INNOVATIVE NANOMATERIALS FOR EFFICIENT CO$_2$ PHOTOCATALYTIC CONVERSION TO FUELS

A Dissertation

by

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DOCTOR OF PHILOSOPHY

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ABSTRACT

Photocatalytic reduction of CO\textsubscript{2} with water by photocatalysts such as TiO\textsubscript{2} to produce solar fuels is an attractive approach to alleviate the environmental influences of greenhouse gasses and in the meantime produce valuable solar fuels. However, TiO\textsubscript{2} has several limitations for CO\textsubscript{2} photoreduction. First, TiO\textsubscript{2} has a large band gap, leading to the low solar energy usage efficiency. Second, the fast charge recombination rate in TiO\textsubscript{2} causes the low photocatalytic performance. Third, relatively insufficient CO\textsubscript{2} adsorption capability results in the low production rate of solar fuels. This work addressed the above limitations by designing innovative TiO\textsubscript{2} based photocatalysts for CO\textsubscript{2} photoreduction with H\textsubscript{2}O from four different aspects: (1) crystal structures, (2) CO\textsubscript{2} gas adsorption capability, (3) exposed facets and (4) defect property.

First, this study demonstrated the high performance of mixed anatase/brookite phase TiO\textsubscript{2} for CO\textsubscript{2} photoreduction with H\textsubscript{2}O. Single-phase anatase and brookite, and mixed-phase anatase/brookite TiO\textsubscript{2} nanomaterials were synthesized and evaluated for CO\textsubscript{2} photoreduction in the presence of water vapor for the production of solar fuels (CO and CH\textsubscript{4}). The results showed that bicrystalline anatase/brookite was more active than single-phase anatase, brookite, and P25. The bicrystalline mixture with a composition of 75\% anatase and 25\% brookite showed the highest photocatalytic activity, likely due to the enhanced interfacial charge transfer between anatase and brookite nanocrystals.

Second, this study showed improved CO\textsubscript{2} adsorption and conversion by combing CO\textsubscript{2} adsorbents LDHs materials with photocatalyst TiO\textsubscript{2}. A novel material of crystallized
titanium-embedded magnesium-aluminum layered double hydroxides (MgAlTi-LDHs) is developed and tested for CO₂ photoreduction with water. Three different materials synthesis methods were explored: (1) coprecipitation, (2) coprecipitation + hydrothermal, and (3) coprecipitation + calcination + reconstruction. The material hydrothermally treated at 150 to 200 °C demonstrated the highest CO production due to a well-balanced TiO₂ crystallinity and specific surface area.

Third, high-performance TiO₂ photocatalysts by combining the effect of oxygen deficiency and exposing facets were synthesized. And atomic layer deposition (ALD) technique was applied to deposit Al₂O₃ thin film on the surface of TiO₂ with thickness of Al₂O₃ controlled by the number of ALD cycles. All the synthesized photocatalysts (ANR, ReANR, and Al₂O₃ coated ReANR) were tested for CO₂ photocatalytic reduction with water. Compared with ANR, ReANR had more than 50% higher CO production and more than ten times higher CH₄ production due to the oxygen vacancies that possibly enhanced CO₂ adsorption and activation. By applying less than 5 cycles of ALD, the Al₂O₃ coated ReANR had enhanced overall production of CO and CH₄ than uncoated ReANR, with 2 cycles being the optimum. Whereas, both CO and CH₄ production decreased with increasing number of ALD cycles when more than 5 cycles were applied. Photoluminescence (PL) analysis showed both 2 and 200 cycles of Al₂O₃ ALD coating on the ReANR were able to reduce the charge carrier recombination rate, likely because of the passivation of surface states. On the other hand, a relatively thick layer (e.g. 200 cycles) of Al₂O₃ may act as an insulation layer to prohibit electron migration to the catalyst surface.
DEDICATION

To my dearest father, without whose support and understanding, I would not be able to complete my Ph.D. study. I am sorry that I could not be there for his last moment, but I believe he knows how much I love him and how much I wanted to be with him. I also believe he would be very happy if he were able to see my completed dissertation.

I also want to dedicate this dissertation to my strong mother, and my younger sister, who took care of my father meticulously without any complaint. No one can imagine how much pressure they suffered. I have to apologize that I did not contribute much during that dark period of our family.

Finally, I would like to dedicate this work to my dear husband, Xiaoru Guo, the love of my life, who is also a Ph.D. candidate, at University of Wisconsin-Milwaukee. Thanks for his support, and all the suggestions and help he has given for my research since 2013. The distance between Texas and Wisconsin is never far enough to impair our love.
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All work for the dissertation was completed independently by the student.

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<tr>
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<tr>
<td>ALD</td>
<td>Atomic Layer Deposition</td>
</tr>
<tr>
<td>ANP</td>
<td>Anatase Nanoparticles</td>
</tr>
<tr>
<td>ANR</td>
<td>Anatase Nanorods</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett and Teller Method</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett-Joyner-Halenda Method</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction Band</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>DRIFTS</td>
<td>Diffuse Reflectance Infrared Fourier Transform Spectroscopy</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersion X-ray Spectroscopy</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionized Detector</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-Resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>LDHs</td>
<td>Layered Double Hydroxides</td>
</tr>
<tr>
<td>LDOs</td>
<td>Layered Double Oxides</td>
</tr>
<tr>
<td>MMO</td>
<td>Mixed Metal Oxide</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
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<td>Re-ANR</td>
<td>Reduced Anatase nanorods</td>
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<tr>
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<tr>
<td>Re-ANP</td>
<td>Reduced Anatase Nanoparticles</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>TCD</td>
<td>Thermal Conductivity Detector</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<td>TGA</td>
<td>Thermogravimetric Analysis</td>
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<tr>
<td>TiO$_2$</td>
<td>A: Anatase B: Brookite R: Rutile</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>UVvis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>VB</td>
<td>Valence Band</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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<td>XRD</td>
<td>X-ray Diffraction</td>
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1. INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

Burning fossil fuel as the energy supply for human activities results in massive amounts of CO$_2$ emissions to the atmosphere, which is the primary cause of the global warming effects. Meanwhile, due to the relatively limited conventional energy source i.e. fossil fuel, in contrast with the enormous energy need by the human society, the development of renewables, e.g. solar energy application technique is essential. The conversion of solar energy into fuels using CO$_2$ as the feedstock by photocatalysts offers significant promise in the development of a sustainable energy technology.$^{1-5}$

CO$_2$ photoreduction with H$_2$O can be understood in two steps. First, CO$_2$ and H$_2$O molecules are adsorbed onto catalyst surface, and this process requires high surface area and low physical and chemical energy barriers. Secondly, the photocatalytic process induces excitons from photons and initiates the photoreduction process. The second step in detail can be described in the following sub-steps (shown in Figure 1): (1) photo-illumination on the surface of photocatalyst induces the generation of charge carriers, i.e. electron-hole (e$^-$–h$^+$) pairs; (2) the excited electrons in the conduction band (CB) of photocatalyst could migrate to the surface and reduce CO$_2$ to solar fuels (e.g., CO, CH$_4$, CH$_3$OH, HCOOH), and (3) the holes left in the valence band (VB) of the photocatalyst could oxidize H$_2$O into oxygen.$^6$ Possible reactions involved in CO$_2$ photoreduction with

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$^1$ Part of this chapter is reprinted with permission from “A review on the effects of TiO$_2$ surface point defects on CO$_2$ photoreduction with H$_2$O” by Huilei Zhao, Fuping Pan and Ying Li, 2016. Journal of Materiomics, 3, 17-32, Copyright [2016] by Elsevier B.V.
H$_2$O on TiO$_2$ and thermodynamic reduction/oxidation potentials of various compounds are listed in Table 1.

Figure 1 Schematic illustration of the photocatalytic process in the CO$_2$ photoreduction with H$_2$O

In the process of CO$_2$ photoreduction with H$_2$O, photocatalysts played a significant role to initiate the reaction and convert photo energy to chemical energy. The appropriate photocatalysts for the artificial photosynthesis need to be cost-effective, earth-abundant, non-toxic, and resistant to photo-corrosion. Besides, the electronic properties of the photocatalyst need to meet the following requirement: (1) the conduction band of the photocatalyst should be more negative than the reduction potential of CO$_2$; and (2) the valence band should be more positive than the oxidation potential of H$_2$O. Due to the thermodynamically stable nature of the CO$_2$ molecule and energetically unfavorable nature of photoreduction processes, advanced photocatalysts design are required to facilitate the CO$_2$ photoreduction and boost the solar energy conversion efficiency.
Table 1 Possible reactions involved in photocatalytic reduction of CO\(_2\) with H\(_2\)O on TiO\(_2\) and thermodynamic reduction/oxidation potentials of various compounds

<table>
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<th>Reaction Equation</th>
<th>Redox pairs</th>
<th>Redox potential(^{9,11-13}) (V vs. NHE @ pH=7)</th>
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<tr>
<td>(2H_2O + 4h^+ \rightarrow 4H^+ + O_2)</td>
<td>(H_2O/O_2)</td>
<td>+0.82</td>
</tr>
<tr>
<td>(CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + H_2O)</td>
<td>(CO_2/CH_4)</td>
<td>-0.24</td>
</tr>
<tr>
<td>(CO_2 + 6e^- + 6H^+ \rightarrow CH_3OH + H_2O)</td>
<td>(CO_2/CH_3OH)</td>
<td>-0.38</td>
</tr>
<tr>
<td>(2H^+ + 4e^- \rightarrow H_2)</td>
<td>(H^+/H_2)</td>
<td>-0.41</td>
</tr>
<tr>
<td>(CO_2 + 4e^- + 4H^+ \rightarrow HCHO + H_2O)</td>
<td>(CO_2/HCHO)</td>
<td>-0.48</td>
</tr>
<tr>
<td>(CO_2 + 2e^- + 2H^+ \rightarrow CO + H_2O)</td>
<td>(CO_2/O)</td>
<td>-0.53</td>
</tr>
<tr>
<td>(CO_2 + 2e^- + 2H^+ \rightarrow HCOOH)</td>
<td>(O_2/HCOOH)</td>
<td>-0.61</td>
</tr>
<tr>
<td>(CO_2 + e^- \rightarrow CO_2^-)</td>
<td>(CO_2/CO_2^-)</td>
<td>-1.9</td>
</tr>
</tbody>
</table>

Compared to other photocatalysts, TiO\(_2\) has the advantages of low cost, low toxicity, high chemical and thermal stability, and abundant availability.\(^7,8\) However, realizing TiO\(_2\) assisted CO\(_2\) photoreduction with commercialized devices faces a great difficulty, owing to the complex chemical reaction pathways and unrevealed underlying mechanism.\(^9\) Besides, TiO\(_2\) itself suffers several limitations for CO\(_2\) photoreduction. First, TiO\(_2\) has a large band gap, leading to the low solar energy usage efficiency. Second, the fast charge recombination rate in TiO\(_2\) causes the poor photocatalytic performance\(^{10}\). Third, relatively insufficient CO\(_2\) adsorption capability results in the low production rate of solar fuels.
1.2 Summary and Literature Review

Literature research has been focused on designing the innovative nanostructure, and composite materials to address the limitation of TiO$_2$ from the following aspects: (1) crystal structure, (2) exposed facets (3) defect property and (4) absorbent modification.

Anatase, brookite, and rutile are naturally existing TiO$_2$ polymorphs.$^{14-17}$ Anatase based catalysts have been demonstrated to be highly active, while rutile is less active,$^{18,19}$ mainly due to the fast e$^-$ and h$^+$ recombination in rutile.$^{20}$ Brookite is rarely studied in photocatalysis likely due to the past difficulties in synthesizing high purity brookite because of its metastable property.$^{21-24}$ A few studies demonstrated the high activity of brookite in photocatalytic oxidation applications.$^{25,26}$ Our previous study$^3$ was the first one to investigate the activity of pure brookite TiO$_2$ for CO$_2$ photoreduction with water; brookite showed higher activity than rutile, and surface-defective brookite was even more active than anatase.

Analogous to anatase/rutile mixed-phase TiO$_2$, anatase/brookite heterojunctions are expected to enhance charge separation as well, probably even superior to anatase/rutile. Possible reasons are: (1) our previous study$^3$ has discovered that brookite itself is more active than rutile in CO$_2$ photoreduction; (2) the CB edge of brookite is slightly above that of anatase,$^{27}$ making it possible for electrons to transfer from brookite to anatase even in the absence of anatase trapping sites. Some experimental evidence exists in the literature indicating that anatase/brookite mixtures are more active than anatase/rutile mixtures (e.g. P25)$^{28}$ and pure anatase$^{17,29}$ for photo-oxidation of organic compounds. While bicrystalline anatase/brookite TiO$_2$ has demonstrated certain
promising photocatalytic oxidation abilities, the relationship between phase composition
and catalytic activity is not clear. In the case of anatase and rutile mixtures, there is an
optimum phase content (i.e., anatase/rutile = 77/23) that corresponds to the highest
photoactivity.\textsuperscript{30,31} The optimum phase composition in an anatase/brookite has never been
explored; moreover, no studies have been reported on its application in CO\textsubscript{2}
photoreduction and the correlation of material properties with photocatalytic activities.

