CO$_2$ Activation on Heterostructures of Bi$_2$O$_3$-Nanocluster Modified TiO$_2$:
Promoting the Critical First Step in CO$_2$ Conversion.

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KEYWORDS: Photocatalysis, CO$_2$, activation, adsorption, heterostructures, reduction, DFT
ABSTRACT: The conversion of CO\textsubscript{2} to fuels is of significant importance in enabling the production of sustainable fuels, contributing to alleviating greenhouse gas emissions. While there are a number of key steps required to convert CO\textsubscript{2}, the initial step of adsorption and activation by the catalyst is critical. Well-known metal oxides such as oxidised TiO\textsubscript{2} or CeO\textsubscript{2} are unable to promote this step. In addressing this difficult problem, recent experimental work shows the potential for bismuth-containing materials to activate and convert CO\textsubscript{2}, but the origin of this activity is not yet clear. Additionally, nanostructures can show enhanced activity towards CO\textsubscript{2}. In this paper we present density functional theory (DFT) simulations of CO\textsubscript{2} activation on heterostructured materials composed of extended rutile and anatase TiO\textsubscript{2} surfaces modified with nanoclusters with Bi\textsubscript{2}O\textsubscript{3} stoichiometry. These heterostructures show low coordinated Bi sites in the nanoclusters and a valence band edge that is dominated by Bi-O states. These two factors mean that supported Bi\textsubscript{2}O\textsubscript{3} nanoclusters are able to adsorb and activate CO\textsubscript{2}. Computed adsorption energies lie in the range of -0.54 eV to -1.01 eV. In these strong adsorption modes, CO\textsubscript{2} is activated, in which the molecule bends giving O-C-O angles of 126 - 130\textdegree and elongation of C-O distances up to 1.28 Å, with no carbonate formation. The electronic properties show a strong CO\textsubscript{2}-Bi-oxygen interaction that drives the interaction of CO\textsubscript{2} to induce the structural distortions. Bi\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} heterostructures can be reduced to form Bi\textsuperscript{2+} and Ti\textsuperscript{3+} species. The interaction of CO\textsubscript{2} with this electron-rich, reduced system can produce CO directly, reoxidising the heterostructure or form an activated carboxyl species (CO\textsubscript{2}^{-}) through electron transfer from the heterostructure to CO\textsubscript{2}. These results highlight that a semiconducting metal oxide modified with suitable metal oxide nanoclusters can activate CO\textsubscript{2}, thus overcoming the difficulties associated with the difficult first step in CO\textsubscript{2} conversion.
1. Introduction

Increasing energy demand is leading to fossil fuel supply issues and ever-increasing CO$_2$ emissions, which are now past 400 ppm and are projected to result in a 2°C rise in average global temperatures. Given these severe societal problems there is an urgent need to find materials that can convert the CO$_2$ produced by combustion of fossil fuels back to fuels or to the precursors for production of more useful chemicals. This will reduce our reliance on non-sustainable fossil fuels and contribute to curbing CO$_2$ emissions. The solar driven photo- or thermal reduction of CO$_2$ to CO (for synthesis gas) or directly to liquid fuels will enable a sustainable approach to producing fuels and storing solar energy in high energy chemical bonds$^{1-11}$.

Using solar energy, e.g. through solar concentrators, coupled with catalysts that can promote activation of CO$_2$ to drive the CO$_2$ reduction process is an attractive strategy to meet this ambitious aim. However, to date, there are no practical catalysts that can exploit solar energy to efficiently reduce CO$_2$ to useful chemical species. One successful photocatalyst to date has been Pt-modified TiO$_2$ nanotubes$^{8,12,13}$. However, the efficiencies for methane production are extremely low and Pt will never be an economically viable catalyst for large scale CO$_2$ conversion. Catalysts based on metallic Cu, oxide-derived Cu or Cu with mixed oxidation states have been demonstrated to reduce CO$_2$ to useful molecules such as methane, methanol or ethanol$^{14-23}$. Recent experimental work indicates the ability of nanocatalysts containing a mix of Cu$^+$ and Cu$^{2+}$ oxidation states and in oxide-like structures to drive CO$_2$ reduction$^{1,2,10,14-16,18,19,22-25}$. However, there is still an urgent need from both a fundamental and a techno-economic perspective to dis-
cover new materials than can activate and reduce CO\textsubscript{2} in particular to produce sustainable fuels, particularly if renewable energy can be used.

Irrespective of how electrons are provided to reduce CO\textsubscript{2}, the key step in any CO\textsubscript{2} conversion process is the initial adsorption and activation of CO\textsubscript{2}. Thereafter there may be transfer of electron(s) to the CO\textsubscript{2} through light absorption, from excess electrons present in the catalyst after catalyst (pre-)reduction or in a combined PV+electrolysis system. Hydrogenation is an attractive route to value-added fuels, so long as the hydrogen is produced in a renewable process. Thus, the key challenge in fuel production from CO\textsubscript{2} is to discover catalysts that will adsorb and activate CO\textsubscript{2}. In particular, the CO\textsubscript{2} should adsorb in an activated form and not form the highly stable carbonates which are unreactive towards further chemistry and poison the surface.

