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Multifunctional photo/thermal catalysts for the reduction of carbon dioxide

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Abstract

The photochemical fixation of CO_2 to energy rich products for solar energy storage or feedstock chemicals is an attractive, albeit daunting, challenge. The overall feasibility of CO_2 conversion is limited by the availability of efficient photo-active materials that meet the energetic requirements for CO_2 reduction and are optically matched to the solar spectrum. Surface modification of TiO_2 with earth abundant metal oxides presents one approach to develop visible active photocatalysts through band gap narrowing, while providing catalytic sites to lower the activation energy for CO_2 reduction. In this work density functional theory was used to model the effect of surface modification of rutile and anatase using MnO_x nanoclusters. The results indicate the formation of inter-band gap states following surface modification with MnO_x, but surface water can change this. Oxygen vacancies are predicted to form in supported MnO_x and the interaction with CO_2 was investigated. MnO_x-TiO_2 was synthesised and characterised using surface analytical methods and photoelectrochemistry. The interaction of CO_2 with the materials under irradiation was probed using in-situ FTIR to interrogate the role of oxygen vacancies in CO_2 binding and reaction. These results provide insights into the requirements of a multifunctional catalyst for CO_2 conversion.

Keywords: Photocatalysis, carbon dioxide, photoelectrochemistry, density functional theory, oxygen vacancies

1 Introduction

The photochemical fixation of CO_2 to energy rich products is an attractive, albeit daunting, challenge that attracts a great deal of recent interest [1-8]. The reduction of CO_2 has a steep uphill thermodynamic barrier and the overall feasibility of CO_2 conversion is limited by the availability of efficient photo-active materials that can meet the energetic requirements, while also being optically matched to the solar spectrum [9].

There are many reports of the heterogeneous photocatalytic reduction of CO_2 on oxide semiconductors, particularly TiO_2. CO_2 reduction is observed, but reaction efficiencies are very low. The conversion of CO_2 by photoactive oxides to energy-rich products is a complex system of reactions requiring novel, multifunctional nanoarchitectures that can harvest visible light, stabilize charge separation, activate CO_2, and control the reaction pathway.

Figure 1 provides a sketch of a potential catalytic cycle for the reduction of CO_2. Small domains of reducible oxides (for MnO_x, but this is extendable to other earth-abundant oxides) are synthesized on supports of appropriate or modified band gap for light harvesting (shown here as TiO_2). MnO_x clusters are examined because they may create band gap states that red-shift TiO_2 for visible light activation – Mn doping was presented in ref [10] and showed that Mn can create in-gap states - and broaden the valence band to favor charge injection (*photocatalysis)*. Reduced metal centers and oxygen deficiencies are created thermally on MnO_x clusters and are sites of CO_2 adsorption and activation (Rx. 1, *thermal catalysis*). A photochemically generated electron (Rx. 2) is transferred to MnO_x and donated to the carboxylate (a specific form of adsorbed CO_2) to achieve a 2-eletron reduction of CO_2, cleaving the C-O bond to produce CO and heal the oxygen vacancy. Water oxidation at the oxidized MnOx (Rx. 3), possibly photo- and thermo-driven, regenerates the active O-vacancy sites by the reverse of the classic Mars-van Krevelen mechanism and injects electrons to the TiO_2 hole (Rx. 4). Crucially, reoxidation of surface vacancies with O_2, which would short-cut the catalytic cycle, is avoided by maintaining very low pO_2. Overall, then, the proposed multi-functional system combines both thermochemical and photochemical cycles for CO_2 reduction and water oxidation.

The purpose of this paper is to probe the efficacy of this model theoretically and experimentally. Using first principles simulations, the effects of supporting MnO_x clusters on various crystal facets of either anatase or rutile TiO_2 [11-13] are explored to determine the extent of band-gap narrowing, the ease of forming oxygen vacancies and the mode of CO_2

surface binding. To validate the theoretical findings experimentally, we compare the influence of synthesis conditions (precursor, support, loading) on light absorption, catalyst reduction and CO_2 activation. The integration of theoretical and experimental findings yields deep insight into the structure and function of this TiO_2-based nanocomposite and indicates the critical features of a multifunctional photo/thermal catalyst tailored for CO_2 reduction.

