Imperial College London

Department of Chemical Engineering

A thesis submitted for the degree of Doctor of Philosophy

CO₂ capture and photoconversion using multifunctional materials

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Abstract

The sustainable production of energy is an exciting area for researchers requiring the development of improved technologies in both carbon dioxide (CO$_2$) capture and CO$_2$ utilization. This thesis presents the development and applications of bifunctional materials for CO$_2$ capture by adsorption and utilization by photocatalytic conversion. Composite materials of solid sorbents and photocatalysts were designed primarily to increase CO$_2$ abundance at the active sites and promote charge separation to aid photocatalytic activity. All materials were characterised using various structural, chemical and optoelectronic techniques. The materials were tested for CO$_2$ capture and photoreduction using a gas-solid photoreactor. Composites of TiO$_2$ and carbon nitride nanosheets (CNNS) were synthesised with control of the exposed TiO$_2$ facets. When evaluated for CO$_2$ adsorption and photocatalytic reduction the exposed TiO$_2$ facets had significant influence in photocatalytic performance, the composite with more {001} facets exposed showed >10 fold higher activity than TiO$_2$. TiO$_2$ composites with metal organic frameworks (MOFs) were also designed; MOFs are an attractive class of materials for CO$_2$ adsorption and their applications as photocatalysts are more recent. TiO$_2$ and MOF (NH$_2$-UiO-66) composites of various composition were evaluated for photocatalytic reduction of CO$_2$ for the first time. The nanocomposites exhibited nanoparticle morphologies, maintained the CO$_2$ adsorption capacity from the MOF component, and photocatalytically, the optimum composite was 1.5 times more active than TiO$_2$ in conversion of CO$_2$ to CO. Further enhancements in the TiO$_2$/MOF composites were made by improving the TiO$_2$-MOF interfaces by forming the MOF onto TiO$_2$ nanofibers to promote more charge transfer. This resulted in a further 2.5-fold increase in photocatalytic reduction of CO$_2$ to CO. A crucial phenomenon behind the improved photocatalytic activity of the composites was revealed by investigations of the charge dynamics, this showed successful formation of heterojunctions had facilitated interfacial charge transfer.
Publications


A. Crake, Metal-organic frameworks based materials for photocatalytic CO₂ reduction, Materials Science and Technology, 33 (2017), 1737-1749


Declaration

I hereby declare that this thesis is my own work, and that any work by others has been clearly indicated and acknowledged in the text, with references to published work as appropriate. Work that has been published or submitted for publication is noted and referenced at the start of their relevant chapter.

Angus Crake

September 2018
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<tr>
<td>AC</td>
<td>Activated carbon</td>
<td>MeCN</td>
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<td>AcOH</td>
<td>Acetic acid</td>
<td>MeOH</td>
<td>Methanol</td>
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<td>ATR</td>
<td>Attenuated total reflectance</td>
<td>MOF</td>
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<td>BE</td>
<td>Binding energy</td>
<td>MS</td>
<td>Mass spectrometer</td>
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<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
<td>NP</td>
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<td>Benzylidihydrionicotinamide</td>
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<td>bpy</td>
<td>2,2'-Bipyridine</td>
<td>PL</td>
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<td>Conduction band</td>
<td>PSA</td>
<td>Pressure swing adsorption</td>
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<td>CCUS</td>
<td>Carbon dioxide capture, utilization and storage</td>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
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<td>Carbon nitride</td>
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<td>Carbon nitride nanosheets</td>
<td>SEM</td>
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<td>Coordination polymers</td>
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<td>Dimethylformamide</td>
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<td>Electron paramagnetic resonance</td>
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<td>Vacuum swing adsorption</td>
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<td>International Union of Pure and Applied Chemistry</td>
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<td>X-ray photoelectron spectroscopy</td>
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<td>LMCT</td>
<td>Ligand to metal charge transfer</td>
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Chapter 1 Introduction

1.1 Background

Climate change is one of the greatest challenges currently faced by mankind. This has been attributed to rising temperatures globally due to ever increasing CO\textsubscript{2} concentration levels in the atmosphere [1] which have exceeded 400 ppm (a 40% increase from 1750) rising at around 2 ppm each year [2, 3]. CO\textsubscript{2} capture, utilization and storage (CCUS) is the method proposed to lower the CO\textsubscript{2} emissions to the atmosphere. This is also likely to subsequently decrease the emission rates of other harmful pollutants [4]. While different ways to capture CO\textsubscript{2} have been investigated for decades enabling some technologies such as amine scrubbing, oxyfuel combustion or calcium looping, they remain energy intensive [5]. Solid adsorbents offer a promising alternative by capturing CO\textsubscript{2} at low temperatures in a less energy demanding process. Materials such as activated carbon, zeolites, metal oxides, amine-modified materials and metal-organic frameworks (MOFs) have emerged as potential CO\textsubscript{2} adsorbents [6]. MOFs are a particularly promising alternative due to their structural tunability, high surface area, high and selective CO\textsubscript{2} adsorption capacity [7-9].

Following CO\textsubscript{2} capture, CO\textsubscript{2} utilisation remains an emerging field. The conversion of CO\textsubscript{2} to chemicals (\textit{e.g.} syngas, methane, methanol and formic acid) \textit{via} chemical, electrochemical or photochemical reactions has been recently proposed and significant efforts are being carried out in this field. Although this pathway will not eliminate the need for long term CO\textsubscript{2} storage, carbon utilization would diversify the range of possibilities and potentially improve the economics of CCUS schemes [10]. Among the routes of CO\textsubscript{2} conversion, chemical fixation by photocatalytic conversion of CO\textsubscript{2} into useful fuels has also attracted a lot of attention recently.
1.2 Scope and Objectives

Photocatalytic reduction of CO$_2$ has the potential to make this process more economically feasible and CO$_2$ emission negative as the energy input could be provided by the sun. Photocatalysts are able to utilise energy from photons to overcome the thermodynamic barriers required for CO$_2$ conversion [16].

The combination of CO$_2$ capture and conversion processes using a bifunctional absorbent-photocatalyst material, could streamline the CCUS process by eliminating the need for desorption, transport and sequestration stages. This is a new field which requires significant development of materials for improved CO$_2$ capture and conversion properties before large scale applications.

### 1.2 Scope and Objectives

The overall objective of this project was the development and investigation of bifunctional materials for combined CO$_2$ adsorption and photocatalytic conversion of CO$_2$.

The scope of the project was to: design and synthesise bifunctional adsorbent-photocatalystic materials capable of CO$_2$ adsorption and photocatalytic CO$_2$ reduction; characterise these materials extensively to investigate their properties; design and assemble a photoreactor system for evaluation of the photocatalytic activity; evaluate the material CO$_2$ adsorption capacity and photocatalytic CO$_2$ reduction; investigate the photocatalytic CO$_2$ reduction reaction further by studying light absorption and charge dynamics, to understand the factors controlling CO$_2$ reduction; use these findings to further develop improved photocatalysts.
The research objectives of the project were:

- **RO 1**: To design and synthesise bifunctional photocatalysts for improved CO₂ adsorption capacity and photocatalytic reduction of CO₂ and investigate their morphology, textural properties and light utilization properties.

- **RO 2**: To investigate the photocatalysts robustness and recyclability for photocatalytic CO₂ reduction.

### 1.3 Thesis Outline

- **Chapter 1** provides the background and motivations of the project, the overall objective and scope of the project, and the project research objectives.

- **Chapter 2** presents the theory and a literature review of research for CO₂ adsorption and photocatalytic CO₂ reduction. It provides the basis of selection of the type of materials investigated in this project, and also the basis of selection of the photoreactor system which was to be built.

- **Chapter 3** describes the synthesis methods used for material synthesis, characterisation techniques employed and how they work, and the photocatalytic testing method developed for evaluation of photocatalytic CO₂ reduction rates.

- **Chapter 4** presents a study of TiO₂/CNNS composite materials which were synthesised, characterised, and evaluated for CO₂ adsorption and photocatalytic reduction. The composites exhibit enhanced adsorption and photocatalytic properties which was attributed to increased surface area and the formation of a heterojunction and the control of TiO₂ facet formation.

- **Chapter 5** is an investigation of TiO₂/MOF nanocomposites. The MOF component was selected to provide increased CO₂ adsorption capacity compared to CNNS used in
Chapter 4. The composites showed improved CO$_2$ adsorption capacity and photocatalytic activity compared to TiO$_2$. A study of the charge generation dynamics shows that the improved activity was attributed charge transfer between the two components.

- Chapter 6 is a further study of TiO$_2$/MOF nanocomposites with a focus on the control of the TiO$_2$ morphology and phase and their impact on CO$_2$ adsorption and CO$_2$ conversion. These materials showed a further improvement in photocatalytic CO$_2$ conversion rates.

- Chapter 7 presents a summary of the conclusions of the project and a discussion on potential future work.

1.4 References

Chapter 2  Literature Review
2.1 Overview

In this chapter a literature review of studies and an overview of the key theories covering CO\(_2\) adsorption and photocatalytic CO\(_2\) reduction are presented. The materials reviewed in detail for application in this project were TiO\(_2\), carbon nitride and metal organic frameworks. In addition, a review of photoreactor design was carried out and used to design the photoreactor system which was to be built. From the metal organic frameworks (MOFs) sections of this chapter ref [1] was prepared.

2.1 Introduction

To achieve the project objectives, it was firstly important to understand the fundamental theories of CO\(_2\) adsorption and photocatalytic CO\(_2\) reduction. Then a review of materials used for CO\(_2\) adsorption and photocatalysis was undertaken to learn from advances made and to use these to design new improved photocatalysts. CO\(_2\) adsorbents materials were reviewed with a focus on carbon nitride (CN) and metal-organic frameworks (MOFs) materials. Carbon nitrides (C\(_3\)N\(_4\)) are polymeric materials, MOFs are crystalline and porous materials, produced via the self-assembly of metal ions and organic ligands via coordination bonds. MOFs microporous structure can result in very high specific surface areas (in the order of several thousands m\(^2\)/g) which is beneficial for gas adsorption such as CO\(_2\) adsorption.

The review of photocatalysts started with TiO\(_2\), the first material demonstrated for photocatalytic CO\(_2\) reduction in 1979 [2]. A focus is then made on materials with higher CO\(_2\) adsorption capacity, carbon nitride and MOFs, as these represent new exciting prospects for photocatalytic reduction of CO\(_2\) [3]. A particularly attractive feature of MOFs for CO\(_2\) photocatalytic reduction is their high porosity, which potentially enables an enhanced
2.2 Carbon dioxide adsorption theory

concentration of CO₂ at the reactive sites. Since first demonstration for photocatalytic CO₂ reduction, MOFs have since inspired notable research [1].

This chapter provides an overview of research achievements and trends in materials for CO₂ adsorption and photocatalytic CO₂ reduction, and inspired the materials synthesised and studied in this thesis. A review of photoreactors used for CO₂ reduction was also carried out to understand the types of reactors employed and their advantages and disadvantages for improved performance. This was basis of selection of the photoreactor system which had to be design and built for this project – described in detail in Chapter 3, Section 3.3.

2.2 Carbon dioxide adsorption theory

Adsorption is defined as an increase of fluid concentration at an interface due to surface forces [4]. This takes place whenever a solid surface is in contact with a fluid, in some scenarios a significant and selective concentration increase occurs; the process therefore becomes dependent on the interfacial surface area. To this end, industrial adsorbents with high surface areas have been developed from highly porous or fine particle size materials. Adsorbents have been utilised on an industrial scale as desiccants, catalyst or catalyst supports, gas storage and/or separation, liquid purification, drug delivery, pollution control and respiratory protection. [5]

Adsorption has been used for millennia since the Egyptians, Greeks and Romans used it in applications such as water desalination or treatment of diseases. Quantification of the process was first reported in the late 17th century for the gas adsorption in charcoal. The first isotherms were recorded for various soils by Van Bemmelen in 1881 [5]. The first mathematical equation to explain isothermal adsorption was proposed by Freundlich in 1906 [6]. Langmuir discovered that adsorption typically starts with initial monolayer formation, the extent of the monolayer
2.2 Carbon dioxide adsorption theory

capacity can be inferred from the Langmuir equation [7-9]. The development of Brunauer-Emmett-Teller (BET) theory pinpointed where monolayer formation is complete and multilayer adsorption begins; the surface area can be estimated from the monolayer capacity [10]. BET theory has since become the standard method for surface area estimation of fine and porous materials [11].

Adsorbents have been developed for industrial scale applications since the 1950s, examples of these are activated carbons, aluminas, and silica gel. Adsorbents have since been developed with well-defined intra-crystalline structures examples of these are zeolites, aluminophosphates, and metal-organic frameworks [5].

Porous materials can be classified by their pore width (International Union of Pure and Applied Chemistry (IUPAC)): micropores (<2 nm), mesopores (2-50 nm), and macropores (>50 nm) [11].

The terms adsorption and desorption indicate the direction from which equilibrium was approached: in the former the substance is captured at the surface, in the latter the substance is released from the surface. The relationship between quantity adsorbed and equilibrium pressure (at constant temperature) is the adsorption isotherm. Adsorption hysteresis can occur when the desorption isotherm does not match the adsorption isotherm due to capillary condensation [12]. Surface area is typically defined as the experimentally accessible surface area per unit mass. Adsorption can arise from two types of surface interactions: physisorption (physical adsorption) from condensations of vapours and deviations from the ideal gas law; and chemisorption (chemical adsorption) from formation of chemical bonds at surface reactive sites. [5] Gas adsorption isotherms are classified based on various characteristic shapes by IUPAC [11] (based on Brunauer-Deming-Deming-Teller (BDDT) classification [13]) with
further additions by Rouquerol et al. [5]. These give an indication on the pore network and structure.

2.3 Carbon dioxide adsorbent materials

2.3.1 Background

One of the principle applications proposed for CO₂ capture on a large scale are on in coal- and gas-fired power plants emission flues - the typical compositions of these flues are presented in Table 2-1. Key considerations for these applications are: selectivity of sorption towards CO₂, for high levels of capture and ease of sequestration of high purity CO₂; sorption strength, CO₂ adsorbed too strongly will induce a large energy penalty for desorption, whereas weakly bound CO₂ would be of low selectivity resulting in a large adsorption bed; and high thermal and chemical stability, to ensure an economical adsorbent lifetime [14]. Solid sorbents offer an attractive alternative to aqueous absorbents due to their lower heat capacity and thus lower energy requirements for CO₂ capture. The milder conditions solid sorbents operate within also provides the opportunity for the process to be combined with gas-solid photocatalytic CO₂ reduction [15]. To this end, the development of potentially industrially deployable sorbents to achieve this has covered various materials: zeolites, activated carbons, carbon nitrides, and MOFs which are discussed below [16].

<table>
<thead>
<tr>
<th>Component</th>
<th>Coal*</th>
<th>Natural Gas*</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>75-80</td>
<td>74-80</td>
</tr>
<tr>
<td>CO₂</td>
<td>12-15</td>
<td>3-5</td>
</tr>
<tr>
<td>H₂O</td>
<td>5-7</td>
<td>7-10</td>
</tr>
<tr>
<td>O₂</td>
<td>3-4</td>
<td>12-15</td>
</tr>
<tr>
<td>SO₂, NOₓ, Hg/As particulates</td>
<td>&lt;1800 ppm</td>
<td>&lt;50 ppm</td>
</tr>
</tbody>
</table>

*composition stated as vol% unless specified otherwise
2.3.2 Zeolites

Zeolites are highly porous aluminosilicate materials with higher chemical and thermal stabilities than alkanoamine solutions, various zeolites have been synthesised to utilise this robustness [16]. At pilot plant scale they have been demonstrated to readily adsorb CO$_2$ in a vacuum swing adsorption process [18]. However, zeolites are typically plagued by a high affinity to water which selectively saturates all pores, leading to a poor levels of CO$_2$ adsorption; this would also be a problem for applications in photocatalytic CO$_2$ reduction using water as a reducing agent. The large CO$_2$ adsorption enthalpy also requires a reasonably high desorption temperature [16].

2.3.3 Activated carbons

Activated carbons (AC) are amorphous carbon-based materials synthesised from the pyrolysis and activation of a carbon-containing precursor. A wide variety of these have been studied as potential CO$_2$ adsorbents such as commercial AC [19], sugars [20], graphite-oxide and its derivatives [21-23], resins [24], and mesoporous carbon [25]. Variation of the pyrolysis temperature and reagents can alter the pore network and surface chemistry. The uniform surface electric potential on ACs results in lower adsorption enthalpies and lower CO$_2$ adsorption capacity than alkanoamine solutions. Improvements to this have been made by nitrogen doping and incorporation of amine groups to increase CO$_2$ affinity and by increasing surface area [16, 26, 27].

2.3.4 Carbon nitride

Carbon nitrides (C$_3$N$_4$) are polymeric materials used for various materials applications [28-31], including CO$_2$ adsorption [32-34], with first derivative synthesised in 1834 [35]. They are promising candidates for CO$_2$ adsorption due to their structural and chemical tuneability,
chemical stability, thermal stability, hardness and semiconductor properties [36]. The theoretical prediction of the $\beta$-C$_3$N$_4$ phase indicated it should be as hard and compressible as diamond [37]. The most stable phase of carbon at ambient conditions is graphitic carbon nitride (g-C$_3$N$_4$), over the past 180 years extensive research has produced various C$_3$N$_4$ derivatives [35]. g-C$_3$N$_4$ is typically synthesised by thermal polycondensation of organic monomers, such as melem and melamine, to form stacked layers of g-C$_3$N$_4$ [28]. Of the triazine and tri-s-triazine allotropes, the latter has been found to be more stable by density-functional theory (DFT) [38]. Stoichiometric carbon nitride would consist only of C-N bonds. In practice, synthesised carbon nitrides deviate from this, incorporating hydrogen which can result in primary and secondary amine groups. Carbon nitrides with alternate stoichiometry (i.e. C$_3$N) maintain the graphitic structure with chemical and thermal stability [36]. Increased surface area and CO$_2$ adsorption capacity can also be achieved by synthesising mesoporous carbon nitride (CN) materials, which can have a lot of NH$_2$ groups on the surface, these can be synthesised by polymerisation reaction. The continued development of carbon nitride materials with improved CO$_2$ adsorption should also lead to improved activation for photocatalytic CO$_2$ conversion [39].

2.3.5 Metal-organic frameworks

Coordination polymers (CPs) are solid materials formed by a network of metal ions or metal clusters linked by polydentate organic molecules, these were first synthesised in the late 1950s [40]. Metal-organic frameworks (MOFs) are subset group of CPs which are crystalline and porous, and assembled with strong metal-ligand coordination bonds. The combination of these three properties are unique to MOFs; consequently, research into developing new MOFs to exploit these attributes has resulted in a highly specialised class of materials. The strength of metal-coordination bond leads to an additional classification of CPs first-, second-, and third-generation polymers based on their response after evacuation of solvent from the pores.
First-generation polymers have a porous network that collapses following the removal of guest molecules; second-generation polymers have a porous network that is more robust leading to high levels of porosity; third-generation polymers have a porous network that is variable depending on external factors – this results in “breathing materials” [41]. As permanent porosity is usually preferred to provide high surface area the second- and third-generation CPs are desirable for use as adsorbents and photocatalysts, and only these generation materials have been applied in this area [42]. Zeolitic imidazolate frameworks (ZIFs) are a subset of MOFs comprised of tetrahedral transition metal ions bonded to imidazolate ligands [43]. Examples of applications of MOFs outside catalysis and adsorption are in drug delivery [44], sensors [45], gas storage, and separation [46-48].

For CO\textsubscript{2} adsorption MOFs are particularly promising due to: very high porosity and adsorption capacity; separation capabilities superior to zeolites or AC; relatively high chemical and thermal stability; low heat capacity; a fully tunable and ordered structure which can be designed from bottom up synthesis and altered by post synthesis modifications [16, 49-51]. Like the other adsorbents reviewed, MOFs have been studied as potential CO\textsubscript{2} adsorbents for both pre- and post-combustion capture by pressure/vacuum swing adsorption (PSA/VSA) and temperature swing adsorption (TSA) respectively [16].

CO\textsubscript{2} adsorption selectivity over other species can be achieved by either: size-based selectivity, where the MOF pore diameter restricts adsorption to molecules below a certain kinetic diameter; and adsorptive selectivity, thermodynamically separation driven by affinity differences or chemical interactions of functional groups towards each gaseous component. For CO\textsubscript{2}/N\textsubscript{2} separation (the most important for post-combustion CO\textsubscript{2} capture), the former would require very narrow pores which are typically not present in MOFs with high CO\textsubscript{2} adsorption capacity. Hence research is currently focused on adsorptive routes by modification of surface
chemistry. This can be enhanced by promoting affinity driven physisorption routes (i.e. altering polarizability) leading to high adsorption enthalpies. Or by functional groups which can be introduced to target CO₂ through chemical interactions. [16]

Instead, selectivity of single components of a gas mixture can be predicted using ideal adsorbed solution theory (IAST) – i.e. a CO₂/N₂ selectivity of PMOF-55 of ≈25% (largely independent of pressure or P_{CO₂}) was found by Hu et al. [52]. Or measurement of the adsorption selectivity for gas mixtures can be inferred from breakthrough experiments. In this setup at CO₂/N₂ mixture is passed through the adsorbent bed and the outlet composition is monitored. Separation efficacy can be gauged from extent separation and time to breakthrough. [16]

CO₂ adsorption of MOFs at near ambient temperature and pressure has been found to be controlled by surface chemistry; those with high affinity functional groups have the highest capacity up to around 27%wt. The adsorption capacity at low CO₂ partial pressures (P_{CO₂}≈0.15 bar) are of particular importance for post-combustion capture from flue gas [16]. Diamine-MOFs have been shown to adsorb CO₂ in a near ideal “step-shaped” fashion; this allowed large amounts of CO₂ to be adsorbed/desorbed over a narrow temperature or pressure range [50, 53]. Significant research has been undertaken in recent years for the development of MOFs with improved CO₂ capture performance, with efforts been made to evaluate MOFs for industrial applications [16].

2.4 Photocatalytic carbon dioxide reduction theory

A photocatalyst is a material capable of facilitating photo-induced molecular transformations or reactions. Photons are absorbed and photoexcite the material which results in electron and/or energy transfer, the subsequent deexcitation processes can proceed via chemical reactions [54]. Upon photoexcitation, the light absorber is elevated to a photoexcited state with photogenerated
electron/hole pairs. These electrons are capable of catalysing reduction reactions (such as CO\textsubscript{2} reduction) – holes are capable of catalysing oxidation reactions. As carbon dioxide is the most oxidised state of carbon, non-polar, and a very stable molecule thermodynamically, both enthalpy and entropy changes for conversion to other higher value chemicals are unfavourable. Photocatalysts are able to utilise energy from photons to generate photoexcited electrons which can catalytically convert CO\textsubscript{2} and overcome these thermodynamic barriers [55].

Semiconductors are the most extensively researched material as photocatalysts since first demonstrated in 1979 for CO\textsubscript{2} reduction [2]. They are suitable as they do not have a continuum of electronic states and have a void energy region known as the bandgap. This is the potential difference from the top of occupied valance band (VB) to the bottom of the vacant conduction band (CB). Photoexcitation by absorbed photons with energy equal to or greater than the bandgap generates an electron-hole pair, with the electron and hole in CB and VB respectively. The lifetime of the electron-hole pair should be long enough to transfer charge to adsorbed species by reduction (donation of electrons) or oxidation (hole migration). Electron-hole recombination is a process which leads to a decrease in electrons available for CO\textsubscript{2} reduction and therefore reduces catalytic activity. This occurs \textit{via} various routes within the bulk material or on the surface [54].