Copper-based catalysts have been widely studied for CO\textsubscript{2} activation and conversion\textsuperscript{2,15,16,18-22,24-29} and this includes Cu metal, oxide-derived Cu and mixed oxidation state Cu. There has also been a great deal of interest in modelling of the interaction of CO\textsubscript{2} with copper oxides using density functional theory (DFT) as this would provide useful and important guidelines for further development of CO\textsubscript{2} activation catalysts. Cu\textsubscript{2}O, with a Cu(I) oxidation state, and CuO, with a Cu(II) oxidation state, have emerged as potential candidates for the CO\textsubscript{2} reduction reaction due to favourable band gap positions and widths\textsuperscript{16}, and studies have focused on the interaction of CO\textsubscript{2} molecules with various cuprous oxide surfaces and terminations\textsuperscript{2,15,16,18,19,22} although issues still persist regarding their stability in solution. Wu et al studied the adsorption of CO\textsubscript{2} at the Cu\textsubscript{2}O (111) surface in which oxygen vacancies were present\textsuperscript{18}, and found that dissociative adsorption was thermodynamically unfeasible. In addition, while oxygen vacancies have a negative effect on the interaction energy, adsorption can lead to the formation of a CO\textsubscript{2}\delta\textsuperscript{6} radical anion species. In another study Wu et al looked at the adsorption of CO\textsubscript{2} and its derivatives at Cu\textsubscript{2}O.
(111) using Hybrid DFT \(^2\) and found adsorption only in non-activated form. This finding is supported by Benavid and Carter in which they reported that physisorption of a linear molecule is favoured over adsorption in a bent anionic (activated) geometry\(^1\). Mishra and colleagues found similar results for CO\(_2\) adsorption at Cu\(_2\)O (111), but reported a strong chemisorption at the high energy Cu-O terminated (110) surface\(^5\). A further study from Mishra et al, reported CO\(_2\) activation, with bending and elongation of bonds, upon the exothermic adsorption of CO\(_2\) at the high energy (011) surface of CuO\(_2\). Uzunova et al studied the conversion of CO\(_2\) to methanol on Cu\(_2\)O nanolayers and clusters \(^\)\(^6\) using Hybrid DFT. The authors considered water as the source of H atoms for the hydrogenation of CO\(_2\) and described a reaction pathway from a carboxyl group (*COOH) to formic acid, which was the rate limiting step, and then onto formaldehyde and finally methanol. In the work of Favaro et al.\(^2\) a model of Cu with susbsurface oxygen was found to describe the ability of CuO\(_x\) to activate CO\(_2\).

The adsorption of CO\(_2\) molecules at different titania surfaces and nanostructures has been studied and the role of oxygen vacancies, low coordinated sites and structure in the CO\(_2\) activation process has been described \(^\)\(^3\)\(^-\)\(^3\)^\(^2\). The presence of excess electrons and holes was shown to affect adsorption and activation of CO\(_2\) at rutile (110) and both bent CO\(_2^-\) anion and CO\(_2^+\) cation configurations were identified \(^3\)^\(^3\). Lee and Kanai\(^2\) used DFT to explore the difference between anatase (101) and a TiO\(_2\) quantum dot for CO\(_2\) activation and hydrogenation. They found that the TiO\(_2\) quantum dot promoted CO\(_2\) activation and hydrogenation. Yang and colleagues showed that sub-nm Pt clusters at the anatase (101) surface enhanced CO\(_2\) activation through provision of additional adsorption sites and the transfer of electron density to the TiO\(_2\) substrate \(^\)\(^3\)^\(^4\).

Other theoretical studies have been conducted into reaction pathways involving the hydrogenation of CO and CO\(_2\) at a variety of catalytic surfaces, including Cu/CeO\(_2\) and Cu/CeO\(_2\)/TiO\(_2\) \(^\)\(^\)\(^1\)^\(^7\),
Cu/ZnO/Al₂O₃ as well as copper surfaces. Enhanced photoreduction of CO₂ with H₂O vapour has been reported for dispersed CeO₂/TiO₂; the role of Ce³⁺ in visible light absorption, photogenerated charge separation and strengthening CO₂-surface bonding was highlighted.

Upon examining recent literature on this topic, the recent experimental work from Rosenthal and co-workers and Walker et al. strongly suggests that p-block metal containing systems, in particular Bismuth, are able to activate CO₂ or convert it to other molecules with good efficiency. The catalysts in refs are Bi-containing materials supported on glassy carbon and Bi nanoparticles, which have large amounts of Bi³⁺. In ionic liquids these can convert CO₂ to alcohols with high efficiency.

The bismuth pyrochlore oxide Bi₂Ti₂O₇ was studied in ref. and has high CO₂ chemisorption capacity. In this system, low energy ion scattering (LEIS) shows clearly that Bi³⁺ species are present in the surface layer. This arises from the well-known stereochemical lone pair in Bi³⁺. By contrast in the pyrochlore Y₂Ti₂O₇ system there is no surface enrichment with Y³⁺ which lacks a lone pair. This Bi-containing pyrochlore was found from infra red spectroscopy to adsorb and activate CO₂. Features in the infra red spectrum corresponding to activated CO₂ were clearly present. The Y₂Ti₄O₇, by contrast, does not strongly adsorb or activate CO₂. This suggests that activation of CO₂ arises from the presence of Bi³⁺ and Bi-O units in the pyrochlore surface.

From the studies in refs., it is reasonable to propose that the presence of the Bi³⁺ cation, with its stereochemically active lone pair, will promote the interaction of the Bi-containing oxide with CO₂. However, the mechanism of CO₂ activation on Bi³⁺-containing materials, as a good exemplar of the p-block metal oxides, still needs to be understood and is to date lacking.
Previously we have used first principles density functional theory (DFT) simulations to design heterostructured materials which are composed of TiO$_2$ (rutile or anatase) surfaces modified with metal oxide nanoclusters. In our work, the emphasis has been on new heterostructured materials with predicted visible light absorption\textsuperscript{44-56} and reduced charge recombination\textsuperscript{45-49, 57-59}. We have recently extended this work to study the interaction of molecules, such as CO$_2$, with these metal oxide nanocluster modified TiO$_2$ heterostructures\textsuperscript{44, 60}. We found that there are modified TiO$_2$ systems, e.g. ZrO$_2$-anatase\textsuperscript{44} where CO$_2$ can adsorb and be activated. There are other heterostructures, such as reduced MnO$_x$-TiO$_2$ where there is no CO$_2$ activation\textsuperscript{60}. There is still much work to be done to understand the factors that drive CO$_2$ activation on metal oxides.

