting of TiO$_2$ and NiO nanoclusters adsorbed at rutile and anatase. Figure 5 presents the atomic structure of the NiO, Ni$_2$O$_3$, Ni$_3$O$_5$, and Ni$_4$O$_7$ nanoclusters, which are chosen as representative NiO nanoclusters, adsorbed on TiO$_2$ anatase (001) and rutile (110) surfaces together with the adsorption energies and the...
numbering of the nanocluster Ni atoms. We compute the coverage of the nanoclusters in terms of Ni atoms per unit area, so 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$^2$. On rutile (110), the corresponding coverages are 0.64, 1.28, 1.92, and 2.56 Ni atoms/nm$^2$. On the larger (4×4) surface supercell, the coverage is 1.28 Ni atoms/nm$^2$. For Ni$_4$O$_4$, the size of the nanocluster on a (2×4) surface supercell will lead to stronger periodic NiO$^-$NiO interactions than for the smaller NiO nanoclusters, which will influence the adsorption structure, due to the NiO nanoclusters being essentially in close proximity, and the effect of this on the change in the electronic properties of NiO-modified TiO$_2$ will be discussed.

All structures show negative adsorption energies, ranging from $-3.18$ to $-6.15$ eV giving an indication of a strong interaction between the nanocluster and the surface and the high stability of individual NiO nanoclusters adsorbed at TiO$_2$, which prevents aggregation of the clusters into larger structures during postheating. For all deposited clusters, detailed information about the geometry is presented in Table 1.

For NiO nanoclusters deposited on anatase, the 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 distorts the surface of TiO$_2$ anatase (001), similar to SnO$_2$ adsorbed at anatase (001).$^{32}$ The same behavior is observed for Ni$_2$O$_2$ deposited at 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 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$_3$O$_3$ 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 Ni$_2$O$_2$, compared to 2.10 Å in bulk NiO. Of the NiO nanoclusters adsorbed at anatase (001), only the Ni$_3$O$_3$ nanocluster shows intermetallic Ni−Ti bonds, with Ni−Ti distances in the range 2.71−2.87 Å, which is consistent with those in the intermetallic NiTi alloy.$^{61}$

At the TiO$_2$ rutile (110) surface, the 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 Ni$_2$O$_2$ cluster 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. Ni$_3$O$_3$ deposition on rutile (110) results in formation of seven new bonds between the
Figure 6 shows the electronic density of states projected while the conduction band is dominated by the Ti 3d states in the well-known O 2p derived VB, with a Ti 3d contribution, anatase TiO₂ surfaces (see the Supporting Information) show an important role in this analysis. The DOS of the clean rutile and rutile (110) (Figure 6e) and Ni₄O₄ clusters adsorbed on anatase (001) (Figure 6a) and Ni₂O₂, Ni₃O₃, NiO clusters adsorbed on Ni 3d and Ti 3d states for NiO, Ni₃O₃, Ni₂O₂, and rutile surfaces. The conduction band of the NiO-modified surfaces can show some dependence on the crystal form of TiO₂. For modified rutile (110), the bottom of the conduction band is dominated by surface Ti 3d states. Interestingly, this is in contrast to the SnO₂/rutile TiO₂ system, where the DOS near the conduction band minimum increases, with the VB unmodified. A close inspection of the conduction band states for anatase indicates that, in some cases, for example, Ni₂O₂, empty NiO cluster levels are generated near the conduction band minimum.

In the NiO/TiO₂ system, the shift of the VB to higher energy has the consequence that the overall band gap of the composite is reduced compared to unmodified TiO₂. We find in the DFT calculations a maximum band gap reduction of 0.8 eV (for NiO/TiO₂ at anatase (001)) compared to the unmodified anatase surface, and this shift is qualitatively comparable to the value determined by the VB-XPS, in Figure 4B. This can further be compared with SnO₂/TiO₂, where anatase modification leads to no band gap change, but rutile modification can reduce the band gap. The narrowing of the band gap will induce visible-light absorption in the composite as shown in Figure 3. Thus, upon modification with NiO nanoclusters, NiO states appear above the VB edge of the TiO₂ surface, which pushes the VB up in energy. There is a case in Figure 6, where the Ni₂O₂ nanocluster on anatase appears to show some empty NiO states just below the anatase conduction band. In general, we can conclude that the NiO modification of TiO₂ will reduce the energy gap by pushing the VB edge up in energy.

We show in Figure 7 the atomic structure and PEDOS of a Ni₄O₄ nanocluster relaxed on the rutile (110) surface with a (4 × 4) surface supercell, which has a coverage of 1.28 Ni atoms/ nm² and an adsorption energy of -4.50 eV. In this case, although the effect of the smaller coverage of NiO at the surface is clear compared to Figure 5f, namely, that the Ni₂O₂ cluster takes a different adsorption structure, the PEDOS shows that the impact of modifying TiO₂ with NiO is unchanged, namely, that there are NiO-derived states found at the top of the VB, which will reduce the energy gap compared to unmodified TiO₂.