2. **Methodology**

2.1 Computational modelling

To model the MnO_x-modified TiO_2 rutile (110) and anatase (101) surfaces, we use a three dimensional periodic slab model within the VASP code [14]; full details of the methodology are given in the supporting information. The cut-off for the kinetic energy is 396 eV and the core-valence interaction is described by PAW potentials [15]. The Perdew-Wang 91 exchange-correlation functional [16] and a Monkhorst-Pack (2×1×1) k-point sampling grid and smearing width of 0.1 eV are used. To describe the Ti 3d and Mn 3d states DFT+U [17-19] is used where U = 4.5 eV for both cations. This value of U is sufficiently large to described localised Ti^{3+} [20-22] and Mn oxidation states and this set-up has been shown to be reliable [12,20].

The rutile (110) and anatase (101) surfaces have two-fold coordinated bridging O atoms terminating the surface layer and 5-fold/6-fold coordinated surface Ti atoms. For both surfaces (2x4) surface supercell expansions, 6 O-Ti-O trilayers thick are employed with a 12 Å vacuum gap. We employ stoichiometric surfaces (no defects and no adsorbed hydroxyls) and surfaces with different water coverages [13] (adsorption energies are computed similarly to Eq (1)) to examine the effect of a wet substrate on nanocluster absorption and the energy gap change.

The convergence criteria for the electronic and ionic relaxations are 0.0001 eV and forces smaller than 0.02 eV/ Å. The Mn_2O_3 nanoclusters are less than 1 nm diameter and based on our previous work [12,21-24] can shift the absorption edge of TiO_2 into the visible. The adsorption energy of the nanoclusters is computed from:

$$E^{ads} = E((Mn_2O_3)\text{-}TiO_2) - \{ E(Mn_2O_3) + E(TiO_2) \} \qquad (1)$$

where $E((Mn_2O_3)\text{-}TiO_2)$ is the energy of an Mn_2O_3 stoichiometry nanocluster supported on a TiO_2 surface and $E(Mn_2O_3)$ and $E(TiO_2)$ are the total energies of the free Mn_2O_3 stoichiometry nanocluster and unmodified TiO_2. A negative adsorption energy indicates that cluster adsorption is stable.

The formation of oxygen vacancies is examined, using the formation energy to assess vacancy stability. After removing different oxygen atoms the vacancy formation energy is calculated from:

$$E^{vac} = \{E(Mn_2O_{3-x}\text{-}TiO_2) + 1/2\ E(O_2)\} - E(Mn_2O_3\text{-}TiO_2) \qquad (2)$$

where $E(Mn_2O_{3-x}\text{-}TiO_2)$ is the energy of modified TiO_2 with an oxygen vacancy in the Mn_2O_3 nanocluster, $1/2\ E(O_2)$ is the energy of oxygen and $E(Mn_2O_3\text{-}TiO_2)$ is the energy of the stoichiometric composite system. Bader charges and spin magnetisations characterise cation oxidation states.

2.2 Catalyst preparation

$MnO_x\text{-}TiO_2$ catalysts were prepared by incipient wetness impregnation. Nanopowders of rutile (Aldrich, 99.5% trace metals basis) or anatase (Aldrich, 99.7% trace metals basis) were calcined in air at 250°C for 2 hours, ground, and sieved. The titania supports were impregnated with a solution of either $Mn(NO_3)_2{\cdot}4H_2O$ (Sigma Aldrich 97.0%) or $Mn(CH_3COO)_2{\cdot}4H_2O$ (Sigma-Aldrich 99.0%) in ultra-pure water in an agate mortar under constant stirring. The concentration of manganese precursor was varied to achieve surface loadings between 0.25 to 8 Mn atoms per nm^2 of support surface area. The impregnated supports dried overnight in ambient air, then at 120°C for 12 hours. These catalysts are referred to by describing the nominal Mn loading (Mn nm^{-2}), the support material (A or R), and precursor anion (nitrate or acetate). For example, an anatase support loaded with 8 Mn nm^{-2} from the $Mn(NO_3)_2{\cdot}4H_2O$ precursor is labelled 8ANO3 and rutile support loaded with 1 Mn nm^{-2} from the $Mn(CH_3COO)_2{\cdot}4H_2O$ precursor is labelled 1ROAc. The as-prepared $MnO_x\text{-}TiO_2$ catalysts were calcined in air at 500°C for 4 h.