In the present paper, we take the ideas from the experimental work on CO$_2$ activation using Bi-containing materials, the ability of nanostructures to activate CO$_2$ and the activity of nanocluster modified TiO$_2$ to use first principles density functional theory to examine in detail the interaction and activation of CO$_2$ at Bi$_2$O$_3$ nanocluster modified rutile and anatase TiO$_2$ surfaces in which both Bi$^{3+}$ species and stabilized nanoclusters are present. The interaction of CO$_2$ with reduced Bi$_2$O$_3$-TiO$_2$ heterostructures, which are formed by removing oxygen from the nanocluster, is also examined. We find that this novel heterostructure is able to activate CO$_2$ with exothermic CO$_2$ adsorption. This results in molecular deformation, primarily bending of the O-C-O angle to \textit{ca.} 130° and elongation of C-O distances up to 1.28Å. In addition, in the case of the partially reduced Bi$_2$O$_3$-TiO$_2$ heterostructures, charge transfer to produce a carboxylate or even direct CO formation are possible. These findings thus demonstrate the potential for Bi-containing materials to convert CO$_2$ to useful molecules.
2. Methods

In the DFT computations, we follow our approach from previous work\cite{58} and prepare heterostructures of Bi$_2$O$_3$ nanoclusters supported on rutile (110) and anatase (101). All DFT computations use a three dimensional periodic surface slab within the VASP code\cite{61-64}, and a plane wave basis set to describe the valence electrons. Projector augmented wave potentials\cite{65, 66}, with 4, 5, 6 and 4 valence electrons for Ti, Bi, O and C describe the core-valence electron interactions and this set-up was extensively tested in our earlier work on Bi$_2$O$_3$-modified TiO$_2$\cite{58}. The cut-off for the kinetic energy is 396 eV and the exchange-correlation functional is the Perdew-Wang 91\cite{67} approximation. A Monkhorst-Pack (2×1×1) k-point sampling grid is used. For consistency with our previous work we apply the DFT+U approach\cite{68, 69} to describe the Ti 3d states, with a value of U = 4.5 eV. The convergence criteria for the electronic and ionic relaxations are 0.0001 eV and 0.02 eV/Å. Methfessel-Paxton smearing is used with σ = 0.1 eV (also for the broadening of the peaks in the projected density of states). We use the Newton-Rhapson relaxation algorithm and all calculations are spin polarised throughout, with no constraints on the spin.

The rutile (110) surface is terminated by two-fold coordinated bridging O atoms, with 3-fold coordinated in-plane oxygen atoms in the surface layer. In the same layer, the Ti atoms take 5-fold and 6-fold coordination. The anatase (101) surface is characterised by two-fold coordinated oxygen atoms terminating the surface layer and the outermost Ti atoms are 5-fold coordinated. (2x4) and (4x2) surface supercell expansions are employed for rutile and anatase, respectively and the vacuum gap in all cases is 12 Å.

In forming these composite structures, we first relax the gas phase metal oxide nanoclusters and the unmodified rutile and anatase surfaces using the same computational set-up described above.
The oxide nanocluster modifier is adsorbed at the TiO$_2$ surfaces in different configurations and each of these are relaxed, as described in Ref.\textsuperscript{45, 54, 58, 70}. We selected the most stable Bi$_2$O$_3$-TiO$_2$ composites for the study of CO$_2$ activation in the present paper. We will use the term Bi$_2$O$_3$-TiO$_2$ throughout this paper to indicate the general Bi$_2$O$_3$ nanocluster modified TiO$_2$ heterostructure, using the precise nanocluster composition and TiO$_2$ surface when necessary.

The stability of the heterostructure is characterised by the computed nanocluster adsorption energy, $E^{ads}$

$$E^{ads} = E[(\text{Bi}_2\text{O}_3)_n\text{-TiO}_2] - \{E[(\text{Bi}_2\text{O}_3)_n] + E[\text{TiO}_2]\}$$ (1)

where $E[(\text{Bi}_2\text{O}_3)_n\text{-TiO}_2]$ is the computed total energy of the Bi$_2$O$_3$ nanocluster-modified TiO$_2$ surface (in which $n$ is the number of Bi$_2$O$_3$ units in the nanocluster so that in this paper $n = 2$ or 3), $E[(\text{Bi}_2\text{O}_3)_n]$ is the computed total energy of the free (Bi$_2$O$_3$)$_n$ nanocluster and $E[(\text{TiO}_2)]$ is the computed total energy of the unmodified TiO$_2$ (rutile/anatase) surface.

The reduction of the Bi$_2$O$_3$-TiO$_2$ heterostructures is studied by removing oxygen from the nanocluster modifier (which is always more stable than removing oxygen from the TiO$_2$ support) and computing the formation energy of the oxygen vacancy as follows:

$$E^{vac} = E\{((\text{Bi}_2\text{O}_3-x)_n\text{-TiO}_2-x) + 1/2E(\text{O}_2)\} - E((\text{Bi}_2\text{O}_3)_n\text{-TiO}_2)$$ (2)

where $E\{((\text{Bi}_2\text{O}_3-x)_n\text{-TiO}_2-x)$ is the total energy of the Bi$_2$O$_3$-TiO$_2$ composite with one oxygen removed and $1/2E(\text{O}_2)$ is the reference energy for oxygen, namely half the total energy of the O$_2$ molecule. Despite the known errors in the DFT energy of the reference O$_2$ molecule, the trends in oxygen vacancy formation are independent of this error.

The CO$_2$ adsorption energy at Bi$_2$O$_3$-modified TiO$_2$ heterostructures is defined in Eqn (3):
\[
E_{\text{ads}} = E(\text{CO}_2@\text{(Bi}_2\text{O}_3)_n\text{-TiO}_2) - \{ E((\text{Bi}_2\text{O}_3)_n\text{-TiO}_2) + E(\text{CO}_2) \} 
\]  
(3)

where \( E(\text{CO}_2@\text{(Bi}_2\text{O}_3)_n\text{-TiO}_2) \) is the computed total energy of the relaxed adsorption structure of \( \text{CO}_2 \) at \( \text{Bi}_2\text{O}_3 \)-modified \( \text{TiO}_2 \) composites, whether stoichiometric or reduced. We examined many \( \text{CO}_2 \) adsorption structures and those shown in the following text are the most stable that we have found. While van de Waals corrections can be added to these computations, we have tested this and find that the change in the adsorption energies is \( \text{ca.} \) 0.15 eV, which is not significant compared to the magnitude of the computed \( \text{CO}_2 \) adsorption energies and furthermore there is no effect of inclusion of vdW corrections on the relative stability of different \( \text{CO}_2 \) adsorption structures.