The position of the band-edge potentials dictate whether or not a semiconductor can transfer electrons/holes to adsorbed species. The CB must be more negative than the reduction reaction redox potentials; similarly, the VB must be more positive than oxidation reaction redox potentials [54]. Table 2-2 lists reaction potentials for possible CO\textsubscript{2} reduction transformations. Of importance is that proton reduction is a competing undesirable reaction and the large reduction potential of -1.90 eV required for single electron CO\textsubscript{2} reduction. Most commonly
used photocatalysts (i.e. metal oxides) have less negative CB than -1.90 V so reduction must proceed via multi-electron transfer reactions.

Table 2-2. CO$_2$ reduction reactions along with the corresponding redox potential [56].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Redox potential (V)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ + e$^-$ → CO$_2^-$</td>
<td>-1.90</td>
</tr>
<tr>
<td>CO$_2$ + 2H$^+$ + 2e$^-$ → HCO$_2$</td>
<td>-0.49</td>
</tr>
<tr>
<td>CO$_2$ + 2H$^+$ + 2e$^-$ → CO + H$_2$O</td>
<td>-0.53</td>
</tr>
<tr>
<td>CO$_2$ + 4H$^+$ + 4e$^-$ → HCHO + H$_2$O</td>
<td>-0.48</td>
</tr>
<tr>
<td>CO$_2$ + 6H$^+$ + 6e$^-$ → CH$_3$OH + H$_2$O</td>
<td>-0.38</td>
</tr>
<tr>
<td>CO$_2$ + 8H$^+$ + 8e$^-$ → CH$_4$ + 2H$_2$O</td>
<td>-0.24</td>
</tr>
<tr>
<td>2H$_2$O → O$_2$ + 4H$^+$ + 4e$^-$</td>
<td>+0.82</td>
</tr>
<tr>
<td>2H$^+$ + 2e$^-$ → H$_2$</td>
<td>-0.41</td>
</tr>
</tbody>
</table>

*vs NHE at pH 7

2.5 Photocatalytic carbon dioxide reduction materials

2.5.1 Background

As mentioned above, photocatalytic CO$_2$ reduction was first demonstrated by Inoue et al. [2] with semiconductors in aqueous suspensions, in this study methanol evolution was only detected for semiconductors with a CB more negative than the H$_2$CO$_3$/CH$_3$OH redox potential. Since then a vast range of materials have been investigated for CO$_2$ reduction: oxides (e.g. TiO$_2$, ZnO$_2$, SnO$_2$), non-oxides (e.g. CdS, GaN, SiC) [57], and carbon based materials (e.g. graphene, carbon nitride and carbon nanotubes) [28-30], zeolites [31], and MOFs [20]. Large band-gap semiconductors such as metal oxides are capable of CO$_2$ reduction due to their favourable redox potentials. These are also readily available, cheap, strong, and non-toxic [58]. However, this band-gap restricts photoexcitation to the UV range. Accordingly, synthesis of materials with a narrower band-gap that can reduce CO$_2$ from visible-light range is highly desirable [59]. Of the solar radiation on the Earth’s surface only around 5% is in the UV region (43% visible, 52% infrared) [60].
The suppression of charge recombination by facilitation of charge separation is an important aspect to consider for improved photocatalytic activity [61]. The use of a co-catalyst forming a heterojunction between two compatible materials can widen the light absorption spectra and facilitate interfacial charge transfer; this results in more photoelectrons and has been investigated for semiconductor photocatalysts [62]. Other challenges for CO$_2$ photoreduction to address are low conversion rates/quantum efficiency, and low catalyst stability when exposed to other gases commonly present in flue gas (i.e. O$_2$) [63, 64].

Various methods have been undertaken to improve the abundance of electrons by either design of materials which generate more electrons or have suppressed charge recombination. Increased charge generation can be achieved by higher light utilisation either by material design or introduction of a photosensitiser. To decrease charge recombination modifications such as composite formation, metal exchange, and metal doping have been investigated. This can result in the light absorber and the active site being located on different molecules leading to charge transfer via a heterojunction [54, 63]. As current CO$_2$ photocatalytic reduction studies typically have very low conversion rates common problems noted include: 1) poor overlay of semiconductor adsorption and solar spectrums, 2) poor charge carrier separation, 3) mass transfer limitations arising from low CO$_2$ solubility in water if liquid phase reaction is used, 4) reversible reactions involved in CO$_2$ reduction, 5) competing reaction of water reduction to hydrogen [65].

Below is a review of the materials investigated in this project starting with TiO$_2$, a widely studied photocatalyst. Then, more recently applied materials for photocatalytic reduction are reviewed: carbon nitride and metal organic frameworks (MOFs). These latter two materials were reviewed in detail primarily due their CO$_2$ adsorption ability. This review combined with
the review of CO₂ adsorbents inspired the design of materials synthesised and studied in Chapters 4-6.

2.5.2 Titanium dioxide

Titanium dioxide (TiO₂) is the most widely investigated photocatalyst (particularly for CO₂ conversion) due to its high stability, low cost, and non-toxic nature [66-68]. It is a semiconductor, typically n type with oxygen deficiencies [69] - its photocatalytic origins are in dye bleaching in the late 1930s [70], and it was first demonstrated for CO₂ reduction in 1979 [2]. Improvements have been made as TiO₂ typically has very low photocatalytic efficiencies for CO₂ reduction due to high electron-hole recombination rates [71]. TiO₂ also has a large bandgap (2.8-3.2 eV) resulting in only around 5% of solar irradiation able to be absorbed [72]. Studies using TiO₂ photocatalysts have therefore made efforts to increase TiO₂ catalytic activity, publications have increased exponentially in the last decade [66]. It remains a benchmark material for photocatalytic reduction [73].

The most common polymorphs of TiO₂ are anatase, rutile, and brookite; the rutile phase is the most thermodynamically stable, anatase/brookite phase TiO₂ can be converted to rutile phase by calcining above 600 °C [72]. Of these phases, the anatase phase has typically been found to be the most active for photocatalysis [74, 75]; this is despite having a larger bandgap than rutile phase (anatase3.2 eV, rutile 3.0 eV). The anatase phase has been found to have high surface reactivity, lower charge recombination, and higher CO₂ adsorption [75].

Mixed phased TiO₂ materials have been prepared to facilitate interfacial charge transfer via a heterojunction. Control of the anatase/rutile phase composition can lead to a catalyst more active than pure phase TiO₂ [76-78]. A commercially available mixed phase TiO₂ material is P25 manufactured by Degussa (Evonik), it is around 70:30 anatase:rutile composition and
shows high photocatalytic activity for various applications [79]. The wide availability and cheap cost of P25 TiO$_2$ allows it to be used as a standard catalyst for comparisons between research groups [76, 79]. The morphology of TiO$_2$ can also be altered to improve photocatalytic activity; for example, rutile nanorods coated in anatase nanoparticles synthesised by Kandiel et al. [80] were more active than rutile nanoparticles coated with anatase nanoparticles. Other morphologies of TiO$_2$ fabricated include nanotubes [81, 82], nanosheets [83], nanofibers [84], and thin films [85].

Recent research has been on the anatase phase for the development of more active catalyst [74, 86, 87]. Control of the exposed TiO$_2$ facets to synthesise TiO$_2$ with increased surface reactivity has resulted in improved photocatalytic activity [66]. Without intervention, anatase TiO$_2$ facets with high surface energy, such as \{001\} will be minimised during crystal growth; anatase facet surface energies have been reported to be in the following order: \{001\} (least stable) > \{101\} > \{100\} > \{110\} > \{111\} (most stable) [88]. The addition of surface adsorbates can lower the surface energy of these facets, allowing TiO$_2$ with dominant \{001\} [89] and \{100\} [90] facets exposed. Compared to \{101\}, the \{001\} and \{100\} surfaces have double the quantity of five-coordinated Ti atoms [91], which can act as photocatalytic sites [92]. The \{001\} facet has been found to have a high density of undercoordinated Ti atoms and increased Ti-O-Ti bond angles, both of which enhance catalytic activity [93]. Efforts in photocatalysis have been made by various routes to synthesise TiO$_2$ with \{001\} facets exposed. By controlling the exposed facets charge separation can be enhanced between \{001\} and \{101\} via formation of a surface heterojunction [87, 94-96].

Improvements in TiO$_2$ photocatalytic performance by other modifications have targeted enhanced light absorption, greater charge separation and lifetime, CO$_2$ reduction selectivity, and CO$_2$ adsorption capacity. These have been made by methods such as impurity doping,
metal deposition, and forming composites with carbon-based materials [97]. Impurity doping can lower the bandgap to increase light utilisation [98]. Doping can be performed by routes such as sol-gel method [99], hydrothermal [100], and self assembly [101]. Impurity doping can also reduce the particle size which can be beneficial for catalytic activity [97].

Deposition of metals on TiO$_2$ has been widely carried out primarily to reduce electron-hole recombination by facilitating electron transfer from TiO$_2$ to the metal nanoparticles, resulting in spatial separation of the electrons and holes [97]. Various metals have been deposited on TiO$_2$ such as Pd [102], Pt [82], Au [103], and Pd [104]. These depositions are carried out by methods such as photochemical deposition, and chemical reduction. Of course, the cost of these rare metals is a disadvantage for large scale applications of these materials.

Coupling TiO$_2$ with carbon based materials has been explored as these are abundant, inexpensive, can be high surface area, highly conductive, tuneable, and high chemical stability [97]. For example, composites with carbon nanosheets and graphene nanosheets have exhibited superior photocatalytic activity owing to increased charge mobility [105, 106]. Carbon nitride and carbon nitride nanosheet TiO$_2$ composites are reviewed in greater detail in Sections 2.5.3.

2.5.3 Carbon nitride

Carbon nitride, a polymeric semiconductor and CO$_2$ adsorbent (reviewed Section 2.3.4), has also been investigated as a photocatalyst recently with the first studies in water splitting [107-109] and organic reactions [110]. Graphitic carbon nitride (g-C$_3$N$_4$) is most commonly used as it is the most stable phase and has narrower bandgap than TiO$_2$ [28]. Many of the properties advantageous for CO$_2$ adsorption are also beneficial as a photocatalyst such as being metal-free, and chemically and thermally stable. As a photocatalyst for CO$_2$ reduction it is promising over metallic semiconductors because it absorbs light from UV into the visible
2.5 Photocatalytic carbon dioxide reduction materials

region, up to around 420 nm [35, 111]. The surface area of g-C₃N₄ synthesised by polycondensation can be low, which would limit active site exposure and access [107]. As with approaches to increase CO₂ adsorption through increased surface, similar efforts have improved photocatalytic activity. The addition of an iron complex increased light absorption up to 650 nm [110].

The difficulty of photocatalytically reducing CO₂ compared to water splitting using g-C₃N₄ requires the development of new CN-based materials, as pure g-C₃N₄ typically does not reduce CO₂ readily to any great extent due to fast electron-hole pair recombination [112]. Modifications by for example, deposition of Pt as a cocatalyst on g-C₃N₄ increased catalytic activity by facilitating charge transfer from g-C₃N₄ to Pt [113].

The formation of composite materials with g-C₃N₄ to form a heterojunction has also been shown to greatly increase catalytic activity by improved charge transfer and separation; materials investigated include NaNbO₃/g-C₃N₄ [62], Ag₃PO₄/g-C₃N₄ [114], RuP/g-C₃N₄ [115], and ZnO/g-C₃N₄ [116]. By coupling CN with TiO₂ for photocatalytic CO₂ reduction, the formation of a TiO₂/g-C₃N₄ heterostructure yields a more active composite material [117-120]. These TiO₂/g-C₃N₄ studies have shown the catalytic performance can be attributed to: adjustment and optimisation of the composite ratio, the heterostructure facilitation of interfacial charge transfer, improved light utilisation and lower bandgap, increased surface area, and the crystallite size.

Bulk graphitic carbon nitride (g-C₃N₄) can be exfoliated to form two-dimensional carbon nitride nanosheets (CNNS); this is readily achievable because bulk g-C₃N₄ layers are bonded by weak van der Waals forces [121]. This can be performed by continuous sonication in water [122] or in other solvents [123]. CNNS can also be synthesised from g-C₃N₄ by post-thermal
oxidation etching [124] and assembled via bottom-up routes [125, 126]. Compared to g-C₃N₄, CNNS has advantages for applications in photocatalysis: the higher surface area allows increased light absorption and mass transfer efficiencies, the nanosheet thickness provides a shorter distance for bulk to surface charge migration and encourages charge transfer in the in-plane direction which both lower charge recombination [121]. Wang et al. [127] synthesised CNNS by “carbothermal activation” of g-C₃N₄ – activation in static air at 550°C. Compared to g-C₃N₄ the CNNS had 5 times higher CO₂ adsorption capacity and 12.5 times higher photocatalytic activity for CO₂ conversion (CO evolution 229 µmol g⁻¹ and CH₄ evolution 112 µmol g⁻¹). These were attributed to the higher surface area and reduced photogenerated charge recombination. Pd as a cocatalyst was grafted on CNNS by Lang et al. [128] with tetrahedron and icosahedron Pd particles. Both composites had increased CO₂ reduction to CO and CH₄, with the icosahedron Pd composite the most active (CO evolution 12 µmol g⁻¹ h⁻¹ and CH₄ evolution 1 µmol g⁻¹ h⁻¹). This showed that control of the catalyst particle shape can lead to a further enhancement of heterojunction charge transfer. CNNS were prepared by exfoliation in a NH₃ atmosphere to NH₃ functionalise the nanosheets for higher CO₂ adsorption [129]. For CO₂ photoreduction the CNNS compared to g-C₃N₄ were 10 and 5 times more active for CH₄ (1.39 µmol g⁻¹ h⁻¹) and CH₃OH (1.87 µmol g⁻¹ h⁻¹) production respectively. Time-resolved PL showed the nanosheets had improved charge separation resulting in longer charge lifetimes.

2.5.4 Metal-organic frameworks

2.5.4.1 Background

MOFs have been studied as photocatalysts since the early 1990’s where a MOF was used for cyanosilylation of aldehydes [130]. The catalytic site in a MOF can reside in the metallic component, organic component or within the pore cavity. Some MOFs are catalytically active as-synthesised, or it is necessary to tailor the MOF to introduce or improve catalytic activity
2.5 Photocatalytic carbon dioxide reduction materials

[131]. The following sections give an overview of catalytic routes in MOFs and reviews papers using MOFs for photocatalytic reduction of CO$_2$. The papers are reviewed by the route the catalyst was designed for improved catalytic activity. A schematic of these different types of materials are shown in Figure 2-1, with a) MOFs that were studied without any synthesis modifications, b) MOFs whose ligands were functionalized, c) MOFs modified via metal exchange and d) MOF-based composites.

![Figure 2-1. MOF-based materials: a) unmodified MOF, b) MOF with ligand functionalisation, c) MOF subjected to metal ion exchange, d) MOF-based composites.](image)

2.5.4.2 **Mechanisms of CO$_2$ photocatalytic reduction using MOF-based materials**

Figure 2-2 below summarises the various routes that have been engineered to facilitate and/or enhance CO$_2$ reduction using MOF-based materials. Most frequently MOFs are catalytic active through either direct (Figure 2-2a, pathway 1) or indirect excitation of the metal cluster (Figure 2-2a, pathway 2). In both instances the metal cluster excited state reduces CO$_2$. For direct excitation, this is generated by metal cluster light excitation by photons of sufficient energy. The metal cluster excited state by indirect excitation is generated by excitation of
another moiety and then subsequent electron transfer to the metal cluster. The effectiveness of indirect excitation can be improved by ligand functionalisation (Figure 2-2b, pathway 3) to broaden the light absorption spectra into longer wavelengths. This results in higher generation of excitation states of the ligand which leads to more electron transfer to the metal cluster where CO$_2$ reduction can take place. The ligand itself can also be intrinsically active or functionalised (Figure 2-2c, pathway 4) to add another CO$_2$ reduction pathway. Post-synthesis metal substitution of the metal cluster has been found to increase catalytic activity; this increases charge separation, as electron transfer occurs between each metal in the metal cluster, leading to more excited states (Figure 2-2c, pathway 4). Similarly, the addition of a co-catalyst to the photochemical system or formation of a composite material (Figure 2-2c, pathways 6) can also increase catalytic activity via cooperative charge separation between each component.

Figure 2-2. MOF photocatalytic reduction of CO$_2$ reaction pathways (numbered 1-6) for the various types of MOF-based materials: a) unmodified MOF, b) MOF with ligand functionalisation, c) MOF subjected to metal ion exchange, d) MOF-based composites.
2.5 Photocatalytic carbon dioxide reduction materials

2.5.4.3 Unmodified MOFs

A number of unmodified MOFs have been reported to be photocatalytically active for CO₂ reduction. Among them, a zirconium MOF (NNU-28) was studied by Chen et al. [132], which, photocatalytically reduced CO₂ into HCOO⁻ (183.3 µmol h⁻¹ mmol⁻¹ MOF⁻¹) under visible light (with TEOA as a sacrificial agent in H₂O). Electron paramagnetic resonance (EPR) showed dual catalytic pathways for this MOF: by direct excitation of the ligand (4,4′-(anthracene-9,10-diylbis(ethyne-2,1-diyl))dibenoic acid), and by ligand to metal charge transfer (LMCT) to the metal cluster. These two catalytic routes were speculated to have led to the catalytic performance of this MOF.

A zirconium based porphyrin (PCN-222) was tested to investigate charge transfer and the role of CO₂ adsorption for photocatalytic reduction of CO₂ [133]. High and selective CO₂ adsorption over N₂ and UV-vis light absorption was observed. Photocatalytically, under visible illumination with TEOA in MeOH, PCN-222 produced HCOO⁻ at a high rate (3 µmol h⁻¹) compared to other MOF photocatalysts. EPR showed that upon illumination Zr⁺ ions were formed, with the charge originating from light absorption from the ligand, showing this MOF had improved electron-hole separation efficiency.

A zinc based porphyrin (Zn/PMOF) reduced CO₂ to CH₄ in a gas phase reactor in the presence of H₂O under UV/visible light [134]. In comparison to ZnO, Zn/PMOF evolved 80 % more CH₄ (8.7 µmol g⁻¹ h⁻¹). Action spectra showed highest activity with highest incident radiation energy (440-500 nm) - activity decreased with decreasing incident energy. Zn/PMOF was observed to deactivate after 4 h due to build up of CH₃OH adsorbed on the surface, so a regeneration step would be required.
Wang et al. [135] investigated three iron based MOFs (MIL-101/53/88B(Fe)) which were photocatalytically active under visible light. For all MOFs tested HCOO\(^-\) was the sole product, MIL-101(Fe) evolved the most (5.9 µmol h\(^{-1}\)). All MOFs had similar absorption spectra and band gap; hence another factor must be driving the improved CO\(_2\) reduction for MIL-101(Fe). EPR analysis confirmed the Fe cluster to be photocatalytically active for all MOFs - light excitation induced charge transfer from O\(^{2-}\) to Fe\(^{3+}\), reducing it to Fe\(^{2+}\), which in turn can reduce CO\(_2\). CO\(_2\) adsorption capacity of MIL-101(Fe) was notably higher than those of MIL-53(Fe) and MIL-88B(Fe). These trends were due to the presence of coordinated unsaturated metal sites for MIL-101(Fe) only.

The MOF morphology has been studied to improve photocatalytic activity. A Ru-based MOF was altered from micro-crystals to nanoflowers [136]. Both morphologies were photocatalytically active for CO\(_2\) reduction to HCOO\(^-\), with TEOA as the sacrificial agent under visible light irradiation. Compared to bulk crystals, the nanoflowers showed 2.5 times higher activity (77.2 µmol g\(^{-1}\)h\(^{-1}\), quantum yield of 0.67% under 475 nm light irradiation). This was attributed to: higher surface area which increased reactant adsorption and exposed catalytic sites, and higher energy-transfer efficiency. Wang et al. [137] synthesised ZIF-67 with different morphologies and tested them for photocatalytic CO\(_2\) reduction with a ruthenium based photosensitiser. Compared to rhombic shape particles, 2D sheets of ZIF-67 had superior CO\(_2\) adsorption capacity and catalytic activity (3890 µmol g\(^{-1}\)h\(^{-1}\)); the latter was explained by TAS and EPR which showed electron transfer from the photosensitiser for the sheet morphology ZIF-67 only. A 2D morphology porphyrin Zn-MOF also showed higher CO\(_2\) adsorption capacity, catalytic activity (11.5 µmol g\(^{-1}\)h\(^{-1}\)), quantum efficiency (0.97% at 435 nm), and selectivity for CO\(_2\) to CO conversion when compared to the bulk material. The improved catalytic ability was attributed to suppressed charge transfer and improved charge lifetime [138].
2.5.4.4 **MOF linker modification**

MOFs structural tunability has resulted in frameworks constructed of numerous organic linkers. These chemical platforms allow various linker modifications to be made to increase photocatalytic performance by addition of functional groups. These were designed in an effort to provide additional reaction pathways or increase light absorption spectra.

2.5.4.4.1 Amine functionalisation

The introduction of amine groups to the organic linker has been carried out due to the basic nature of this group which has been speculated to promote interactions with the acidic CO$_2$ molecules. Fu et al. [139] investigated amine functionalisation of MIL-125(Ti) to reduce CO$_2$ to HCOO$^-$ under visible and UV irradiation. Functionalisation increased CO$_2$ adsorption and was speculated to have led to the higher catalytic activity observed (16.3 µmol g$^{-1}$h$^{-1}$). Their proposed mechanism was that upon photoexcitation, charge separation leads to electron transfer from ligand to the metal-oxo cluster, generating a Ti$^{III}$ ion which then facilitates CO$_2$ transformation to HCOO$^-$.  

Amine functionalisation of UiO-66 to NH$_2$-UiO-66 was also studied by the same research group. As observed with NH$_2$-MIL-125 [139], amine functionalisation of UiO-66 increased CO$_2$ adsorption capacity. Under visible light irradiation, HCOO$^-$ was the sole product formed when using NH$_2$-UiO-66 (26.4 µmol g$^{-1}$h$^{-1}$), while unmodified UiO-66 showed no photocatalytic activity. EPR and photoluminescence analysis indicated photoexcited electron transfer from the organic linker to the Zr-O linker, generating Zr$^{III}$ which catalyses CO$_2$ reduction with TEOA as a hydrogen source. Partial addition of a second NH$_2$ group increased light absorption and resulted in higher CO$_2$ adsorption capacity and further enhancement of catalytic activity. The same impact on absorbance and catalytic activity was also found by Lee et al. for (NH$_2$)$_2$-UiO-66(Zr) [140].
Amine-functionalization has also been carried out for MIL-101/53/88B(Fe)) [135]. Enhanced CO$_2$ adsorption and catalytic activity was observed in each case. The amine group was speculated to provide an additional pathway for conversion acting as a light antenna, the photo-generated electron can then transfer to catalytically active Fe-O center, increasing activity. NH$_2$-MIL-101(Fe) was the most active, evolving 178 µmol HCOO$^-$ in 10 h, with a quantum efficiency of $1.3 \times 10^{-4}$ at 450 nm.

### 2.5.4.4.2 Molecular catalyst addition

In addition to amine functionalisation, another route explored to enhance the photocatalytic activity of MOF is the addition of metallic molecular catalysts. These have been bonded to MOF linkers mostly to promote charge separation. The stability of molecular catalysts can also be improved when anchored to a MOF.

A Re(I)(CO)$_3$(dcbpy)Cl (H$_2$L$_4$) ligand was integrated into UiO-67 by Wang et al. [141] and evaluated for CO$_2$ photoreduction producing CO and H$_2$ under visible irradiation. Prior to the incorporation of the Re-containing moiety, the unmodified UiO-67 was not found to be photocatalytically active. The reaction was therefore deemed to proceed via the Re complex. A CO turn over number (TON) of this composite of 10.9 over 20 h was achieved (compared to a CO TON of 3.5 over 20 h for the homogeneous Re(I)(CO)$_3$(dcbpy)Cl (H$_2$L$_4$) ligand). In addition, decomposition of the Re-containing ligand was also found to be greatly suppressed when attached to the MOF.