2.3 Catalyst Characterisation

The optical absorption properties of the materials were measured with diffuse reflectance UV-vis spectroscopy (DRUV-vis) using a Shimadzu UV-3600 spectrophotometer equipped with a Harrick Praying Mantis diffuse reflectance holder. Powdered polytetrafluoroethylene (Aldrich, 35 μm particle size) was the reflectance standard. Pseudo-absorption spectra were obtained by transforming the raw reflectance spectra using the Kubelka-Munk function. Band gap energies were estimated by linear fitting of Tauc plots[25].

The reducibility of the $MnO_x\text{-}TiO_2$ composites was assessed by temperature programmed reduction (TPR) using a T.A. Instruments Q500 Thermogravimetric Analyzer. Samples of the $MnO_x\text{-}TiO_2$ composites calcined at 500°C for 4 hours were loaded into the TGA instrument

and subjected to temperature programmed oxidation up to 500°C (10°C min^{-1}, 10 mL min^{-1} O_2 flow), were cooled to ambient temperature under 10 mL min^{-1} He, and were then subjected to another temperature ramp to 500°C (5°C min^{-1}, 10 mL min^{-1} of a mixture of 5 % H_2, 5% Ar, and balance He). Mass loss was measured by the TGA instrument.

In situ FTIR spectra were collected using a Nicolet 6700 (Thermo Scientific) IR spectrometer and a mercury cadmium telluride detector. Each spectrum was obtained by taking an average of 256 scans collected at 4 cm^{-1} resolution using a custom fabricated IR cell and sample preparation protocol previously described [26-29].

The samples were loaded into the cell, evacuated and heated at 5°C/min to 350°C, held at that temperature under vacuum for 15 min, then 30 torr of ultra-high purity O_2 (99.999%) was admitted to the cell. After 15 min the cell was evacuated, then 30 Torr of ultra-high purity H_2 (99.999%) was admitted. The materials were reduced in this atmosphere for a further 15 minutes, then the heating element was turned off and the materials were allowed to cool to ambient temperature before being evacuated again. Background spectra were recorded before introducing 30 Torr of ultra-high purity CO_2 (99.999%) and sealing the cell. Difference spectra were recorded after 30 min of adsorption time.

2.4 Photoelectrochemical Characterisation

The powder samples were suspended in anhydrous methanol (Sigma Aldrich) to give a 5% by weight suspension and sonicated. Films were spray coated on titanium foil (20 x 25 mm^2) using a lab spray gun (Badger Model 250-2) to give a coated area of 20 x 20 mm^2 with a catalyst loading of 1mg cm^{-2}. The samples were annealed in air at 400^oC (ramp 2^oC up, 1^oC/min down). Electrical connection was made to the foil using copper wire and conductive silver epoxy (circuit works CW2400). Any area of the electrode not coated with catalyst was insulated with SU8 photoresist (Microchem) leaving an area of 20 x 20 mm^2 of catalyst exposed.

Electrochemical measurements were performed with a three electrode cell modified with a quartz window. The supporting electrolyte was 0.1 M $NaHCO_3$. The counter electrode was a Pt gauze electrode and the reference electrode was a saturated calomel electrode (SCE). Potentiostatic control was implemented using an Autolab PG30 Stat and irradiation was provided by a 450 W xenon lamp with or without and a 435 nm cut off filter or monochromator (Horiba Jobin Yvonne Gemini 120). A chopper (Uniblitz) was used for chopped irradiation. All potentials are reported vs SCE.