3. Results and Discussion

3.1 \( \text{Bi}_2\text{O}_3 \)-Modified Rutile and Anatase \( \text{TiO}_2 \) Heterostructure

\( \text{Figure 1} \) shows the atomic structure of \( \text{Bi}_4\text{O}_6 \)-and \( \text{Bi}_6\text{O}_9 \)-nanocluster modified anatase (101) and rutile (110) surfaces. We have described these heterostructured systems in detail in previous work\(^8\), we briefly summarise the key features required for this paper. The computed adsorption energies relative to the gas phase \( \text{Bi}_2\text{O}_3 \)-stoichiometry nanoclusters are -5.18 eV, -5.18 eV and -5.72 eV for \( \text{Bi}_4\text{O}_6 \)-rutile, \( \text{Bi}_6\text{O}_9 \)-rutile and \( \text{Bi}_4\text{O}_6 \)-anatase, respectively. These energies indicate strong binding of the nanocluster modifier at both \( \text{TiO}_2 \) surfaces. This is primarily driven by formation of new interfacial bonds between the nanocluster and the surface.
On Bi$_4$O$_6$-rutile, there are three bonds from Bi to bridging surface oxygen, with two Bi-O distances of 2.17 Å and a third of 2.54 Å. The Bi cations are 3-fold coordinated and the nanocluster not bound to the surface are 2-fold coordinated. There are three new bonds between nanocluster oxygen and 5-fold coordinated Ti surface atoms; the Ti-O distances are in the range of 1.83 Å to 2.05 Å. In the Bi$_6$O$_9$-rutile nanocluster, there is a new Bi-O bond (2.37 Å) to bridging oxygen. Nanocluster oxygen binds to surface Ti atoms, with Ti-O distances of 1.94 and 1.86 Å. Here the terminal Bi cations, furthest away from the cluster-surface interface, are 3-fold coordinated and there are 2-fold coordinated oxygen sites in the nanocluster.

In Bi$_6$O$_9$-anatase, four new Bi-O bonds are formed to the surface, with Bi-O distances of 2.14, 2.14, 2.24 and 2.17 Å. The two Bi cations furthest away from the cluster-surface interface are 3-fold coordinate and the remaining Bi cations are 4-fold coordinate. There are five bonds between nanocluster oxygen and surface Ti, with distances of 1.87, 1.89, 2.0, 2.01 and 2.06 Å. There are three 2-fold coordinated oxygen sites: one is the terminal oxygen in the nanocluster and the remaining two sites bridge the nanocluster and the anatase (101) surface.

Figure 1: Relaxed atomic structure for Bi$_2$O$_3$-nanocluster modified rutile (110) and anatase (101). (a): Bi$_4$O$_6$-rutile (110), (b): Bi$_6$O$_9$-rutile (110) and (c): Bi$_6$O$_9$-anatase (101). The colour
coding in this and subsequent figures is Ti = light gray sphere, O = red sphere and Bi = purple sphere. Bi and O atoms in the adsorbed nanoclusters are depicted by larger radius spheres.

The other important aspect of the Bi$_2$O$_3$-TiO$_2$ composites for the interaction with CO$_2$ is their electronic properties and in **Figure 2** we show the projected electronic density of states (PEDOS) for the Bi$_2$O$_3$-rutile and Bi$_2$O$_3$-anatase systems. Bi$^{3+}$ is an interesting species as it has a stero-
chemically active lone pair which results in the presence of Bi-derived electronic states at the top of the valence band. This gives rise to the distorted structure of bulk Bi$_2$O$_3$ and the Bi-rich surface region in the pyrochlore Bi$_2$Ti$_2$O$_7$. Other metal oxides with +3 cations do not show these structural distortions.

In the PEDOS of the Bi$_2$O$_3$-TiO$_2$ heterostructures, the Bi electronic states are present at the valence band edge of all composite systems studied. For modified rutile (110), we see Bi (5s+5p) and O 2p states originating from the nanoclusters lying at higher energy than the corresponding TiO$_2$ valence and conduction band edges, which should result in a small red shift in light absorption. For anatase, the Bi$_2$O$_3$ derived states lie just below the anatase valence band edge, which results in no predicted red shift. The key finding is that the Bi states lie at the top of the valance band edge and this will be crucial for the discussion of CO$_2$ activation on Bi$_2$O$_3$-TiO$_2$. 
**Figure 2:** Projected electronic density of states (PEDOS) projected onto Bi 6s, Ti 3d and O 2p states (nanocluster and surface) for (a): Bi$_4$O$_6$ rutile (110), (b): Bi$_6$O$_9$-rutile (110) and (c): Bi$_4$O$_6$-anatase (101). The zero of energy in all cases is the Fermi level. The left panels show the cation PEDOS and the right panels show the oxygen 2p PEDOS.

3.2 Activation of CO$_2$ at Stoichiometric Bi$_2$O$_3$-TiO$_2$ Heterostructures

We now discuss the adsorption and activation of CO$_2$ at Bi$_2$O$_3$-nanocluster modified TiO$_2$ heterostructures and in this section we focus on the stoichiometric compositions. Table 1 presents the
computed adsorption energies of the two most stable adsorption configurations of CO$_2$ at each Bi$_2$O$_3$-TiO$_2$ heterostructure and **Figure 3** shows the relaxed atomic structures for these CO$_2$ adsorption configurations.