A MOF-253 Ru carbonyl MOF complex (MOF-253-Ru(CO)$_2$Cl$_2$) was synthesised by Sun et al. [142] to reduce CO$_2$ to CO, HCOO$^-$ and H$_2$ under visible light irradiation. The Ru complex was selected as both a photocatalyst and a photosensitizer. The light absorption edge of MOF-253 (no photocatalytic activity) was extended from 370 to 470 nm after coordination of
Ru(II) with MOF-253 (moderate catalytic activity), and then further to 630 nm after subsequent photosensitisation of MOF-253-Ru(CO)$_2$Cl$_2$ with Ru(bpy)$_2$Cl$_2$ (highest catalytic activity, 0.67 µmol HCOO$^-$ and 1.86 µmol of CO after 8 h). Homogenous Ru(CO)$_2$Cl$_2$ had low catalytic activity compared to the MOF-253-Ru(CO)$_2$Cl$_2$.

A rhodium molecular catalyst was incorporated into a UiO-67 by post synthesis linker exchange to produce UiO-67 complexes [143]. The catalytic activity of the MOF complex was observed to be similar to the homogenous system and increased with photocatalyst loading to 10 %mol (HCOO$^-$ TON 47 in 16 h). Compared to the homogenous system though, the photocatalyst attached to the MOF was found to retain catalytic activity and stability.

A Mn molecular catalyst has also been grafted onto UiO-67 [144]. Photocatalytic tests aided by a Ru photosensitiser, BNAH (sacrificial reductant), and TEAO (sacrificial agent) evolved HCOO$^-$. Compared to homogenous Mn catalyst and UiO-67, Mn-UiO-67 incorporation increased HCOO$^-$ TON by 57% and 189% respectively, with a quantum yield of 13.8% using 470 nm irradiation. The enhanced activity was accredited to high CO$_2$ adsorption capacity, electron transfer from the photosensitiser, and increased Mn catalyst stability supported by the MOF.

Postsynthetic exchange of UiO-66 has incorporated Cr- and Ga-monocatecholato groups onto the linker [145]. In the presence of MeCN, TEOA and BNAH, CO$_2$ was photoreduced to HCOOH, with Cr-UiO-66 (quantum yield 1.83 ± 0.16% at 450 nm) roughly twice as active as Ga-UiO-66 - unmodified UiO-66 was not active. The catalytic trend was explained by TR-PL, which showed lowest charge recombination and longer lifetime for Cr-UiO-66, indicating charge transfer from the linker to Cr.
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A Re modified ligand was designed by Huang et al. [146] to synthesise a Re-Uio type MOF. CO and H\textsubscript{2} were evolved photocatalytically with TEOA and various solvents as sacrificial agents - CO selectivity was highest with MeCN. PL spectra revealed the reduction proceeded via the Re center with electrons provided from photooxidation of triethanolamine by the photogenerated metal to ligand charge transfer state. The catalyst framework was observed to partially decompose during the process.

2.5.4.4.3 Porphyrin MOF metalation

MOFs built using porphyrin linkers have also been reported for CO\textsubscript{2} reduction. These attracted interest as the porphyrin can be metalated to induce or enhance photocatalytic properties [147]. Copper insertion into MOF ((5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin), TCPP) was investigated by Liu et al. [148] The significance of the Cu\textsuperscript{2+} center was elucidated by a comparison with the MOF without Cu. Despite having 20% lower BET surface area, the Cu-MOF exhibited 80% higher CO\textsubscript{2} adsorption capacity. Importantly, hysteresis observed for the Cu-MOF CO\textsubscript{2} adsorption isotherms was attributed to chemisorption of CO\textsubscript{2} at the Cu sites. The consequent 7-fold increase in photocatalytic activity for CO\textsubscript{2} reduction to methanol (262.6 ppm g\textsuperscript{-1} h\textsuperscript{-1}) using this material was attributed to this interaction.

A porphyrin containing zirconium MOF (MOF-525) was studied for incorporation of Co and Zn [149]. Under visible irradiation with TEOA as a sacrificial agent, photoreduction of CO\textsubscript{2} yielded CO and CH\textsubscript{4} as products. Co-MOF-525 showed highest catalytic activity (CO evolution 200.6 µmol g\textsuperscript{-1} h\textsuperscript{-1} and CH\textsubscript{4} evolution 36.76 µmol g\textsuperscript{-1} h\textsuperscript{-1}) and CO\textsubscript{2} adsorption capacity compared to Zn-MOF-525 and MOF-525. Both metallised MOFs exhibited increased charge separation, particularly the Co-MOF-525 which also showed greatest energy transfer efficiency. This combined with in-situ FTIR showing CO\textsubscript{2}-Co\textsuperscript{II} adsorption for Co-MOF-525, explained the enhanced activity for this MOF.
2.5.4.5 MOF metal ion exchange

Post-synthesis metal exchange of a MOF has been pursued to increase catalytic activity by altering the redox potentials and promoting charge separation. Li and colleagues substituted Ti into NH$_2$-UiO-66(Zr) via post-synthetic exchange to form NH$_2$-UiO(Zr/Ti) [150]. In comparison to NH$_2$-UiO-66(Zr), Ti doping yielded a 70% increase in CO$_2$ reduction to formate (5.8 mmol) and a 22% increase in CO$_2$ adsorption capacity. The increase in catalytic activity was not solely attributed to the larger adsorption capacity; Ti addition was also found to act as an electron transfer mediator. Molecular simulations and EPR indicated electron transfer from Ti$^{3+}$ to Zr$^{4+}$ which promoted electron transfer from the MOF linker to the metal clusters.

Similarly post-synthetic exchange of Ti into NH$_2$-UiO-66(Zr) has also been investigated by Lee et al. [140]. This was carried out for MOFs constructed of mixed terephthalic acid linkers with a single and dual NH$_2$ groups. Evidence of increased charge transfer of photoexcited electrons from the linker to the metal clusters was indicated by photoluminescence spectroscopy— as observed by Sun et al. [150] with EPR.

2.5.4.6 MOF based composites

MOF based composites have been explored primarily to increase photocatalytic activity by formation of a heterojunction to increase charge separation. Additionally, MOFs higher and selective CO$_2$ adsorption capacity could aid this by the increase in reactant concentration at the active sites.

2.5.4.6.1 TiO$_2$ composites

As mentioned previously, TiO$_2$ has been researched extensively as a photocatalyst for CO$_2$ reduction. TiO$_2$/MOF composites have been explored in an effort make further improvements in photocatalytic activity. Li et al. [151] grafted anatase phase TiO$_2$ particles onto HKUST-1
(Cu₃(BTC)₂) microcrystals to create a TiO₂/HKUST-1 composite around 33 %wt TiO₂. The CO₂ adsorption capacity of the material decreased by around a third compared to HKUST-1, indicating the CO₂ capacity of the MOF was not inhibited by the presence of TiO₂. In comparison to TiO₂, CH₄ production from HKUST-1@TiO₂ was around 5 times higher (2.64 μmol g⁻¹ TiO₂ h⁻¹) than TiO₂ (no CO evolution was observed for HKUST-1). Transient absorption spectroscopy revealed electron transfer from TiO₂ CB to the Cu sites on the HKUST-1.

A ternary TiO₂(mixed anatase and rutile phase)/Cu₂O/HKUST-1 composite was investigated by He et al. [152], in this case the MOF was synthesised onto TiO₂/Cu₂O which provided the copper source. For CO₂ photoreduction the composite evolved twice as much CO (144 μmol g⁻¹ h⁻¹) and four times as much CH₄ (132 μmol g⁻¹ h⁻¹) compared to TiO₂ (HKUST-1 showed no activity). The increase in catalytic activity was probed by investigation of the reaction mechanism which showed activation of adsorbed CO₂ on the coordinatively unsaturated HKUST-1 copper sites, with electrons supplied from the Cu₂O and TiO₂ via a heterojunction.

Anatase phase TiO₂ has also been assembled onto CPO-27-Mg. This MOF was selected due to its high CO₂ capacity [153]. Photocatalytic CO₂ reduction was performed under UV illumination in the gas phase in a CO₂ and H₂O atmosphere yielding CO, CH₄ and H₂ as products. The TiO₂/CPO-27-Mg composite (39.3 %wt CPO-27-Mg) showed CO₂ capacity proportional to the MOF content. The CO (40.9 μmol g⁻¹ h⁻¹) and CH₄ (23.5 μmol g⁻¹ h⁻¹) evolutions from the composite was higher than TiO₂ and CPO-27-Mg (which showed no activity). The improved CO₂ conversion was accredited to the CO₂ adsorption capacity and the open alkaline earth metal sites on CPO-27-Mg.
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Co-ZIF-9 has also been coupled with anatase phase TiO$_2$ to form TiO$_2$/Co-ZIF-9 composites of various TiO$_2$ loadings [154]. The TiO$_2$ crystals were deposited directly onto the Co-ZIF-9 sheets via an in-situ growth synthesis. The absorption spectra of the TiO$_2$/Co-ZIF-9 composites was shown to shift from UV (TiO$_2$ absorption) towards visible (Co-ZIF-9 absorption). Photocatalytic reduction of CO$_2$ evolved CO and CH$_4$ as products, the TiO$_2$/Co-ZIF-9 composite with 3% wt Co-ZIF-9 showed highest activity (CO evolution 7.16 µmol g$^{-1}$ h$^{-1}$, CH$_4$ evolution 1.26 µmol g$^{-1}$ h$^{-1}$) - Co-ZIF-9 alone did not show any activity. The synergistic effects of this composite were determined by XPS, revealing the photoreduction proceeds via Co-ZIF-9 aided by electron transfer from TiO$_2$.

TiO$_2$/ZIF-8 composites with various MOF loadings have been synthesised by forming ZIF-8 on a TiO$_2$ film (mixed anatase and rutile phase) [155]. With increased MOF loading the composites had increased CO$_2$ adsorption capacity and decreased charge recombination probed by PL. The composite with intermediate MOF loading had the highest yield of CO (0.53 µmol g$^{-1}$ h$^{-1}$) and CH$_4$ (0.18 µmol g$^{-1}$ h$^{-1}$) evolution when tested in a gas/solid setup with H$_2$O as the electron source. ZIF-8 was also used by Cardoso et al. [156] who grafted ZIF-8 onto Ti/TiO$_2$ nanotubes by a layer-by-layer synthesis. The composite had increased CO$_2$ adsorption, broader light absorption and formed methanol (0.15 mmol L$^{-1}$) and ethanol (2.75 mmol L$^{-1}$) when evaluated for photocatalytic CO$_2$ reduction. A TiO$_2$/UiO-67 composite was synthesised using hydrolysis of a titania precursor in the presence of the MOF [157]. The composite exhibited improved CO$_2$ reduction to HCOOH by a factor of 80 when compared to UiO-67, the authors attributed this increase to the composite having a wider light absorption spectrum.
2.5.4.6.2 Metal deposition

It is well established for semiconductor photocatalysts that the addition of noble metals can lower the band gap and promote charge separation [158], MOFs are also suitable candidates for this. NH2-MIL-125(Ti) noble metal doping has also been investigated with Pt and Au doping [159]. Both metals were found to exist as nanoparticle clusters bonded to the MOF on the amine group on the organic linker. Photocatalytic experiments of these catalysts under visible light irradiation yield both HCOO\(^-\) and H\(_2\). H\(_2\) formation was attributed to the noble metals which are known to act as electron traps; this also indicated that electron transfer from the linker to the metal nanoparticles had occurred. Lower HCOO\(^-\) production compared to H\(_2\) was observed only for Au/NH2-MIL-125(Ti); Pt/NH2-MIL-125(Ti) exhibited higher catalytic activity for HCOO\(^-\) production (32.4 µmol g\(^{-1}\) h\(^{-1}\)) compared to NH2-MIL-125(Ti).

2.5.4.6.3 Other composites

The coupling of carbon nitride (g-C\(_3\)N\(_4\)) with Co-ZIF-9 has also been undertaken [160]. g-C\(_3\)N\(_4\) was chosen as it is a noble-metal free semiconductor and is photochemically stable. Photoreduction of CO\(_2\) was carried out in bpy (2,2\('\)-Bipyridine) and TEOA under visible light irradiation producing CO (10.4 µmol g\(^{-1}\) h\(^{-1}\)) and H\(_2\) (1.7 µmol g\(^{-1}\) h\(^{-1}\)). Elimination of either: light, g-C\(_3\)N\(_4\), or the sacrificial agent (TEOA) led to photocatalytic inactivity – indicating each element had role in the photoreduction. Aprotic solvents were also found to aid CO\(_2\) solubility and lead to increased catalytic activity. PL analysis was used to prove the synergistic effect of both g-C\(_3\)N\(_4\) and bpy for effective charge separation – analogous to findings by Wang et al. [161].

Carbon nitride nanosheets (CNNS) have also been coupled with UiO-66 via an electrostatic self-assembly synthesis [162]. Under visible light in the presence of MeCN/TEOA CO\(_2\) was reduced to CO for CNNS and CNNS/UiO-66 (no products were detected for UiO-66). The CO
evolution (10.4 \( \mu \text{mol g}_{\text{CN}}^{-1} \text{h}^{-1} \)) for the composite was 1.6 times larger than bulk CNNS per \( g_{\text{CN}} \) and was attributed to high CO\(_2\) adsorption capacity of the CNNS/UIO-66 which was similar to UIO-66 (CNNS was around 10% of UIO-66) and did not suppress the CO\(_2\) capacity of the MOF. The catalytic trends were explained by ESR and photoluminescence of the composites which showed favourable electron transfer from CNNS to UIO-66. Xu et al. [163] assembled CNNS onto a boron imidazolate framework (BIF-20). The composite had improved CO\(_2\) adsorption and CO\(_2\) conversion (CO evolution 59.87 \( \mu \text{mol g}^{-1} \text{h}^{-1} \), CH\(_4\) evolution 15.52 \( \mu \text{mol g}^{-1} \text{h}^{-1} \)) compared to CNNS. The improved catalytic activity was attributed to CO\(_2\) activation by B-H bonds, and charge transfer from CNNS to BIF-20 investigated by photoluminescence and electron paramagnetic resonance (EPR).

Liu et al. [164] synthesised ZIF-8 onto Zn\(_2\)GeO\(_4\) nanorods; Zn\(_2\)GeO\(_4\) was selected as a semiconductor as it is a known photocatalyst for CO\(_2\) reduction. CO\(_2\) adsorption isotherms indicated Zn\(_2\)GeO\(_4\)/ZIF-8 nanorods had less than 50% capacity when compared to ZIF-8, but around double that of unmodified Zn\(_2\)GeO\(_4\). Photocatalytic experiments with the composite showed a 62% increase in methanol production (0.143 \( \mu \text{mol g}^{-1} \text{h}^{-1} \)) compared to Zn\(_2\)GeO\(_4\), with trace amounts of small hydrocarbons. This trend was explained by increased CO\(_2\) adsorption and wider light absorption spectra. Further improvements were also made by addition of Pt to the composites as a co-catalyst.

2.5.4.6.4 Co-catalyst addition

MOF photocatalytic activity can also be enhanced by the addition of a co-catalyst to the reactor system. Wang et al. [165] synthesised Co-ZIF-9 for photoconversion of CO\(_2\) in CO (TON 41.8) under visible light with an estimated quantum yield of 1.48% at 420 nm. H\(_2\) was also produced (TON 29.9). The reactor system used was liquid phase with acetonitrile, TEOA (sacrificial agent), and [Ru(bpy)]\(_3\)Cl\(_2\).6(H\(_2\)O) (photosensitiser/co-catalyst) – no CO was observed in the
absence of the co-catalyst. Recyclability tests indicated that the dye is photosensitive as it degraded notably, resulting in lower catalytic activity.

CdS with Co-ZIF-9 as a co-catalyst was studied by Wang et al. [161]. This was explored because unlike this group’s previous work [165], it did not require a photosensitive dye as a light harvester. Co-ZIF-9 with CdS reduced CO$_2$ to CO (TON 50.4) under mild reactor conditions and visible light irradiation, the quantum yield was measured to be 1.93% at 420 nm, H$_2$ was also evolved (TON 11.1). Elimination of Co-ZIF-9 suppressed production generation severely, indicating Co-ZIF-9 enhanced the CdS catalytic activity by facilitating electron transfer.

2.6 Photoreactor design

As photoreactors aim to optimise photocatalytic CO$_2$ conversion, they require high light harvesting efficiency to limit photon loss and increase access to the catalyst. The photoreactor design therefore has a large impact on catalyst activity [63], so a review of photoreactors used for CO$_2$ reduction was undertaken. The two main categories of reactor: slurry and fixed bed, are reviewed briefly in turn below. This review was the basis of selection for the reactor design which was to be built.

2.6.1 Slurry reactors

A typical slurry photoreactor is a gas-liquid heterogeneous system carried out as a batch process. The solid catalyst is suspended in solution to promote conversion – agitation is provided by a magnetic stirrer to prevent agglomeration. The system is purged of air by vacuum and is replaced with CO$_2$, and the reaction is initiated by lamp irradiance [65]. This scheme was initially selected by researchers due to high active surface areas aiding effective mass
transfer. Its simple operation allows rapid assessment of various catalysts. Following the reaction, additional catalyst recovery processes by filtration or centrifugation are needed. Catalyst agglomeration, condensation of nanoparticles and poor light penetration are other common issues observed when using fluidised beds [166]. Light harvesting efficiency can be enhanced by immersing the lamp within the slurry, this reduces losses arising from reflection [167].

2.6.2 Fixed bed reactors

Photocatalysts are normally in powder form so they need to be attached to a support for fixed bed gas-phase operation. A typical fixed bed reactor was used by Yamagata et al. [168] who supported the catalyst on a glass disc foam under UV irradiation from a Hg lamp. CO_2 was reduced to CH_4 under H_2 atmosphere in a closed loop system, Figure 2-3a. On-line gas samples (by gas syringe) were analysed by gas chromatography (GC). Similarly, Li et al. [151] supported their HKUST-1@TiO_2 catalyst on a glass sinter on a quartz boat floating in water to reduce CO_2 into CH_4. This arrangement resulted in the catalyst being surrounded by water vapor as the reducing agent - Figure 2-3b. Hwang et al. [169] deposited Pt (~3 %wt) onto TiO_2-coated glass plate used for CO photooxidation. This was housed in a stainless steel cell with a quartz window for UV irradiation. Gas was flowed through the reactor at a constant flowrate, as part of a closed-circulation setup.
Figure 2-3. Gas photoreactor systems, catalyst supported a) on foam glass [168], reproduced with permission from Elsevier, b) a glass sinter afloat in water [151], reproduced with permission from John Wiley and Sons.

Seeking higher solar efficiency, different catalyst supports have been designed to increase exposed catalyst surface area. Gui et al. [170] used a continuous operation to reduce CO₂ in a reactor system comprised of a quartz tube which housed catalyst coated on glass rods. Water vapour was used as the reducing agent, and was added to the inlet stream by bubbling the CO₂ through water. The catalyst was illuminated by a 15 W energy saving bulb. Gas was sampled periodically in gas bags and analysed by a GC. Lo et al. [171] used Pyrex pellets as a catalyst support, housed within a quartz tube irradiated by four UV lamps. This was part of a closed loop reactor system with periodic sampling by GC. A high irradiation area of photocatalyst was attained by Nguyen and Wu [172] who supported a Cu-Fe/TiO₂ catalyst on the inner surface of optical fibers. Concentrated light was shone along the tube to reduce CO₂ into methane and ethylene. Continuous operation was used, illumination was provided by a 150 W Hg lamp with the temperature maintained at around 75 °C. CO₂ and H₂O vapour (provided by bubbling CO₂ through distilled water) was flowed into the reactor.

2.6.3 Photoreactor selection

It can be seen above that various photoreactor systems have been employed for photocatalytic CO₂ reduction, with recent advances in fixed bed catalyst supports. Of the MOF papers in
Section 2.5.4 reviewed, the vast majority operated in liquid phase, with the photocatalyst slurry dispersed in an organic sacrificial agent and often further aided by photosensitiser. Liquid operation has notable disadvantages for photocatalysis such as low light utilization, product/catalyst separation, catalyst agglomeration, catalyst attrition, mass transfer limitations, and problematic scale up [63, 171, 173]. For detection and quantification of evolved gases a GC was selected as this was the standard method used for gas analysis; this was often combined with a mass spectrometer for isotopic tracing experiments.

Specifically, for bifunctional CO\(_2\) adsorbent-photoncatalyst materials, the low CO\(_2\) solubility would not allow their high CO\(_2\) adsorption capacity to be fully utilised to promote catalytic activity [151, 171]. CO\(_2\) reduction using semiconductors was carried out exhaustively in liquid phase from 1980-2000. A move from liquid towards high active surface gas phase operation has occurred for photocatalytic CO\(_2\) reduction using semiconductors, with improved conversion [173]. Hence, a gas-solid system was selected to test the adsorbent-photoncatalyst materials in this project. This could facilitate milder reaction conditions (without potent sacrificial agents i.e. TEOA), as demonstrated with semiconductors (i.e. H\(_2\)O and CO\(_2\), H\(_2\) and CO\(_2\) photoreactor systems). By evaluating both the CO\(_2\) adsorption and photoreduction under ambient conditions in a heterogeneous gas/solid set-up, we can imitate both CO\(_2\) capture and fixation in a single step process. These systems also allow flexibility in terms of batch or continuous operation, and the reducing agent used (H\(_2\) or H\(_2\)O).

### 2.7 Current challenges and paths forward

Considering the materials and photoreactor systems reviewed above, the focus remains on promoting CO\(_2\) conversion - usually without a specific target product, though it is observed that CO, HCOO\(^-\), and CH\(_4\) are most commonly evolved with TEOA as a sacrificial agent. In
addition, there is no agreed metric to compare photocatalytic efficiency between studies [158]. Reporting only evolution rates makes it very difficult to compare due to significant differences in reactor setup (i.e. irradiation spectra/power, sacrificial/reducing agents and gas/liquid). Rate is most commonly expressed as amount of product per gram of catalyst per unit time, alternate units are sometimes reported. In the case of composite materials, there is also no convention for reporting per gram of material or per gram of active site. Additionally activity is often time dependent and there is no standard testing duration adhered to – 24 h has been suggested [174].

Moving forward, more accurate comparisons between studies could be made by measuring how efficient absorbed photons are utilised [158] or comparison with a standard catalyst. In terms of evolution rates for large scale deployment, this remains a significant challenge. It has been speculated conversion rates in the order of mol g⁻¹ h⁻¹ which are required for industrial scale applications (at present mmol g⁻¹ h⁻¹ have been achieved for semiconductor photocatalysts). A conversion rate: 10 mol g⁻¹ h⁻¹ would convert 1 Gton CO₂ per year per ton of catalyst over 250 locations [175].

Focusing on CO₂ adsorption capacity and its importance in photocatalytic conversion, it can be seen from the high CO₂ adsorbent based materials, such as MOFs, the influence of this remains unclear and CO₂ adsorption capacity was often not reported. When reported, higher CO₂ adsorption generally coincides with higher catalytic activity. Hence, further investigation into the surface chemistry and textural properties for CO₂ adsorption could deepen knowledge in this area.

Regarding catalyst design, the control of crystal growth in terms of exposed facets had a large influence on the activity as seen with studies using TiO₂. Investigations of morphology showed increased surface area by formation of 2D sheets with TiO₂ and CN improved CO₂ adsorption
capacity and catalytic activity by improved charge transport properties. The formation of composites has improved activity by facilitating interfacial charge transfer via a heterojunction.