Except for crystal phases, the photocatalytic property of TiO\textsubscript{2} is also related to
exposed facets. Among the three low-index facets of anatase {100}, {001} and {101},
{100} facets was demonstrated to have a higher photocatalytic ability.\textsuperscript{32,33} Both {100} and
{001} facets have higher surface energy than {101},\textsuperscript{34-36} and have 100\% fivefold
coordinated Ti (Ti\textsubscript{5C}). By contrast {101} facets have only 50\% Ti\textsubscript{5C} sites. Ti\textsubscript{5C} sites are
more active than Ti\textsubscript{6C} sites due to unsaturated coordination of Ti\textsubscript{5C}, and Ti\textsubscript{5C} can act as the
active sites for CO\textsubscript{2} activation and conversion.\textsuperscript{34,37} Meanwhile, both theoretical
calculations and experimental results suggested that the {100} is more active than
{001}.\textsuperscript{38-40} Pan \textit{et al.} tested the photocatalytic H\textsubscript{2} evolution on TiO\textsubscript{2} with different
dominant facets, and TiO\textsubscript{2}-{100} showed the highest H\textsubscript{2} evolution.\textsuperscript{34} In addition, the order
of CO\textsubscript{2} photoreduction to methane on different anatase facets was reported as {100} >
{101} > {001}.\textsuperscript{33} This is because the conduction band (CB) values for {100}, {101}, and
{001} are -0.52eV, -0.49eV, -0.45eV, respectively, resulting in the driving force for CH\textsubscript{4}
production (E\textsuperscript{0} (CO\textsubscript{2}/CH\textsubscript{4}) = -0.24 eV vs. NHE, pH = 7.0)) in the order of {100} > {101} >
{001}. In this work, {100} is used to refer both {100} and {010} facets, since these two
surfaces in anatase are isostructural.\textsuperscript{41}
Also, oxygen deficient TiO$_2$ has shown better performance for CO$_2$ photoreduction compared to pristine TiO$_2$ because surface V$_O$ can serve as the active sites for CO$_2$ adsorption$^{42,43}$, activation$^{44,45}$, and conversion$^{44,46}$. Also, the light absorption of TiO$_2$ can be improved due to the rising local states under the CB band minimum caused by the V$_O$.\(^47\)

The promising results of combining the advantages of active facets and defect effects in our previous work$^{37}$ have inspired the design of novel TiO$_2$ material with high percentage {100} facets exposed and high density of surface oxygen vacancies. However, as the concentration of the surface defects increases, the local surface states increase$^{48}$, which results in the formation of recombination centers near/on the defect sites. To suppress the recombination, a very thin layer (in ångström level) of metal oxide such as ZrO$_2$$^{49}$, Al$_2$O$_3$$^{50}$ on the surface of semiconductors was applied by atomic layer deposition (ALD). Amorphous Al$_2$O$_3$ was popularly used as the surface passivation coating material on Si for solar cell application by two passivation mechanisms: chemical passivation by reducing the interface state density and field effect passivation caused by the fixed charges in the thin film.$^{51,52}$ ALD can precisely control the thickness of the Al$_2$O$_3$ layer because of the self-limiting reaction of the dosed precursor gasses.$^{53,54}$

To address the poor CO$_2$ adsorption capability of TiO$_2$, Surface modification of TiO$_2$ with stronger CO$_2$ adsorbent could improve CO$_2$ adsorption and reduction on TiO$_2$. Xie et al.$^{55}$ added a variety of metal oxides to Pt-loaded TiO$_2$ for CO$_2$ photoreduction and discovered a linear correlation between the amount of chemisorbed CO$_2$ on metal oxides and the CH$_4$ yield. Our recent study demonstrated that CO$_2$ photoreduction was significantly improved by using a hybrid adsorbent–photocatalyst (i.e., MgO/TiO$_2$).
microspheres) due to great CO$_2$ adsorption ability of MgO.$^{56,57}$ Layered double hydroxides (LDHs), known as a class of anionic clays or hydrotalcite (HT)-like materials, and their derivatives, e.g. layered double oxides (LDOs) obtained upon calcination of LDHs have both been applied as CO$_2$ adsorbents. $^{58-61}$ LDOs can be reconstructed to LDHs upon rehydration.$^{62}$ Our recent work reported an integrated CO$_2$ capture and photocatalytic reduction process by a hybrid TiO$_2$/MgAl-LDO material where captured CO$_2$ on MgAl-LDO can be converted to CO by TiO$_2$ under UV light irradiation.$^{63}$ Hong et al.$^{64}$ assembled MgAl-LDHs nanosheets with carbon nitride (C$_3$N$_4$) photocatalyst, which was demonstrated to yield more CH$_4$ from photoreduction of CO$_2$ than C$_3$N$_4$ alone in aqueous solution with Pd as the cocatalyst. The main reason was identified to be the enrichment of CO$_2$ adsorption on the catalyst surface by MgAl-LDHs. Other LDHs like ZnAl-LDHs, ZnCr-LDHs and NiAl-LDHs did not make significant improvement of CH$_4$ production since they have very limited CO$_2$ adsorption capacity.$^{64}$
2. BICRYSTALLINE TiO$_2$ WITH CONTROLLABLE ANATASE-BROOKITE PHASE CONTENT FOR ENHANCED CO$_2$ PHOTOREDUCTION$^2$

2.1 Introduction

Mixed-phase TiO$_2$ nanomaterials other than commercial P25 TiO$_2$ nanoparticles are scarcely studied in CO$_2$ photoreduction, and the interactions of the different phases during the CO$_2$ photoreduction reactions have not been explored. It is believed that the junctions between different phases of TiO$_2$ play a significant role in improving its photo-oxidation activity.$^{16,17}$ Several studies have explored the mechanism for the enhanced activity of anatase and rutile mixtures such as P25; however, the findings are not conclusive. Some studies suggested that photoinduced electrons tend to transfer from the higher-level anatase conduction band (CB) to the lower-level rutile CB,$^{65}$ while the holes in the anatase valance band (VB) could migrate to the rutile VB.$^{66}$ On the contrary, other studies suggested that electrons transfer from rutile to anatase.$^{20,67-69}$ Among them, Hurum et al.$^{20,69}$ used electron paramagnetic resonance (EPR) spectroscopy to monitor the direction of electron migration; they suggested that electrons transfer from rutile to anatase because the energy levels of the electron trapping sites in anatase are lower than that of the rutile CB. Also, the interfacial sites between anatase and rutile facilitate the electron transport and prevent the recombination of e$^-$ and h$^+$.$^{20,69}$ However, some recent studies

$^2$ Part of this chapter is reprinted with permission from “Bicrystalline TiO$_2$ with controllable anatase–brookite phase content for enhanced CO$_2$ photoreduction to fuels” by Huilei Zhao, Lianjun Liu, Jean M Andino, and Ying Li, 2013. Journal of Materials Chemistry A, 1, 8209-8216, Copyright [2013] by the authors.
reported that there are no interactions between the two phases in P25, and anatase and rutile independently catalyze reactions.\textsuperscript{70}

According to the literature review in Chapter 1, heterojunction between two crystal phases in the anatase and brookite bicrystalline system can enhance photocatalytic activity for CO\textsubscript{2} photoreduction. In this topic, we have synthesized pure phase anatase, brookite, and mixed-phase anatase/brookite catalysts with a controllable brookite fraction. We have investigated the effect of TiO\textsubscript{2} phase fractions and nanostructures on CO\textsubscript{2} photoreduction, including the optimum phase composition for CO\textsubscript{2} photoreduction. The in situ spectroscopic studies was also conducted to investigate the CO\textsubscript{2} reduction mechanism.

2.2 Materials and Methods

2.2.1 Catalyst Preparation

TiO\textsubscript{2} nanocrystals of single-phase anatase and brookite and mixed-phase anatase/brookite were prepared using a hydrothermal method.\textsuperscript{71} In a typical preparation process, 10 ml titanium bis (ammoniumlactate) dihydroxide (50\% in H\textsubscript{2}O, Sigma-Aldrich), was mixed with 90 ml urea solution (with varying concentration of urea) and sealed in a 250 ml Teflon-lined autoclave, which was then sealed and placed in an electric oven at 160 °C for 24 h. After the hydrothermal process, the autoclave was naturally cooled down to room temperature. The precipitates were centrifuged, washed with de-ionized water, dried at 60°C for 12 h, ground and finally calcined at 400 °C for 3 h. To prepare pure phase anatase, the urea concentration in the precursor solution was 0.1 M. A urea concentration above 0.1 M led to the formation of an anatase/brookite mixture, and
the brookite content increased with the urea concentration. At 7.0 M, pure brookite was formed. Table 2 summarizes the relation between the urea concentration and the phase composition. The prepared TiO$_2$ mixtures were denoted as A$_x$B$_y$, where x and y are the phase fraction of anatase and brookite, respectively.

2.2.2 Catalyst Characterization

The crystal structures of the prepared TiO$_2$ samples were identified by X-ray diffraction (Scintag XDS 2000) using Cu Kα irradiation at 45 kV and a diffracted beam monochromator operated at 40 mA in the 2θ range from 20° to 50° at a scan rate of 2°/min. The crystallite sizes of catalysts were calculated by the Scherrer Equation. Quantitative phase composition analysis of as prepared TiO$_2$ was performed using Rietveld refinement method by the MAUD software (version 2.33). The XRD data of as prepared TiO$_2$ samples together with the known standard data of anatase (tetragonal) and brookite (orthorhombic) were loaded into the MAUD software. The isotropic model and anisotropic model were chosen for anatase and brookite, respectively. Peak positions and scale factors were adjusted before quantitative analysis.

Raman spectroscopy was carried out with a Renishaw 1000B system in the range of 100-700 cm$^{-1}$. The specific surface areas of all synthesized catalysts were obtained by nitrogen adsorption/desorption at 77 K using the Brunauer-Emmett-Teller (BET) method (Micrometrics, ASAP 2020). UV–vis spectra of the catalysts were obtained by a diffuse reflectance UV–vis spectrophotometer (Ocean Optics) using BaSO$_4$ as the background. The morphologies of TiO$_2$ polymorphs were characterized by Scanning electron microscopy (SEM, Hitachi S4800), using a secondary electron detector (SE) at an
accelerating voltage range of 5~10 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were carried out with 300 keV electrons in a Hitachi H9000NAR instrument with 0.18 nm point and 0.11 nm lattice resolutions, to obtain crystal structure, morphology, and lattice information of TiO$_2$ nanocrystals.

2.2.3 Photocatalytic Activity Measurement

The photocatalytic reduction of CO$_2$ over the TiO$_2$ samples was conducted in a photoreactor operating in a continuous-flow mode. The experimental setup was similar to that described in our previous work.$^4$ A solar simulator (Oriel, 150 W) was used as the light source. The light intensity was 69.6 mW/cm$^2$ for 200 < $\lambda$ < 1000 nm and 12.5 mW/cm$^2$ for 200 < $\lambda$ < 400 nm (UV region), as measured by a spectroradiometer (International Light Technologies ILT950). The photoreactor was cylindrical shape with a stainless steel housing and a quartz window (dia. = 7.5 cm). For each test, 100 mg TiO$_2$ powder catalyst was evenly dispersed onto a glass-fiber filter that was placed at the bottom of the photoreactor facing the light source.

Ultrapure CO$_2$ (99.999%, Praxair) regulated by a mass-flow controller (MFC) continuously passed through a bubbler that contained de-ionized water. The resulting gas mixture (CO$_2$ and 2.3 vol% H$_2$O vapor) was introduced to the photoreactor. A gas chromatograph (GC, Agilent 7890A) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) was used to continuously analyze the gaseous products. A Carboxen-1010 PLOT capillary column coupled with the TCD was used for
CO measurement, and a HP-PLOT-Q capillary column coupled with the FID was used for CH₄ measurement.

2.2.4 In-situ DRIFTS Analysis

To evaluate the interaction of CO₂-H₂O with the photocatalyst (A75B25) during the reaction process, in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was applied in a simulated reaction condition. The in situ experiments were conducted under such a sequential procedure: (1) the A75B25 catalyst was purged with He at 200 °C to remove the residual water and hydroxyl groups on the surface, (2) a CO₂/H₂O mixture was continuously introduced to the DRIFTS cell for 30 min when the intensities of adsorption peaks of CO₂ and H₂O reached saturation levels, and (3) the light from the solar lamp was introduced to the DRIFTS cell by a liquid guide. The IR spectra were recorded as a function of time to monitor the surface adsorbed species during H₂O and CO₂ adsorption in the dark (step 2) and the surface intermediates during the photocatalytic reaction process (step 3).