From table 1, we can see that there is at least one strongly interacting CO$_2$ adsorption configuration at each Bi$_2$O$_3$-modified TiO$_2$ composite – the corresponding adsorption energies are -0.54 eV, -1.01 eV and -0.82 eV on Bi$_4$O$_6$-rutile, Bi$_6$O$_9$-rutile and Bi$_4$O$_6$-anatase. Compared to computed adsorption energies of CO$_2$ on other metal oxide modified TiO$_2$ systems, e.g. in ref.44 or on polymorphs of TiO$_2$ itself$^{10,31,71}$ the adsorption energies of CO$_2$ on Bi$_2$O$_3$-modified TiO$_2$ are notably larger, indicating that these heterostructures are significantly more active towards CO$_2$ adsorption and activation. Given that the adsorption of CO$_2$ is the crucial first step in the catalytic conversion of CO$_2$ to useful molecules, and is generally difficult on stoichiometric metal oxides, our finding that CO$_2$ interacts strongly with Bi$_2$O$_3$-modified TiO$_2$ is a first key result of this work.

<table>
<thead>
<tr>
<th>Adsorption Configuration</th>
<th>$E^{ads}$/ eV</th>
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<tbody>
<tr>
<td><strong>On Rutile (110)</strong></td>
<td></td>
</tr>
<tr>
<td>Bi$_4$O$_6$-Rutile (110) + CO$_2$ (activated)</td>
<td>-0.37 eV</td>
</tr>
<tr>
<td>Bi$_6$O$_9$-Rutile (110) + CO$_2$ (activated)</td>
<td>-0.54 eV</td>
</tr>
<tr>
<td>Bi$_6$O$_9$-Rutile (110) + CO$_2$ (linear)</td>
<td>-0.28 eV</td>
</tr>
<tr>
<td>Bi$_4$O$_6$-Rutile (110) + CO$_2$ (activated)</td>
<td>-1.01 eV</td>
</tr>
<tr>
<td><strong>On Anatase (101)</strong></td>
<td></td>
</tr>
<tr>
<td>Bi$_4$O$_6$-Anatase (101) + CO$_2$ (linear)</td>
<td>-0.51 eV</td>
</tr>
<tr>
<td>Bi$_4$O$_6$-Anatase (101) + CO$_2$ (activated)</td>
<td>-0.82 eV</td>
</tr>
</tbody>
</table>

**Table 1**: Computed adsorption energies, in eV, of CO$_2$ at Bi$_2$O$_3$-modified rutile (110) and anatase (101) heterostructures.
Figure 3: Relaxed adsorption structures of CO$_2$ at Bi$_2$O$_3$-modified rutile (110) and anatase (101) composites; the composition is indicated in each case. (a), (b): CO$_2$ adsorption at Bi$_4$O$_6$-Rutile (110) (c), (d): CO$_2$ adsorption at Bi$_6$O$_9$-Rutile (110) and (e), (f): CO$_2$ adsorption at Bi$_4$O$_6$-anatase (101). Colour coding is the same as figure 1, with the additional inclusion of a gray sphere for carbon. The Bi and O atoms in supported Bi$_2$O$_3$ nanoclusters are depicted with the larger diameter spheres.

Examining the atomic structures for adsorbed CO$_2$ we see that there are adsorption configurations on Bi$_6$O$_9$-rutile and Bi$_4$O$_6$-anatase, namely the configurations in Figure 3(c) and 3(e) which have the weakest interactions and show a linear CO$_2$ that is unchanged from the gas phase. This is a non-activated CO$_2$ physisorption mode.

The other adsorption modes in figure 3 are of more interest from the perspective of CO$_2$ activation and these result in distortions to the atomic structure of bound CO$_2$ at the Bi$_2$O$_3$ nanoclusters.
and the stabilization of this bound adsorption configuration. Table 2 presents the important C-O distances and O-C-O bending angles in the activated CO$_2$ adsorption mode as well as the computed vibrational modes of the adsorbed CO$_2$. The common feature of these adsorption modes of CO$_2$ is that the molecule is clearly bent (gas phase CO$_2$ is linear, with an O-C-O angle of 180°). The O-C-O angles in adsorbed CO$_2$ are 131°, 127° and 130° on Bi$_4$O$_6$-rutile, Bi$_6$O$_9$-rutile and Bi$_4$O$_6$-anatase, Table 2. This is consistent with the bending of activated CO$_2$ observed on other materials, including transition metal carbides or on ceria-modified rutile (110)$^4,72,73$.

<table>
<thead>
<tr>
<th>Structure</th>
<th>C-O / Å</th>
<th>O-C-O Angle / °</th>
<th>CO$_2$ vibrational frequencies / cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutile (110)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi$_4$O$_6$-Rutile (110) + CO$_2$</td>
<td>1.27, 1.26, 1.39</td>
<td>131</td>
<td>1617, 1250, 924, 774</td>
</tr>
<tr>
<td>Bi$_6$O$_9$-Rutile (110) + CO$_2$</td>
<td>1.26, 1.29, 1.39</td>
<td>127</td>
<td>1531, 1304, 1028, 774</td>
</tr>
<tr>
<td>Anatase (101)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi$_4$O$_6$-Anatase (101) + CO$_2$</td>
<td>1.26, 1.27, 1.39</td>
<td>130</td>
<td>1593, 1243, 917, 790</td>
</tr>
</tbody>
</table>

Table 2: Computed C-O and Bi-O distances and CO$_2$ vibrational frequencies for CO$_2$ adsorbed in activated forms at Bi$_2$O$_3$-modified rutile (110) and anatase (101). The first two C-O distances in column 2 are in the adsorbed molecule and the third C-O distance is to oxygen in the Bi$_2$O$_3$ nanocluster. Our computed vibrational frequencies of free CO$_2$ are 2354, 1325, and 632 cm$^{-1}$, with the latter being degenerate. These can be compared with experimental data: 2349 (C=O asymmetric stretch), 1388 cm$^{-1}$ (C=O symmetric stretch) and 667 cm$^{-1}$ (C=O bonding, degenerate).