Focusing on MOFs, in terms of photocatalyst choice, a wide range of MOFs has been investigated which should aid further catalyst design. Notably the UiO series has been utilised most frequently, the high chemical and thermal stability of this MOF family allows various post synthesis modifications to be made to enhance photocatalytic activity. Similarly, the ZIF series has also been used to form composites by several groups. Overall since the first MOF photocatalytic CO\textsubscript{2} reduction study in 2011 [141], photocatalyst selection has broadened from MOFs with modifications studied for other applications (i.e. CO\textsubscript{2} adsorption) towards more targeted MOFs often with incorporation of heavy metal molecular catalysts or composites. Until now, the synthesis of MOF composites, although promising, has been seldom explored. This may be because MOF synthesis chemistry is complex and thus forming MOF-based composites with enhanced performance remains challenging.

The photoreactor reactor design is important as some studies showed inactivity for catalysts other researchers had activity with in different photoreactors. Most photoreactors using MOFs operated in liquid phase, with the photocatalyst slurry dispersed in an organic sacrificial agent and often further aided by photosensitiser, the use of these agents also limits the overall benefit of CO\textsubscript{2} reduction in terms of carbon management. Additionally, liquid operation has notable drawbacks for photocatalytic activity, specifically for high CO\textsubscript{2} adsorbent materials, the low CO\textsubscript{2} solubility in water does not allow this attribute to be utilised for improved catalytic activity. Instead the design of gas-solid photoreactors with high catalyst exposure using reducing agents with lower environmental impact (i.e. H\textsubscript{2} or H\textsubscript{2}O) may lead to higher catalytic activities. The irradiation ranges used were in the UV-Vis or visible light spectra (420-800 nm) - a region which contains the majority of the solar spectrum [176]. The latter represents a
challenge in terms of material selection, as it means it must have a smaller bandgap than UV-only active materials such as TiO$_2$. The robustness of the catalysts could also be investigated deeper, as often the materials require expensive precursors. The recyclability is often reported which shows under repeated experimental conditions the materials are relatively stable photocatalytically. Studies with additional post-reaction characterisation could investigate any catalyst degradation.

2.8 Summary

Recent research of CO$_2$ adsorbent materials and photocatalytic materials for CO$_2$ reduction has been collated and reviewed. This showed novel synthesis and analytical methods have been carried to investigate and enhance material performance. By reviewing these studies, the diversity and innovation of this emerging field is evident. The routes to incorporate and improve the photocatalytic CO$_2$ reduction activity of TiO$_2$, carbon nitride and MOF based materials in various photochemical systems were reviewed and evaluated. There was notable research developing titanium dioxide, with recent efforts into other types of materials such as carbon nitride and MOFs. These are exciting materials for photocatalytic applications as compared to titanium oxide as they have the potential for a higher CO$_2$ adsorption capacity and broader light utilisation, both of which could be beneficial for photocatalytic CO$_2$ reduction. Carbon nitride and MOFs were therefore selected for development, synthesis, and testing in this project. Overall by combining both the CO$_2$ adsorption and photoreduction under ambient conditions in a heterogeneous gas/solid set-up we aim to combine both CO$_2$ capture and fixation in a single step process.

In relation to achieving the project objectives: carbon nitride and MOFs are both CO$_2$ adsorbents and photocatalytically active for CO$_2$ reduction (Research Objective 1). Their
applications are relatively new in the field so further investigations into the role of their morphology, textural properties, and light utilisation are required to understand their roles in CO$_2$ adsorption and CO$_2$ conversion (Research Objective 1). Similarly, the lack of studies into their robustness and recyclability for photocatalytic CO$_2$ reduction requires investigation (Research Objective 2).

2.9 References

2.9 References


[67] Y. Cao, Q. Li, C. Li, J. Li, J. Yang, Surface Heterojunction between (001) and (101) Facets of Ultrafine Anatase TiO2 Nanocrystals for Highly Efficient Photoreduction CO2 to CH4, Applied Catalysis B: Environmental, 198 (2016) 378-388.
References


Chapter 3  Methods
In this chapter the synthesis methods, characterisation techniques, and photoreactor used in this project are described and explained.

### 3.1 Synthesis methods

The following section gives an overview of the synthesis methods used in this project. Further details of the material syntheses are presented in their respective chapters.

#### 3.1.1 Autoclave

Hydrothermal syntheses were carried out using autoclaves (Anton Paar, PTFE liner) shown in Figure 3-1a. Once loaded with the synthesis reagents these were sealed and then heated for a set duration in an oven. After the reaction, solid products were washed and recovered by centrifugation. This method was used for the synthesis of titanium oxide, and also for altering the crystalline phase of titanium oxide.

#### 3.1.2 Open vessel

Round bottom flasks were used to form MOFs as shown in Figure 3-1b. The reagents were loaded into the vessel, sonicated if necessary, and heated for a set duration by partial submersion in a heated silicon oil bath. After the reaction, the solid products were washed (solvent exchange of DMF with ethanol) and recovered by centrifugation.

#### 3.1.3 Microwave

A microwave was also used for the synthesis of MOFs. This technique was similar to the open vessel method except the vessels are sealed, with heat input provided by microwave irradiation. Compared to open vessel synthesis, this method typically results in faster crystal formation and
3.2 Photocatalytic CO₂ reduction experiments

A smaller crystal size. After the reaction, the solid products were washed (solvent exchange of DMF with ethanol) and recovered by centrifugation.

**Figure 3-1.** a) autoclaves used for hydrothermal synthesis, b) round bottom flask used for synthesis of MOF, photograph showing MOF NH₂-Uio-66 formed in DMF after 24 h at 150 °C.

3.2 Photocatalytic CO₂ reduction experiments

3.2.1 Photoreactor setup description

A gas/solid reactor setup was assembled as presented in Figure 3-2. Research grade (99.999%) CO₂ from a cylinder and H₂ (99.9995%, Peak Scientific PH200 hydrogen generator) were flowed at controlled rates using mass flow controllers (Omega Engineering, 0-50 mL/min) – see Figure 3-3a. Water vapour was generated by a saturator (room temperature, 20 °C). A stainless steel cylindrical cell (total volume 35 mL) with a glass window was used as the photoreactor – Figure 3-3b-d. The photocatalysts were deposited on a stainless steel plate with a fixed area and mass of 9.6 cm² and 25 mg respectively. For experiments in Chapter 5, a
different reactor was used; in this case the glass reactor (total volume 132 mL) was used with fixed catalyst area and mass of 4.5 cm$^2$ and 3 mg respectively.

A xenon arc lamp (300 W and 150 W, $\lambda > 325$ nm, spectra: Figure 3-4a, LOT Quantum Design,), equipped with a water filter were used as the irradiation source – see Figure 3-3e. Evolved gases were analysed by a gas chromatograph mass spectrometer (GC-MS) with gas sampling valves connected directly to the photoreactor. The GC (Agilent Technologies, 7890B) was equipped with hayesep (Agilent J&W 6 foot, 1/8 inch, 2 mm, HayeSep Q Column 80/100 SST) and mol sieve (Agilent J&W 6 foot, 1/8 inch, 2 mm, MolSieve 5A, 60/80, preconditioned) packed columns in series for the GC, a GS-GASPRO capillary column (Agilent J&W HP-5ms GC Column, 30 m, 0.25 mm, 0.25 µm) for the MS, thermal conductivity (TCD), flame ionisation (FID) and mass spectrometer (MS) detectors – see Figure 3-4b for full configuration. The GC carrier gas was nitrogen (99.9995%), for experiments requiring detection of oxygen this was switched to helium (99.9995%) A vacuum pump (ultimate vacuum 99.995%) was also connected to the setup.

![Figure 3-2. Configuration of photocatalytic gas-solid reactor setup used to evaluate photocatalytic CO$_2$ reduction: 1) CO$_2$ cylinder, 2) H$_2$ generator, 3) mass flow controllers, 4) non-return valves, 5) H$_2$O saturator, 6) photoreactor, 7) xenon arc lamp, 8) pressure transducer, 9) gas chromatograph, 10) vacuum pump.](image-url)
3.2 Photocatalytic CO2 reduction experiments

Figure 3-3. Photographs of the photoreactor system: a) mass flow controllers to control flow of CO2 and H2, b) photoreactor open with catalyst mounted inside, c) photoreactor closed, d) photoreactor illuminated, and e) xenon arc lamp (150 W) with power supply unit.
3.2 Photocatalytic CO\textsubscript{2} reduction experiments

3.2.2 Photocatalytic CO\textsubscript{2} reduction method

Prior to photocatalytic testing the catalysts were dispersed onto a stainless steel disc as shown in Figure 3-3b, this ensured the catalyst mass and exposed area was constant for all materials tested. The dispersion was performed by preparing 2.5 mL solution of catalyst in H\textsubscript{2}O (10 mg\textsubscript{cat}/mL\textsubscript{H\textsubscript{2}O}). This solution was sonicated for 20 mins and then drop casted onto the

Figure 3-4. a) Xenon arc lamp emission spectra, 150 W and 300 W, (LOT Quantum Design), equipped with a water filter, and b) gas chromatograph mass spectrometer instrument configuration.
stainless steel disc using a plastic pipette. The H$_2$O was removed by drying in a drying oven at 65 °C for 3 h, then vacuum dried at 120 °C overnight. The catalyst was then placed into the photoreactor cell which was then sealed (Figure 3-3c).

The most common photoreactor test was performed with a CO$_2$ and H$_2$ atmosphere as a batch reaction and was performed as follows. The photoreactor was evacuated and replenished with CO$_2$ and H$_2$ five times to remove air from the system. Then, CO$_2$ and H$_2$ (1.5 vol/vol ratio) was passed over the catalyst bed in the photoreactor for 15 residence times before it was sealed at 1.25 bara and illuminated. For experiments in a CO$_2$ and H$_2$O atmosphere, the H$_2$ flow was isolated and the CO$_2$ flow was directed through the H$_2$O saturator (20°C).

After a reaction period of 6 h the contents of the photoreactor was analysed by GC. The GC was calibrated using a calibration gas (SIP Analytical) of composition presented in Table 3-1. The detection limits in Table 3-1 of each species was measured by analysis of diluted calibration gas. The total number of moles in the photoreactor was calculated using the ideal gas law assuming a molar volume of 24.7 L/mol (at 25°C) and the reactor volume – Equation [3-1]. The GC provided the concentration of gases in the reactor (% vol), this was converted to moles of each compound using Equation [3-2] and evaluated as an evolution rate of μmol/gh using the photocatalyst mass and reaction duration.

To assess the stability of the photocatalysts, the process above was repeated after each 6 h illumination without opening the photoreactor. The stability of evolution of the 6 h experiment was measured by sampling the reactor at 2, 4, 6 h durations.
3.2 Photocatalytic CO2 reduction experiments

\[ n_{Total} = \frac{V_{Total}}{V_m} \]  
\[ n_x = c_x n_{Total} \]

Equation [3-1]
Equation [3-2]

Where:

- \( n_{Total} \) = total number of moles in photoreactor (mol)
- \( V_m \) = gas molar volume (L/mol)
- \( V_{Total} \) = photoreactor volume (L)
- \( n_x \) = moles of \( x \) (moles)
- \( c_x \) = concentration (% vol)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (ppm)</th>
<th>Detection limit (ppm)</th>
<th>Detector</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>10000</td>
<td>5.0</td>
<td>TCD</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>500</td>
<td>2.5</td>
<td>FID</td>
</tr>
<tr>
<td>CH₄</td>
<td>15000</td>
<td>3.0</td>
<td>FID</td>
</tr>
<tr>
<td>CO</td>
<td>20000</td>
<td>4.0</td>
<td>FID</td>
</tr>
<tr>
<td>CO₂</td>
<td>balance</td>
<td></td>
<td>FID</td>
</tr>
</tbody>
</table>

**Table 3-1.** Calibration gas composition, measured GC detection limits and detector used for each compound.

3.2.3 Photocatalytic CO₂ reduction verification

To verify the photocatalytic nature of evolved products, experiments with a N₂ and H₂ atmosphere and isotopic tracing (¹³CO₂) were performed. For the N₂/H₂ reaction the procedure in Section 3.2.2 above was carried out except the CO₂ source (Figure 3-2, item 1) was replaced with N₂ (99.9995%). For isotopic tracing experiments, the procedure in Section 3.2.2 above was carried out except the CO₂ source (Figure 3-2, item 1) was replaced with ¹³CO₂ (BOC, >99%, >98% atom ¹³CO₂ compared to ¹²CO₂), with gases being analysed on the GC (TCD and FID) and MS (SIM).
3.3 Characterisation techniques

3.3.1 X-ray diffraction

Powdered X-ray diffraction measurements (XRD) were performed with a PANalytical X’Pert PRO instrument at room temperature (reflection mode at 40 kV and 40 mA using Cu Kα radiation ($\lambda = 1.54178$ Å). The powder samples were placed on a diffraction plate with the surface flattened by compression with a glass slide, this was then mounted in the goniometer stage. XRD was used to identify the crystalline structure of the materials, the X-ray beam was directed onto the sample in the $2\theta = 5$ to $80^\circ$ range with an X-ray detector measuring the reflected X-rays. When Bragg’s law (Equation [3-3]) was met, constructive interference resulted in a peak in the XRD pattern. The XRD peak pattern was characteristic of the crystalline structure and allowed the material and phase to be identified by comparison to XRD databases, literature, or simulated patterns. The interplanar spacing of an XRD peak was also calculated using Bragg’s law (Equation [3-3]).

$$2d \sin \theta = n\lambda$$

Equation [3-3]

Where:

- $d$ = interplanar distance (nm)
- $\theta$ = scattering angle ($^\circ$)
- $n$ = positive integer
- $\lambda$ = wavelength (nm)

3.3.2 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out under a nitrogen flowrate of 100 mL min$^{-1}$, from 25 to 900 °C at a heating rate of 10 °C min$^{-1}$ using a Netzsch TG 209 F1 Libra instrument.
3.3 Characterisation techniques

TGA provided output of the sample mass as the temperature was ramped. This provided insight into the thermal stability of the sample, for example, a reduction in sample mass was indicative of thermal degradation at that temperature. TGA analysis of composite materials, with distinct degradation profiles, allowed the composition to be calculated. Prior to TGA the samples were stored in a vacuum oven at 120 °C for 24 h. A sample of mass of ~20 mg (TGA balance accuracy ±0.0001 mg) in an aluminium oxide crucible was used in each analysis.

3.3.3 Attenuated total reflection Fourier transform infrared spectroscopy

Attenuated total reflection Fourier transform-infrared (ATR-FTIR) spectra were collected at room temperature using a Perkin-Elmer Spectrum 100 Spectrometer equipped with an ATR cell at room temperature. The spectra were generated, collected 8 times, averaged and corrected for the background noise. The powered samples were analysed by compression onto the diamond crystal stage, without KBr addition. ATR-FTIR spectra were measured in the 500-3600 cm\(^{-1}\) range measuring % transmission (%T). The chemistry of the sample determines which wavelengths are absorbed as these induce vibrational states in atomic bonds, the vibrational modes that induce changes in the dipole moment are said to be “IR active”. This results in bands at certain wavelengths that can be used to identify molecular groups in the sample by comparison with literature. [1]

3.3.4 Nitrogen gas sorption

Nitrogen adsorption and desorption isotherms were measured using a Micrometrics 3Flex sorption analyser at -196 °C. The shape of the nitrogen isotherms provides an indication of the type of porosity of the material defined by the International Union of Pure and Applied Chemistry (IUPAC). The pore type of materials are defined as: micropores (<2 nm), mesopores (2-50 nm), macropores (<50 nm), and nanopores (less than ~100 nm) [10]. The isotherms were
analysed to calculate: surface area, total pore volume, micropore volume, and mesopore volume.

The surface area was calculated from the Brunauer-Emmett-Teller method [2]. The BET method involves two stages for calculated BET surface area, $\alpha$(BET), estimation from physisorption isotherms: calculation of monolayer capacity calculation, then surface area evaluation. First the physisorption data is plotted using the BET equation in linear form - Equation [3-4]. Interpretation of the gradient linear portion and the intercept yields the monolayer capacity and C. The application of BET theory was used adhering to: the P/P$_0$ region where the BET equation (Equation [3-4]) was increasing and linear, and that the BET constant (C) must be positive. The BET surface area, $\alpha$(BET), was then calculated from Equation [3-5].

The total volume of pore was calculated using the volume adsorbed at P/P$_0$=0.97 and Equation [3-6]. The volume of micropores was determined using the t method [4]. The volume of mesopores was calculated as the difference between the total pore volume and the volume of micropores (Equation [3-7]).
\[
\frac{p/p^0}{n(1 - p/p^0)} = \frac{1}{n_m C} + \frac{C - 1}{n_m C} \left( \frac{p}{p^0} \right)
\]
Equation [3-4]

\[\alpha(\text{BET}) = n_m \cdot L \cdot \sigma\]
Equation [3-5]

Where:

\[p = \text{equilibrium pressure (Pa)}\]
\[p_0 = \text{saturation pressure (Pa)}\]
\[n = \text{adsorption capacity (mol/g)}\]
\[n_m = \text{monolayer capacity (mol/g)}\]
\[C = \text{BET constant related to the enthalpy of monolayer adsorption}\]
\[L = \text{Avogadro’s constant (6.022x}10^{23}/\text{mol)}\]
\[\sigma = \text{average area occupied by each molecule on the monolayer (} \sigma(\text{N}_2) = 0.162 \text{ nm}^2\).\]

\[V_{\text{total}} = \frac{PV_{\text{ad}}V_m}{RT}\]
Equation [3-6]

\[V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}\]
Equation [3-7]

Where:

\[V_{\text{total}} = \text{total pore volume (cm}^3/\text{g)}\]
\[P = \text{pressure (Pa)}\]
\[V_{\text{ad}} = \text{adsorbed gas volume (cm}^3/\text{g)}\]
\[V_m = \text{liquid nitrogen molar volume (34.7 cm}^3/\text{mol)}\]
\[R = \text{ideal gas constant (8.314 J/mol K)}\]
\[T = \text{temperature (K)}\]
\[V_{\text{meso}} = \text{mesopore volume (cm}^3/\text{g)}\]
\[V_{\text{micro}} = \text{mircopore volume (cm}^3/\text{g)}\]
3.3 Characterisation techniques

3.3.5 Carbon dioxide gas sorption

CO$_2$ sorption was also evaluated up to 1 bar using the same instrument as nitrogen sorption but measured at 25 °C. Prior to the measurements the samples were degassed at 0.2 mTorr, 120 °C for 24 h. This provided the CO$_2$ adsorption capacity of the material (mmol/g) up to 1 bar at 25 °C.

3.3.6 Scanning electron microscopy

Scanning electron microscopy (SEM) images were taken using a high resolution LEO Germini at 1525 at 5 kW in secondary electron mode (InLens detector). Energy-dispersive X-ray (EDX) spectroscopy was performed using an Oxford Instruments silicon drift detector attached to the SEM. Prior to analysis, the samples were ground and mounted on carbon tape and coated with 20 nm chromium. SEM works by rastering a focused high energy electron beam across a sample area under high vacuum, these produce secondary electrons which were detected to produce an image [5]. SEM was used to capture high resolution (up to 150 k magnification) images of materials for analysis of their morphology and particle size.

3.3.7 Transmission electron microscopy

Transmission electron microscope (TEM) images were taken by a JEOL 2100Plus instrument at an acceleration voltage of 200 kV, energy dispersive x-ray (EDX) spectroscopy was captured using an Oxford Instruments INCA energy dispersive analytical system attached to the TEM. Before analysis, the sample were sonicated in ethanol and then drop casted on a carbon coated copper grid (holey carbon film, 300 mesh). TEM produces an image by passing a focused high energy electron beam through the sample and onto a detector. Some electrons interact with the atoms in the sample, these electrons scatter and weaken the beam hitting the detector, resulting in image of the sample comprised of the unscattered electrons [6]. TEM was used to capture
3.3 Characterisation techniques

images of sample morphology and particle size. The high resolution (up to 800 k magnification) also allowed lattice spacing of the crystals to be observed and measured.

3.3.8 Ultraviolet-visible spectroscopy

Diffuse reflectance ultraviolet-visible (DR-UV/Vis) was measured using a Agilent Cary 500 UV-Vis-NIR spectrometer equipped with an integrating sphere. Spectral band width was set to 2 nm, with Spectralon as a standard. The samples were compressed onto a KBr backed pellet for analysis. DR-UV/Vis spectra measured the reflection of light from a sample at different wavelengths (200-800 nm), which allowed the bandgap of the material to be calculated using the following method. The absorption coefficient was calculated from the collected spectra (% reflectance) using Equation [3-8]. The bandgap is calculated from the Kubelka-Munk function (Equation [3-9]), a Tauc plot of \((h\nu\kappa)^{1/n}\) vs \(h\nu\) was plotted, with the extrapolation of the linear part intercepting the x axis at the bandgap [7].

\[
\kappa = \frac{(1 - R/100)^2}{2(R/100)} \quad \text{Equation [3-8]}
\]

\[
\kappa = \frac{B_T(h\nu - E_g)^n}{h\nu} \quad \text{Equation [3-9]}
\]

Where:

- \(\kappa\) = absorption coefficient
- \(B_T\) = a constant related to the average dipolar momentum matrix element
- \(h\) = Planck's constant \((6.626 \times 10^{-34} \text{ m}^2 \text{ kg/s})\)
- \(\nu\) = frequency \((1/\text{s})\)
- \(E_g\) = bandgap \((\text{eV})\)
- \(n\) = direct \((0.5)\) and indirect \((2)\) band gap transitions
3.3 Characterisation techniques

3.3.9 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) measurements were performed using two instruments by Dr Spyridon Zafeiratos in the University of Strasbourg, and by Mr Benjamin Moss at Imperial College London. The former used a ultrahigh vacuum spectrometer equipped with a VSW Class WA hemispherical electron analyser with a dual anode Al Kα X-ray source (1486.6 eV) as incident radiation, a constant pass energy mode (44 and 22 eV for survey and high resolution spectra respectively) was applied in all XPS measurements. The latter XPS instrument was a Thermo Scientific K-Alpha spectrometer equipped with an Al Kα X-Ray source (1486.6 eV) and an 180° double focusing hemispherical analyzer with a 2D detector at an operating pressure of 1x10⁻⁸ mbar and a flood gun to minimise charging from photoemission. For XPS analysis, the powder samples were mounted onto conductive carbon tape adhered to a sample holder. The Binding energies (BEs) of all peaks were referenced to the C 1s main peak at 285 eV. XPS spectroscopy works by irradiating a sample surface with X-rays, resulting in the emission of photoelectrons. The quantity and kinetic energy of the emitted photoelectrons is measured, the latter property allows the binding energy of the electron to be determined. This allows the elements to be identified as they have characteristic peaks at specific binding energies, these are related to the chemical state of the atoms [8]. Shifts or additional XPS peaks can be indicative of a modification of the atomic chemical state. The valance band was also measured by ultraviolet photoemission spectroscopy, which uses lower energy irradiation (ultraviolet photons).