The oxidation state of the metal oxide surface modifier can also affect the photocatalytic activity of TiO₂. A Bader charge analysis on Ni for the NiO nanoclusters deposited on both surfaces gives net charges on Ni ranging from 8.7 to 8.9 electrons, which are consistent with a Ni⁴⁺ oxidation state. Moreover, in TiO₂, the computed net Bader charges are approximately +1.3 electrons, which is typical for the Ti³⁺ oxidation state. The oxidation states of Ni and Ti are in agreement with those determined by XPS.

On the basis of these results above, the NiO surface modification effect on the photocatalytic activity of P-2S can be rationalized as follows and indicated in Figure 8. NiO clusters possess a strong interaction with the anatase and rutile surfaces through Ni–O–Ti bonds for anatase and rutile and additional Ni–Ti bonds for rutile. As a result of the mixing of the Ni 3d levels, the VB maximum of TiO₂ rises significantly, while new vacant levels are generated near the conduction band minimum of anatase that is the major phase of P-2S.
Upon visible-light irradiation of NiO/P-25, the electrons in the surface Ni 3d sub-band are excited to the TiO\textsubscript{2} conduction band. This surface-to-bulk interfacial electron transfer (IET) enhances the charge carrier separation. The holes generated at the surface d sub-band oxidize adsorbed 2-naphthol and p-cresol. On the other hand, the electrons in the TiO\textsubscript{2} conduction band are consumed by O\textsubscript{2} reduction. This process can be the key to increasing photocatalytic activity in the oxidative decomposition of organic pollutants.\textsuperscript{63,64} Figure 8 suggests that the excited electrons in the anatase conduction band can be transferred to the surface levels of the NiO species, which further assists the electron transfer to O\textsubscript{2} as previously

Figure 6. Spin polarized PEDOS on Ni 3d and Ti 3d states for (a) NiO, (b) Ni\textsubscript{2}O\textsubscript{2}, (c) Ni\textsubscript{3}O\textsubscript{3}, and (d) Ni\textsubscript{4}O\textsubscript{4} clusters supported on the anatase (001) surface and for (e) NiO, (f) Ni\textsubscript{2}O\textsubscript{2}, (g) Ni\textsubscript{3}O\textsubscript{3}, and (h) Ni\textsubscript{4}O\textsubscript{4} clusters supported on the TiO\textsubscript{2} rutile (110) surface.

Figure 7. (a) Atomic structure and (b) PEDOS for a Ni\textsubscript{4}O\textsubscript{4} cluster adsorbed at the rutile (110) surface in a (4 × 4) surface supercell.
confirmed by the electrochemical experiments. This action by the NiO clusters should also operate under UV-light irradiation. Consequently, the NiO surface modified P-25 causes the high activities under illumination of visible light and UV light. A final point is that, in the experiments, an optimum Ni loading for photocatalytic activity is found (Figure 2A,B), although above this loading, the NiO–TiO$_2$ system displays a continuous decrease in the band gap. With the results of this work showing that the increased loading of NiO results in a rise in the VB edge of the composite system compared to unmodified TiO$_2$, we can explain this finding as follows. The low VB edge in unmodified TiO$_2$ imparts good oxidative power to the holes formed after light excitation, while an upward shift of the VB edge will weaken the oxidation power of the holes. Thus, with an increase in NiO loading, the VB edge is shifted upward (Figures 3, 4, and 6), which therefore weakens the oxidative power of the holes and results in an optimal loading of NiO on TiO$_2$. A similar result has been found for other metal oxide nanocluster modified TiO$_2$ indicating that this phenomenon is quite general; that is, there will be an optimum loading of a second metal oxide on TiO$_2$ that shifts the VB edge such that visible-light absorption is realized but that the oxidative power of the photoexcited holes is not reduced too much.

4. CONCLUSIONS

We have shown that the surface modification of P-25 (anatase/ rutile = 4:1 w/w) with NiO clusters gives rise to high visible-light activities for 2-naphthol and p-cresol concomitantly with significant increases in the UV-light activities. We have presented DFT simulations of nickel oxide clusters adsorbed on TiO$_2$ anatase (001) and rutile (110) surfaces to understand the origin of visible-light activity in these heterostructures. We find that NiO clusters are deposited on TiO$_2$ surfaces with large adsorption energies ranging from $-3.18$ to $-6.15$ eV, with metallic Ni–Ti bonds leading to extra stabilization on rutile (110) compared with anatase (001). The deposited clusters cause the narrowing of the TiO$_2$ band gap, which pushes the photoactivity into the visible region due to the presence of NiO states at the top of the valence band of TiO$_2$. The present energy level alignments enhance the charge separation and the electron transfer to O$_2$, which are the origins of photocatalytic efficiency enhancement. These results are consistent with experimental data.

ASSOCIATED CONTENT

Supporting Information

Photocatalytic activities of metal oxide surface modified P-25 (Degussa) for 2-naphthol degradation; Ni 3d and O 2p PEDOS for NiO nanocluster modified TiO$_2$; electronic DOS for unmodified rutile (110) and anatase (001) surfaces. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: michael.nolan@tyndall.ie (M.N.); h-tada@apch.kindai.ac.jp (H.T.).

Notes

The authors declare no competing financial interest.

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