In the more strongly bound monodentate CO$_2$ adsorption mode on Bi$_4$O$_6$-rutile, the C-O distances in adsorbed CO$_2$ elongate to 1.26 and 1.27 Å, while the C-O distance to nanocluster oxygen is 1.39 Å. This is a notable elongation in the C-O distances over those in the gas phase molecule (which are 1.16 Å). Similarly, on Bi$_6$O$_9$-rutile, the resulting bidentate adsorption configuration has elongated C-O distances of 1.26 and 1.29 Å in the molecule, while the C-O distance to the
nanocluster is 1.39 Å. On Bi$_4$O$_6$-anatase, the carbon atom binds in a monodentate fashion to one oxygen in the nanocluster, with a C-O distance of 1.39 Å, while the C-O distances in the molecule are 1.26 and 1.27 Å. Clearly on Bi$_2$O$_3$-modified TiO$_2$, the CO$_2$ molecule does not adsorb as a carbonate, where the three C-O distances are equal (~1.29 Å). These changes in geometry of the adsorbed CO$_2$ are consistent with and characteristic of formation of an activated CO$_2$ species.

We have also computed the vibrational modes of adsorbed CO$_2$ on Bi$_2$O$_3$-modified TiO$_2$. The computed gas phase vibrational modes of CO$_2$ are 2354, 1325, and 632 cm$^{-1}$, with the latter being degenerate. These correspond to the asymmetric C=O stretch, the symmetric C=O stretch and the O-C-O bending mode. We see that upon adsorption at the Bi$_2$O$_3$-TiO$_2$ heterostructures, there are significant red shifts in the asymmetric C=O stretch of 737, 823 and 761 cm$^{-1}$ on Bi$_4$O$_6$-rutile, Bi$_6$O$_9$-rutile and Bi$_4$O$_6$-anatase. The degeneracy of the O-C-O bending mode is lifted upon adsorption at Bi$_2$O$_3$-TiO$_2$. Again, this large red shift in the C=O stretch is consistent with activation of CO$_2$ upon adsorption. CO$_2$ adsorbed on Bi$_6$O$_9$-rutile shows the largest red shift of the C=O stretch which is consistent with its larger adsorption energy and more distorted CO$_2$ geometry. This shift in the C=O stretching mode correlates with the strength of the CO$_2$-Bi$_2$O$_3$-TiO$_2$ interaction and it has been observed in experimental studies of CO$_2$ adsorption on a range of materials.$^{74-76}$

When we examine the local atomic structure of the Bi$_2$O$_3$ nanoclusters around the adsorption site of CO$_2$, we find that the oxygen site in the supported Bi$_2$O$_3$ nanocluster that promotes CO$_2$ adsorption is a two-fold coordinated oxygen atom which bridges two Bi cations in the nanocluster. Such lower coordinated oxygen species abound in sub-nm metal oxide nanoclusters. Importantly, we also find that the most favourable CO$_2$ adsorption modes have a common structural motif in which one of the Bi-O bonds involving this two-fold oxygen can break upon formation of the
new C-O bond. In Bi\(_4\)O\(_6\)-rutile, we did not find any adsorption modes where one of these Bi-O bonds involving the 2-fold coordinated oxygen is broken and this structure has the least favourable CO\(_2\) interaction energies.

Finally, we briefly examine the electronic structure. **Figure 4** shows the projected electronic density of states for C and O atoms in CO\(_2\), and Ti and Bi atoms for the examples of CO\(_2\) adsorbed on Bi\(_6\)O\(_9\)-rutile and Bi\(_4\)O\(_6\)-anatase. In both cases the CO\(_2\) derived C 2p and O 2p electronic states lie at the top of the valence band. Furthermore, there is a strong interaction between the Bi 5s/5p states and the carbon and oxygen 2p states of CO\(_2\). This is consistent with the strong interaction and distortion of CO\(_2\) when adsorbed at the supported Bi\(_2\)O\(_3\) nanoclusters. We have also computed the Bader atomic charges upon CO\(_2\) adsorption. These do not show a significant charge transfer between Bi\(_2\)O\(_3\)-TiO\(_2\) and CO\(_2\), indicating that the activation of CO\(_2\) takes place without any charge transfer.

The atomic and electronic structure of Bi\(_2\)O\(_3\)-nanocluster modified TiO\(_2\) permits the interaction of Bi-O electronic states at the top of the Bi\(_2\)O\(_3\)-TiO\(_2\) valance band with the C and O atoms of CO\(_2\). The atomic structure of the Bi\(_2\)O\(_3\) nanoclusters can further facilitate CO\(_2\) adsorption due the flexibility in these supported nanoclusters upon relaxation. We can also relate these findings to the work from Walker et al\(^{41}\) on the Bi-containing pyrochlore. In this system the surface is terminated by a Bi-O layer, similar to our Bi\(_2\)O\(_3\)-nanocluster modified TiO\(_2\), and the Bi 5s/5p electronic states are mixed with O 2p states at the top of the valence band. Thus, the pyrochlore has a suitable electronic structure to permit interaction with CO\(_2\) and an atomic structure that also facilitates the interaction with CO\(_2\).
Figure 4: PEDOS projected onto the Ti 3d, Bi 6s/6p and CO\textsubscript{2} 2p states after adsorption of CO\textsubscript{2} onto (a) Bi\textsubscript{6}O\textsubscript{9}-rutile and (b) Bi\textsubscript{4}O\textsubscript{6}-anatase.

3.3 CO\textsubscript{2} Activation at Reduced Bi\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} Heterostructures

In this section we consider the interaction of CO\textsubscript{2} at reduced Bi\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} heterostructures. The reduced heterostructures are prepared by removing oxygen atoms from the Bi\textsubscript{2}O\textsubscript{3} nanoclusters and computing the oxygen vacancy formation energy. From these results, the most stable reduced structures are shown in Figure 5. The computed formation energies for these oxygen vacancies are 1.75 eV for Bi\textsubscript{4}O\textsubscript{6}-rutile (110), 1.64 eV for Bi\textsubscript{6}O\textsubscript{9}-rutile (110) and 3.0 eV for Bi\textsubscript{4}O\textsubscript{6}-anatase (101). The other oxygen sites have formation energies larger than 2 eV on Bi\textsubscript{2}O\textsubscript{3}-rutile and between 3.4 and 3.7 eV on Bi\textsubscript{4}O\textsubscript{6}-anatase. The computed oxygen vacancy formation energies
for the most favourable sites are all smaller than on the corresponding bare TiO$_2$ surfaces (3.5 eV for rutile (110) and 3.6 – 4.1 eV for anatase (101)$^{77}$) and indicate a moderate cost to reduce the heterostructures so that reduction should be possible under moderate conditions.