3.0 Results and discussion

3.1 DFT Modelling of Mn_2O_3-nanocluster modified rutile and anatase TiO_2

3.1.1 Mn_2O_3 Nanocluster Adsorption at TiO_2 Surfaces

Figure 2 shows the atomic structure of dry rutile (110) and anatase (101) modified with an Mn_4O_6 nanocluster and with water coverages of 1 monolayer (ML) for rutile and ¾ ML for anatase; the supporting information (figures S1 and S2) shows the atomic structure of the dry and water covered TiO_2 surfaces modified with Mn_4O_6 and Mn_6O_9 nanoclusters. Water is stable at different coverages on rutile and anatase (see SI) [13].

The relaxed atomic structures of the Mn_4O_6 nanocluster adsorbed at dry TiO_2 and with 1 monolayer (ML) and ¾ ML water coverage on rutile (110) and anatase (101), respectively, are shown in Figure 2. The adsorption energies of Mn_4O_6 are -7.20 eV and -5.33 eV on dry rutile and anatase and -1.69 eV and -4.94 eV and rutile and anatase with water; the adsorption energy of Mn_6O_9 on dry rutile is -6.02 eV. In general (see SI) strong Mn_4O_6 nanocluster adsorption energies persist on water covered surfaces; although the rutile (110) surface with 1 ML water has a smaller adsorption energy, this is still reasonable.

After relaxation on water covered TiO_2, hydrogen migrates from surface water, forming new bonds to nanocluster oxygen, passivating oxygen and forming hydroxyls. On rutile, as the water coverage increases, more hydrogen atoms migrate to the nanocluster (figure S2), passivating more oxygen species. On anatase there is less hydrogen migration from adsorbed water to the nanocluster. This is consistent with the more negative adsorption energies of Mn_4O_6 at anatase compared to rutile.

Figure 2 shows the projected electronic density of states (PEDOS) for Mn_4O_6 modified dry and wet rutile (110) and anatase (101). On the dry TiO_2 surfaces, new states, originating from the nanocluster, are found in the valence to conduction band energy gap of TiO_2. We predict a strong red shift of light absorption resulting from the reduced energy gap between the highest occupied and lowest unoccupied electronic states of the composite system.

The PEDOS for Mn_4O_6 modified water covered TiO_2 shows that for modified rutile(110), the key effect of water is an apparent reduction in the electronic states in the TiO_2 energy gap which have almost disappeared at 1 ML water coverage (Figure 2, Figure S3). Surface water appears to prevent strong nanocluster-surface interactions needed to modify the rutile TiO_2 energy gap. Passivating nanocluster oxygen by hydrogen can also remove nanocluster

derived states from the energy gap, ultimately giving no red shift. For modified anatase with water, the reduced hydrogen migration and strong nanocluster-surface interaction means that the Mn_4O_6 derived states persist in the TiO_2 energy gap so that modification of anatase with Mn_4O_6 gives a red shift. Given the nature of the valence and conduction band edges, we suggest an interfacial charge transfer process [30] from supported Mn_2O_3 to TiO_2; a similar process has been described in our earlier work, refs [11-13].

We studied oxygen vacancies in Mn_4O_6-modified rutile and anatase (with no surface water). Figure 3 (a), (b) shows the structure of the most stable oxygen vacancy site in Mn_4O_6-modified rutile (110) and anatase (101). Formation energies are +0.59 eV and +1.1 eV on rutile and anatase. The vacancy originates in Mn_4O_6, consistent with our earlier work on surface modified TiO_2 [31]. There is a low cost to form the O vacancy in the composite, compared to *ca.* 3.5 eV on bare rutile and anatase. On Mn_4O_6-rutile (110), the two electrons reduce two Mn^{3+} sites to Mn^{2+}. On Mn_4O_6-anatase (101), one electron reduces an Mn^{3+} site to Mn^{2+} and the second electron reduces a surface Ti atom in anatase.