2.3. Results and Discussion

2.3.1 Crystal Structure and Morphology of TiO₂ Polymorphs

The urea concentration in the precursor solution was directly related to the phase content of the prepared TiO₂ nanocrystals (Table 2). The crystal structure of TiO₂ with different ratios of anatase/brookite was confirmed by XRD, as shown in Figure 2a. The anatase/brookite ratios were calculated by the Rietveld refinement method. Figure 2b shows the Rietveld refinement result of A50B50 as an example. At the lowest concentration
of urea (0.1 M), pure phase anatase (JCPDS No. 21-1272), i.e., A\textsubscript{100}, was obtained. With an increasing concentration of urea up to 1.5 M, bicrystalline anatase/brookite mixtures with an increasing brookite fraction, i.e., A\textsubscript{96}B\textsubscript{4}, A\textsubscript{75}B\textsubscript{25}, A\textsubscript{50}B\textsubscript{50}, and A\textsubscript{37}B\textsubscript{63} were formed. At the highest urea concentration (7.0 M), pure brookite (JCPDS No. 29-1360) was obtained. The existence of brookite in the resultant powders is readily discernible from its unique (121), (221), and (032) diffraction peaks at 30.81, 42.34, 46.07° (2θ), respectively (Figure 2a). Clearly, through adjusting the concentration of urea, anatase, brookite or mixtures with controllable anatase/brookite phase fractions were successfully prepared.

**Table 2** The characteristics of prepared TiO\textsubscript{2} catalysts including crystal phase content, BET specific surface area, pore size and pore volume, band gap, and the corresponding urea concentration in the precursor solution during material synthesis.

<table>
<thead>
<tr>
<th>Catalyst Conc.</th>
<th>Urea Conc. (M)</th>
<th>Anatase Phase (%)</th>
<th>Brookite Phase (%)</th>
<th>BET Specific Surface Area (m\textsuperscript{2}/g)</th>
<th>Pore Size (nm)</th>
<th>Pore Volume (cm\textsuperscript{3}/g)</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A\textsubscript{100}</td>
<td>0.1</td>
<td>100</td>
<td>0</td>
<td>145.6</td>
<td>6.2</td>
<td>0.23</td>
<td>3.08</td>
</tr>
<tr>
<td>A\textsubscript{96}B\textsubscript{4}</td>
<td>0.25</td>
<td>96</td>
<td>4</td>
<td>134.5</td>
<td>5.9</td>
<td>0.20</td>
<td>3.12</td>
</tr>
<tr>
<td>A\textsubscript{75}B\textsubscript{25}</td>
<td>0.5</td>
<td>75</td>
<td>25</td>
<td>140.3</td>
<td>5.5</td>
<td>0.20</td>
<td>3.15</td>
</tr>
<tr>
<td>A\textsubscript{50}B\textsubscript{50}</td>
<td>1.0</td>
<td>50</td>
<td>50</td>
<td>84.5</td>
<td>7.0</td>
<td>0.18</td>
<td>3.15</td>
</tr>
<tr>
<td>A\textsubscript{37}B\textsubscript{63}</td>
<td>1.5</td>
<td>37</td>
<td>63</td>
<td>70.2</td>
<td>10.7</td>
<td>0.19</td>
<td>3.20</td>
</tr>
<tr>
<td>B\textsubscript{100}</td>
<td>7.0</td>
<td>0</td>
<td>100</td>
<td>76.6</td>
<td>18.4</td>
<td>0.35</td>
<td>3.22</td>
</tr>
</tbody>
</table>
Figure 2 XRD patterns of the prepared TiO$_2$ catalyst powders with different fractions of anatase and brookite phases (a); Rietveld refinement result for the A$_{50}$B$_{50}$ sample (b).

The morphologies of the prepared TiO$_2$ nanocrystals were examined by SEM, as shown in Figure 3. Pure anatase, A$_{100}$, consisted of agglomerate sphere-shaped nanoparticles, while pure brookite, B$_{100}$, was rod-shaped nanoparticles. For anatase/brookite mixtures, the brookite nanorods appeared to have a lower aspect ratio (brick-shaped) than those observed in pure brookite (rod-shaped). With an increasing brookite fraction in the anatase/brookite mixtures, the number of nanobricks/nanorods increased and the size became larger. Eventually, the brookite crystals evolved from nanobricks to nanorods as the brookite content approached 100%.
Figure 3 SEM images of A\textsubscript{100} (a), A\textsubscript{96}B\textsubscript{4} (b), A\textsubscript{75}B\textsubscript{25} (c), A\textsubscript{50}B\textsubscript{50} (d), A\textsubscript{37}B\textsubscript{63} (e) and B\textsubscript{100} (f). The circled areas in black indicate brookite nanobricks.

The particle size, morphology, and lattice structure of A\textsubscript{75}B\textsubscript{25} were further evaluated by TEM and HRTEM, as shown in Figure 4. A mixture of spherical and rod-shaped nanoparticles were observed (Figure 4a). The spherical particles are in the range of 5~10 nm and the nanorod has a width of 20 nm and length of 60 nm. HRTEM images in Figure 4 b-c clearly demonstrated that the spherical nanoparticle was anatase (lattice
spacing = 0.35 nm, corresponding to the (101) plane) and the nanorod was brookite (lattice spacing = 0.91, 0.35 nm, corresponding to (100) and (210) plane, respectively).³

Figure 4 TEM images of A₇₅B₂₅ (a), and HRTEM images of A₇₅B₂₅ (b, c).

Figure 4b-c also demonstrated the overlapping anatase and brookite particles and the interface between them. In Figure 4b the lattice fringe becomes fuzzy and even discontinued (Region 1) where the anatase and brookite crystals overlap. An anatase particle was also located at the edge of brookite (Region 2). Besides those simple attachments of anatase particles to brookite particles, a coherent interface between anatase and brookite could be formed. As shown in Figure 4c, the lattice spacing of the anatase (101) plane matches that of the brookite (210) plane (0.35 nm) in the region where the two particles overlap (Region 3). This observation agrees with theoretical simulation results that the brookite (210) surface and the most stable anatase (101) plane have the same type of building block, and both phases may share a common boundary.⁷⁴ On anatase (101) all the octahedron units are closely packed, while on brookite (210) the rotated units are closely packed only along the [001] direction.⁷⁴ This difference may cause a distortion at the interface between the two crystal phases. The HRTEM images in Figure 4
demonstrated that when anatase and brookite nanocrystals grow in the same orientation, a unique interface between them could be possibly formed.

**Figure 5** Raman spectra of A100, B100, and A75B25 samples.

Raman spectra (Figure 5) have further proved the existence of both anatase and brookite crystals in the A/B mixture (A75B25). Brookite has the most intense Raman bands at ~245, ~320, ~399, ~410, and ~637 cm\(^{-1}\), while anatase has intense Raman bands at ~399, ~519, and ~639 cm\(^{-1}\). As compared with the spectra of A100 and B100, the Raman spectrum of A75B25 included all the bands of the two crystal phases, thus indicating a mixed phase of anatase and brookite.

2.3.2. Textural and Optical Properties of TiO\(_2\) Polymorphs

**Figure 6** shows that the N\(_2\) adsorption/desorption isotherms for all the six TiO\(_2\) samples are Type IV, characteristics of materials with mesoporous structures. The isotherms of B100 and A37B63 have a similar shape and close at a higher relative pressure compared to those of A100, A96B4, A75B25, and A50B50. Correspondingly, the calculated
pore sizes of anatase-rich TiO$_2$ are smaller than those of brookite-rich TiO$_2$ (Table 2).

This is because the inter-particle spaces between the agglomerated anatase TiO$_2$ nanoparticles were smaller than those between the nanobricks/nanorods in brookite-rich TiO$_2$. Table 2 also compared the BET specific surface areas of the various TiO$_2$ catalysts. The surface areas of anatase and anatase-rich samples (A$_{100}$, A$_{96}$B$_4$, and A$_{75}$B$_{25}$) were close
(around 140 m²/g) and were twice as much as those of brookite-rich and pure brookite TiO₂ (A₃₇B₆₃ and B₁₀₀). The sharp decrease in surface area from A₇₅B₂₅ to A₅₀B₅₀ can be explained from their SEM images in Figure 3: for A₇₅B₂₅, brookite nanobricks are embedded in agglomerated anatase nanoparticles; whereas, for A₅₀B₅₀, a smaller amount of anatase nanoparticles are dispersed on the surfaces of brookite nanobricks. The surface area of the larger brookite crystals is smaller than that of the smaller anatase crystals.

**Figure 7** The UV-Vis diffuse reflectance spectra (displayed in absorbance) of the prepared TiO₂ catalysts.

**Figure 7** compares the UV-vis spectra, displayed in absorbance units, of the prepared TiO₂ catalysts. The absorption edge of A₁₀₀ is around 402 nm, corresponding to a band gap at 3.08 eV, close to the value reported in the literature.³⁻⁷⁶ An increase in the brookite fraction in the anatase/brookite mixture results in a blue shift in the absorption
spectra and an increase in the band gap (listed in Table 2). \( B_{100} \) has the largest band gap at 3.22 eV. The observed larger band gap of brookite than anatase agrees with that reported in the literature,\(^{25}\) as the conduction band of brookite is positioned at 0.14 eV more negative than that of anatase.\(^{77}\) The band gaps stayed the same before or after 4 hours photo illumination.

2.3.3 Photocatalytic Activity for CO\(_2\) Reduction

The photocatalytic activities of the prepared TiO\(_2\) catalysts were tested for CO\(_2\) photoreduction with H\(_2\)O vapor. Background experiments were first conducted under the following conditions: (1) blank glass-fiber filter in the reactor without loading catalysts under the irradiation of solar simulator in a CO\(_2\)+H\(_2\)O flow; (2) catalysts loaded on a glass-fiber filter in the dark in a CO\(_2\)+H\(_2\)O flow; and (3) catalysts loaded on a glass-fiber filter under simulated solar radiation in a He+H\(_2\)O flow. In all cases, no carbon-containing products were detected. These background tests indicated that any carbon-containing products formed (described in the subsequent part of this paper) were generated solely from the reaction of CO\(_2\)+H\(_2\)O over the photocatalysts under light irradiation, not from any surface impurities on the catalysts.

As consistent with our previous studies,\(^2,3\) CO was the major product and CH\(_4\) was the minor product formed during CO\(_2\) photoreduction with H\(_2\)O vapor, and no other products (such as H\(_2\)) were detected. The absence of H\(_2\) production was consistent with the literature that H\(_2\) production is prominent only in the presence of noble metal co-catalysts (e.g., Pt, Ag)\(^4,78\) or in the presence of sacrificial agents (e.g., CH\(_3\)OH).\(^4,79\) CH\(_4\) production was much lower than CO production, likely because the formation of CH\(_4\)
requires the complete reduction of \( \text{CO}_2 \) to \( \text{C} \), and a subsequent reaction with available \( \text{H} \) atoms from the decomposition of water vapor on the same catalyst surface. If the \( \text{CO} \) desorbs from the surface before it can be fully reduced, then the formation of \( \text{CH}_4 \) is impacted.

**Figure 8** compares the apparent production rates of \( \text{CO} \) on various TiO\(_2\) catalysts. The test for each sample was repeated twice (a fresh catalyst was used each time), and the errors were within reasonable experimental uncertainties. The \( \text{CH}_4 \) production rates are not plotted in Figure 8 because they were too low (in the range of 0.001~0.005 \( \mu \text{mol h}^{-1} \)) and did not vary significantly for different catalysts. \( \text{B}_{100} \) had the lowest activity among all the catalysts, with a \( \text{CO} \) production rate at 0.073 \( \mu \text{mol h}^{-1} \). \( \text{A}_{100} \) had a \( \text{CO} \) production rate at 0.123 \( \mu \text{mol h}^{-1} \), higher than that of \( \text{B}_{100} \).

![Figure 8](image)

**Figure 8** The production rates of \( \text{CO} \) using various TiO\(_2\) catalysts (the reactants were a gas mixture of 97.7 vol\% \( \text{CO}_2 \) and 2.3 vol\% \( \text{H}_2\text{O} \)).
The bicrystalline samples with dominating anatase phase (A\textsubscript{96}B\textsubscript{4} and A\textsubscript{75}B\textsubscript{25}) or equal anatase-brookite content (A\textsubscript{50}B\textsubscript{50}) were the most active ones, having a CO production rate from 0.157 to 0.209 \( \mu \)mol h\(^{-1}\). The activity of A\textsubscript{75}B\textsubscript{25} was nearly twice as high as that of A\textsubscript{100} and three times as high as that of B\textsubscript{100}. Further increasing the brookite content (i.e., brookite-rich A\textsubscript{37}B\textsubscript{63}) led to a lower CO production rate at 0.115 \( \mu \)mol h\(^{-1}\). Commercial TiO\textsubscript{2} P25 was also tested as comparison; it had a CO production rate of 0.130 \( \mu \)mol h\(^{-1}\), lower than the anatase-rich bicrystalline anatase/brookite samples. The above results demonstrate that the anatase-rich bicrystalline anatase/brookite mixtures are superior to single crystalline anatase or brookite and anatase/rutile mixtures (i.e., P25).