3.3.10 Transient absorption spectroscopy

Transient absorption spectroscopy (TAS) experiments were conducted by researchers in Prof. James Durrant’s group: Dr Andreas Kafizas and Dr Robert Godin. TAS is a form of laser flash spectroscopy that can monitor the generation, recombination, trapping and charge transfer
3.4 References


Chapter 4 Exploring nanocomposites for improved CO₂ reduction

Abstract

In this chapter, inorganic/organic composite photocatalysts for CO₂ capture and reduction comprised of titanium dioxide (TiO₂) and carbon nitride nanosheets (CNNS) were synthesized using a hydrothermal in-situ growth method. Pre-formed CNNS were used as seeds to synthesize TiO₂/CNNS heterostructures with control of the TiO₂ facet formation. The materials were characterised by various spectroscopic, imaging, and analytical techniques to investigate their structural, chemical, and optical properties. TiO₂ nanoparticles were efficiently grown on the CNNS. The CO₂ adsorption capacity of the composites was measured, and they were tested for CO₂ photoreduction under UV-Vis illumination with hydrogen as the reducing agent. The composites exhibited enhanced CO₂ adsorption capacity and photocatalytic CO₂ conversion compared to their constituent materials (> ten-fold increase) and outperformed the P25 TiO₂ benchmark material. The TiO₂/CNNS composite with more {001} TiO₂ facets was the most catalytically active. Further investigations using transient absorption spectroscopy (TAS) revealed the control of facet formation improved interfacial transfer at the TiO₂/CNNS junction. A photocatalytic mechanism was proposed based on the spectroscopic analyses as well as the CO₂ adsorption, and CO₂ conversion results.
4.1 Overview

To take advantage of the complementary features of inorganic (high photocatalytic activity) and organic (high CO\textsubscript{2} adsorption capacity) materials, the synthesis of inorganic-organic composite materials was explored. The materials for this study comprised of titanium dioxide (TiO\textsubscript{2}) and carbon nitride nanosheet (CNNS) composites; in addition, the TiO\textsubscript{2} facet formation was also controlled, and the findings presented in this chapter. Based on this chapter ref \cite{1} was prepared.

4.2 Introduction

As reviewed in Section 2.5.3, composites of g-C\textsubscript{3}N\textsubscript{4} and TiO\textsubscript{2} (g-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2}) have shown improved photocatalytic activity for various applications including CO\textsubscript{2} reduction \cite{2-4}. Most prepared TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} heterostructures have used bulk g-C\textsubscript{3}N\textsubscript{4} and have been synthesised by calcination of TiO\textsubscript{2} nanoparticles and organic precursor mixtures but were hindered by aggregation and low surface area \cite{5, 6}. Instead, exfoliation of g-C\textsubscript{3}N\textsubscript{4} to CNNS and then formation of TiO\textsubscript{2}/CNNS composites was investigated to enhance CO\textsubscript{2} adsorption capacity and CO\textsubscript{2} conversion. These composites targeted improvement in these properties through improved photogenerated charge lifetime owing to the formation of a heterojunction, broader light absorption into visible irradiation from CNNS, and lower TiO\textsubscript{2} aggregation due to preferential growth onto CNNS resulting in higher surface area and CO\textsubscript{2} adsorption. Despite these potential advantages of using CNNS and TiO\textsubscript{2} crystals with controlled facet formation, TiO\textsubscript{2}/CNNS composites had never been applied in CO\textsubscript{2} photocatalytic reduction until this study.

Another key aspect of this study was the control of the TiO\textsubscript{2} facet formation to study the TiO\textsubscript{2}-CNNS heterojunction in more detail. Anatase phase TiO\textsubscript{2} was selected as it is generally the most photocatalytically active phase for CO\textsubscript{2} reduction. The \{001\} facet has been shown
to have enhanced activity due to the high density of unsaturated Ti atoms and active surface oxygen atoms [7, 8]. As reviewed in more detail in Section 2.5.2, studies have shown that optimisation of {001}/[101] ratio can be achieved by using hydrofluoric acid to control crystal facet formation; this has been shown to greatly improve charge separation via a surface heterojunction where electrons and holes migrate to different facets [8-10]. This technique was used to form TiO$_2$ with more and less exposed {001} facets to form nanosheet (NS) and isometric (ISO) TiO$_2$ respectively. TiO$_2$/CNNS composites with each of these TiO$_2$ shapes were synthesised (Ti-ISO/CN and Ti-NS/NS) and all materials were studied using a variety of analytical, imaging, and spectroscopic techniques.

### 4.3 Material synthesis

All reagents used in this study were of analytical grade and used without further purification. Hydrofluoric acid (48%), melamine (99%) and titanium butoxide (97%) were purchased from Sigma-Aldrich.

#### 4.3.1 Synthesis of carbon nitride nanosheets (CNNS)

Carbon nitride (g-C$_3$N$_4$) was synthesized from heating melamine in a muffle furnace to 560 °C at a 5 °C/min ramp under static air for 4 h. Carbon nitride nanosheets (CNNS) were prepared by firstly sonicating the as prepared g-C$_3$N$_4$ in water for 4 h. This was centrifuged at 1000 rpm for 10 min, the recovered supernatant was then centrifuged at 12,000 rpm for 30 min to recover CNNS. The CNNS were then dispersed in ethanol by sonication for 4 h and further centrifuged at 2000 rpm for 10 min. The CNNS in the supernatant was then collected. The stock solution of CNNS in ethanol had a CNNS concentration of 2.25 mg/mL, determined by thermogravimetric analysis.
4.3.2 Synthesis of TiO$_2$

A hydrothermal synthesis was used to produce TiO$_2$. Specifically, TiO$_2$ nanosheets (TiO$_2$-NS, ‘NS’ for nanosheet) were synthesized by adding titanium butoxide (3 mL), hydrofluoric acid (1.2 mL), and ethanol (30 mL) to a PTFE autoclave liner under mixing. The autoclave was sealed, then the mixture was heated to 180°C for 24 h. Following the reaction, the collected material was washed by centrifugation (10,000 rpm for 10 min) with 0.2 M NaOH, then deionized water until a neutral pH was reached, and finally with ethanol prior to drying overnight at 65 °C. Hydrofluoric acid was used to control the crystal facet formation and in particular for the development of nanocrystals with exposed {001} facets. For TiO$_2$ isometric bipyramidal (TiO$_2$-ISO, ‘ISO’ for isotropic) synthesis the same procedure was used but 1.2 mL of deionised water was used instead of HF.

4.3.3 Synthesis of TiO$_2$/CNNS composites

A hydrothermal *in-situ* synthesis was used to form TiO$_2$ in the presence of preformed CNNS to obtain TiO$_2$/CNNS composites as shown in Figure 4-1. Titanium butoxide (3 mL), hydrofluoric acid (1.2 mL), and CNNS stock solution (30 mL) were added to a PTFE autoclave liner under mixing. The autoclave was sealed and heated to 180 °C for 24 h. Following the reaction, the collected material was washed by centrifugation (10,000 rpm for 10 min) with 0.2 M NaOH, then deionized water until a neutral pH was reached, and finally with ethanol prior to drying overnight at 65 °C. The TiO$_2$/CNNS composite synthesised in the presence of HF was named Ti-NS/CN. For synthesis in the absence of HF, named Ti-ISO/CN, 1.2 mL of deionised water used instead of HF. In this study, we assumed that the effect of F$^-$ on the morphology of TiO$_2$ particles remains the same either for the pure of the composite material.
Figure 4-1. Schematic of the synthesis process used to produce TiO$_2$/CNNS composites. Following exfoliation of g-C$_3$N$_4$ to CNNS by sonication, TiO$_2$ was synthesised in an autoclave in the presence of CNNS to form TiO$_2$/CN nanocomposites. The TiO$_2$ crystal shape was controlled by the addition of either HF or H$_2$O to the synthesis vessel, leading to the formation of composites with TiO$_2$ nanosheets (NS) and TiO$_2$ isometric (ISO) structures, respectively.

4.4 Results and Discussion

4.4.1 Structural and chemical characterisation

The TiO$_2$/CNNS composites synthesis via an *in-situ* route with TiO$_2$ formation in the presence of preformed CNNS (see Figure 4-1) was primarily done to promote nanoscale mixing of the two components and improve charge carrier dynamics [11]. This formed strong links between the materials physical/chemical features and their adsorptive and photocatalytic properties; as such, the materials were characterised by various techniques to get an understanding of the materials from the nano- to the microscale.

4.4.1.1 Crystalline structure

The crystalline structure of the materials was analysed to confirm the synthesis of TiO$_2$ and CNNS and the presence of both these components in the composites using XRD. The patterns of the composites are presented alongside those of the parent materials in Figure 4-2a. Anatase phase TiO$_2$ was observed for all TiO$_2$ containing samples (single phase and nanocomposite
4.4 Results and Discussion

Materials) either in the presence (TiO\textsubscript{2}-NS) or absence (TiO\textsubscript{2}-ISO) of the stabilizing agent (HF) [12]. The g-C\textsubscript{3}N\textsubscript{4} XRD pattern displayed peaks at 13.0\textdegree (100), characteristic of 0.680 nm interplanar spacing of the tri-s-triazine units, and at 27.4\textdegree (002), characteristic of 0.322 nm bulk CN interlayer stacking [13, 14]. Successful exfoliation of g-C\textsubscript{3}N\textsubscript{4} to CNNS was evident from the significant intensity decrease in the interlayer stacking peak (27.4\textdegree). The TiO\textsubscript{2}/CNNS composites showed patterns which were a combination of the TiO\textsubscript{2} and CNNS diffraction patterns confirming that both species were present and that the TiO\textsubscript{2} synthesis was not altered significantly by the presence of CNNS. The effect of the stabilizing agent (HF) on TiO\textsubscript{2} facet growth can be observed by comparing the XRD patterns of TiO\textsubscript{2}-NS and TiO\textsubscript{2}-ISO. The (004) diffraction peak provides an indirect indicator of the number of exposed \{001\} facets. The (101) peak became sharper when using HF, indicating an increase of the exposed \{001\} facets. This is because more exposed \{001\} facets results in a plate morphology with larger particles with larger\{001\} facets [15]. Additionally, this increased crystallinity was in line with reported studies [8, 16].

![Figure 4-2. Material characterisation analyses confirming the formation of the TiO\textsubscript{2}/CNNS composites: a) XRD patterns, b) ATR-FTIR spectra.](image)

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4.4 Results and Discussion

4.4.1.2 Material chemistry

ATR-FTIR spectroscopy was used to probe the chemical makeup of the materials and provide further confirmation of a close TiO$_2$/CNNS interaction from any deviations from their constituent materials (Figure 4-2b). g-C$_3$N$_4$ showed the expected band vibrations: C=N (1627 cm$^{-1}$) and C-N (1312 cm$^{-1}$) stretching, as well as out-of-plane C-N bending (803 cm$^{-1}$) [17-19]. The spectrum of the CNNS was similar to bulk g-C$_3$N$_4$ showing exfoliation did not alter its chemical features. TiO$_2$ is relatively inactive in the IR region with broad Ti-O-Ti stretching bands across 1000-400 cm$^{-1}$ evident for both TiO$_2$ samples (TiO$_2$-NS and TiO$_2$-ISO) [20]. The band at around 1630 cm$^{-1}$ for these samples is assigned to the bending vibration of the O-H bond [21] from surface hydroxyl groups or water molecules. The scarcity of TiO$_2$ features in the 1800-1000 cm$^{-1}$ region allowed the presence of CNNS in the TiO$_2$/CNNS nanocomposites spectra to be clearly visible in Figure 4-2b. In addition, the Ti-O-Ti stretching band (1000-400 cm$^{-1}$) was observed on the composites spectra confirming the presence of TiO$_2$ in these samples.

4.4.1.3 Material composition

XPS in this section was performed and analysed by Dr Spyridon Zafeiratos in the University of Strasbourg.

Investigation of the composite composition was carried out using XPS and TGA. The presence of Ti, O, C, and N in the nanocomposites was confirmed (Figure 4-A1a in Appendix 4). No fluorine was detected in the TiO$_2$-NS and TiO$_2$-NS/CN composite materials verifying its successful removal with the washing process applied. The CNNS and pure TiO$_2$-NS were characterized by two dominant contributions, C and N for the CNNS and Ti and O for the TiO$_2$-NS (no nitrogen was detected on TiO$_2$). The Ti 2$p_{3/2}$ binding energy (BE) for all TiO$_2$ containing materials was found at 458.4 eV corresponding to Ti$^{4+}$ surface species in TiO$_2$ [42].
CNNS presented the typical chemical states of C and N in g-C$_3$N$_4$. The N 1$s$ peak of the CNNS appeared at 398.6 eV (Figure 4-A1a in Appendix 4), characteristic of sp$^2$ hybridised nitrogen and the major contribution in the C 1$s$ region centered at 288.4 eV was ascribed to sp$^2$ bonded carbon (N = C (– N)$_2$) [55]. Both Ti-ISO/CN and Ti-NS/CN composites presented N 1$s$ peaks centered at the same position as the CNNS sample (Figure 4-A1b in Appendix 4). The unchanged BE of both Ti 2$p$ and N 1$s$ in the composites compared with the bare TiO$_2$ and CNNS materials, respectively, verified that the crystal structure of the individual parts in the composites was unaltered. This observation suggested the formation of a composite rather than modification of the crystal lattice structure, i.e. N doping of TiO$_2$ via decomposition of CNNS. This is in line with the ATR-FTIR data presented above. The amount of TiO$_2$ in the composites was measured by TGA under a nitrogen atmosphere (Figure 4-3) using the differences in decomposition profiles of CNNS, which decomposed around 500°C, and the relatively thermally stable TiO$_2$. From these the TiO$_2$ content of Ti-NS/CN and Ti-ISO/CN composites was calculated to be 96.2 %wt and 97.1 %wt respectively - accurate to ±1 %wt.

**Figure 4-3.** Thermogravimetric analysis of g-C$_3$N$_4$, CNNS, TiO$_2$, and TiO$_2$/CNNS composites under nitrogen (100 ml min$^{-1}$) heating rate 10 °C min$^{-1}$. 

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4.4.1.4 Materials morphology

In addition to the above techniques, which allowed us to gain insights into the bulk structure and chemistry of the composites, imaging with SEM and TEM were employed for an in-depth understanding of the nanocomposite formation and more details of the TiO$_2$ facet growth. SEM of TiO$_2$-NS (Figure 4-4a) revealed agglomerated TiO$_2$ NS forming large sheets. The average particle size of the TiO$_2$-NS was approximately 20 nm based on TEM (Figure 4-4j). Lattice spacings corresponding to the (101) and (001) anatase TiO$_2$ planes were measured for the top down and side on views respectively of the NS (Figure 4-4b) [16]. The interfacial angle between these planes was in agreement with results reported in previous studies on TiO$_2$ [22, 23]. This confirmed the formation of nanoplatelets with exposed {001} facets [9]. TEM of CNNS also confirmed exfoliation of g-C$_3$N$_4$ to CNNS; the nanosheets were observed 100s of nanometres in length and around 300 nm in width (Figure 4-4c). TEM of Ti-NS/CN showed CNNS coated with TiO$_2$-NS particles (Figure 4-4d). The TiO$_2$ particle size and shape were not affected by the presence of CNNS. Additional evidence of the composite formation was provided by TEM-EDX of Ti-NS/CN (Figure 4-4e-f), with images of TiO$_2$ particles covering a carbon nitride nanosheet on a nanometre scale. The EDX spectra (Figure 4-4f) showed only C and N atoms on the uncovered CNNS region (Area A in Figure 4-4e), with predominantly Ti and O atoms on the TiO$_2$ covered region (Area B in Figure 4-4e).

The control of TiO$_2$ facet growth, previously analysed by XRD patterns, was further confirmed by TEM of Ti-ISO/CN (Figure 4-4g). TiO$_2$ nanoparticles on carbon nitride nanosheets were observed showing successful nanocomposite synthesis for this composite. Compared to Ti-NS/CN (Figure 4-4d), the morphology of the TiO$_2$ crystals was different: an isometric bipyramidal shape was formed, with a smaller mean particle size of 15 nm (Figure 4-4j). Further details of the crystal planes(Figure 4-4h) showed lattice spacings corresponding to the (001) and (101) anatase TiO$_2$ planes [16]. The interfacial angle between the (101) and (011)
planes aligned with the theoretical value [23]. Overall, TEM provided direct evidence of TiO$_2$/CNNS nanocomposite formation as well as the successful control of TiO$_2$ crystal growth. Synthesis in the presence of HF resulted in nanosheet TiO$_2$ formation with more {001} facets; while the absence of HF led to the formation of isometric bipyramidal TiO$_2$ with less {001} facets.

Figure 4-4. Electron microscope images of the materials showing the formation of the composites and highlighting the control over the TiO$_2$ morphology: a) SEM image of TiO$_2$-NS; TEM images of b) TiO$_2$-NS, c) CNNS, d) Ti-NS/CN (a few TiO$_2$ nanoplates are highlighted in blue), e) Ti-NS/CN with uncovered CNNS (Area A), TiO$_2$ nanoparticles (Area B), and blank control (Area C – hole in the TEM grid), f) EDX spectra of e), g) Ti-ISO/CN (a few bipyramidal TiO$_2$ are highlighted in orange), h) Ti-ISO/CN, j) TEM histogram data of
4.4 Results and Discussion

TiO₂-NS (average particle size 20 nm) and TiO₂-ISO (average particle size 15 nm), data from measurement of 100 TiO₂ particles.

4.4.1.5 Textural properties

The surface of the materials was analysed as this is an important aspect of a photocatalyst to quantify the porosity which relates to the number exposed catalytic sites. The textural parameters of the materials are presented in Table 4-1 (see Figure 4-5 for N₂ isotherms). TiO₂-NS exhibited a low surface area with some degree of mesoporosity. Considering that no mesopores are expected for single-crystal nanosheets, the observed mesoporosity can be assigned to void space between aggregates of NS. TiO₂-ISO exhibited a higher surface area [24] and pore volume comprised of both mesopores and some micropores. The higher surface area of TiO₂-ISO was attributed to its smaller particle size and less crystalline nature. Further evidence of exfoliation of g-C₃N₄ to CNNS was proven by the threefold increase of surface area of the CNNS [25], and the transition from a Type H4 to H3 hysteresis loop [24]. The surface area and porosity of Ti-NS/CN were enhanced compared to the parent materials and this material exhibited the highest surface area of all materials in this study. The increased porosity in Ti-NS/CN was assigned to the self-assembly of TiO₂-NS in the presence of CNNS forming a porous structure. This structure was deemed important in photocatalytic reactions to provide potential charge transport pathways and to increase the concentration of reactants close to catalytic sites. On the other hand, Ti-ISO/CN exhibited an isotherm dominated by the TiO₂ component with a similar surface area to TiO₂. It was thought that the different trends observed for the two types of composites may be due to the distinct morphologies of TiO₂-NS and TiO₂-ISO: TiO₂-NS may have allowed a particular assembly of the TiO₂ nanosheets and CNNS due to their similar 2D morphology to form meso- and microporous structures with higher surface area.
Table 4-1. Textural parameters derived from N\textsubscript{2} sorption isotherms at -196 °C, and CO\textsubscript{2} adsorption capacities at 1 bara and 25 °C.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>BET (m\textsuperscript{2} g\textsuperscript{-1})</th>
<th>(V\textsubscript{Tot}^a) (cm\textsuperscript{3} g\textsuperscript{-1})</th>
<th>(V\textsubscript{Meso}^b) (cm\textsuperscript{3} g\textsuperscript{-1})</th>
<th>(V\textsubscript{Micro}^c) (cm\textsuperscript{3} g\textsuperscript{-1})</th>
<th>CO\textsubscript{2} ad\textsuperscript{d} (mmol g\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO\textsubscript{2}-NS</td>
<td>50</td>
<td>0.085</td>
<td>0.085</td>
<td>0.000</td>
<td>0.167</td>
</tr>
<tr>
<td>TiO\textsubscript{2}-ISO</td>
<td>115</td>
<td>0.332</td>
<td>0.300</td>
<td>0.032</td>
<td>0.294</td>
</tr>
<tr>
<td>Ti-NS/CN</td>
<td>174</td>
<td>0.294</td>
<td>0.242</td>
<td>0.052</td>
<td>0.488</td>
</tr>
<tr>
<td>Ti-ISO/CN</td>
<td>119</td>
<td>0.334</td>
<td>0.299</td>
<td>0.035</td>
<td>0.521</td>
</tr>
<tr>
<td>CNNS</td>
<td>53</td>
<td>0.141</td>
<td>0.125</td>
<td>0.016</td>
<td>0.294</td>
</tr>
<tr>
<td>g-C\textsubscript{3}N\textsubscript{4}</td>
<td>17</td>
<td>0.058</td>
<td>0.058</td>
<td>-</td>
<td>0.060</td>
</tr>
</tbody>
</table>

\(^a\) Calculated from the volume adsorbed at P/P\textsubscript{0} = 0.97, \(^b\) Calculated from \(V\textsubscript{meso} = V\textsubscript{total} - V\textsubscript{micro}\), \(^c\) Calculated from the Dubinin-Radushkevich method. \(^d\) CO\textsubscript{2} adsorption capacity measured at 25 °C and 1 bara.

Figure 4-5. a) N\textsubscript{2} adsorption-desorption isotherms at -196 °C and b) CO\textsubscript{2} adsorption-desorption isotherms at 25 °C of g-C\textsubscript{3}N\textsubscript{4}, TiO\textsubscript{2}, CNNS and TiO\textsubscript{2}/CNNS composites.
4.4 Results and Discussion

4.4.2 CO₂ capture capacity

CO₂ adsorption capacities of the materials were measured to quantify the CO₂ concentration at the catalytic surface as this is an important factor in photocatalysis. This was measured at 25 °C up to 1 bar (Figure 4-5b, Figure 4-6a). The materials displayed varying CO₂ uptakes and the overall trend followed the surface area. Both TiO₂ materials had a CO₂ adsorption capacity typical for materials of this kind [11]. The slightly higher capacity of TiO₂-ISO compared to TiO₂-NS may be related to its higher surface area. The exfoliation of g-C₃N₄ to CNNS resulted in a five-fold increase in the CO₂ capacity, similar to reports in other studies [26]. Both nanocomposites exhibited around a twofold increase in CO₂ adsorption compared to their component materials. Ti-ISO/CN exhibited a capacity of 0.521 mmol g⁻¹ which was similar to that of Ti-NS/CN (0.488 mmol g⁻¹), which, given their similar composition, was expected as chemical features take precedence over porosity in controlling CO₂ adsorption at ambient pressure. The small difference observed may be due to a slightly different proportion of reactive sites or access to these sites. The increase in CO₂ uptake for the composite materials was highly desirable, as a higher concentration of CO₂ on the catalyst surface is expected to improve photocatalytic activity [11, 27].
Figure 4-6. Evaluation of TiO$_2$, g-C$_3$N$_4$, CNNS, and TiO$_2$/CNNS composites for: a) CO$_2$ adsorption at 25°C, 1 bar, b) CO production. The panel shows CO evolution rates from photocatalytic CO$_2$ reduction under UV-Vis illumination for a duration of 6 hours with H$_2$ or
H$_2$O as sacrificial agents. The performance of the benchmark TiO$_2$ P25 material is added for comparison. c) Ti-NS/CN CO evolution over a 6 hour photocatalyst test under UV-Vis illumination with H$_2$ as the reducing agent, d) CO evolution for repeated Ti-NS/CN photocatalytic tests under UV-Vis illumination with H$_2$ as the sacrificial agent, f) Mass spectrometer chromatographs (29 m/z) of evolved gases using $^{13}$CO$_2$ and $^{12}$CO$_2$ with photocatalyst Ti-NS/CN.