We examined the interaction of CO_2 with the defective structures to investigate if the oxygen vacancy and the reduced metal sites can participate in CO_2 activation. Figure 3 (c) – (e) show relaxed adsorption modes for CO_2 at defective Mn_4O_6-rutile (110). We identify non-interacting (Figure 3 (c)), bidentate (two Mn-O bonds between the nanocluster and CO_2), Figure 3 (d), and bidentate carbonate (Figure 3 (e)); the computed adsorption energies are -0.21 eV, -0.55 eV and +0.68 eV; the carbonate-like adsorption mode is not stable. Similar CO_2 adsorption energies are found at other nanocluster-modified TiO_2 composites [32]. In the bidentate adsorption mode, the C-O distances in CO_2 are elongated to 1.24 and 1.26 Å and the molecule has a bent structure.

Figure 3 (e) shows the relaxed adsorption structure of CO_2 at defective Mn_4O_6-anatase in which a C-O bond in CO_2 breaks and CO is released, with a small energy gain of 0.37 eV, and the vacancy is healed.

3.2 Catalyst characterisation

Normalized Kubelka-Munk pseudo-absorbance spectra for the MnO_x-TiO_2 (anatase) composites are presented in Figure 4. Anatase supported materials showed a red shift in the absorbance edge relative to the bare anatase support, which arises from the modification of TiO_2. They also show broad absorbance in the visible light range, which increases with Mn loading (due to transitions within supported MnO_x). The rutile-supported materials showed a small extension of absorbance into the visible light range (Figure S5), but to a much lesser extent than for anatase supported materials.

Band gap energies of the composites and the bare supports were calculated by linear fitting of Tauc plots and are shown in Table S1. The anatase-supported materials with 0.25 Mn nm^{-2} loading show a negligible shift in band gap relative to the 3.15 eV band gap of bare anatase, but a significant trend of decreasing band gap is evident at higher loadings with the highest Mn loading materials showing a band gap of 2.74 eV (8ANO3) and 2.30 eV (8AOAc). The red shift is greater in the AOAc materials than the ANO3 materials at all Mn loadings and the differences grow with increasing Mn loading. For all of the MnO_x-TiO_2 rutile composites there is no marked change in the band gap energy at any Mn loading. These results point to the influence of both support and precursor on the structure and optoelectronic properties of MnO_x-TiO_2 materials.

The photoresponse of the anatase-supported materials is consistent with computational results for small clusters of Mn_2O_3 composition on anatase (101) that predict the introduction of states above the valence band of anatase, resulting in decreased band gap energy. As shown computationally, the presence of water on the surface of rutile can change the effect of the nanocluster modifier and result in no significant change to the energy gap, as observed experimentally.

There are potential differences between computation and experimental results. The computational results are obtained for very small (< 1nm diameter) clusters of Mn_2O_3, however the size of the MnO_x domains in the MnO_x-TiO_2 composites synthesized for this study is likely much larger, especially at higher Mn loadings. Also, the computations were focused on idealised crystal surfaces, whereas the surfaces of the support materials used in the experiments contain defects and can have additional exposed facets beyond anatase (101) and rutile (110). Furthermore, the Mn precursor and the nature of the titania support material may influence the final composite structures in ways that cannot not be captured by computational modelling. Nevertheless, the qualitative agreement for the red shift on modified anatase (with or without water present on the anatase surface) and the effect of water on the energy gap change for rutile is reasonable.

TPR curves for the MnO_x-TiO_2 composites are shown in Figure 5. The plots show the negative first derivative of catalyst mass with respect to temperature. Peaks correspond to mass loss associated with reduction of the catalyst and generation of oxygen vacancies. The curves for the MnO_x-TiO_2 composites show two main features. The first is a low temperature feature centered between 150-300°C. This peak is also present in the bare anatase and rutile curves and represents the reduction of the titania to generate oxygen vacancies and accompanying Ti^{3+} sites. The feature is supressed in low loading composites, but reappears at higher loadings and trends towards lower temperature with increased Mn loading. The

second feature is a broad peak between 250-500°C that becomes larger in area and devolves into two or more distinct peaks with increasing Mn loading. This feature is not present in the bare support materials and is likely a result of the generation of oxygen vacancies in the MnO_x domains. At lower Mn loadings, the broad feature indicates multiple populations of oxygen vacancies over that range. As the Mn loading increases, especially on the anatase supported materials, two distinct peaks appear, a result that is consistent with the presence of bulk-like MnO_2 domains undergoing a two-step reduction. This behaviour is more pronounced on the anatase supported materials, especially ANO_3, than on rutile.