Considering that pure anatase A\textsubscript{100} had the largest specific surface area and the smallest band gap (Table 2), the higher activity of bicrystalline anatase/brookite is very likely ascribed to the interactions between the anatase and brookite nanocrystals. This interaction between anatase and brookite seems to be more effective than that between anatase and rutile (as in P25). In addition, it is reasonable to find that anatase-rich A/B mixtures are more active than brookite-rich A/B mixtures since pure anatase is more active than pure brookite.

The experimental results in Figure 8 indicate that anatase rich A/B mixture with 75\% anatase and 25\% brookite, i.e., A\textsubscript{75}B\textsubscript{25} is the most active among all the prepared catalysts. There are three possible reasons for its superior activity: (1) the more negative CB band of brookite may induce electron transfer from brookite to anatase, thus enhancing charge separation; (2) the facilitated formation of the intrinsic defect sites in brookite may enhance electron trapping,\textsuperscript{3,80} and (3) the distorted interfaces between anatase and brookite.
crystals (as evidenced in the HRTEM images) may facilitate interfacial electron transport and prevent the recombination of electron-hole pairs.81

Additional experiments were conducted to explore the potential O₂ production from H₂O oxidation using the sample of anatase-rich A₇₅B₂₅. Prior to the photocatalytic reaction, the photoreactor was purged with a CO₂/H₂O gas mixture to eliminate the air inside the reactor. However, even after purging for a few hours, there was still background O₂ (in a few hundred ppm range) together with N₂ detected in the reactor effluent gas. Hence, a better indicator of O₂ production by the catalyst is the volumetric ratio of O₂/N₂ in the effluent gas, as also suggested in the literature and in our previous work.²,82

Figure 9 Time dependence of the volumetric ratio of O₂/N₂ before, during and after the photoreduction of CO₂ with H₂O on the A₇₅B₂₅

Figure 9 shows the O₂/N₂ ratio before, during and after the photoreaction, when the reactor effluent gas was sampled every 15 min. Before turning on the light (in the dark), the O₂/N₂ ratio was steady. Immediately upon photo-illumination, the O₂/N₂ ratio
dramatically decreased in the first 60 min and then gradually increased. The sharp decrease is probably due to the consumption of residual O$_2$ in the reactor through the reaction with photogenerated electrons O$_2$ + e$^-$ → O$_2^-$ and consecutive reactions.$^2$ The gradual increase in the O$_2$/N$_2$ ratio after 60 min photo irradiation indicated the generation of O$_2$ through oxidation of H$_2$O with photogenerated holes, H$_2$O + 2h$^+$ → 2H$^+$ + (1/2) O$_2$. Because the increasing amount of generated O$_2$ overweighed the previous concurrent O$_2$ consumption process, the net result was that the O$_2$/N$_2$ ratio gradually increased with time and finally reached in a steady state after 200 min. After turning off the light (the second dark period), the O$_2$/N$_2$ ratio dropped. This result again verified the generation of O$_2$ during the photocatalytic CO$_2$ reduction with H$_2$O vapor process.

2.3.4 In-situ DRIFTS Investigation on Surface Chemistry and Reaction Intermediates

As shown in Figure 10, in the dark, CO$_2$/H$_2$O adsorption on A$_{75}$B$_{25}$ resulted in the formation of bicarbonate (HCO$_3^-$, 1220 and 1420 cm$^{-1}$), bidentate carbonate (b-CO$_3^{2-}$, 1360 and 1570 cm$^{-1}$), monodentate carbonate (m-CO$_3^{2-}$, 1300 and 1540 cm$^{-1}$), and carboxylate (CO$_2^-$, 1250 and 1673 cm$^{-1}$)$^{2,83,84}$ The intensities of the peaks remained almost unchanged from 20 min to 30 min, indicating that the adsorption of CO$_2$/H$_2$O reached the saturated level on the surface of A$_{75}$B$_{25}$. Immediately upon photo-irradiation for 15 min, the peaks for HCO$_3^-$ and CO$_2^-$ species decreased or even disappeared, while the peak for surface H$_2$O (1639 cm$^{-1}$)$^2$ and CO$_3^{2-}$ increased. Upon increasing the photo-illumination time from 15 min to 3 h, the intensities of the H$_2$O and CO$_3^{2-}$ peaks gradually increased, while that of HCO$_3^-$ was gradually decreased and CO$_2^-$ completely disappeared.
**Figure 10** In situ DRIFTS spectra of CO$_2$ and H$_2$O adsorption on A$_{75}$B$_{25}$ for 30 min in the dark (short-dash lines), and subsequent photoreduction process under the UV-vis light irradiation for 3 h (solid lines)

In our previous studies,$^{85}$ we found that HCO$_3^-$ and CO$_2^-$, formed from CO$_2$ interaction with OH groups and Ti$^{3+}$ sites, are the possible intermediates for CO$_2$ photoreduction to CO and C$_1$ fuels (e.g., CH$_4$) once the dissociative H atom is available. The DRIFTS study here again demonstrated the importance of the HCO$_3^-$ and CO$_2^-$ as the CO$_2$ reduction intermediates, evidenced by the weakened HCO$_3^-$ peak and the disappearance of CO$_2^-$ upon photo-illumination. The increase of CO$_3^{2-}$ species could result from HCO$_3^-$ transformation. The increase in surface H$_2$O may be explained as follows. It is known that H$_2$O and CO$_2$ competitively adsorb on TiO$_2$. H$_2$O and CO$_2$ adsorption reached equilibrium in the dark. Upon photo-illumination, this equilibrium was broken
when adsorbed CO₂ species was reduced to CO and desorbed into the gas phase. Hence, some surface sites like OH groups became available for incoming gas molecule adsorption. Because H₂O has a higher binding energy with surface OH groups than CO₂, once the OH groups were re-exposed, most of them may be occupied by H₂O, and thus preventing subsequent CO₂ adsorption on the surface. The lack of continuous formation of active CO₂ adsorption species (HCO₃⁻ and CO₂, not CO₃²⁻) species may cause the observed catalyst deactivation over a few hours observed in the photocatalytic activity measurements. The above described DRIFTS results have provided significant insights into the reaction mechanism and catalyst deactivation which have been rarely studied in the literature.

2.4 Conclusions

Anatase-rich anatase/brookite mixtures showed superior activity for the photocatalytic reduction of CO₂ to fuels. The interfaces between anatase and brookite nanocrystals are believed to enhance photo-induced charge transfer and electron-hole separation, and thus they are more active than single-phase anatase or brookite. Anatase-rich A/B mixtures are more active than brookite-rich A/B mixtures since the anatase nanoparticles used in this study have higher specific surface area and smaller band gaps than the brookite nanorods that were used. The anatase-rich A/B mixture (A₇₅B₂₅) was far more active than the anatase-rich A/R mixture with similar anatase fraction (i.e. P25). This important finding suggests a new direction for the development of efficient catalysts for CO₂ photoreduction to fuels, i.e. brookite-containing mixed phase TiO₂ nanocrystals.
3. CO₂ PHOTOREDUCTION WITH WATER VAPOR BY Ti-EMBEDDED MgAl LAYERED DOUBLE HYDROXIDES³

3.1 Introduction

A general pathway for TiO₂ assisted CO₂ photoreduction with H₂O was described as follows: reactants adsorbed on the surface of TiO₂, photogeneration of electrons and holes, activation of the adsorbed reactants by charge carriers, formation of intermediates adsorbed on the surface of TiO₂, conversion of intermediates to products, desorption of products from catalyst surface, and regeneration of the catalyst.⁸⁶ However, fast recombination rate of photogenerated electrons and holes, and poor CO₂ adsorption capability on the surface of TiO₂ limit its photocatalytic activity. Surface modification of TiO₂ with stronger CO₂ adsorbent could improve CO₂ adsorption and reduction on TiO₂. LDHs themselves have also been demonstrated as photocatalysts thanks to their highly tunable chemical compositions. Silva et al.⁸⁷ reported O₂ evolution from water under visible light on ZnTi, ZnCr and ZnCe-LDHs. Parida et al.⁸⁸ reported photocatalytic H₂ generation from water by a MgAlFe-LDH. Ti-containing LDHs (NiTi, ZnTi and MgAlTi-LDHs) have been reported to enhance H₂ production from photocatalytic water splitting by providing highly dispersed TiO₆ units in the LDHs structure.⁸⁹ In general, Ti species in MgAlTi-LDHs remain as amorphous phase in LDHs prepared by a conventional coprecipitation method.⁶² However, reconstructed LDHs, prepared by calcination at 400

³ Part of this chapter is reprinted with permission from “CO₂ photoreduction with water vapor by Ti-embedded MgAl layered double hydroxides” by Huilei Zhao, Jinye Xu, Lianjun Liu, Guiying Rao, Cunyu Zhao, and Ying Li, 2016. Journal of CO₂ Utilization, 15, 15-23, Copyright [2016] by Elsevier B.V.
While both MgAlTi-LDHs (with amorphous Ti species) and crystalline TiO$_2$ embedded in MgAl-LDH are demonstrated as photocatalysts, it is not clear in the literature which material is more active, particularly for CO$_2$ photoreduction with water.

According to the literature review in Chapter 1, the photocatalytic activity for CO$_2$ reduction can be improved by modifying TiO$_2$ with CO$_2$ adsorbent. In this work, we have prepared three types of MgAlTi-LDHs photocatalyst materials with different Ti species and structures and compared their activities in CO$_2$ photoreduction with water. The first type is prepared using a conventional coprecipitation method. The second method is coprecipitation followed by hydrothermal treatment to increase the crystallinity of TiO$_2$. This method has not been reported in the literature before and is inspired by the idea that amorphous TiO$_x$ species can be transformed to crystalline TiO$_2$ by hydrothermal treatment.$^{90,91}$ The third method is to reconstruct LDHs by calcination and rehydration, which was anticipated to crystalize TiO$_2$ while maintaining the layered structure. We have carefully characterized the three types of materials and correlated their materials properties with their photocatalytic activities in CO$_2$ reduction.

### 3.2 Materials and Methods

#### 3.2.1 Material Preparation

The first type of MgAlTi-LDH was fabricated with a coprecipitation method reported by Lu et al.$^{62}$ In a typical preparation process, solution A containing 1.6 M NaOH and 0.16 M Na$_2$CO$_3$ and solution B containing 0.6 M Mg(NO$_3$)$_2$•6H$_2$O, 0.2 M
Al(NO₃)₃•9H₂O, and 0.3 M TiCl₄ were prepared in two separated beakers. Then solution A was added dropwise into solution B with rigorous stirring until pH 10. The resultant white mixture was aged in a silicon oil bath of 60°C for 18 h. The precipitates were then collected by vacuum filtration and dried overnight at 80°C. The powders were finally grinded and sieved. The atomic ratio of Mg: Al: Ti was 6:2:3. The as synthesized Ti-containing MgAl-LDHs from coprecipitation was denoted as MgAlTi(CP) or simply CP.

The MgAlTi(CP) powders were re-dispersed in water (1wt%) and stirred for 30 min. Then the mixture was transferred into a hydrothermal vessel and heated at varies temperature (100, 150, or 200°C) for 24 h. After the hydrothermal reaction, powders were obtained by filtration, vacuum drying and grinding. The samples were denoted as MgAlTi(HT100), MgAlTi(HT150), and MgAlTi(HT200) or simply HT100, HT150 and HT200, where the number designates the hydrothermal temperature.

The MgAlTi(CP) powders were first calcined in a muffle furnace at 400, 500, or 600°C for 2 h and then dispersed in water and rigorously stirred at room temperature for 24 h for reconstruction. Powders were collected after filtering and drying at 80°C. The samples were denoted as MgAlTi(R400), MgAlTi(R500), and MgAlTi(R600) or simply R400, R500 and R600, where the number designates the calcination temperature.

3.2.2 Material Characterization

Crystal structures of samples were characterized with X-ray diffraction (XRD, Scintag XDS 2000) using Cu Kα irradiation (λ=0.1540562 nm) at 45 kV and a diffracted beam monochromator at 40 mA in the 2θ range of 5°-70° at a scan rate of 2°/min. UV–visible diffuse reflectance spectra (UV–vis DRS) were obtained by an UV–visible
spectrometer (Ocean Optics) using BaSO$_4$ as the background. Scanning electron microscopy (SEM) (Hitachi S4800) was used to visualize the catalyst morphology. Porous textual characterization was performed with nitrogen adsorption–desorption at 77 K using the Brunauer–Emmett–Teller (BET) method for surface area estimation and Barrette-Joynere-Halenda (BJH) method for cumulative pore volume analysis (Micrometrics, ASAP 2020). CO$_2$ adsorption capacity of different samples were investigated by CO$_2$ adsorption isotherms taken with the thermogravimetric analyzer (TGA-DAT-2960 SDT).