4.4.3 Optical and photophysical properties, and photocatalytic CO$_2$ reduction

4.4.3.1 Light absorption

Besides CO$_2$ adsorption, another important property of a photocatalyst is light absorption to create photogenerated electrons. This aspect was first investigated using UV-Vis spectroscopy. The Kubelka-Munk formula was used to convert the data into a Tauc plot (Figure 4-A2 in Appendix 4) from which the bandgap energies were measured (Table 4-2) - the TiO$_2$ and carbon nitride samples were treated as indirect and direct semiconductors respectively [25, 28, 29]. As expected, the TiO$_2$ samples both exhibited light absorption onsets in the UV region with a bandgap energy around 3.2 eV for anatase TiO$_2$ [30], g-$C_3N_4$ absorbed in the visible range (bandgap of 2.86 eV). Following exfoliation to CNNS, a blue shift of 0.11 eV was measured. This shift had been reported before [31] and was attributed to the quantum size effect in nanostructures, which led to a shift of the valence and conduction bands in opposite directions [13]. The TiO$_2$/CNNS composites exhibited light absorption spectra in between those of their TiO$_2$ and CNNS components.
Table 4-2. Photocatalyst bandgaps derived from the Kubelka-Munk UV-vis absorption.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>( E_g ) (eV)</th>
<th>( E_g ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)-NS</td>
<td>3.17</td>
<td>391</td>
</tr>
<tr>
<td>TiO(_2)-ISO</td>
<td>3.20</td>
<td>388</td>
</tr>
<tr>
<td>CNNS</td>
<td>2.86</td>
<td>434</td>
</tr>
<tr>
<td>g-C(_3)N(_4)</td>
<td>2.77</td>
<td>448</td>
</tr>
</tbody>
</table>

4.4.3.2 Photocatalytic CO\(_2\) reduction

The materials were evaluated for CO\(_2\) photocatalytic conversion under UV-visible illumination (150 W), for 6 h, under a CO\(_2\)/H\(_2\) or CO\(_2\)/H\(_2\)O vapor atmosphere with the evolution rates in \( \mu \text{mol g}^{-1} \text{h}^{-1} \) presented in Figure 4-6b and Table 4-3. Under these conditions, all photocatalysts reduced CO\(_2\) into CO. Considering the TiO\(_2\) photocatalysts, TiO\(_2\)-ISO evolved CO at a higher rate than TiO\(_2\)-NS; indeed, optimisation studies of TiO\(_2\) {001} facet formation have shown high F\(^-\) concentrations can result in a lower catalytic activity [8, 10]. g-C\(_3\)N\(_4\) was the least active material; in comparison, CNNS reduced CO\(_2\) at almost twice the rate, proving that exfoliation lead to a superior photocatalyst. Both TiO\(_2\)/CNNS nanocomposites showed enhanced CO evolution when compared to their components. Ti-NS/CN was observed to be the most active photocatalyst and notably produced CO at a rate over 12 times higher than TiO\(_2\)-NS. A physical mixture of Ti-NS and CNNS with the same composition as Ti-NS/CN evolved CO at the same rate as Ti-NS, this showed the formation of the nanocomposites using an in-situ synthesis had successfully improved the photocatalytic activity. Also of note was that the CO production of Ti-NS/CN was 37% higher than TiO\(_2\) P25 (tested under the same conditions).

As Ti-NS/CN was the most active photocatalyst, further investigations into the photocatalytic process using it were undertaken. Kinetic data of the CO evolution from Ti-NS/CN over the
6 h testing period (Figure 4-6c) produced a linear progression, indicating a constant catalytic activity. Repeated catalytic tests of Ti-NS/CN (Figure 4-6d) showed a decrease in activity, but the catalyst remained active for three cycles, this may due to formation of surface products and the lack of any catalyst regeneration process. A control test under a N₂ and H₂ atmosphere for Ti-NS/CN yielded no CO₂ reduction products (Table 4-3, entry 9). Additionally, isotopic tracing experiments using $^{13}$CO₂ yielded $^{13}$CO (Figure 4-6e). These two tests prove the photocatalytic origin of CO detected [32]. Following completion of the above tests, the XRD pattern, porosity, UV-Vis absorption profile, and ATR-FTIR spectra were maintained with no significant alterations (Figure 4-A3 in Appendix 4). The influence of the reducing agent was also studied by testing Ti-NS/CN with H₂O vapor (Figure 4-6c). CO and H₂ were detected at rates of $0.80 \mu\text{mol g}^{-1}\text{ h}^{-1}$ and $2.67 \mu\text{mol g}^{-1}\text{ h}^{-1}$ respectively. This represents a third of the CO production rate obtained when using H₂ as a reducing agent. The generation of photocatalytic oxidation products was also investigated with H₂O as the reducing agent: O₂ was detected (test performed with a 300 W lamp under UV-Vis irradiation with water; evolution rates: CO: $1.96 \mu\text{mol g}^{-1}\text{ h}^{-1}$, O₂: $0.98 \mu\text{mol g}^{-1}\text{ h}^{-1}$). This confirmed the holes generated from the photoexcitation process were being used in a photocatalytic oxidation reaction.
Table 4-3. Photocatalytic evolution tests under UV illumination (150 W).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Photocatalyst</th>
<th>CO Evolution (µmol g⁻¹ h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TiO₂-NS</td>
<td>0.16</td>
</tr>
<tr>
<td>2</td>
<td>TiO₂-ISO</td>
<td>1.32</td>
</tr>
<tr>
<td>3</td>
<td>Ti-NS/CN</td>
<td>2.04</td>
</tr>
<tr>
<td>5</td>
<td>Ti-ISO/CN</td>
<td>1.55</td>
</tr>
<tr>
<td>6</td>
<td>CNNS</td>
<td>0.19</td>
</tr>
<tr>
<td>7</td>
<td>g-C₃N₄</td>
<td>0.10</td>
</tr>
<tr>
<td>8</td>
<td>P25</td>
<td>1.49</td>
</tr>
<tr>
<td>9</td>
<td>Ti-NS/CN</td>
<td>n.d</td>
</tr>
<tr>
<td>10</td>
<td>Ti-NS/CN</td>
<td>0.80</td>
</tr>
</tbody>
</table>

N₂ and H₂ atmosphere control test, H₂O as sacrificial agent

4.4.3.3 Transient light absorption

Transient absorption spectroscopy (TAS) in this section were carried out and analysed by Dr. Robert Godin at Imperial College London.

Considering the above spectroscopic and photocatalytic results, multiple factors could have impacted the photocatalytic activity of the prepared materials. Such as CO₂ adsorption playing a key role as evidenced by the improvement in CO evolution from exfoliation of g-C₃N₄ to CNNS, and the high activity of the composite materials. In addition, it is also well known that activity is linked to the ability to photogenerate and separate charges. In the prepared materials, it was thought it was likely that a combination of both the enhancement of CO₂ adsorption at the active sites and improved charge separation influenced the photoactivity. Additionally, it was clear the TiO₂ facets in the composites had a large impact on the photocatalytic activity. Whilst the enhanced photocatalytic activity of the TiO₂/CN composites compared to their
4.4 Results and Discussion

Parent materials can be explained by complimentary optoelectronic and textural properties (i.e. higher surface area, CO₂ adsorption, and higher UV-visible light absorption), the difference in performance between the two composites and therefore the effect of TiO₂ nanoparticle morphology on the photoactivity of the nanocomposites was thought to be related to the contact interface between TiO₂ and CNNS. Specifically, as TiO₂-NS was more of a two-dimensional (2D) structure compared to TiO₂-ISO, this was postulated to enable a more effective contact interface with the 2D morphology of CNNS. This interface could have an impact on the charge dynamics leading to more efficient interfacial charge transfer. As such, a detailed study using Transient absorption spectroscopy (TAS) was undertaken to analyse the photo-excitation and relaxation processes in these materials.

Photoexcitation of TiO₂-NS produced a broad absorption from the visible and NIR spectral ranges which was present for hundreds of milliseconds (Figure 4-7a). The initial signal, at 1 µs, had a larger amplitude at shorter wavelengths and as the spectra evolved the dominant signal shifted to longer wavelengths. These spectral signatures of charges in TiO₂ have been well studied and allowed the distinction between the electron and hole charge carriers. Hole absorption typically increases toward shorter wavelengths while electron absorption peaks at longer wavelengths (~900 nm) [33]. This is consistent with our observations, at early timescales, we observed significant contribution of both hole and electron signals (Figure 4-7b). For spectra deconvolution into reference electron and hole spectra, plotted in red and blue in Figure 4-7 panels b-c, the reference electron spectra was taken as the long-lived signal of TiO₂, while the reference hole spectra was taken as the long-lived signal of Ti-ISO/CN. Over time, the hole component decreased more quickly compared to the electron signal (Figure 4-7a). As balanced electron-hole recombination was expected for TiO₂,[34] we assigned the faster sub-ms decay of holes to scavenging by residual organic surface adsorbates [35]. As a result, only long-lived electrons were observed after hundreds of milliseconds since
all holes have been consumed. We note that the influence of these surface organics complicate interpretation of the decay kinetics and may explain why the TiO₂ absorption spectra in this chapter differed at early timescales from the TiO₂ materials studied in Chapters 5 and 6. We therefore limited the analysis to the distinct shape of the TAS spectra for the different samples.

Turning our attention to the Ti-NS/CN composite absorption spectra (Figure 4-A4a in Appendix 4), a much less distinct spectral evolution on the microsecond – millisecond timescales was observed. While the spectra at longer times were similar to those observed for the TiO₂-NS sample in comparison the hole signal at 1 µs was suppressed (Figure 4-7c). This suggested sub-µs hole transfer from the TiO₂ to the CNNS, a process in line with the favorable energetics from the relative valence band potentials of these materials. The spectra of CNNS alone instead showed a broad absorption peaking between 550–700 nm (Figure 4-A4b in Appendix 4) [36]. It was assumed that the CNNS spectrum was dominated by the electron signal and as such the spectral signature of holes localised on CN was too weak to be observed.

The TiO₂/CN composite prepared without the stabilizing agent to form bipyramidal TiO₂ (Ti-ISO/CN) exhibited a spectrum dominated by a signal peaking near 500 nm (Figure 4-A4c in Appendix 4). The spectrum did not show temporal evolution over the micro-millisecond range, indicating that the same species were dominant throughout. The shape of the spectra was consistent with a TiO₂ hole signal, and the long-lived signal of Ti-ISO/CN was therefore taken as the reference hole spectra. Compared to the Ti-NS/CN composite, no long-lived electron signal was observed. In addition, the Ti-ISO/CN initial spectrum (Figure 4-7d) was dominated by signal from TiO₂ holes, unlike the Ti-NS/CN spectra, indicating a lack of hole charge transfer in Ti-ISO/CN. Thus, the {001} facet stabilizing agent (HF) was deemed to have played a key role in dictating the trapping of charges in the TiO₂ component of the TiO₂/CNNS composites: in the Ti-ISO/CN hole transfer to CNNS was impeded and holes instead
accumulated on TiO$_2$ leading to low electron concentration in TiO$_2$, owing to faster charge recombination, and lower CO$_2$ reduction yields; and in contrast, hole transfer from TiO$_2$ to CNNS was facilitated in the Ti-NS/CN, resulting in higher electron concentration in TiO$_2$ due to lower charge recombination rates, and higher CO$_2$ reduction yields.

**Figure 4-7.** TAS spectra used to study photoexcitation processes in the powdered samples. a) spectra at different delay times of TiO$_2$-NS following photoexcitation. b-d) Initial spectra at 1 µs for: b) TiO$_2$-NS, c) Ti-NS/CN, d) Ti-ISO/CN. The hole contribution is shaded in blue and the electron contribution is shaded in red. The sum of the two is indicated as the ‘Total’
by a green line, and is compared to the experimental values shown in the black line and squares. All samples were photoexcited by 100 µJ/cm² pulses of 355 nm laser light. TAS was carried out Dr. Robert Godin at Imperial College London.

4.4.4 Proposed reaction pathway

Taking the above results into account, a possible reaction pathway is proposed for photocatalytic CO₂ reduction over Ti-NS/CN (Figure 4-8). The band structure was constructed using the bandgap measured in this study (Table 4-2). The conduction bands were taken from computational studies in literature relative to the SHE of 4.44 eV: -0.96 V for CNNS [37], and -0.28 V for anatase TiO₂ [38]. As shown in Figure 4-8, the composite heterojunction was Type II. Under UV-vis illumination, both the CNNS and TiO₂ absorbed photons with sufficient energy to generate electron-hole pairs. Both CNNS and TiO₂ reduced CO₂ to CO as both sets of photoexcited electrons possess sufficient electrochemical potential. The enhanced photocatalytic activity of the Ti-NS/CN can be explained by two main factors: availability of CO₂, and availability of photoexcited electrons. Compared to their constituent materials, CO₂ concentration was increased at the catalytic sites owing to their increased CO₂ adsorption capacity. Recombination of electron-hole pairs was suppressed by interfacial charge transfer via the heterojunction present in this material. This increased the abundance of electrons available for catalysis and resulted in a further increase in CO₂ conversion.
4.5 Conclusions

This chapter presents the design, synthesis, characterisation, and testing of inorganic/organic TiO$_2$/CNNS nanocomposites for CO$_2$ capture and photocatalytic conversion. These composites were formed via an *in-situ* synthesis of TiO$_2$ in the presence of CNNS. Particular attention was paid to controlling the TiO$_2$ crystal growth and the formation of {001} facets due to their enhanced photocatalytic activity. Electron microscopy imaging and spectroscopic analyses provided direct and indirect indication of the formation of TiO$_2$ on the CNNS, and demonstrated the control of TiO$_2$ facet growth. Both nanocomposites showed enhanced CO$_2$ adsorption capacity and photocatalytic activity (*i.e.* CO$_2$ photoreduction) compared to their component materials, also exceeding the performance of the TiO$_2$ P25 benchmark material. CO production using the composites was observed when using either H$_2$ or water vapour as the sacrificial agent. The TiO$_2$/CN with increased number of TiO$_2$ {001} facets was more
catalytically active than the composite with isometric TiO₂. TAS analyses provided insights into the observed catalytic trends, sub-μs hole transfer from TiO₂ to CN was observed for Ti-NS/CN but not Ti-ISO/CN. This showed the control of TiO₂ crystal growth enabled charge transfer via a TiO₂-CN heterojunction to produce a more active photocatalyst. The study overall demonstrated that the photocatalytic reduction of CO₂ could be improved greatly by forming composite materials with increased CO₂ adsorption capacity and which can suppress electron-hole recombination by facilitation of charge transfer.

In relation to the research objectives the above study addressed each by the following findings:

**RO 1: To design and synthesise bifunctional photocatalysts for improved CO₂ adsorption capacity and photocatalytic reduction of CO₂ and investigate their morphology, textural properties and light utilization properties.**

- The TiO₂/CNNS composite materials were bifunctional materials capable of combined CO₂ adsorption and CO₂ photoreduction.
- The TiO₂/CNNS materials had increased CO₂ adsorption capacity by a factor of 3 and increase CO₂ reduction by a factor of 10 when compared to TiO₂-NS.
- The formation of TiO₂/CNNS composites with TiO₂ particles coating CNNS was confirmed and they had increased surface area and CO₂ adsorption capacity compared to their constituent materials.
- A broader light absorption spectra into visible wavelengths was attributed to the CNNS component, light utilization was improved by increased charge generation achieved by the control of the {001} facet in the Ti-NS/CN composite.
- These improved morphology, textural and light utilization properties were all shown to have contributed to the improved CO₂ photoreduction rates.
RO 2: To investigate the photocatalysts robustness and recyclability for photocatalytic CO$_2$ reduction.

- The TiO$_2$/CNNS composites photocatalytically reduced CO$_2$ at a stable rate over the 6 h testing period.
- Repeated photocatalytic tests with no regeneration step showed a decrease in photocatalytic activity, the materials crystallinity was unchanged.

4.6 References

Chapter 5  Investigation of TiO$_2$/MOF nanocomposites

Abstract

TiO$_2$ and metal-organic framework (NH$_2$-UiO-66) were effectively coupled via an *in-situ* growth strategy to form bifunctional composite materials for the combined capture and photocatalytic reduction of CO$_2$ under UV-visible light irradiation. These materials were chosen to take advantage of the high CO$_2$ adsorption capacity of the metal-organic framework (MOF) and the photocatalytic properties of pre-formed TiO$_2$ nanosheets in a single material. The prepared materials were thoroughly characterised using a variety of techniques and were tested for CO$_2$ adsorption and CO$_2$ photocatalytic reduction using a heterogeneous gas/solid set-up. The adopted synthesis process allowed the development of a tight interaction between TiO$_2$ and NH$_2$-UiO-66, forming a heterojunction, while maintaining the high CO$_2$ uptake and porosity of NH$_2$-UiO-66. The nanocomposites were proven durable and significantly more efficient in reducing CO$_2$ to CO than their single components. Photocatalytic activity was greatly affected by the nanocomposites composition with the optimum TiO$_2$ content presenting 1.5 times increased CO evolution rate compared with the pure TiO$_2$. The improved photoactivity was assigned to the enhanced abundance of long lived charge carriers, revealed by transient absorption spectroscopy (TAS). This most likely occurred due to the effective charge transfer via the TiO$_2$-MOF interface.


5.1 Overview

In this chapter a study of TiO$_2$/MOF composites for photocatalytic CO$_2$ reduction is presented. The MOF’s tunability allowed selection of a photocatalytically active MOF with increased light absorption, high surface area, and increased CO$_2$ adsorption capacity. The coupling of MOFs with TiO$_2$ was investigated with the primary aim of forming composites with improved CO$_2$ reduction and adsorption properties. Compared to the TiO$_2$/CNNS composites studied in Chapter 4, the MOF component in TiO$_2$/MOF composites should result in significantly higher surface area to increase exposed catalytic sites, and higher CO$_2$ adsorption capacity to increase CO$_2$ abundance at these sites. TiO$_2$ was synthesised with TiO$_2$ facet formation controlled to form nanosheets, then the MOF was synthesised in the presence of TiO$_2$ to form composite materials, the MOF content in these composites was varied and optimised. Based on this chapter ref [1] was prepared.

5.2 Introduction

MOFs have recently been studied as photocatalysts for CO$_2$ reduction [2, 3] – these were reviewed in more detail in Chapter 2, Section 2.5.3. Whilst progress has been made, of note was that the photoactivity of MOFs was not comparable to that of inorganic semiconductors mostly due to the low photogenerated charge formation and low charge separation efficiency. Among the MOFs explored, NH$_2$-UiO-66 has attracted attention due to its chemical stability and visible light adsorption [4-7]. Targeting improved performance, MOFs have been effectively coupled with other photocatalysts [5, 8-10]. As reviewed in Chapter 2 Section 2.5.3.5.1, the coupling TiO$_2$ and MOFs to form TiO$_2$/MOF composites has resulted in materials with increased catalytic activities. For example, TiO$_2$ particles have been grafted onto preformed HKUST-1 microcrystals by hydrolysis to create a TiO$_2$/HKUST-1 composite [8].
More recently, TiO$_2$ nanoparticles were grown on Co-ZIF-9 and the prepared composites were applied for CO$_2$ photoreduction under UV-visible light irradiation [11]. These studies have shown that the establishment of synergistic effects leading to improved activity is greatly affected by the nature of the coupled materials. The interaction between semiconductors and MOFs was identified as the critical parameter for enhanced photoactivity [11, 12].

For this study bifunctional TiO$_2$/MOF nanocomposites were developed for the combined capture and photocatalytic reduction of CO$_2$. The TiO$_2$ component was selected primarily for its photocatalytic activity while the MOF component was hypothesized to enhance CO$_2$ uptake and provide the pore space needed to promote access to the catalytic sites. In an effort to control in parallel both the TiO$_2$/MOF interaction as well as the activity of the TiO$_2$ component, an \textit{in-situ} synthesis process was adopted to develop NH$_2$-UiO-66 in the presence of pre-synthesised large TiO$_2$ nanosheets (NS) with exposed \{001\} facets. The MOF content in the composites was also controlled and optimised. The materials were applied for CO$_2$ adsorption and photoreduction, and various analytical and spectroscopic techniques were used to fully understand these processes.

### 5.3 Material synthesis

All reagents used in this study were of analytical grade and used without further purification. 2-aminoterephthalic acid (99%), hydrochloric acid (HCl, 37 %), hydrofluoric (48%), titanium butoxide (97%), and zirconium (IV) chloride (ZrCl$_4$, 99.5%) were purchased from Sigma-Aldrich. N,N-dimethyl formamide (DMF, 99.9%, anhydrous) was purchased from VWR.
5.3.1 Synthesis of TiO$_2$ nanosheets (NS)

TiO$_2$ NS were prepared by a solvothermal method [13] – see Figure 5-1. 30 mL of titanium butoxide was added into a Teflon cup. Then, 3 mL of HF (48%) was slowly added into the solution under stirring. The solution was then stirred for 10 minutes and then the Teflon cup was sealed in a stainless steel autoclave and placed in an oven at 180 °C for 24 h. After that, the autoclave was naturally cooled to room temperature, the white solid was collected, separated, and washed by centrifugation with deionized water once and then ethanol three times. The powder was dried overnight at 65 °C, vacuum treated at 120 °C and finally calcined at 300 °C for 4 h under static air to remove any remaining organics.

5.3.2 Synthesis of NH$_2$-UiO-66

NH$_2$-UiO-66 was synthesised based on a previously reported procedure [14], scaled up to increase the product yield. 1.25 g of zirconium (IV) chloride (ZrCl$_4$), 50 mL N,N-dimethyl formamide (DMF), and 10 mL concentrated hydrochloric acid (37 %) were combined in beaker and placed in a sonication bath for 20 minutes. 1.34 g of 2-aminoterephthalic acid (99%) and additional 100 mL DMF were added. The mixture was sonicated for 20 min, transferred to a round bottom flask, and then heated under stirring to 150 °C for 24 h in an oil bath. After cooling, the solid particles were recovered by centrifugation and washed three times with ethanol, vacuum dried at 120 °C and then stored in a desiccator.

5.3.3 Synthesis of TiO$_2$/NH$_2$-UiO-66 composites

For the synthesis of the nanocomposites, an in-situ approach was adopted for the development of NH$_2$-UiO-66 in the presence of pre-synthesised TiO$_2$ NS – see Figure 5-1. The synthesis was based on the pure NH$_2$-UiO-66 synthesis process with the addition of TiO$_2$ NS in the solution. A fixed amount of TiO$_2$ (0.5 g) was sonicated for 30 min in DMF. The TiO$_2$ content in the nanocomposites was controlled by scaling the NH$_2$-UiO-66 synthesis. Herein, the
NH$_2$-UiO-66 sample is referred to as MOF and the obtained nanocomposites are named $x$-TiMOF, where an increase $x$ ($x = 1, 2, 3, 4$) denotes an increase in NH$_2$-UiO-66 content (from 19 to 37 wt.%).

**Figure 5-1.** Schematic of the TiO$_2$/NH$_2$-UiO-66 nanocomposites synthesis. TiO$_2$ nanosheets (NS) were synthesised hydrothermally from titanium butoxide. The TiO$_2$ NS were then added to an open vessel NH$_2$-UiO-66 synthesis flask for MOF growth in the presence of TiO$_2$ NS to form TiO$_2$/NH$_2$-UiO-66 nanocomposites ($x$-TiMOF), where $x$ denotes an increase in MOF %wt, controlled by scaling the MOF synthesis volume.
5.4 Results and Discussion

5.4.1 Structural and chemical characterisation

5.4.1.1 Material composition, crystalline structure, and thermal stability

TGA was first used to quantify the TiO$_2$ and NH$_2$-UiO-66 content in the nanocomposites and assess their thermal stability. It can be seen from Figure 5-2a that TiO$_2$ was stable up to 900 °C. The small mass drop from 300 to 700°C of 2.8 %wt can be attributed to impurities from the TiO$_2$ synthesis as this material was calcined at 300 °C. NH$_2$-UiO-66 exhibited stability up to around 200 °C. The lack of mass drop prior to this shows no detectable guest species (i.e. DMF) remaining in the pore network after synthesis. As expected, the organic ligands and hence the framework decomposed above 200 °C [14, 15]. The thermal degradation profiles of TiO$_2$/NH$_2$-Uio-66 nanocomposites displayed characteristics of both TiO$_2$ and NH$_2$-UiO-66, allowing the TiO$_2$ content to be quantified from the residual mass at 900 °C (Table 5-S1 in Appendix 5). The TiO$_2$ content of the composites ranged from 63.2 to 81.0 %wt.
5.4 Results and Discussion

![Thermogravimetric curves of TiO₂, NH₂-UiO 66 and TiO₂/NH₂-UiO-66 nanocomposites (x-TiMOF) under N₂ atmosphere](image)

![XRD patterns of TiO₂, NH₂-UiO-66 and TiO₂/NH₂-UiO-66 nanocomposites (x-TiMOF).](image)

**Figure 5-2.** a) Thermogravimetric curves of TiO₂, NH₂-UiO 66 and TiO₂/NH₂-UiO-66 nanocomposites (x-TiMOF) under N₂ atmosphere b) XRD patterns of TiO₂, NH₂-UiO-66 and TiO₂/NH₂-UiO-66 nanocomposites (x-TiMOF).