These results indicate that the MnO_x-TiO_2 materials are reduced to form oxygen vacancies, including some at relatively mild temperatures, as predicted in the DFT calculations. The reducibility of the materials increases with Mn loading and appears to be greater for anatase- than for rutile-supported materials. The data also show the appearance of features associated with bulk-like MnO_2, especially at higher Mn loading. This underlines one possible limitation in comparing the computational results and experimental work - the size of supported MnO_x clusters generated experimentally is likely much larger than what can be modelled, accounting for differences with DFT results that suggest reducibility is not strongly affected by the support.

3.3 Photoelectrochemical characterisation

To investigate the effective band gap, photocurrent measurements were performed under UV-vis and visible only irradiation. The onset potential for anodic current shifted positive with increased MnO_x loading. Samples with the highest MnO_x loading showed an oxidation peak around +0.25 V, which correlates to previous reports relating to Mn^{2+} oxidation [33]. Under UV-Vis irradiation the MnO_x modification gave a lower photocurrent as compared to unmodified TiO_2. Linear sweep voltammograms (LSVs) for anatase and 0.25AOAc MnO_x-TiO_2 are shown in Figure S6. Photocurrent was difficult to determine at higher Mn loadings due to increased dark current. Under visible only irradiation, very small photocurrents were observed with the anatase and 0.25ANO3 MnO_x-TiO_2 samples (Figure S7). A more noticeable photocurrent was observed with higher loadings of MnO_x; however, the observed photocurrents under visible irradiation were only a fraction of the photocurrent observed under UV-Vis irradiation. To further investigate any red shift in absorption the spectral photocurrent response at fixed potential was determined using monochromatic irradiation. The spectral response for the anatase and 0.25ANO3 samples is shown in Figure 6. The anatase sample shows a typical response with maximum photocurrent in the UV. The anatase sample also shows a small visible response due to defect sites. The MnO_x-TiO_2 has a relatively lower UV response and no real improvement in the visible photocurrent

response is observed. These results correlate with previous spectral photocurrent measurements on N,F-TiO_2 samples, where a red shift in the optical absorption spectrum was observed, however, no real shift in the photocurrent spectrum was observed [34].

The change in the open circuit potential (E_{OC}) under polychromatic UV-Vis and visible only irradiation is shown in Figure S8 for the anatase and 0.25ANO3 MnO_x-TiO_2. The E_{OC} shifts negative from ca +750 mV (dark) to -300 mV under UV-Vis irradiation while the E_{OC} MnO_x-TiO_2 also shifts negative, but not as much as the anatase sample. Under visible only irradiation, the negative shift in the E_{OC} is more pronounced for the MnO_x-TiO_2 sample as compared to anatase. Although the photocurrent under visible irradiation is similar for both samples, the negative shift in E_{OC} is more pronounced for the MnO_x-TiO_2 as compared to the anatase, indicating that visible light excitation of the MnO_x-TiO_2 gives a negative shift in the Fermi energy level of the material but photogenerated electrons cannot be collected as photocurrent, probably due to rapid recombination at defect sites.

Figure 7 shows the open circuit photopential (E_{OCP}, the potential under irradiation minus the dark equilibrium potential) as a function of wavelength for monochromatic irradiation. It is observed that as the MnO_x loading increases the negative shift in the E_{OCP} under UV irradiation becomes less while the visible E_{OCP} shifts more negative. This agrees to previous findings where it was observed that the E_{OCP} gives a better correlation to the optical absorption spectra for the materials as compared to the photocurrent spectra [34].