For each test, 15-20 mg of sample was loaded in an Al$_2$O$_3$ container and heated to 150°C at a ramp of 10°C/min under an argon flow (100 ml/min). After the weight was stabilized, the argon flow was replaced with a moisturized CO$_2$ flow (120 ml/min). The weight versus time was recorded and analyzed. Thermal stability analysis of the MgAlTi(CP) material was also carried out on the same thermogravimetric analyzer (TGA) at a heating ramp of 10°C/min from room temperature to 800°C in air flow. Temperature programmed desorption (TPD) of CO$_2$ (10°C/min) was recorded with a mass spectrometer (MS). To characterize the surface chemistry of the MgAlTi(CP) under thermal treatment, Fourier transform infrared spectra (FTIR) were recorded on a Nicolet 6700 spectrometer (Thermo Electron) equipped with a liquid nitrogen-cooled HgCdTe (MCT) detector. The sample was loaded in a reaction chamber (Harrick Scientific, HVCDRP) equipped with a heater and a programmed temperature controller, as well as cooling water circulation.

3.2.3 Activity Tests for CO$_2$ Photoreduction

For each CO$_2$ photoreduction test, 50 mg of samples were dispersed on a clean glass fiber filter paper and loaded on the inner wall of a quartz tube reactor. CO$_2$ (99.999%,
Praxair) controlled by mass flow controller (MFC) was continuously passed through a water bubbler to allow a mixture of CO₂ and 2.3 vol% H₂O vapor to flow through the photoreactor. A 400 W UV lamp (Oriel) was used as the light source, and the light intensity is about 420 mW cm⁻² in the range of 200-1000 nm. Our previous studies found that slightly increasing the reaction temperature could aid desorption of the surface intermediates and thus promote the photocatalytic reduction of CO₂ with water vapor.⁵⁶,⁵⁷ Therefore, in this work two 250 W infrared lamps were applied to heat up the photoreactor to a temperature of 150°C, the optimal temperature found in our previous work.⁵⁶ The photoreactor was operated in a continuous-flow mode, and the gaseous products in the reactor effluent were continuously analyzed by a gas chromatograph (GC, Agilent 7890A) equipped with both a thermal conductivity detector (TCD) and a flame ionization detector (FID).

### 3.3 Results and Discussion

#### 3.3.1 Crystal Structure and Morphology

Crystal structures of MgAlTi-LDH samples were examined by XRD as shown in Figure 11. The XRD pattern of MgAlTi(CP) sample shows peaks at 2θ around 12° (003), 23° (006), 35° (009)/(102), 61° (110) and 64° (113) that match the typical rhombohedral structure of MgAl-LDHs reported in literature.⁶⁴,⁹² The basal spacing corresponding to (003) plane is calculated to be 0.759 nm using Bragg’s equation.⁹³ Assuming 3-layer rhombohedral (3R) stacking sequence of MgAlTi-LDHs, the unit cell parameter c was calculated to be 2.276 nm, three times that of the layer-to-layer distance. By applying
Bragg’s equation to (110) plane, the unit cell parameter \( a \) was obtained to be 0.305 nm, which is the averaged metal-to-metal distance within the layers. These calculated parameters were comparable to those reported in the literature.\(^{95,96}\) By applying the Scherrer equation on the (003) peak, the crystallite size, i.e. disk diameter\(^ 97\) in the stacking direction of the MgAlTi(CP) sample was determined to be 8.3 nm.

**Figure 11** XRD patterns of MgAlTi(CP), MgAlTi(HT100), MgAlTi(HT150), MgAlTi(HT200), MgAlTi(R400), MgAlTi(R500), and MgAlTi(R600) samples. (* refers to Al\(_2\)O\(_3\) phase; S refers to spinel MgAl\(_2\)O\(_4\); A refers to anatase TiO\(_2\) )

**Figure 11** also shows the crystal structure changes of MgAlTi(CP) treated with hydrothermal or calcination/reconstruction. The (101) diffraction peaks for anatase type TiO\(_2\) (JCPDS no. 21-1272) appeared for HT150, HT200 and R600 samples at \( 2\theta = 25.3^\circ \), 25.2\(^\circ\) and 25.7\(^\circ\), respectively. Hydrothermal at lower than 150 °C or calcination lower
than 600 °C did not result in anatase TiO$_2$ formation. Yanagisawa et al.$^{90}$ attributed the reason that crystallization temperature required in hydrothermal condition was lower than that in calcination in air to the acceleration of nucleation by water. At a higher hydrothermal temperature, the nucleation by structural rearrangement of the TiO$_6$ octahedral units in the amorphous TiO$_2$ might proceed quickly and heterogeneously followed by immediate growing, leading to larger anatase crystals.$^{98}$ That explains why the anatase crystallite size for HT(200), 12.3 nm, is larger than that of HT(150) 8.4 nm.

Reconstructed LDHs generally preserved the original LDH structure, as seen in the R400, R500 and R600 samples; however, reflection peaks of impurities like Al$_2$O$_3$ and spinel MgAl$_2$O$_4$$^{99-101}$ were identified on the R600 sample, indicating permanent structure change due to high temperature calcination.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CP</th>
<th>HT100</th>
<th>HT150</th>
<th>HT200</th>
<th>R400</th>
<th>R500</th>
<th>R600</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(003) (nm)</td>
<td>0.759</td>
<td>0.751</td>
<td>0.753</td>
<td>0.767</td>
<td>0.751</td>
<td>0.758</td>
<td>0.759</td>
</tr>
<tr>
<td>(003) disk diameter (nm)</td>
<td>8.3</td>
<td>11.9</td>
<td>14.4</td>
<td>19.9</td>
<td>4.8</td>
<td>5.5</td>
<td>6</td>
</tr>
<tr>
<td>a (nm)</td>
<td>0.305</td>
<td>0.304</td>
<td>0.304</td>
<td>0.305</td>
<td>0.303</td>
<td>0.304</td>
<td>0.306</td>
</tr>
<tr>
<td>Anatase crystallite size (nm)</td>
<td>/</td>
<td>/</td>
<td>8.4</td>
<td>12.3</td>
<td>/</td>
<td>/</td>
<td>30.1</td>
</tr>
</tbody>
</table>

Crystal structural parameters of MgAlTi-LDHs samples calculated from XRD results were summarized in Table 3. The lattice parameters of LDHs structures remained
similar after hydrothermal and reconstruction treatments, basal spacing \( d(003) = 0.751-0.767 \) nm and unit cell parameter \( a = 0.303-0.306 \) nm, consistent with the literature.\(^6\) But the crystallinity changed significantly (disk diameter = 4.8~19.9 nm). Hydrothermal treatment at 100, 150, and 200 °C increased the crystallite size of LDHs from 8.3 nm to 11.9, 14.4 and 19.9 nm, respectively. Whereas, reconstructed samples at 400, 500, and 600 °C calcination have a decreased crystallite size to 4.8, 5.5 and 6.0 nm. It is highly possible that during hydrothermal treatment, LDHs crystallites prong to grow larger via Ostwald ripening.\(^1\) This phenomenon was also reported by Xu et.al\(^3\) that LDHs particles disaggregated at a lower temperature and followed by the growth of LDHs individual crystallite via 3-D process (dissolution, diffusion, and deposition). At a higher temperature, the development of LDHs accelerated could be due to the faster diffusion of ions, e.g. Mg\(^{II}\), Al\(^{III}\) cations. Reconstructed samples were prepared by calcination and reconstruction method, using the memory effect of LDHs materials. Amorphous phase is often produced during the calcination-reconstruction process simultaneously,\(^4\) which led to a smaller crystallite size compared with the unmodified LDH materials. Increasing calcination temperature of LDHs samples may boost the agglomeration of crystals, which could give rise to the growing of crystals in the reconstructed LDHs as well.

Morphologies of the samples obtained by SEM are shown in **Figure 12-Figure 13**. The pristine CP sample (**Figure 12**) was composed of densely aggregated small nanoflakes (~50 nm). Porous flower-like morphologies were observed for all the hydrothermal and reconstruction treated samples (**Figure 13**). Increasing the hydrothermal temperature resulted in larger flakes with diameters of ~100, ~500 and
~1000 nm for HT100, HT150, HT200, respectively, which matches the increased crystallite size observed in the XRD results (Table 3). Whereas, the reconstructed samples (R400, R500, and R600) consisted of relatively small flakes (~100 nm) and no obvious change of flake size was observed with increased calcination temperature.

![SEM images of MgAlTi(CP)](image)

**Figure 12** SEM images of MgAlTi(CP)

![SEM images of MgAlTi-LDHs after hydrothermal treatment (HT100, HT150, and HT200) and calcination + reconstruction treatment (R400, R500, and R600)](image)

**Figure 13** SEM images of MgAlTi-LDHs after hydrothermal treatment (HT100, HT150, and HT200) and calcination + reconstruction treatment (R400, R500, and R600)
3.3.2 Temperature Dependent Properties

To better understand the crystal structural change of the MgAlTi(CP) as a function of calcination temperature, the MgAlTi(CP) sample was calcined at 200, 400, 500, and 600 °C, respectively (without the reconstruction step), and the XRD patterns are shown in Figure 14(A). At a lower temperature (200 °C), broadened LDH characteristic peaks were observed, suggesting that LDH layered structure started to collapse upon thermal treatment. When the calcination temperature was raised to 400-500 °C, the layered structure was completely lost, leaving mixed metal oxide (MMO) of MgO and Al₂O₃. When the calcination temperature further increased to 600 °C, crystal TiO₂ (anatase type, JCPDS no. 21-1272) and spinel phase MgAl₂O₄ appeared.

The XRD pattern change of the MgAlTi(CP) sample upon thermal treatment was consistent with TGA result, as shown in Figure 14(B). Three stages with a total weight loss of 34.4% were identified: 20-216 °C, 216-410 °C, and 410-800 °C. In the first stage, water molecules from the material surface and interlayer gallery were lost, but the layered structure was still preserved. In the second stage, dehydroxylation of the brucite-like sheet layers and decarbonation occurred, leading to gradual deformation of the layered structure. In the third stage, carbonates in the interlayer space were further eliminated. Desorption of CO₂ as a result of decarbonation during the heating process (20 to 600 °C with a ramp of 10 °C/min) was recorded as the TPD profile shown in Figure 14(C). The peak centered at 420 °C coincided well with the transition from the second to the third stage weight loss shown in the TGA curve.
Figure 14 XRD patterns of MgAlTi(CP) after calcined at 200~600°C for 2 h (A); TGA curve of MgAlTi(CP) (B), TPD profile of MgAlTi(CP) for CO$_2$ desorption (C); and FTIR spectra of MgAlTi (CP) heated at different temperatures in air (D).

FTIR spectra of the sample heated to 50-500 °C (the sample was continuously purged with an air flow) were recorded in Figure 14(D). At 50 °C, the high frequency bands at 3550 and 3100 cm$^{-1}$ were ascribed to vibrations of H$_2$O and OH$^-$ groups. The band around 1643 cm$^{-1}$ was attributed to bending mode of interlayer water and the one around 1413 cm$^{-1}$ belonged to asymmetric stretching of the interlayer carbonate or bicarbonate. As the temperature increased, the 1643 and 1413 cm$^{-1}$ bands gradually decreased and finally disappeared at 300 °C, but new bands at 1566 and 1327 cm$^{-1}$ for bidentate carbonate (b−CO$_3^{2−}$) appeared from 150°C and reached the maxima at 300°C.
When the temperature was further raised to 500 °C, bands at 1731, 1450 and 1299 cm\(^{-1}\) for bridged carbonate (d-CO\(_3^{2-}\))\(^{85}\) were observed. The FTIR results also agree with the TGA analysis on the structural transformation of the LDH material.

3.3.3 Textual Properties

Table 4 Textual parameters of samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CP</th>
<th>HT100</th>
<th>HT150</th>
<th>HT200</th>
<th>R400</th>
<th>R500</th>
<th>R600</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S_{\text{BET}}) (m(^2)/g)</td>
<td>169.9</td>
<td>181.4</td>
<td>117</td>
<td>78.3</td>
<td>111.4</td>
<td>102.1</td>
<td>73.8</td>
</tr>
<tr>
<td>Pore size (nm)</td>
<td>5.5</td>
<td>6.3</td>
<td>10.8</td>
<td>14.3</td>
<td>4.2</td>
<td>4.4</td>
<td>5.7</td>
</tr>
<tr>
<td>Pore volume (cm(^3)/g)</td>
<td>0.25</td>
<td>0.3</td>
<td>0.38</td>
<td>0.33</td>
<td>0.14</td>
<td>0.16</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Nitrogen adsorption/desorption isotherms were taken at 77K to analyze textual properties of the samples. As shown in Figure 15A, all of the samples display a type IV isotherm (IUPAC classification) and type H3 hysteresis loop,\(^{106,107}\) indicating mesoporous structures formed by aggregates of flakes or slit pores between edged flakes. The relative pressure (P/P\(_0\)) at the loop closing point for HT150 and HT200 (0.6-0.7) was higher than that for the rest of samples (~0.4), suggesting larger pore sizes for HT150 and HT200 samples. The BET surface area decreased from 169.9 m\(^2\)/g for the CP sample to 117.0 and 78.3 m\(^2\)/g at 150 and 200 °C hydrothermal treatment temperatures. However the HT100 sample had slightly increased BET surface area of 181.4 m\(^2\)/g. A similar trend was also observed for the reconstructed samples, with the BET surface area decreased to 111.4, 102.1 and 73.8 m\(^2\)/g as the calcination temperature raised from 400 to 500 and 600°C. The
decreased specific surface area could be attributed to the increase in LDH crystallite size at higher calcination temperature.