Figure 5: Atomic structure and spin density isosurfaces of the most stable reduced Bi$_2$O$_3$-TiO$_2$ heterostructures in this work. (a): Bi$_4$O$_6$-rutile (110), (b): Bi$_8$O$_{10}$-rutile (110) and (c): Bi$_4$O$_6$-anatase (101). Spin density isosurfaces enclose spin densities up to 0.02 electron / Å$^3$. Colour coding of the atoms is the same as Figure 1.

After reduction of the Bi$_2$O$_3$ nanoclusters, the local atomic structure shows some changes. On Bi$_4$O$_6$-rutile (110), the removal of the oxygen results in formation of a structure that shows symmetry, with two 2-fold coordinated oxygen atoms terminating the nanocluster. The Bi cations are 3-fold coordinated and each Bi atom binds to a bridging oxygen atom from the rutile (110) surface, with Bi-O distances in the range of 2.17 – 2.18 Å. Furthermore each Bi atom also coordinates to one oxygen from the nanocluster which itself binds to a surface Ti atom, with Bi-O distances of 2.07 – 2.15 Å and Ti-O distances of 2.03 Å.
On Bi$_6$O$_9$-rutile, the formation of the most stable oxygen vacancy results in small changes to the nanocluster structure. Two Bi cations are coordinated to the surface bridging oxygen sites, with Bi-O distances of 2.20 – 2.23 Å. Two nanocluster oxygen bind to surface 5-fold coordinated Ti with Ti-O distances of 1.89 and 2.02 Å, while after relaxation, four oxygen take a 2-fold coordination environment, by breaking bonds to Bi cations (giving long Bi-O distances of 2.51 and 2.56 Å).

On Bi$_4$O$_6$-anatase, two Bi cations are 3-fold coordinated and the remaining cations are 4-fold coordinated. Typical Bi-O distances range from 1.86 – 2.15 Å and the Bi-O distances to the surface are 2.12 – 2.16 Å. One oxygen atom from the surface migrates outwards to bind to a Bi cation in the nanocluster, with three oxygen in the nanocluster binding to surface Ti sites; these Bi-O distances are 1.86 – 1.90 Å.

The localisation of the two electrons released upon removal of the neutral oxygen atom is shown by the spin density isosurfaces in Figure 5. For both Bi$_2$O$_3$-nanocluster modified rutile (110) composites, the electrons preferentially localise on Ti sites in the rutile (110) surface, with computed Ti Bader charges of +1.65 / 1.71 electrons in Bi$_4$O$_6$-rutile and +1.65 / 1.69 electrons in Bi$_6$O$_9$-rutile, and spin magnetisations of 0.92-0.94 μB. The first electron localises on a subsurface Ti site and the second electron localises onto a surface 5-fold coordinated Ti$_3^+$ site that has no interaction with the supported nanocluster. These values are typical of reduced Ti$_3^+$ species in rutile (110).

In contrast, on Bi$_4$O$_6$-anatase (101), the two electrons localise on a surface 5-fold coordinated Ti$_3^+$ site and on a Bi site in the nanocluster, which results in formation of a reduced Bi$_2^+$ species. The computed Bader charges are +1.74 electrons on Ti and +2.99 electrons on Bi; the latter
compares to a computed Bi Bader charge of +2.1 electrons in stoichiometric Bi$_2$O$_3$ nanoclusters, indicating reduction of the Bi species. The computed spin magnetisations on Ti and Bi are 0.96 and 0.7 $\mu_B$. This Bi site binds to the oxygen that migrated out of the surface and this particular oxygen bridges the two reduced Ti$^{3+}$ and Bi$^{2+}$ sites.

We then examined the interaction of reduced Bi$_2$O$_3$-TiO$_2$ heterostructures with CO$_2$ in a number of adsorption configurations. **Figure 6** shows the most stable relaxed structures after relaxation of adsorbed CO$_2$ on each reduced Bi$_2$O$_3$-TiO$_2$ heterostructure. The computed interaction energies for CO$_2$ are: -0.45 eV on reduced Bi$_4$O$_6$-rutile (110), -0.53 eV on reduced Bi$_6$O$_9$-rutile (110) and -0.93 eV on reduced Bi$_4$O$_6$-anatase (101). These energies indicate a moderately strong interaction between the initially reduced metal oxide heterostructure and the CO$_2$ molecule.

**Figure 6**: Atomic structure of the most stable CO$_2$ adsorption structures on reduced Bi$_2$O$_3$-TiO$_2$ composites. (a): Bi$_4$O$_6$-rutile (110), (b): Bi$_6$O$_9$-rutile (110) and (c): Bi$_4$O$_6$-anatase (101). The colour coding is the same as Figure 3
CO$_2$ binds to reduced Bi$_4$O$_6$-rutile (110) with the formation of two Bi-O bonds, with Bi-O distances of 2.45 and 2.52 Å. The carbon of CO$_2$ binds to oxygen in the nanocluster, with a C-O distance of 1.38 Å. The C-O distances in adsorbed CO$_2$ are elongated to 1.27 Å and the O-C-O angle is 130°. Thus the CO$_2$ molecule is activated upon interaction with the reduced Bi$_4$O$_6$ nanocluster.

On Bi$_6$O$_9$-rutile (110) relaxation of initially adsorbed CO$_2$ leads to spontaneous breaking of a C-O bond in the molecule which results in the release of a free CO molecule, with no energy barrier to this process. At the same time the Bi$_6$O$_9$ nanocluster is re-oxidised. Examining the atomic structure, we see that the free CO has a C-O distance of 1.14 Å that is typical of gas phase CO and the Bi-O distances are similar to those in the stoichiometric Bi$_6$O$_9$-rutile system.