Although the E_{OCP} shifts are always negative, the actual measured E_{OC} becomes more positive with increasing MnO_x loading. This indicates a positive shift in the E_{OC} probably being determined by the redox potential of the Mn^{4+}/ Mn^{2+} couple.

3.4 CO_2 binding under UV irradiation

In contrast to theoretical findings, we did not detect CO_2 conversion to CO or any other product on any of the synthesized MnO_x-TiO_2 composites. In order to explain these results, we evaluated CO_2 binding at the material surface with FTIR. The spectra in Figure S9 reveal that the 0.25ANO3 material shows greater relative intensity of the peak (at 1247 cm^{-1}) associated with carboxylate species than does the bare anatase support. In contrast, the 0.25AOAc spectrum is almost identical to that of anatase. Compared to anatase, the highly Mn-loaded 8ANO3 and 8AOAc spectra show relatively greater intensity for peaks associated with bidentate carbonates (1281, 1324, 1555 cm^{-1}) and bicarbonates (1222, 1398, 1418 cm^{-1}) [28,29,35-38] and relatively lower intensity for peaks associated with carboxylates (1247, 1670 cm^{-1}). Spectra for rutile supported composites show a similar trend of increased

relative intensity of features associated with monodentate and bidentate carbonates as well as bicarbonates.

The FTIR spectra (Figure S9) present evidence of CO_2 binding in a variety of configurations, including carboxylate and bidentate carbonate, which are both associated with interactions between CO_2 and oxygen vacancies and/or electron donation from associated Ti^{3+} sites [28,29]. Since the bare titania and MnO_x-TiO_2 composites were reduced during the pre-treatment, it is likely that the same mechanism is at play here, with electron donation from a reduced Ti center in the case of anatase/rutile or a reduced Ti or Mn center in the case of the MnO_x-TiO_2 composites. However, the spectra for the MnO_x-TiO_2 composites show a greater proportion of the bound CO_2 in the form of carbonates and bicarbonates, than carboxylates, which was observed on the bare titania. Carboxylates include the CO_2^- moiety, which is believed to be an important intermediate in CO_2 photoreduction [28,29,39-41] whereas carbonates and bicarbonates are relatively stable and may not yield CO_2 reduction products. Therefore, while CO_2 is observed to bind to MnO_x-TiO_2, it does not do so in the activated state that is advantageous for CO_2 reduction.

4.0 Concluding Remarks

We propose a novel nanoarchitecture of MnOx clusters supported on TiO_2 that cycles between Mn^{3+} and Mn^{2+} with an input of thermal and light energy using CO_2 to produce CO and heal oxygen vacancies. DFT predicts that this composite shows band gap narrowing and visible light activity, facile formation of oxygen vacancies and reduced Mn-centers, and possible CO_2 reduction to CO. The presence of water on TiO_2 may, however, unfavourably affect these interactions, particularly the red-shift after MnO_x modification.

Experimental studies yield new insights into the structure and function of the multifunctional catalyst. Only MnO_x supported on anatase displayed a red-shift which increased with MnO_x loading. In contrast, photoelectrochemistry revealed that increased MnO_x loading decreased total anodic photocurrent, with a minor enhancement in visible light current; this was attributed to electron trapping by MnO_x defects. Although these defects are detrimental to anodic current, they may be favourable for CO_2 reaction. In agreement with theory, TPR shows that oxygen vacancies were easily formed, particularly on anatase supports. However, FTIR results indicate that CO_2 adsorption does not occur in the preferred carboxylate configuration, failing to heal oxygen vacancies and produce C-O cleavage. Oxygen vacancies on MnO_x clusters, with low formation energies, may be too stable for oxidation by CO_2 and our ongoing efforts are focused on evaluating metal oxide clusters that produce more reactive defects. Finally, these results illustrate the value of integrating theory and experiments to understand the complex structure-function relationships required for the

photoreduction of CO_2. There is a clear influence of both the crystal form of TiO_2 and the surface coverage of water on the red shift in the composite and on vacancy formation. These are important factors in the design of surface modified TiO_2 photocatalysts.

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