Figure 15 N₂ adsorption-desorption isotherms (A) and Pore size distribution (B)

Pore size distribution of the samples Figure 15B were plotted using BJH desorption data. Average pore size and pore volume were summarized in Table 4. For the pristine CP sample, two peaks at 3.8 and 6.3 nm were observed, which was consistent with the values in the literature.¹⁰⁶ Hydrothermal treatment at 100°C did not change the pore size distribution significantly, although the second peak was slightly broadened. When the hydrothermal temperature was raised to 150 and 200°C, the first peaks shrank significantly and the second peaks grew and shifted to 8.4 and 10.8 nm respectively. The average pore size for HT150 and HT200 was 10.8 and 14.3 nm, larger than that of 6.3 and 5.5 nm for
the HT100 and CP samples. This increase in pore size could be the result of increased LDHs flake size due to hydrothermal treatment. Reconstructed samples had similar pore size distribution with the pristine CP sample. R400 and R500 had only the sharp peaks at 3.7 and 3.5 nm while the R600 sample had two peaks at 3.4 and 5 nm. Average pore sizes were 4.2, 4.4 and 5.7 nm for R400, R500 and R600 respectively. The increasing trend with temperature in pore size agreed well with the flake size changes observed in SEM analyses.

3.3.4 Optical Property and CO$_2$ Adsorption Capability

Band gaps of the samples measured from UV-Vis absorption spectra are listed in Table 5. The CP sample had a band gap of 3.40 eV, in consistent with the reported value for amorphous TiO$_2$.\textsuperscript{108} Hydrothermal treatment at 100 °C (HT100) did not change the band gap. But when the hydrothermal temperatures were raised to 150°C and 200°C, the band gaps were slightly narrowed down to 3.32 and 3.31 eV, which could be attributed to the presence of anatase TiO$_2$ in the two samples. Band gaps of reconstructed samples were determined to be 3.42, 3.35 and 3.30 eV at calcination temperatures of 400, 500 and 600°C. The results indicate that all the treatments did not significantly change the band gap of the MgAlTi-LDH materials.

CO$_2$ adsorption capacities were measured from CO$_2$ isotherms obtained by the TGA instrument and shown in Table 5. The CP sample had a CO$_2$ adsorption capacity of 2.07 wt% or 0.47 mmol/g, the highest among all samples tested. The decrease in CO$_2$ adsorption capacity for the HT150, HT200, R400, and R600 was probably caused by the decreased surface area after hydrothermal and reconstruction treatment. All MgAlTi-
LDHs have a much higher CO₂ adsorption capacity than commercial TiO₂-P25 nanoparticles, which is a mixture of anatase and rutile crystal phases\textsuperscript{109}.

**Table 5 Optical and CO₂ adsorption parameters of MgAl-Ti-LDHs**

<table>
<thead>
<tr>
<th>Sample</th>
<th>CP</th>
<th>HT100</th>
<th>HT150</th>
<th>HT200</th>
<th>R400</th>
<th>R500</th>
<th>R600</th>
<th>P25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band gap (eV)</td>
<td>3.40</td>
<td>3.40</td>
<td>3.32</td>
<td>3.31</td>
<td>3.42</td>
<td>3.35</td>
<td>3.30</td>
<td>3.20</td>
</tr>
<tr>
<td>CO₂ adsorption capacity (wt%)</td>
<td>2.07</td>
<td>N/M*</td>
<td>0.66</td>
<td>0.62</td>
<td>0.85</td>
<td>N/M*</td>
<td>0.59</td>
<td>0.11</td>
</tr>
<tr>
<td>CO₂ adsorption capacity (mmol/g)</td>
<td>0.470</td>
<td>N/M*</td>
<td>0.150</td>
<td>0.141</td>
<td>0.193</td>
<td>N/M*</td>
<td>0.134</td>
<td>0.025</td>
</tr>
<tr>
<td>CO₂ adsorption capacity per unit surface area (µmol/m²)</td>
<td>2.77</td>
<td>N/M*</td>
<td>1.28</td>
<td>1.80</td>
<td>1.73</td>
<td>N/M*</td>
<td>1.82</td>
<td>0.5</td>
</tr>
</tbody>
</table>

* N/M: not measured

### 3.3.5 Photocatalytic Activity for CO₂ Photoreduction with H₂O

The photocatalytic activity of MgAlTi-LDHs were tested for CO₂ photoreduction by UV light irradiation for 5 h with continuous moisturized CO₂ feeding. Baseline experiments were first carried out in the dark with the photocatalyst or in the absence of photocatalyst under light irradiation, and CO₂ reduction products were observed. Under light irradiation in the presence of photocatalyst, CO was identified as the major product with only trace amount of CH₄ detected, which was consistent with our previous reports on TiO₂ based photocatalysts for CO₂ reduction\textsuperscript{2}. 
Figure 16 Amount of CO (normalized by catalyst mass) evolved by CO$_2$ photoreduction with water vapor during 5 h UV irradiation.

The amounts of CO production evolved within 5 h with moisturized CO$_2$ feeding were compared for all the MgAlTi-LDHs samples and commercial TiO$_2$-P25 nanopowders. The experiments were repeated two to three times for each material and the results (average and deviation) of CO production per unit gram of active photocatalyst material (TiO$_2$) are shown in Figure 16. P25 had the lowest CO production at around 10 µmol/g. The CP sample, with amorphous TiO$_2$, produced 33 µmol/g CO, more than two times of that by P25. This result indicates that amorphous TiO$_2$ in MgAlTi-LDH is photocatalytically active. The much higher activity of CP than that of P25 is likely due to the much large surface area (BET specific area of CP and P25 are 169.9 and 50 m$^2$/g, respectively) and thus better dispersion of Ti species, as well as the facilitated CO$_2$
adsorption capacity due to the MgAl-LDH. All the hydrothermal treated (HT) samples showed enhanced photoactivity compared to the CP sample. HT150 showed the highest CO production at around 50 µmol/g, 50% higher than that of the CP sample and four times higher than that of P25. Either lower (100 °C) or higher (200 °C) hydrothermal temperature did not improve photocatalytic activity significantly compared with the CP sample. For the reconstructed samples, however, only R400 showed slightly increased CO production, while the R500 and R600 showed rather decreased CO production compared with the CP sample. Nevertheless, they all had photocatalytic activities higher than P25.

Figure 17 Amount of CO (normalized by catalyst surface area) evolved by CO₂ photoreduction with water vapor during 5 h UV irradiation
The results of CO production by the various catalysts were also normalized by surface area and compared in Figure 17, which further demonstrated the better performance of hydrothermally treated sample over those prepared by calcination-reconstruction method. The CO\textsubscript{2} adsorption capability normalized by surface area was also added in Table 5. HT200 had the highest CO production per unit surface area and was twice as high as those of CP and P25 samples. Even though HT200 and R600 had similar CO\textsubscript{2} adsorption capacity per unit surface area, the photoactivity of HT200 was greater than that of R600. Since HT200 and R600 had similar band gap energies, a possible reason is that HT200 had a smaller anatase crystallite size (12.3 nm) than R600 (30.1 nm), which resulted in more number of surface active sites. However, HT150 had the smallest anatase crystallite size (8.4 nm), but the surface area normalized photoactivity of HT150 was slightly less than that of HT 200. This maybe because the CO\textsubscript{2} adsorption capacity of HT150 per unit surface area was lower and its band gap was slightly larger than HT200. The above results suggest there exists an optimal anatase crystallite size for CO\textsubscript{2} photoreduction, due to the balance between band gap and surface active sites of TiO\textsubscript{2} particles.\textsuperscript{110,111}

By correlating Figure 16 and Figure 17 with the materials properties, it can be concluded that the materials properties that may affect the CO\textsubscript{2} photoreduction activities include TiO\textsubscript{2} crystallinity and crystallite size, band gap, surface area, and CO\textsubscript{2} adsorption ability. Among all the samples tested, the two samples HT150 and HT200 showed the highest overall CO production. HT150 was the most active catalyst when normalized by mass and HT200 was the most active one when normalized by surface area. It is likely the
combination of the following properties made them superior catalysts to others: (1) their band gaps were among the smallest (3.31-3.32 eV), (2) HT150 had a relatively high surface area (117.0 m$^2$/g), (3) both had crystalized anatase TiO$_2$ with small crystallite size (8.4 and 12.3 nm for HT150 and HT200, respectively), and (4) the LDH composition and structure enhanced their CO$_2$ adsorption capacities. Although R600 also had anatase TiO$_2$ nanocrystals and relatively small band gap, its relatively large crystallite size (30.1 nm) and low surface area (74 m$^2$/g) prevented improvement in the overall photocatalytic activity. However, the general higher activity of all MgAlTi-LDH materials than P25 suggests the advantages of this type of new photocatalyst materials because of their better TiO$_2$ dispersion and higher CO$_2$ adsorption capacity.

3.4 Conclusions

In this study, a new series of photocatalysts, MgAlTi-LDHs, with different materials structures have been fabricated and demonstrated for CO$_2$ photoreduction with water vapor to produce CO. The MgAlTi(CP) sample prepared by a coprecipitation method had amorphous TiO$_2$ species but was fairly active and had much higher photoactivity than the commercial TiO$_2$-P25. Hydrothermal treatment at 150-200°C converted the amorphous Ti species in the LDHs to anatase nanocrystals while maintaining the characteristic LDH structures. The optimum hydrothermal temperature was identified to be in the range of 150 to 200 °C (corresponding to photocatalysts HT150 and HT200). HT150 was four times more active than P25 and 50% more active than the CP sample, when normalized by catalyst mass. HT150 was four times more active than P25 and 50% more active than the CP sample, when normalized by catalyst mass. The
activity of HT200 was twice as high as those of CP and P25, when normalized by catalyst surface area. Alternatively, reconstructing the CP sample at a calcination temperature of 600°C resulted in crystal anatase TiO₂, but the larger anatase crystallite size and relatively low surface area of R600 made its catalytic activity inferior to the HT150 and HT200 samples. In general, distributed crystalline TiO₂ in LDHs has better photocatalytic activity than amorphous TiO₂ for CO₂ photoreduction with H₂O. Band gap, specific surface area, and TiO₂ crystallinity and crystallite size are all important factors affecting the photocatalytic activity, and the enhanced CO₂ adsorption capacity introduced by the MgAl-LDH is particularly beneficial to CO₂ photoreduction. The discovery of this new type of MgAlTi-LDH (HT) material is important in the development of efficient CO₂ reduction photocatalysts.
4. ENHANCING PHOTOCATALYTIC CO₂ REDUCTION BY COATING AN ULTRATHIN Al₂O₃ LAYER ON OXYGEN DEFICIENT TiO₂ NANORODS THROUGH ATOMIC LAYER DEPOSITION⁴

4.1 Introduction

Among anatase, brookite and rutile, anatase is the most studied TiO₂ crystal phase because it is easier to synthesis compared to brookite and more active compared to rutile. A basic anatase crystal formed naturally has a truncated bipyramidal structure usually enclosed by eight {101} facets and two {001} facets, and because the surface energy of {001} is greater than {101}, the exposed facet of anatase is dominated by {101} at 94%.¹¹² Recently, anatase nanomaterials with well-defined exposed facets {101}, {001} or {100} have been successfully prepared and investigated for the facet-dependent photoactivity of TiO₂. The effect of exposed facet attracted more attention. The promising results of combining the advantages of active facets and defect effects in our previous work³⁷ have inspired on the design of novel TiO₂ material with high percentage {100} facets exposed and high density of surface oxygen vacancies. To further improve the photocatalytic activity of TiO₂, ALD was used in this work to coat a layer of Al₂O₃ on the surface of TiO₂. The thickness of Al₂O₃ layer deposited on TiO₂ was controlled by ALD. The mechanism of the enhanced photocatalytic activity was proposed based on the materials characterization and activity test results. We have found that when the layer of Al₂O₃ was

⁴Part of this chapter is reprinted with permission from “Enhancing photocatalytic CO₂ reduction by coating an ultrathin Al₂O₃ layer on oxygen deficient TiO₂ nanorods through atomic layer deposition” by Huilei Zhao, Jiatang Chen, Guiying Rao, Wei Deng and Ying Li, 2017. Applied Surface Science, 404, 49-56, Copyright [2017] by Elsevier B.V.
very thin, the surface passivation ability of Al$_2$O$_3$ over TiO$_2$ could enhance the photocatalytic activity, but a thick layer of Al$_2$O$_3$ as an insulator could hinder the electron transfer to the surface, thus lowering the rate of CO$_2$ photocatalytic conversion.