XRD was used to verify the formation of both the TiO₂ and NH₂-UiO-66 components in the composites. Figure 5-2b presents the XRD patterns of the pure TiO₂ and NH₂-UiO-66 materials and the x-TiMOF composites, all samples showed high levels of crystallinity. For the TiO₂ sample only anatase (A) phase TiO₂ was detected [16]. NH₂-UiO-66 displayed the typical diffraction pattern of that particular MOF [4, 6, 7, 14]. As evidenced by the XRD patterns of the x-TiMOF composites, the phase composition and crystallinity of TiO₂ did not change after the synthesis process applied for the MOF nucleation and growth. Similarly, no obvious changes were detected in the diffraction peaks of the nanocomposites corresponding to the NH₂-UiO-66 part. The nanocomposites showed a combination of the TiO₂ and NH₂-UiO-66 patterns with intensity proportional to abundance. Hence, the XRD data provided direct evidence that both TiO₂ and NH₂-UiO-66 structures were present and not noticeably altered by the synthesis process applied for the development of the nanocomposites.
XPS in this section was performed and analysed by Dr Spyridon Zafeiratos in the University of Strasbourg.

X-ray photoelectron spectroscopy (XPS) was employed to investigate the chemical state and the composition of the outermost surface (ca. 5 nm). The survey spectra confirmed the presence of Zr, Ti, O, N, and C elements (Figure 5-A1 in Appendix 5) while in the case of pure TiO$_2$ and the nanocomposites F originating from HF used to synthesize TiO$_2$, was also detected. The Ti $2p$ core level spectra of TiO$_2$, and 2-TiMOF samples are shown in Figure 5-3a. The Ti $2p_{3/2}$ binding energy (BE) for the pure TiO$_2$ sample was found at 458.5 eV in agreement with previous published results for Ti$^{4+}$ in TiO$_2$ [17]. The Ti $2p$ spectrum of 2-TiMOF was shifted at lower BEs and has a broader line shape (the width of Ti $2p_{3/2}$ increases to 1.8 eV instead of 1.5 eV in the pure TiO$_2$). The analysis of the Ti $2p$ peak using two doublets with fixed spin-orbit splitting and $2p_{3/2}/2p_{1/2}$ area ratio, indicated an additional Ti $2p$ component at 457.9 eV. This new Ti component could not be attributed to reduced Ti$^{3+}$ species, since typically the BE of Ti$^{3+}$ is reported around 457 eV or lower [17, 18]. The Zr $3d$ peaks of NH$_2$-UiO-66 and 2-TiMOF samples are displayed in Figure 5-3b. As in the case of Ti $2p$, the Zr $3d$ core levels are split into two components, due to the spin-orbit coupling effect. The Zr $3d$ peak of NH$_2$-UiO-66 at 182.6 eV is characteristic of Zr$^{4+}$ [19], while in case of 2-TiMOF the spectrum becomes broader and shifts to higher BEs. The fitting procedure indicates that this is due to the contribution of an additional Zr $3d$ peak at 183.2 eV. The appearance of the additional Ti and Zr components at 457.9 eV and 183.2 eV respectively, suggested a modification in the surface chemical states of Zr and Ti in the composite and supported an interaction between the TiO$_2$ and NH$_2$-UiO-66 with a possible formation of an effective path for charge carrier migration. Based on the obtained Zr/Ti surface atomic ratio equal to 0.42, it can be concluded that although most of the TiO$_2$ NS is incorporated within the inner part of MOF particles, part of the TiO$_2$ particles is also present at the surface of the composite. The C $1s$, O $1s$ and N $1s$ peaks are
shown in Figure 5-A2 in Appendix 5. In the C 1s spectra the component at ca. 288.5 eV, that is due to sp² C atoms bonding to N or O=C-O [20, 21], is enhanced in MOF and 2-TiMOF as compared to the pure TiO₂. Similarly, the O 1s peak at 529.4 eV, attributed to the lattice oxygen ions of the TiO₂ network, is shifted by ca. 0.2 eV to higher BE in the nanocomposite.

**Figure 5-3.** Core level XPS spectra of the pure TiO₂ and NH₂-UiO-66 and 2-TiMOF nanocomposite in the: a) Ti 2p and b) Zr 3d regions. XPS was performed by Dr Spyridon Zafeiratos in the University of Strasbourg.

### 5.4.1.2 Material chemistry

ATR-FTIR spectroscopy was then used to get further insight into the interactions between the two composite components (Figure 5-4). The NH₂-UiO-66 and TiO₂ samples showed similar characteristics to those reported in literature [4, 11, 22]. Key differences were detected for the x-TiMOF nanocomposites when compared with the pure reference materials. Particularly, the NH₂-UiO-66 bands at 1338 cm⁻¹ and 1255 cm⁻¹ corresponding to the Cₛ₋N stretching vibration modes [23] decreased in intensity for the nanocomposites while the latter shifted to 1262 cm⁻¹. The NH₂-UiO-66 band centred at 1568 cm⁻¹ assigned to the OCO asymmetric stretching vibration mode shifted to 1581 cm⁻¹ for the composites. In addition, the intensity of the low frequency bands (763-473 cm⁻¹), which are a combination of OH and CH bending and Zr–O
modes, was significantly decreased in the nanocomposites. These changes suggest an alteration of the organic moiety ligation to the metal cluster [24]. Changes were also detected on the amine group bands, the band centered at 3474 cm\(^{-1}\) ascribed to the asymmetric N–H stretching vibration mode [25] shifted to 3487 cm\(^{-1}\) in the nanocomposites. Overall, the presence of NH\(_2\)-UiO-66 bands in the IR spectra of \(x\)-TiMOF nanocomposites suggested the presence of the MOF in the composites and suggested that the structural features of the MOF are maintained in the presence of TiO\(_2\). In addition, the observed differences compared with the pure NH\(_2\)-UiO-66 suggested the presence of interactions between the two components of the nanocomposites.

![Figure 5-4. ATR-FTIR of TiO\(_2\), NH\(_2\)-UiO-66 and TiO\(_2\)/NH\(_2\)-UiO-66 nanocomposites \((x\)-TiMOF\).](image)

5.4.1.3 Materials morphology

By visualizing the morphology of the composites, SEM brought further evidence of the intimate contact between TiO\(_2\) NS and NH\(_2\)-UiO-66 particles. As seen in Figure 5-5a, TiO\(_2\)
presented a nanoplate morphology with an average side length of ca. 105 nm and thickness of ca. 32 nm. These were observed in the form of agglomerates formed through the stacking of TiO$_2$ NS. At this point, it is highlighted the deviation from the typical octahedral bipyramidal morphology observed for natural anatase [26]. This was attributed to the presence of F$^-$ ions (HF used for TiO$_2$ synthesis) controlling the morphology and favouring the growth of $\{001\}$ facets [27, 28]. The pure NH$_2$-UiO-66 (Figure 5-5b) exhibited smooth and clean surfaces presenting an average particle size of ca. 400 nm, similar to those reported previously for that material. [7, 29, 30] The nanocomposites exhibited features intermediate between those of pure TiO$_2$ and NH$_2$-UiO-66 (Figure 5-5c). The presence of TiO$_2$ during the MOF synthesis created a composite material with an uneven and rough surface. This might be due to the fact that the presence of the TiO$_2$ nanoparticles altered the formation process of the MOF particles and agglomerates. Crucially there was a uniform distribution of TiO$_2$ NS within the composite structure confirmed by EDX (Figure 5-5d), which highlighted the even dispersion of Ti and Zr atoms. Also of importance was that compared with the pure TiO$_2$, no agglomerates or isolated TiO$_2$ particles were detected in the nanocomposites. Overall, the SEM data confirmed the successful formation of heterostructures and suggested a tight interaction between the two parts with a possible formation of a heterojunction.
5.4 Results and Discussion

Figure 5-5. SEM images of: a) TiO$_2$, b) NH$_2$-UiO-66, c) 2-TiMOF with TiO$_2$ particles (white arrows) and NH$_2$-UiO-66 particles (red arrow) indicated, and d) EDX of 2-TiMOF with zirconium and titanium element mapping.

5.4.1.4 Textural properties

As explained above, one of the key aspects of the use of MOFs in building the composites was to create the porosity necessary to capture CO$_2$ and also to favour access of CO$_2$ molecules to the catalytic sites. Hence the porosity of the materials was evaluated using nitrogen sorption isotherms (Figure 5-A3 in Appendix 5). Table 5-1 summarises the BET surface area, pore volume, and CO$_2$ adsorption capacity (obtained at 1 bar, 25 °C). As expected, the surface area of TiO$_2$ was found to be very low when compared to NH$_2$-UiO-66 with values similar to those reported, exhibiting typical adsorption/desorption isotherm features of a mesoporous material [4, 14]. The nanocomposites contained micropores owing to the presence of NH$_2$-UiO-66 and their surface increased linearly with increasing NH$_2$-UiO-66 content. Overall, surface area based on the total weight of the nanocomposite was significantly lower than that of the pure NH$_2$-UiO-66 (871 m$^2$ g$^{-1}$). This was expected taking into consideration the low content of the
MOF in the final composites. In fact, the experimentally observed surface area values of the nanocomposites were similar to the theoretical values - calculated by linear combination of their constituent surface areas using the content extracted from TGA (Table 5-1). Of importance to note was that the mesoporous volumes for all composites, except 4-TiMOF, were higher than those of both TiO$_2$ and NH$_2$-UiO-66. This must originate from the incorporation of the TiO$_2$ nanoparticles within the MOF structure; at the MOF-TiO$_2$ interface MOF formation may have been altered leading to missing ligands increasing mesoporosity. On the other hand, the microporosity was not significantly altered when normalized to the MOF content.

**Table 5-1.** Textural parameters derived from N$_2$ sorption isotherms at -196 °C, CO$_2$ adsorption capacities at 1 bar and 25 °C, and titanium dioxide content for TiO$_2$, NH$_2$-UiO-66 and TiO$_2$/NH$_2$-UiO-66 composites.

<table>
<thead>
<tr>
<th></th>
<th>BET (m$^2$ g$^{-1}$)</th>
<th>$V_{\text{Tot}}$ (cm$^3$ g$^{-1}$)</th>
<th>$V_{\text{Meso}}$ (cm$^3$ g$^{-1}$)</th>
<th>$V_{\text{Micro}}$ (cm$^3$ g$^{-1}$)</th>
<th>CO$_2$ ad (mmol g$^{-1}$)</th>
<th>$X_{\text{TiO}_2}$ (% mass)</th>
<th>BET$_{\text{calc}}$ (m$^2$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>42</td>
<td>0.149</td>
<td>0.149</td>
<td>-</td>
<td>0.061</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>1-TiMOF</td>
<td>173</td>
<td>0.213</td>
<td>0.173</td>
<td>0.040</td>
<td>0.32</td>
<td>81.0</td>
<td>200</td>
</tr>
<tr>
<td>2-TiMOF</td>
<td>202</td>
<td>0.233</td>
<td>0.164</td>
<td>0.049</td>
<td>0.36</td>
<td>80.5</td>
<td>204</td>
</tr>
<tr>
<td>3-TiMOF</td>
<td>268</td>
<td>0.256</td>
<td>0.165</td>
<td>0.071</td>
<td>0.47</td>
<td>75.5</td>
<td>245</td>
</tr>
<tr>
<td>4-TiMOF</td>
<td>284</td>
<td>0.215</td>
<td>0.138</td>
<td>0.077</td>
<td>0.56</td>
<td>63.2</td>
<td>347</td>
</tr>
<tr>
<td>NH$_2$-UiO-66</td>
<td>871</td>
<td>0.410</td>
<td>0.135</td>
<td>0.275</td>
<td>1.30</td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>

$^a$. Calculated from the volume adsorbed at P/P$_0$ = 0.97, $^b$. Calculated from $V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$, $^c$. Calculated from the t-plot method, $^d$. CO$_2$ adsorption capacity measured at 25 °C and 1 bar, $^e$. BET$_{\text{calc}} = x_{\text{NH}_2\text{-UiO-66}} \times \text{BET}_{\text{NH}_2\text{-UiO-66}} + x_{\text{TiO}_2} \times \text{BET}_{\text{TiO}_2}$.
As the porosity of the composites was confirmed, the amount of CO$_2$ captured was then investigated (Figure 5-6, Table 5-1). The nanocomposites presented moderate adsorption capacity (ranging from 0.32 to 0.56 mmol g$^{-1}$) when compared with the pure NH$_2$-UiO-66 (1.30 mmol g$^{-1}$). However, CO$_2$ uptake was significantly improved when compared with the pure TiO$_2$ nanoparticles (0.061 mmol g$^{-1}$) and increased linearly with increasing MOF content. Hence, the CO$_2$ adsorption on the nanocomposites was attributed to the presence of NH$_2$-UiO-66. This is also supported by the CO$_2$ adsorption capacity of the x-TiMOF materials normalized to the NH$_2$-UiO-66 content, which is approximately equal to that of NH$_2$-UiO-66. These results clearly indicate that the incorporation of TiO$_2$ into the MOF did not alter its structure or inhibit CO$_2$ uptake of the MOF. The observed enhanced CO$_2$ adsorption by the nanocomposites compared with the pure TiO$_2$ may have an impact in photoactivity by increasing the CO$_2$ concentration on the photocatalyst surface [9].

Figure 5-6. CO$_2$ sorption isotherms measured at 25 °C for TiO$_2$, NH$_2$-UiO-66 and TiO$_2$/NH$_2$-UiO-66 composites (x-TiMOF).
5.4 Results and Discussion

5.4.2 Optical and photophysical properties of the materials and photocatalytic CO$_2$ reduction

5.4.2.1 Light absorption

As the materials were to be evaluated for the photocatalytic reduction of CO$_2$, their optical absorption properties were studied by DR-UV/Vis. The converted UV-Vis absorption spectra are given Figure 5-7a and the corresponding Tauc plots used to estimate the $E_g$ values in Figure 5-7b. TiO$_2$ was treated as an indirect and NH$_2$-UiO-66 as a direct semiconductor [26, 31, 32]. The absorption edge of the pure TiO$_2$ was around 380 nm while for the pure NH$_2$-UiO-66 the absorbance was extended up to 440 nm. These correspond to $E_g$ values of 3.20 eV and 2.70 eV, respectively [8, 26]. In the nanocomposites an obvious shift of the absorption band towards visible wavelengths was detected which can be exclusively attributed to the presence of NH$_2$-UiO-66.
Figure 5-7. a) Kulbelka-Munk absorption spectra and b) Tauc plot of TiO$_2$, NH$_2$-UiO-66 and TiO$_2$/NH$_2$-UiO-66 composites.

5.4.2.2 Photocatalytic CO$_2$ reduction

The photocatalytic activity of the prepared materials was then evaluated for gas phase photocatalytic reduction of CO$_2$ at ambient temperature using H$_2$ as a sacrificial agent. Figure 5-8a presents the CO evolution after 6 hours reaction time under UV-Vis irradiation. The pure NH$_2$-UiO-66 presented the lowest activity. Recently, NH$_2$-UiO-66 [4] as well as other amino-functionalized [33] and Zr-cluster containing MOFs [34] have been proven active for CO$_2$ reductions but reactions have been carried out in the liquid phase using light irradiation of higher power. Here, a gas/solid phase setup was selected to mimic the conditions needed for a
combined CO$_2$ capture and CO$_2$ conversion process as a way towards carbon management. In the case of the TiO$_2$-based materials, all nanocomposites showed superior photoactivity compared with the pure TiO$_2$ indicating a synergistic effect between TiO$_2$ and NH$_2$-UiO-66 (red bars in Figure 5-8a). CO evolution first increased and then decreased with increasing MOF content. The nanocomposite containing moderate amounts of NH$_2$-UiO-66, 2-TiMOF (ca. 20 \%wt), presented the highest activity, 1.5 times more active than the pure TiO$_2$. It is important to note that no CO$_2$ reduction was observed over CdS/NH$_2$-UiO-66 composites in ref [5]. The difference in the findings of the present study and in ref [5] highlight the importance of the proper choice of the individual parts for the development of composites with improved catalytic activity.
5.4 Results and Discussion

Figure 5-8. a) Photocatalytic CO evolution from TiO$_2$, NH$_2$-UiO-66 and TiO$_2$/NH$_2$-UiO-66 composites ($x$-TiMOF) under UV-Vis illumination (150 W) with H$_2$ as the reducing agent, b) 2-TiMOF photocatalytic CO evolution as a function of time, c) 2-TiMOF CO evolution repeated for three 6 h photocatalytic cycles, d) 2-TiMOF XRD patterns before and after photocatalytic testing.

In order to establish the contribution of a heterojunction formation in photoactivity, a physical mixture containing the same weight ratio of TiO$_2$/NH-UiO-66 as that of the 2-TiMOF nanocomposite was prepared and tested. The activity of the mechanically mixed sample
resembled that of the TiO\textsubscript{2} portion. This indicates that the *in-situ* process applied herein for the synthesis of the nanocomposites is prerequisite for the development of an interfacial interaction between the two components, which in turn has a crucial role in activity. The close interaction formed between TiO\textsubscript{2} and NH\textsubscript{2}-UiO-66 probably diminished the need of an assistant electron transfer material which is required in catalytic systems obtained by physically mixing of two materials [5]. It is highlighted that no CO was detected in all reference reactions carried out in the dark, in the absence of catalyst or under a N\textsubscript{2}/H\textsubscript{2} atmosphere. These results clearly indicate that CO originated from the photocatalytic reduction of CO\textsubscript{2}. In terms of catalyst stability, the CO evolution from 2-TiMOF was observed to proceed at a near constant rate over the 6 hour testing period (Figure 5-8b). Additionally, no obvious decrease in CO evolution was detected when using the same catalyst for three consecutive times highlighting the stability of the prepared materials which did not require of any regeneration process (Figure 5-8c). Stability was further verified by acquiring the XRD patterns of the used catalysts. The XRD patterns of the materials remained unaltered after the reactions indicating the potential robustness of the materials (Figure 5-8d).

There are different and non-exclusive factors that could account for the enhanced CO\textsubscript{2} reduction observed over the prepared nanocomposites. The MOF may act as an interface spacer preventing agglomeration of TiO\textsubscript{2} nanoparticles to provide additional exposed surfaces, facilitating increased activity. This was evidenced by SEM in the nanocomposites (Figure 5-5). The observed superior CO\textsubscript{2} uptake of the nanocomposites compared to the pure TiO\textsubscript{2} could also improve photoactivity [9] by increasing the CO\textsubscript{2} concentrations close to the photoactive surfaces. Light absorption properties of the prepared nanocomposites were also improved with absorption edge of the TiO\textsubscript{2}/NH\textsubscript{2}-UiO-66 nanocomposites red-shifted by approximately 70 nm compared to the pure TiO\textsubscript{2} NS. However, light absorption and CO\textsubscript{2} adsorption alone cannot explain the observed trend in the nanocomposite series since 4-TiMOF was less active than
2-TiMOF. Regarding the actual trend in CO evolution rate observed within the TiO$_2$/NH$_2$-UiO-66 samples, as TiO$_2$ was the most active phase of CO$_2$ photoreduction process (Figure 5-8a), the drop of photoactivity at high MOF loadings might be related to the decrease of TiO$_2$. Alternatively, considering that both phases (TiO$_2$ and MOF) are photoexcited under the applied conditions, excess NH$_2$-UiO-66 may have also decreased the number of hetero-interfaces in the nanocomposites, which in turn decreased charge transfer in heterostructures [35]. It is well known that both the ability to produce photogenerated charges but also their efficient separation are essential [36].

5.4.2.3 Transient light absorption

Transient absorption spectroscopy (TAS) in this section were carried out and analysed by Dr. Andreas Kafizas at Imperial College London.

Transient absorption spectra (TAS) were recorded to evaluate charge transfer processes in an effort to relate the electronic properties with catalytic activity. For this study, TAS measurements were focused on long lived charge carriers (micro- to millisecond), as it has been shown that these are the timescales most relevant to CO$_2$ reduction kinetics (typically several hundred microseconds) [37]. The transient change in absorption 10 µs after a laser pulse is shown in Figure 5-9a. TiO$_2$ displayed a broad spectrum that increased in absorption into the near-IR, while the pure NH$_2$-UiO-66 MOF showed a more structured spectrum, with a maximum absorption at ~650 nm. The composite, 2-TiMOF, exhibited a spectral signature almost identical to that of the MOF. Considering the composite was mostly composed of TiO$_2$ (approximately 80 %wt TiO$_2$ and 20 %wt MOF), the laser excitation would mostly be absorbed by the TiO$_2$ component. Hence, the spectral signature of the composite indicated charge transfer from TiO$_2$ sites to the MOF. Previous TAS studies of TiO$_2$ have shown that transient absorption is dominated by the absorption of photogenerated holes in the visible region [38].
This means that the change in the spectral signature of the composite was likely due to interfacial charge transfer. This charge transfer was apparent in the increase in transient absorption for the composite, which approximately doubled in comparison to either of its pure counterparts (Figure 5-9a). However, these photo-generated charges in the composite did not recombine more slowly than in the pure MOF, and in fact, recombined at a similar rate to the pure TiO$_2$ sample (Figure 5-9b). We therefore attributed the increase in the number of charge carriers present in the composite to early timescale inhibition of recombination. This was most likely caused by an increase in charge carrier separation due to charge transfer between TiO$_2$ and the MOF. On the micro- to millisecond timescales, recombination was slightly faster in the composite compared to the pure MOF. However, the number of charge carriers that remained present on timescales relevant to CO$_2$ reduction was superior in the composite. This correlated with our photocatalytic studies, which showed that the composite, 2-TiMOF, was significantly more active than either of its counterparts. More detailed results of our transient absorption studies are provided in Appendix 5 (Figure 5-A3).
5.4 Results and Discussion

Figure 5-9. Transient absorption spectroscopy study of TiO$_2$, NH$_2$-UiO-66 and TiO$_2$/NH$_2$-UiO-66 composite (2-TiMOF): a) transient absorption spectrum 10 µs after a laser pulse, and b) kinetics of charge carrier recombination at 650 nm, with the normalized kinetics shown inset ($\lambda_{exc} = 355$ nm, $\sim$2 mJ cm$^{-2}$, 6 ns pulse width, 0.6 Hz). Transient absorption spectroscopy (TAS) was carried out Dr. Andreas Kafizas at Imperial College London. Experiments were carried out in diffuse reflectance mode, a UV laser (355 nm, $\sim$2 mJ cm$^{-2}$) was used to photoexcite the nanopowder.