Finally, on Bi$_4$O$_6$-anatase (101) the C-O distances in adsorbed CO$_2$ are 1.25 and 1.27 Å, again showing a significant elongation over the free molecule. The bending of CO$_2$ upon interaction with the nanocluster is also apparent, with an O-C-O angle of 130°. CO$_2$ binds to the nanocluster through a Bi-O bond which has a distance of 2.42 Å and a Bi-C bond of 2.37 Å involving a second Bi atom in the nanocluster. Similar to the other systems, this adsorption configuration indicates that the CO$_2$ adsorbs in an activated binding mode.

The computed vibrational frequencies for activated CO$_2$ are shown in Table 3. The large red shift in the C=O stretching mode of 760 and 767 cm$^{-1}$ on Bi$_4$O$_6$-rutile and Bi$_4$O$_6$-anatase are again consistent with activated CO$_2$, as is the breaking of the degeneracy in the CO$_2$ bending mode upon adsorption. We note that on Bi$_4$O$_6$-anatase the splitting of the degeneracy in the CO$_2$ bending mode is larger and the origin of this is likely due to one oxygen of CO$_2$ not binding with
the Bi₂O₃ nanocluster. By contrast the two oxygen atoms in CO₂ bind with the nanocluster in Bi₄O₆-rutile so that the split in the degeneracy of the two modes is smaller.

<table>
<thead>
<tr>
<th>Reduced structure</th>
<th>Bi₂O₃-TiO₂</th>
<th>Heterostructure</th>
<th>CO₂ vibrational frequencies / cm⁻¹</th>
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Table 3: Computed CO₂ vibrational frequencies for activated CO₂ at reduced Bi₂O₃-TiO₂. Our computed vibrational frequencies of free CO₂ are 2354, 1325, and 632 cm⁻¹.

Examining the electronic structure, in the CO₂-Bi₄O₆-rutile system, the computed Bader charges on the previously reduced Ti atoms are now +1.3 electrons signifying the presence of oxidised Ti⁴⁺ species. Interestingly, we find that the charge on two Bi cations in the nanocluster changes to 2.8 and 3.2 electrons, indicating that these Bi cations are partially reduced. One of these Bi binds to oxygen of CO₂, suggesting a rearrangement of charge upon CO₂ adsorption.

In the Bi₆O₉-rutile system the computed Bader charges of Ti and Bi are +1.3 and +2.2 electrons, consistent with the presence of only oxidised Ti⁴⁺ and Bi₃⁺ species. The electrons on the TiO₂ surface after reduction are therefore transferred to CO₂ to allow the formation of new Bi-O bonds and a free CO molecule.
Finally, in the Bi$_4$O$_6$-anatase system, the Bader charges on the CO$_2$ molecule indicate a charge transfer of *ca.* 1.5 electrons to the molecule from the reduced composite. The computed Bader charges of 1.3 and 2.1 electrons on previously reduced Ti and Bi further support this electron transfer, which re-oxidises Ti and Bi. This process then results in the formation and stabilisation of a carboxyl, CO$_2^-$ species. This is one of the activated CO$_2$ species that is important in CO$_2$ conversion. In the gas phase the potential required for formation of CO$_2^-$ is prohibitively high, but in the reduced Bi$_2$O$_3$-modified anatase system, the presence of both low coordinated active sites and excess electrons after reduction appears to facilitate electron transfer to the adsorbed CO$_2$ molecule.

**Conclusions**

We have studied the interaction of CO$_2$ with novel heterostructure of Bi$_2$O$_3$ nanoclusters supported on rutile and anatase TiO$_2$ surfaces. Experimental work has shown that Bi-containing materials are able to activate and convert CO$_2$ to more useful molecules. We find that CO$_2$ adsorbs strongly at supported Bi$_2$O$_3$ nanoclusters, with adsorption energies ranging from -0.54 to 1.01 eV; van der Waals interactions simply shift these energies by *ca.* 0.15 eV but do not change the overall trends in CO$_2$ activation.

CO$_2$ adsorbs in an activated adsorption mode, with no charge transfer to the molecule, but instead some charge rearrangement. In this activated adsorption mode, the O-C-O angle in the molecule is reduced from 180° to *ca.* 130°, a characteristic feature of CO$_2$ activation. The C-O distances in the molecule elongate from 1.16 Å to 1.28 Å, which is also characteristic of CO$_2$ activation. Finally, the computed vibrational modes of adsorbed CO$_2$ show a significant red shift of
over 750 cm$^{-1}$ in the C=O stretching mode and a breaking of the degeneracy in the O-C-O bending mode. The magnitude of the red shift in the C=O stretching mode correlates with the strength of adsorption of CO$_2$.

The Bi$_2$O$_3$-TiO$_2$ heterostructures can be reduced, with moderate energy costs, resulting in reduction of Ti sites and in some cases Bi sites in the nanocluster are also reduced. The interaction of the reduced heterostructures with CO$_2$ can result in direct C formation, which is exothermic, or charge transfer to CO$_2$ (reoxidising Bi and Ti cations) to give an activated carboxylate species.

These results show that the unique properties of bismuth-containing oxides can be exploited to adsorb and activate carbon dioxide which is the key first step in the reductive conversion of CO$_2$ to useful molecules. The combination of a non-bulk like nanocluster containing Bi$^{3+}$ species which is also moderately reducible provides an interesting material that can activate CO$_2$, whether that be by strong adsorption and distortion, electron transfer to form a carboxylate or by direct breaking of a C-O bond and we propose that these heterostructures can be synthesized and tested for CO$_2$ activation.

**CONFLICTS OF INTEREST**

There are no conflicts of interest to declare
ACKNOWLEDGMENTS

Financial Support from Science Foundation Ireland through the Starting Investigator Research Grant Project EMOIN SFI/SIRG/09/12160 and the Science Foundation Ireland US-Ireland R&D Partnership Program Project SusChem SFI/US/14/E2915 is gratefully acknowledged. Access to the computational resources at the Science Foundation Ireland/Higher Education Authority funded Irish Center for High End Computing is acknowledged. We are grateful for support from the COST Action CM1104 “Reducible Metal Oxides, Structure and Function” We acknowledge important discussions with Profs. K. A. Gray, E. Weitz and J. A. Byrne.

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