4.2 Material and Methods

4.2.1 Material Preparation

Anatase nanorods (ANR) were prepared by a two-step hydrothermal method. Firstly, TiO$_2$ P25 (Evonik) was dispersed into a 10M NaOH solution, sealed in a Teflon-lined autoclave, and heated in an electric furnace at 140°C for 24 h to produce sodium titanates. The products were washed and centrifuged several times with D/I water till pH 10. Next, 2 g sodium titanates were mixed with D/I water and subject to a second hydrothermal process at 200 °C for 12 h. The resulting solids were separated from the liquid by centrifuge and washed with D/I water till pH 7. The anatase nanorods were obtained after drying the sample at 60 °C for 12 h.

The reduced anatase nanorods (ReANR) were prepared by mixing the ANR with NaBH$_4$ (1:1) in a mortar, and thermally treated in Ar at 300 °C for 30 min. The resulting mixed solids were washed with D/I water and centrifuged till pH 7. The ReANR was obtained after drying in the oven at 60 °C for 12 h. For comparison, pure anatase nanoparticles (ANP) were prepared by a simple hydrothermal method reported in our precious work.$^{113}$ Briefly, titanium (IV) bis(ammonium lactato) dihydroxyde (TALH) was mixed with 0.1 M urea, and hydrothermally treated at 160 °C for 24 h. The sample was washed and dried using the same method as in the procedure for ANR. The ANP was
finally calcined at 450 °C for 2 h to remove any possible organic residuals on the surface. The reduced ANP (ReANP) was also prepared using the same method as ReANR.

To obtain ALD coated Al₂O₃ on ReANR, a commercial ALD system (Savannah S200, Ultratech) was applied. For each coating process, ANR powders were loaded into a home-designed particle holder, which was placed in the middle of the reaction chamber of the ALD. To ensure adequate coating on porous materials, the ALD system was set in an “expo mode” assisted with a soft pump, which can prolong the time for precursor molecules to contact with the surface of ANR by slowing down the pressure decreasing rate. The pulse time of both the H₂O and Trimethylaluminum (TMA) was 0.03 s, and the reaction chamber was set at 200 °C. No external heater was applied to the TMA cylinder. The Al₂O₃ coated samples were denoted as xAl_ReANR, where x is the number of ALD cycles applied.

4.2.2 Material Characterization

X-ray diffraction (XRD, BRIKER D8) using Cu Kα irradiation at 45 kV and 40 mA diffracted beam monochromator was applied to detect the crystal structures of the photocatalyst samples. The surface morphology was obtained by scanning electron microscopy (SEM, JEOL JSM7500F) equipped with a cold cathode UHV field emission conical. The Energy-dispersive X-ray spectroscopy (EDS, Oxford) associated with SEM was used for surface elemental mapping and quantitative elemental composition analysis. Transmission electron microscopy (TEM) and high resolution-TEM (HR-TEM) taken by an FEI Tecnai G2 F20 ST instrument with 0.24 nm point and 0.15 nm information limitation at 200 keV was used to obtain the lattice structure of ANR and identify the
Al$_2$O$_3$ coating layer. UV–vis diffuse reflectance spectra were obtained by a Hitachi U4100 UV-Vis-NIR Spectrophotometer with Praying Mantis accessory. Photoluminescence (PTI QuantaMaster series Spectrofluorometer) was used to investigate the charge recombination emission using 360 nm incident light, scanning from 370 to 700 nm with scan rate 0.1nm/s. A 380 nm long pass filter was applied to the detector. X-ray photoelectron spectroscopy (XPS) was used to identify the chemical states of Ti, O and Al elements, using an Omicron XPS system using Omicron's DAR 400 dual Mg/Al X-ray source. All region and components were calibrated using C 1s peak at 284.8 eV.

4.2.3 Photocatalytic CO$_2$ Photoreduction

Photocatalytic activity test for CO$_2$ photoreduction with water vapor was performed in a cylindrical quartz tube reactor. For each activity test, 10 mg catalyst was dispersed on a piece of glass fiber filter paper. The filter paper was placed in the middle of the reactor, with the catalyst side facing the light irradiation direction. CO$_2$ (99.999%, Airgas) continuously passed through a water bubbler and brought the mixed CO$_2$ and H$_2$O gas (2.3vol% of H$_2$O) into the reactor. The reactor was first purged at 100 ml/min for 1 h to eliminate air and then maintained at 4 ml/min (continuous-flow mode) for the whole photoreaction process. A 450 W Xe lamp (Newport) was used as the UV-vis source. The light intensity is about 267.15 mW/cm$^2$ in the range from 250 to 1050 nm, and 17.15 mW/cm$^2$ in the UV range (<390 nm). The spectrum of the light source was shown in Figure 18. A 250 W infrared (IR) lamp was applied to keep the reactor at 100 °C, this is because a relatively higher reaction temperature can facilitate the desorption of the products and improve the activity of photo-activated TiO$_2$.\textsuperscript{114} In addition, Slamet et
reported elevated CO$_2$ photocatalytic conversion to CH$_4$ by increasing the reaction temperature to 100 °C. The effluent from the reactor was analyzed continuously by a gas chromatograph (GC, Fuel Cell GC-2014ATF, Shimadzu) equipped with a thermal conductivity detector (TCD) and a methanizer assisted flame ionization detector (FID).

**Figure 18** Irradiation spectrum of the Xe lamp used for CO$_2$ photoreduction experiments

### 4.3 Results and Discussion

#### 4.3.1 Crystal Structure

The crystal structure of the materials synthesized was characterized by XRD. **Figure 19** shows the XRD patterns of the ReANR and 200Al_ReANR, both of which show characteristic peaks for anatase TiO$_2$ (tetragonal, space group I41/amd, JCPDS 21-1272). Peaks at 25.3, 37.1, 37.8, 38.9, 48.0, 53.9, and 55.0 degree can be assigned to (101), (103), (004), (112), (200), (105), and (211) crystal plane of anatase TiO$_2$, respectively. The full width at half maximum (FWHM) for peaks at 25.3, 37.8, and 48.0° was calculated.
to be 0.011, 0.006, and 0.012, which are indexed to crystal planes (101), (004) and (200), respectively. Compared with the FWHM of anatase nanocuboids (0.11, 0.26, 0.09) with 95% {100} exposed facet reported in the literature, the ANR synthesized in this work with much smaller FWHM had better crystallinity. The peak intensity ratio $I_{(101)}: I_{(004)}: I_{(200)}$ was 100:14:40, while the standard ratio of anatase is 100:18:23, suggesting that the preferential crystallographic orientation of anatase nanorod synthesized was along [100] direction. For ALD coated catalyst, there was a very broad peak at 20-50°, observed from the intensity difference between ReANR and 200Al_ReANR (inset of Figure 19). The broad peak matched the amorphous Al$_2$O$_3$ by ALD reported in the literature, indicating the successful coating of amorphous Al$_2$O$_3$ layer on nanorods.

![XRD patterns of ReANR and 200Al_ReANR](image)

**Figure 19** XRD patterns of ReANR and 200Al_ReANR (Inset figure is intensity by subtracting intensity of ReANR from 200Al_ReANR)
4.3.2 Morphology

Figure 20 SEM images of ANR (a), ReANR (b), 200Al_ReANR (c), the enlarged image of the circled area (d), and the simulated geometry model of ANR (e)

The morphology of the photocatalysts was characterized by SEM in Figure 20. The rod-shape ANR (Figure 20a) and ReANR (Figure 20b) have well-defined lateral facets with sharp edges, and the adjacent parallel facets \{100\} and \{010\} are perpendicular as boxed off in Figure 20d. The rectangular shape has a width \(a\) of ~53 nm, and a depth \(b\) of ~58 nm, suggesting \(a\) is approximately equal to \(b\). Thus, a geometry model of the ANR can be built based on the measurement in SEM, TEM, and HRTEM images, as shown in Figure 20e. The exposed facets of ANR were composed by four \{100\}/\{010\} facets as the lateral planes, two \{001\} as the end planes, and four \{101\} facet as the connecting planes. Although the anatase nanorods exhibited different lengths (along [001] direction), the aspect ratios of the rods are similar. The model parameters are estimated to
be a:b:c:H:h₁:h₂ = 1:1:0.3:10:9:0.5. The percentage of {100} facets exposed was calculated to be 91.5\% using the method described in our previous work.\textsuperscript{37} As shown in Figure 20c, after ALD coating of Al₂O₃ for 200 cycles on the surface of TiO₂, the size of the nanorods became larger, and the edges became blurry, suggesting the successful coating of Al₂O₃ on ANR.

4.3.3 Lattice Structure of ANR and Identification of Al₂O₃ Coating Layer

**Figure 21** EDS mapping images of ReANR with different cycles of ALD Al₂O₃ coating (a), and the EDS elemental analysis spectrum of 200Al_ReANR (b), and the XPS for 2Al_ReANR (c).

The EDS mapping images and elemental analysis spectrum in Figure 21 further confirm the existence of the Al₂O₃ layer. In Figure 21a, as the ALD cycle increased from
2 to 200, the size of nanorods increased. Moreover, the number of the green dots, which were corresponding to Al element, also increased with the increasing ALD cycle number. The surface quantitative elemental composition analysis (Figure 21b) shows an even higher concentration of Al (21.69 wt.%) than Ti (15.01 wt.%) on 200Al_ReANR. All the above results demonstrate the successfully coating of an ALD layer of Al₂O₃ whose thickness increases with an increasing ALD cycle number. For the sample 2Al_ReANR, the presence of the ultrathin layer of Al₂O₃ was also demonstrated by XPS results in Figure 21c. The broad peak at 74.75 eV represents typical characteristic of Al 2P (oxide).
TEM and HRTEM were applied to obtain crystal structure information and verify the surface Al₂O₃ coating layer. Figure 22 compares the morphology of 2Al_ReANR and 200Al_ReANR. The rod-shaped structure shown in Figure 22a and Figure 22c agrees well with the SEM observation and literature report. The lattice spaces of TiO₂ are measured to be 0.48, 0.35, and 0.35 nm in Figure 22b and Figure 22d based on the inset fast Fourier transform (FFT) images, corresponding to the (002), (101), and (10\overline{1}) facets, respectively. For 2Al_ReANR in Figure 22b, the fuzzy edges may be attributed to the ultra thin layer of Al₂O₃ on the surface of TiO₂. The amorphous layer of Al₂O₃, which is outlined by dashed lines, can be observed clearly in Figure 22d. The amorphous Al₂O₃ gave the circle signal in the inset FFT image (Figure 22d). The thickness of the Al₂O₃ from the edges of the nanorod to the dashed lines was estimated to be 5 nm for the 200Al_ReANR sample, which also matches the average thickness measured in Figure 22c. Therefore, the growth rate of the Al₂O₃ overlayers estimated to be ~0.25 Å per cycle.

4.3.4 Optical and Charge Transfer Properties

![Figure 23 XPS O 1s spectra (a) and Ti 2p spectra of ANR, ReANR and 2Al_ReANR](image_url)

**Figure 23** XPS O 1s spectra (a) and Ti 2p spectra of ANR, ReANR and 2Al_ReANR
<table>
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<th>Sample</th>
<th>O 1s</th>
<th>Ti 2p\textsubscript{1/2}</th>
<th>Ti 2p\textsubscript{3/2}</th>
<th>Fraction of Ti\textsuperscript{3+}/Ti\textsuperscript{4+}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(O_V)</td>
<td>(O_L)</td>
<td>Ti\textsuperscript{4+}</td>
<td>Ti\textsuperscript{3+}</td>
</tr>
<tr>
<td></td>
<td>(eV)</td>
<td>(eV)</td>
<td>(eV)</td>
<td>(eV)</td>
</tr>
<tr>
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<td>530.1</td>
<td>464.7</td>
<td>463.3</td>
</tr>
<tr>
<td>ReANR</td>
<td>532.2</td>
<td>530.1</td>
<td>464.9</td>
<td>463.7</td>
</tr>
<tr>
<td>2Al_ReANR</td>
<td>531.9</td>
<td>530.1</td>
<td>464.7</td>
<td>463.2</td>
</tr>
</tbody>
</table>

Based on the UV-vis absorption result (Figure 24a) and the Tauc plot (Figure 24b), the band gap of ANR was calculated to be 3.12 eV, while ReANR had a slightly reduced band gap, 3.04 eV. This agrees with the color change from white to grey after the reduction treatment by NaBH\textsubscript{4}, due to the formation of Vo, which was confirmed by XPS shown in Figure 23.\textsuperscript{120} According to the O 1s XPS spectra in Figure 23a, the oxygen vacancy peak (~532.0 eV) of ReANR and 2Al_ReANR was higher than that of ANR, suggesting more oxygen vacancies were formed after reduction.\textsuperscript{121,122} Also, quantitative analysis of Ti\textsuperscript{3+} is given in Table 6 in terms of the Ti\textsuperscript{3+}/Ti\textsuperscript{4+} fraction. It was found that after reduction, the Ti\textsuperscript{3+}/Ti\textsuperscript{4+} fraction increased from 0.35 (ANR) to 0.48 (ReANR). The increased formation of Ti\textsuperscript{3+} is another evidence of Vo formation.\textsuperscript{123} With 2 cycles of Al\textsubscript{2}O\textsubscript{3} ALD coating, the band gap was slightly increased to 3.08 eV, compared to uncoated ANR, which may be because the surface Vo were partially consumed by H\textsubscript{2}O during the ALD pulsing process.
The charge recombination property of the photocatalysts was characterized by photoluminescence. Promoted charge separation lowering the rate of radiative or non-radiative recombination leads to the quenching of the photoluminesces intensity. According to the photoluminescence results (Figure 25), the reduced sample ReANR had a much lower intensity of emission peak around 550 nm than ANR, suggesting a reduced charge recombination on ReANR. This is likely because the ReANR had more surface $V_0$, which can generate donor states below the conduction band (CB), promoting the charge separation and transportation. After the surface of ReANR was coated with 2 or 200 cycles of Al$_2$O$_3$ ALD, the height of the 550 nm emission peak of 2Al_ReANR and 200Al_ReANR was further lowered, indicating the coated overlayer further helped to suppress the surface charge recombination. The photoluminesces intensities of 2Al_ReANR and 200Al_ReANR were quite close to each other, indicating the ultrathin layer of Al$_2$O$_3$ coating in the range from 0.5 Å to 5 nm was capable to promote the charge.

Figure 24 UV-vis absorption spectra (a) and band gap measurement using Tauc plot (b)
separation. This is consistent with existing literature reports that the thickness of Al$_2$O$_3$ for the surface passivation effect varies from several tenths of Å to tens of nm.$^{126-128}$

Figure 25 Photoluminescence spectra of anatase nanorod photocatalysts

Figure 26 SEM (a) and HRTEM (b) of ANP, UV-vis spectra (c) and bandgap measurement using Tauc plot (d) of ANP and ReANP
The morphology, crystal structure, and optical property characterization results of anatase nanoparticles (ANP) are shown in Figure 26. The reduction process did not change the morphology and the crystal structure of ANP, thus only SEM and TEM images of ANP were shown. The SEM image in Figure 26a shows the fine nanoparticle morphology of the ANP, which resulting in the high surface area of ANP. The HRTEM image in Figure 26b shows the lattice space of ANP crystals is 0.35 nm, attributed to the most common {101} facet of anatase. The estimated band gap energies of ANP (2.95 eV) and ReANP (2.85 eV) (as seen in Figure 26d-c) are smaller than those of ANR (3.12 eV) and ReANR (3.04 eV).

4.3.5 Photocatalytic Activity for CO₂ Photoreduction with H₂O under UV-Vis Irradiation

Figure 27 The production of CO and CH₄ during a 4 h UV-vis irradiation period by anatase nanorods and nanoparticles
The photocatalytic activity of the synthesized photocatalysts for CO$_2$ photoreduction was tested by UV-vis light irradiation for 4 h with continuous CO$_2$ and H$_2$O vapor feeding. Two control experiments were conducted: (1) in the dark with the photocatalyst, and (2) under light irradiation without photocatalyst. In both cases, no CO$_2$ reduction products were detected. Under light irradiation in the presence of photocatalysts, CO and CH$_4$ were detected as the major products of CO$_2$ photoreduction with H$_2$O.

The production of CO and CH$_4$ from CO$_2$ photoreduction with H$_2$O within 4 h was compared among ANR, ReANR, ANP and ReANP, as shown in Figure 27. As shown in Figure 26a-b, ANP has isotropic nanoparticle structure, and {101} as the dominating facet. Even though ANP had a larger surface area than ANR due to the much smaller particle size of ANP (5-10 nm, Figure 26a-b, which was also reported in our previous work$^{113}$) than ANR (a few hundred nm in length as shown in Figure 20), ANP produced 50% less amount of CO (8.2 µmol/g) than ANR (17.1 µmol/g). There are two possible reasons for the higher CO production on ANR over ANP was because the following reasons. First, ANR has a very high percentage (91.5%) of exposed {100} facet that has 100% active Ti$_{5C}$ sites; by contrast, ANP has zero percent {100} facet. Second, the anisotropic structure of ANR may also enhance charge separation between different facets. The reduced sample ReANR had 50% higher CO production and 10 times higher CH$_4$ production than ANR. The improvement by ReANR can be attributed to the enhanced light absorption and formation of surface oxygen vacancies. The light absorption of ReANR was enhanced as evidenced by the narrowed band gap of 3.04 eV, compared with 3.12 eV for ANR. In addition, ReANR prepared by reducing ANR with NaBH$_4$ had Vo
created on the surface rather than in the bulk.\textsuperscript{129} The Vo in the bulk is believed to be recombination centers for electrons and holes,\textsuperscript{130} whereas, Vo on the surface facilitates CO\textsubscript{2} adsorption and activation\textsuperscript{42,43}, and promote electron transfer. The promoted CH\textsubscript{4} production was attributed to the increased local electron density by Vo, since CH\textsubscript{4} formation involves 8 electrons, while only 2 electrons are required for CO formation. When comparing the activity of ReANR and ReANP, one can find that the production of both CO and CH\textsubscript{4} were higher by ReANR and the overall production of CO and CH\textsubscript{4} by ReANR was 22\% higher than ReANP. The results reveal the superior photocatalytic activity of ReANR that takes the advantages of the active exposed facet and surface defect effects. However, it can also be noticed that the activity difference between nanoparticles and nanorods became smaller after reduction. It may be because ReANP may have more Vo formed than ReANR due to the high surface area of ReANP. In addition, the band gap of anatase nanoparticles was reduced from 2.95eV to 2.85eV after NaBH\textsubscript{4} reducing treatment (Figure 26c-d). The further narrowed band gap of ReANP compared to ReANR (3.04 eV) leads to higher light absorption capability of ReANP, which may be another reason for the less difference in activity between the reduced nanorods and nanoparticles.

The CO\textsubscript{2} photocatalytic reduction with H\textsubscript{2}O was also conducted on Al\textsubscript{2}O\textsubscript{3} coated ReANR with varied thickness of Al\textsubscript{2}O\textsubscript{3} coating layer. \textbf{Figure 28} compares the CO and CH\textsubscript{4} production on ReANR with different cycles (0-200) of ALD coated Al\textsubscript{2}O\textsubscript{3}. By applying less than 5 cycles of ALD, the Al\textsubscript{2}O\textsubscript{3} coated ReANR had enhanced overall (CO+CH\textsubscript{4}) production than uncoated ReANR, with 2 cycles being the optimum, about 40\% higher overall production (45.2 $\mu$mol/g in total with 40.8 $\mu$mol/g CO and 4.4 $\mu$mol/g
CH$_4$) than ReANR (32.1 µmol/g in total). A thin layer of Al$_2$O$_3$ deposited on the surface can passivate the trapping states caused by the surface oxygen vacancies, and consequently reduce the recombination of electrons and holes, as revealed by the photoluminescences results. The electrons can still reach to the surface by tunneling or other effects and react with the gas molecules to produce CO and CH$_4$ when the layer of Al$_2$O$_3$ coating is very thin. Due to the passivation effect of Al$_2$O$_3$, the surface recombination was suppressed, resulting in the enhanced CO production, and the increase of the overall electron involved. At the same time, the surface electron density was decreased, which can explain the decline of CH$_4$ selectivity.

![Figure 28](image.png)

**Figure 28** The production of CO and CH$_4$ during a 4 h UV-vis irradiation period by Al$_2$O$_3$ coated ReANR with different ALD cycles
However, both CO and CH$_4$ production decreased with increasing number of ALD cycles when more than 5 cycles were applied. When more than 100 cycles of ALD was applied, the overall production was reduced to ~12 µmol/g with negligible amount of CH$_4$. The insulating property of a thick layer of Al$_2$O$_3$ may have decreased the surface electron density, which leads to an overall low product yield and low selectivity of CH$_4$. Future studies will continue to focus on the application of ALD on the design of innovative photocatalyst, and the effect of varied coating materials on the performance of TiO$_2$.

To confirm the catalyst was active under UV light, 2Al_ReANR was tested for CO$_2$ photoreduction with H$_2$O under UV irradiation (mercury lamp, UVP LLC, USA; $\lambda$ = 365 nm, I = 13.12 mW/cm$^2$). The production under UV irradiation was compared to that under UV-vis irradiation (450 W Xe lamp, Newport, USA; I ($\lambda$ < 390 nm) = 17.15 mW/cm$^2$, I ($390 \text{ nm} < \lambda < 1050 \text{ nm}$) = 250 mW/cm$^2$) in Figure 29. Note that although different light sources were used, the intensities of the UV portion from the two lights were close to each other. The production of CO and CH$_4$ in 4 h UV irradiation was 2.8, and 2.0 µmol/g, respectively, demonstrating the catalysts prepared in this work are photoactive for CO$_2$ photoreduction under UV only irradiation. While, under UV-vis irradiation, the production of CO (40.8 µmol/g) and CH$_4$ (4.4 µmol/g) was 14 and 2 times as much as those under UV only. The result suggests both UV and visible lights contributed to the production of CO and CH$_4$ production while the visible light activity was superb. Thus, catalysts with a smaller band gap, or higher visible light absorption capability may have higher photocatalytic activity for CO$_2$ photoreduction.
The stability of 2Al_ReANR, which has the optimal thickness of Al₂O₃ coating layer, was tested by 5 cycles (8 h/cycle) of activity tests. After each 8h cycle test, the photocatalysts were wetted by DI water and dried at 60 °C prior to the next cycle test. The cycling performance results are presented in Figure 30. It shows the production rate of CO+CH₄ after 5 cycles maintained ~80% of the initial value, suggesting a relatively high stability of 2Al_ReANR. In addition, the color of ReANR and Al₂O₃ coated ReANR remained the same gray color for months, which also indicates the prepared materials are very stable.
Three materials innovations have been applied in this work to synthesize a unique nanostructured photocatalyst (TiO$_2$ anatase nanorods with over 90% exposed {100} facet, oxygen-deficient surface, and ALD coated Al$_2$O$_3$ overlayer), which demonstrated significantly enhanced capability for CO$_2$ photoreduction with H$_2$O to produce CO and CH$_4$. ANR with dominating {100} facets, despite a smaller surface area, was much more active than ANP. Reduced ANR facilitated CO$_2$ adsorption and activation due to surface oxygen vacancies. However, the density of surface states increased with increasing oxygen vacancies, which may be detrimental to photocatalytic reactions. An ultrathin
overlayer of Al₂O₃ deposited by ALD demonstrated the ability to passivate the surface states of reduced ANR and thus further enhanced the yield of CO₂ photoreduction. The thickness of the Al₂O₃ coating is found to be critical to the photocatalytic performance of TiO₂. Two cycles of ALD coating or approximately 0.5 Å Al₂O₃ corresponded to the optimum CO and CH₄ production. However, when more than five ALD cycles was applied, the CO and CH₄ production decreased, likely because the relatively thick overlayer inhibited electron transfer to the catalyst surface, although the surface passivation effect was still in effect. The strategy of ALD coating of a surface passivation layer can be applied to other photocatalysts beyond TiO₂ and other engineered surfaces and nanostructures, which may lead to the discovery of efficient, stable photocatalysts for CO₂ photoreduction with H₂O.
5. SUMMARY AND PROPOSED FUTURE WORK

The urgent need to reduce CO₂ emission and produce alternative energy raises the attention to advanced technologies of CO₂ utilization. Photocatalysts assisted CO₂ photoreduction is a very promising approach because it can convert CO₂ to value added products using photo energy. TiO₂ is the most extensively studied photocatalyst in this application but its catalytic performance is limited because of intrinsic materials properties such as large band gap and fast electron-hole recombination. This dissertation focuses on the innovative design of TiO₂ based nanomaterials for improve CO₂ photoreduction from the four direction (1) crystal structures, (2) CO₂ gas adsorption capability, (3) exposed facets and (4) defect property.

(1) The interfaces between anatase and brookite nanocrystals are believed to enhance photo-induced charge transfer and electron-hole separation

(2) New type of MgAlTi-LDH (HT) material, i.e. MgAl-LDHs with TiO₂ crystals showed higher CO₂ photoreduction because of the enhanced CO₂ adsorption capability.

(3) TiO₂ anatase crystals with active {100} facet exposed exhibited higher photocatalytic activity of CO₂ conversion compared to TiO₂ with {101} as the dominating facet.

(4) The photocatalytic activity of TiO₂ for CO₂ photoreduction was greatly improved by introducing surface defects. And a ultrathin layer of Al₂O₃ coating could further promote the photocatalytic performance due to the surface passivation effect of the coating layer.
Based on the current knowledge of design of TiO$_2$ based material and the research results, the future work was proposed in the following directions.

(1) Better understanding about the mechanism of the complicated reaction path of CO$_2$ photoreduction in gas adsorption, activation and reduction, and charge transfer.

(2) Investigate the defects effects on CO$_2$ photoreduction.

(3) Surface modification of photocatalyst using ALD technique.
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