Compared with previous transient absorption studies of MOFs, NH$_2$-UiO-66 and the TiO$_2$/MOF composites show substantially longer electron-hole lifetimes [39-42]. Previous studies have shown that the half-time for recombination in MOF-5 (Zn$_4$O clusters linked orthogonally to terephthalate) was $\sim$50 µs [39, 40]. Substantially lower half-times ($\sim$8 µs) were observed by Garcia et. al. in CAU-8 (AlO$_6$ octahedra MOF, connected by benzophenone dicarboxylate linkers) [41]. Epitaxial films of SURMOF 2 (Zn$_4$O clusters linked to porphyrin
rings) showed similarly fast electron-hole recombination [42]. In this work, NH$_2$-UiO-66 showed recombination half-times in the region of 1500 µs, which were substantially longer lived than the pure TiO$_2$ sample (~180 µs). Of note, previous TAS studies have also focused on the ultra-fast charge-carrier dynamics (from the femto- to nanosecond timescale) of MOF systems capable of reducing CO$_2$ [8, 43]. Li et. al. found that photogenerated electrons transferred from anatase TiO$_2$ to HKUST-1 within several picoseconds [8]. Also, Zhang et. al. found that MOF-525 (composed of Zr$_6$ clusters and porphyrin-based molecular units) can transfer charge onto impregnated Co centres within 10 ps [43]. Herein, although no direct charge transfer at short timescale was observed, the data acquired on longer timescales (micro- to millisecond) suggest transfer of short lived charges.

5.4.3 Proposed Reaction Mechanism

Given the analysis above close inspection of the catalytic results (Figure 5-8) suggested that although the light absorption and CO$_2$ uptake properties may have impacted photoactivity, they are not the sole factors governing the photocatalytic efficiency. The composition (TiO$_2$:MOF) must have had a crucial role in the photoactivity. On the basis of these observations and the charge transfer measured by TAS, it is suggested that CO$_2$ is photocatalytically reduced to CO by TiO$_2$ and NH$_2$-UiO-66. In the TiO$_2$/NH$_2$-UiO-66 nanocomposites photoactivity was mainly governed by two parameters: (a) the TiO$_2$ that controls the available sites for CO$_2$ reduction and (b) the presence of NH$_2$-UiO-66 as charge separator and CO$_2$ adsorbent. The actual content of the two parts would control activity. However, improved catalytic activity was mainly attributed to the enhanced abundance of photogenerated charges driven by the interfacial charge transfer.
5.5 Conclusions

In this chapter TiO$_2$/NH$_2$-UiO-66 nanocomposites were synthesised for the first time via an *in-situ* process allowing intimate contact between the two components. The composites exhibited enhanced photocatalytic CO$_2$ reduction to CO in the presence of H$_2$ compared to the parent materials. TiO$_2$/NH$_2$-UiO-66 displayed several features that promoted catalytic activity. The composite heterostructures maintained a high surface area preventing TiO$_2$ aggregation and exposing more active sites. The large CO$_2$ adsorption capacity also increased the CO$_2$ concentration on the surface (owing to the presence of the MOF porosity), facilitating intimate contact of CO$_2$ with the photocatalytic sites. The optical properties of the composite were improved for the targeted reaction, with an absorption shift towards visible light compared to TiO$_2$. Transient absorption spectroscopy revealed increased charge generation enabled by efficient charge transfer, resulting in additional photo-excited electrons. This study demonstrated photocatalytic CO$_2$ reduction over TiO$_2$ can be greatly improved with the use of a MOF (NH$_2$-UiO-66) as CO$_2$ adsorbent, charge generator, and charge separator.

In relation to the research objectives the above study addressed each by the following findings:

**RO 1: To design and synthesise bifunctional photocatalysts for improved CO$_2$ adsorption capacity and photocatalytic reduction of CO$_2$ and investigate their morphology, textural properties and light utilization properties.**

- The TiO$_2$/MOF composite materials were bifunctional materials capable of combined CO$_2$ adsorption and CO$_2$ photoreduction.
- The TiO$_2$/MOF materials had increased CO$_2$ adsorption capacity by a factor of 6 and increased CO$_2$ reduction by 50% when compared to TiO$_2$. 

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The formation of TiO$_2$/MOF composites with TiO$_2$ nanosheets coating and dispersed within the MOF was confirmed and they had increased surface area and CO$_2$ adsorption capacity compared to theoretical mixture of these materials.

A broader composite light absorption spectra into longer wavelengths was attributed to the MOF component, light utilization was improved by increased charge generation achieved by the control of the TiO$_2$/MOF heterojunctions in the composites.

These improved morphology, textural and light utilization properties were shown to have contributed to the improved CO$_2$ adsorption capacity and photoreduction rates.

**RO 2: To investigate the photocatalysts robustness and recyclability for photocatalytic CO$_2$ reduction.**

The TiO$_2$/MOF composites photocatalytically reduced CO$_2$ at a stable rate over the 6 hour testing period.

Repeated photocatalytic tests with no regeneration step showed no significant decrease in activity and the materials crystallinity was unchanged.

### 5.6 References


5.6 References


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Chapter 6 Further studies of TiO$_2$ morphology and phase in TiO$_2$/MOF composite materials

Abstract

Titanate nanofibers and metal organic frameworks (MOFs) composites were synthesised using a rapid microwave assisted method. Control of the MOF (NH$_2$-UiO-66) loading in the composites was achieved by altering the quantity of the titanate nanofibers present during synthesis. The titanate/MOF nanocomposites were studied using various techniques and they exhibited increased CO$_2$ adsorption capacities. Their photocatalytic activities were evaluated in a gas/solid heterogenous reactor under UV-Vis illumination. All composites were more active than their component materials, the composite with the highest MOF loading most active. Anatase phase fibers were also formed for further improvements in photocatalytic activity. Photocatalytically, the anatase fibers were 6 more active than titanate and the anatase TiO$_2$ fiber/MOF composite was 9 times more active than titanate. Detailed studies confirmed successful composite formation, transient absorption spectroscopy highlighted charge transfer between the two composite components. Using X-ray photoemission spectroscopy, we demonstrated that electrons transfer from TiO$_2$ into the MOF, and holes from the MOF into anatase TiO$_2$. 
6.1 Overview

In this chapter, a further study of TiO\textsubscript{2}/MOF composites for photocatalytic CO\textsubscript{2} reduction is presented. These composites were formed using the same MOF as in Chapter 5 (NH\textsubscript{2}-UiO-66), but with further control of the TiO\textsubscript{2}-MOF interfaces; this was achieved by greater control of both the TiO\textsubscript{2} morphology and MOF growth sites. TiO\textsubscript{2} with fiber morphology was synthesised, then TiO\textsubscript{2}-MOF composites were formed using a microwave-antenna synthesis which induced of “super-hot” dots on the TiO\textsubscript{2} fibers for localised MOF growth on the fiber. The MOF content and TiO\textsubscript{2} phase of the fibers were also investigated. Based on this chapter ref [1] was prepared.

6.2 Introduction

The morphology of TiO\textsubscript{2} has been studied to improve photocatalytic activity, it has been shown that the TiO\textsubscript{2} morphology (e.g. 1D structures), crystalline form (e.g anatase, rutile, brookite, and titanate), and composition (e.g. heterojunction, heterostucture formation) all are critical factors for this [2, 3]. Another example of semiconductor that can be considered as a derivative of titania is titanate. Titanate materials are photocatalytically active, with a crystalline structure similar to anatase TiO\textsubscript{2} and a one-dimensional morphology. Compared to conventional TiO\textsubscript{2}, titanates exhibit attractive properties for photocatalysis such as a high surface area, a well-defined morphology, an improved photogenerated charge separation, and a small bandgap [4-6].Titanates have been used for photocatalysis [7-10], and in particular for CO\textsubscript{2} photoreduction [11, 12]. Recent photocatalytic improvements routes using titanate – not limited to CO\textsubscript{2} photoreduction – include the formation of composite materials for improved charge separation [5, 10, 13, 14], and the conversion to a mixed phase anatase/titanate material hydrothermally,
whilst retaining the fiber morphology [15-17]. Specifically, mixed phase TiO$_2$ has been shown to have improved charge separation and catalytic activity [18-20].

As presented in Chapter 5, the formation of TiO$_2$/MOF composites increased the photocatalytic activity owing to a synergistic effect between the coupled materials. From this study, it was shown the interface between the titania and MOF particles, and therefore the morphology of the respective particles, had a large influence the photoreduction of CO$_2$. For the development of higher performing TiO$_2$/MOF composites, it was hypothesised that increasing the number of ‘points of contact’ between the TiO$_2$ and MOF would further improve photocatalytic activity by increasing the charge separation and transfer.

Herein a study dedicated to testing the above hypothesis is presented. Nanocomposites of titanium oxide nanofibers with NH$_2$-UiO-66 for combined CO$_2$ capture and photocatalytic conversion were synthesised. To study and improve the TiO$_2$-MOF interactions for CO$_2$ conversion, the MOF loading, TiO$_2$ morphology, and TiO$_2$ phase were controlled. A 1D nanofibers morphology was selected for the TiO$_2$ part, and the MOF particles were grown in-situ on top of these preformed fibres (Figure 6-1) in an effort to maximise charge transfer. A microwave-antenna synthesis was used, for the induction of “super-hot” dots on the TiO$_2$ fibers for TiO$_2$/MOF composite formation [21, 22]. This rapid technique has low energy requirements and was selected to promote MOF formation directly on the fiber and form TiO$_2$/MOF composites [23]. The nanocomposites were studied by various analytical, imaging, and spectroscopic techniques and were evaluated for CO$_2$ adsorption and photocatalytic reduction. A comparison with the as TiO$_2$/MOF composite with nanoparticle (NP) morphology, the highest performing composite in Chapter 5 (denoted “TiO$_2$/MOF NP”), was also made.
6.3 Material synthesis

All reagents used in this study were of analytical grade and used without further purification. Titanium oxide P25 (≥99.5% trace metals), sodium hydroxide (≥98%), zirconium chloride (≥99.5% trace metals), polyvinylpyrrolidone (PVP, average molecular weight 10,000), N,N-dimethyl formamide (99.9%), hydrochloric acid (37%wt), and acetic acid (≥99.7%) were purchased from Sigma-Aldrich.

6.3.1 Synthesis of titanium dioxide nanofibers

A hydrothermal synthesis was used to produce TiO$_2$ nanofibers (NF), see Figure 6-1, following a previously reported method [24]. P25 (5 g) was dispersed in 10 M sodium hydroxide (70 mL), the mixture was then sealed in an autoclave (polytetrafluoroethylene liner) and heated to 180 °C for 48 h. After cooling, the white solid was collected and washed by filtration with 1 M hydrochloric acid until the pH of the filtrate reached 1. Finally, the white solid was washed by filtration with deionised water until the filtrate was pH neutral - the titanate product was denoted “t”.

Thermal treatment of titanate was undertake for phase conversion of the TiO$_2$ nanofibers – from titanate to titania (Figure 6-1 route b) [25]. “t”(600 mg), 30 mL deionised water, and ethanol (20 mL) were added to a PTFE autoclave liner under stirring. This was then sealed and heated to 150 °C for 17 h, the white solid product was recovered and washed by centrifugation (3 ethanol washes), vacuum dried at 120 °C and stored in a desiccator. The thermally treated titanate was denoted “T”.

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6.3.2 Synthesis of TiO$_2$/NH$_2$-UiO-66 nanocomposites and NH$_2$-UiO-66

An *in-situ* growth method was used to synthesise NH$_2$-UiO-66 on the as-synthesised TiO$_2$ nanofibers – Figure 6-1 route a. The formation of the NH$_2$-UiO-66 particles was based on a previously reported method [26], but applying much lower temperature (80 °C) to suppress MOF formation in the bulk solution. A CEM MARS 5 microwave oven with XP-1500 Plus vessels was used for all microwave syntheses. The following was added to reaction vessels: zirconium chloride (291 mg), 2-aminoteraphthalic acid (226 mg), titanate (varied mass), N,N-dimethyl formamide (30 mL), acetic acid (8.4 mL), and deionised water (540 µL). The mixture was sonicated for 30 minutes before heating at 80°C for 1 h. After synthesis, the solid product was recovered and washed by centrifugation (3 ethanol washes), vacuum dried at 120°C and stored in a desiccator. The MOF/TiO$_2$ ratio of the nanocomposites was controlled by altering the mass of titanate present in the synthesis. These were labelled t-x-MOF, where x refers to the mass of titanate in mg used during synthesis, and MOF is NH$_2$-UiO-66. NH$_2$-UiO-66 was synthesised using the same procedure above but with no titanate present.

The thermally treated titanate, T, was also used for the synthesis of a TiO$_2$/MOF nanocomposites using the same procedure as above. This composite was labelled T-300-MOF to identify its thermally treated TiO$_2$ component (T), and the quantity of TiO$_2$ present during synthesis (300 mg).

To assess the role of the particles morphology on the photoreduction process, the materials in the present study were compared to a composite of the same materials in Chapter 5 in which the morphology of the titania and the MOF synthesis sites were not controlled [27]. The TiO$_2$/NH$_2$-UiO-66 nanocomposite formed had a MOF content of 19.5%wt and was the most photocatalytically active for CO$_2$ to CO conversion, in this chapter it was referred to as TiO$_2$/MOF composite with nanoparticle (NP) morphology, and denoted “TiO$_2$/MOF NP”.
Figure 6-1. Schematic of the TiO$_2$/NH$_2$-UiO-66 nanocomposites synthesis routes. TiO$_2$ nanoparticles (P25) were first hydrothermally converted to titanate nanofibers (t). These fibers were then subjected to one of two routes: a) the titanate nanofibers were added to a synthesis vessel with NH$_2$-UiO-66 precursors and heated using microwaves to 80°C to form t/NH$_2$-UiO-66 composites, b) the titanate nanofibers were converted to anatase phase nanofibers (T) hydrothermally, these were then added to a synthesis vessel and heated using microwaves to form T/NH$_2$-UiO-66 composites. The microwave induced hot spots on the TiO$_2$ promoted direct growth of the MOF on the fibers.
6.4 Results and Discussion

6.4.1 Structural and chemical characterisation

6.4.1.1 Material composition, crystalline structure, and thermal stability

A schematic of the composites synthesis routes is provided in Figure 6-1. Overall, a microwave-assisted synthesis was used to form NH$_2$-UiO-66 particles on the surface of preformed titanate fibers – Figure 6-1 route a. To study and optimise the titanate:NH$_2$-UiO-66 for photocatalytic CO$_2$ reduction, the quantity of titanate present in the synthesis was varied. This was denoted as t-x-MOF, where x is the quantity in mg of titanate used and MOF is NH$_2$-UiO-66. Further improvements in composite photocatalytic activities were pursued by investigating the conversion of the TiO$_2$ phase, whilst retaining the desirable nanofiber morphology – Figure 6-1 route b. A nanocomposite using this material was labelled T-300-MOF.

The titanate structure (t, H$_2$Ti$_2$O$_5$.H$_2$O) was confirmed by XRD as shown in Figure 6-2a, with peaks at 11.6° (200), 25.2° (110), and 48.7° (020) [28]. The titanate interlayer distance, derived from the 11.6° peak, was calculated to be 0.8 nm. The peaks at 25.2° and 48.7° are characteristic of a crystalline tri-titanate structure [13]. NH$_2$-UiO-66 displayed a diffraction pattern typical for this MOF [26, 27]. The t-x-MOF patterns were a combination of these two materials, indicating the presence of both materials and that the titanate did not alter the MOF crystal growth. The XRD pattern of the thermally treated nanofiber, T, was assigned to anatase phase TiO$_2$ (Figure 1a), with peaks at 25.5° (101), 38.1 (004), 44.3° (003), 48.3° (200), 54.1° (105), and 55.2° (211) [29, 30]. This showed that under hydrothermal conditions at 150 °C, the titanate phase was converted to anatase phase TiO$_2$, as previously reported by Yu et al. [15]. The
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The composite T-300-MOF XRD pattern was a combination of the TiO\textsubscript{2} and NH\textsubscript{2}-UiO-66 components, confirming the presence of both species.

Thermal gravimetric analysis (TGA) was used to assess the thermal stability of the materials, and to quantify the MOF content of the nanocomposites (Figure 6-A1 in Appendix 6). Under a nitrogen atmosphere, NH\textsubscript{2}-UiO-66 was stable up to around 200 °C when the organic ligands began to decompose [26, 27]. The titanate remained stable at the highest temperature tested (900 °C), with a small mass drop from 200-350 °C attributed to the removal of interlayer water [28]. As expected, the composite materials displayed thermal degradation profiles which were a combination of the titanate and NH\textsubscript{2}-UiO-66. The final masses (at 900 °C) of the materials were used to quantify the MOF loadings of the composites, shown in Table 6-A1, these ranged from 20-33%wt. The highest MOF loading was obtained for the intermediate TiO\textsubscript{2} seed content in t-300-MOF (33%wt). A possible reason for this is proposed below when discussing the surface area (Section 6.4.1.4). The anatase nanofiber, T, remained thermally stable at 900 °C (Figure 6-A2 in Appendix 6), with a similar degradation profile to the untreated titanate. The TiO\textsubscript{2}/MOF composite synthesised with the anatase nanofibers, T-300-MOF, had a MOF content of 15%wt. This was around half the MOF loading when compared to the analogous titanate/MOF composite (t-300-MOF) which indicated the MOF growth was affected and hindered by altering the titanium oxide phase.

6.4.1.2 Material chemistry

ATR-FTIR spectroscopy was used to probe possible chemical interactions between the titanate and the organic moieties of the MOF and is shown in Figure 6-2b. The NH\textsubscript{2}-UiO-66 transmittance spectra was similar to those reported [27, 31]. The main titanate bands were H-O-H bending at 1630 cm\textsuperscript{-1}, Ti-O-Ti bending across 1000-400 cm\textsuperscript{-1}, and a broad surface O-H stretching band at 3398 cm\textsuperscript{-1} [13, 16]. The relatively low IR interactions of titanate allowed the
MOF in the composite materials to be easily distinguished in the 1700-1000 cm\(^{-1}\) region. The broad H-O-H and Ti-O-Ti bending titanate peaks also confirmed the titanate component in the composites. The thermally treated nanofibers, T, showed ATR-FTIR spectra similar to other anatase (Figure 6-2b), with an O-H absorption bands at 1653 cm\(^{-1}\) and 3400 cm\(^{-1}\) [32, 33]. The reduction of the titanate peaks across the 1000-1500 cm\(^{-1}\) region provided further evidence of titanate to anatase phase conversion. Transmission spectra of T-300-MOF confirmed the presence of both components in the composite, with features of both T and NH\(_2\)-UiO-66 visible.
6.4 Results and Discussion

**Figure 6-2.** Structural and chemical characterisation of titanium oxide nanofibers, NH$_2$-UiO-66, and TiO$_2$/NH$_2$-UiO-66 composites: a) XRD patterns, b) ATR-FTIR spectra, c) N$_2$ sorption isotherms at 77 K.

X-ray photoemission spectroscopy in the section below was performed and analysed by Mr. Benjamin Moss at Imperial College London.

X-ray photoemission spectrum from anatase nanorods (T) also indicated that annealing of titanate (t) produced high purity TiO$_2$. Indeed, Ti 2$p$ core lines (Figure 6-A3a) exhibited a
doublet (458.5 eV, 464.3 eV) consistent with a single Ti$^{4+}$ environment, split by spin-orbit coupling.$^{[34]}$ The O 1$s$ spectrum confirmed the formation of TiO$_2$ with the strongest emission peak arising from O$^{2-}$ anions in the TiO$_2$ lattice (529.8 eV, Figure 6-A3c).$^{[35]}$ Like for other particulate TiO$_2$ systems, we observed small amounts of adventitious carbon on the TiO$_2$ surface (C-C at 284.8 eV, C-O 288.1 eV, Figure 6-A3b; and C-O 532.1 eV, Figure 6-A3c).$^{[36]}$ NH$_2$-UiO-66 exhibited core line emission broadly consistent with previous reports of this material.$^{[27]}$ We observed a single Zr$^{4+}$ 3$d$ environment (Zr 3$d_{5/2}$ at 283 eV)$^{[37]}$ (Figure 6-A4a). The carbon emission spectrum reflected the carbon oxidation states in the linker: O=C-O at 288.9 eV and C-C at 284.8 eV and a less oxidised C-O environment at 286.1 eV, Figure 6-A4b). For the oxygen environment, we observed: a small peak with a binding energy typical of oxide anions in a ZrO$_2$ environment (i.e. a ZrO$_6$ octahedral environment from the MOF) (530.2 eV)$^{[38]}$ and a large peak at 532.0 eV consistent with the carboxyl groups in the linker. T-300-MOF composite did not exhibit further chemical environments to those indicated above and the Ti:Zr ratio of 8:1 measured by XPS was in line with that obtained from TGA (Figure 6-A5 a-d). Surprisingly, we note a strong shift to higher binding energy (0.6 eV) in all core levels associated with TiO$_2$ (Figure 6-A6 c-d.). This was attributed to a shift in the Fermi level of TiO$_2$ upon forming a junction with NH$_2$-UiO-66 (see discussion for a detailed appraisal of this effect). Considering the O 1$s$ spectrum of the composite and the peaks attributable to the MOF, we observed a carboxyl to oxide area ratio of 10:1, which is consistent with the structure of the MOF.

6.4.1.3 Materials morphology

While the former analyses confirmed the successful synthesis of the composites and provided insights into their structures, they did not inform on their morphology which represents a main aspect of this study. Hence, electron microscopy images of the materials were captured to visualise the nanofiber morphology and to provide direct evidence of titanate/NH$_2$-UiO-66
composite formation. The titanate material (t) was confirmed to be a nanofiber/nanowire morphology with a smooth surface (Figure 6-3a-b), ranging in diameters 25-250 nm, and up to several microns in length. The titanate interlayer spacing (200) was 0.8 nm [15, 16, 39]; this also aligned with the interlayer spacing derived from XRD (Figure 6-2a). The NH₂-UiO-66 (Figure 6-3c) formed agglomerated crystals around 25-50 nm in diameter [23, 40]. Imaging the nanocomposites showed the titanate nanofibers coated in MOF particles in Figure 6-3e-f. The titanate nanofiber was unaltered during the MOF synthesis, with the MOF growth directly on the fiber surface as seen on Figure 6-3f on a nanometer scale. The MOF particles on the titanate were larger than those synthesised in the absence of titanate; indicating the presence of titanate created “super-hot” spots on the fiber [21] for preferential MOF growth at those sites and the formation of a composite material. TEM images of T, Figure 6-3g-i, confirmed that the nanofiber morphology was retained following thermal treatment at 150 °C. The fiber was observed to be more coarse and porous [15]; this conversion of titanate to anatase phase via the formation of nanocavities was described as “anti-crystal growth” by Han et al. [41]. The lattice spacing was observed to be anatase phase TiO₂ (101) [42]. SEM and TEM images of T-300-MOF (Figure 6-3j-l) showed direct growth of NH₂-UiO-66 on the TiO₂ fiber; confirmation of successful composite formation. Compared to the most analogous titanate/MOF composite in terms of composition (t-300-MOF), the MOF particles in T-300-MOF were observed to be half the size. The MOF formation on the anatase surfaces was probably less favourable than on titanate, which may explain this observation and that made based on the thermogravimetric analyses. A smaller MOF particle size is expected to improve photocatalytic properties, owing to increased light utilization and charge separation due to the shortened charge transfer pathway [23]. The composites morphologies must be compared to that of a TiO₂/MOF composite for which the titania particles shape was not controlled (TiO₂/MOF NP). SEM images of the TiO₂/MOF NP composite can be found in Chapter 5.
6.4 Results and Discussion

Figure 5-5. Clearly, the latter material exhibited a random structure with no evident particle shape. In addition, the mixing between the two phases – MOF and titania – occurs at the 10 nm scale.

Figure 6-3. Electron microscopy images highlighting the well-defined morphology of the materials: of a-b) titanate fibers (t), c) NH$_2$-UiO-66, and d-f) t-300-MOF composite, g-i) anatase fibers (T), j-l) T-300-MOF composite.
6.4.1.4 Textural properties

The textural properties of the materials were analysed by measuring nitrogen sorption isotherms at 77 K (Figure 6-2c, Table 6-A1), with the BET surface area and other textural parameters presented. Titanate (t) had a low surface area (45 m$^2$g$^{-1}$) with a Type IV isotherm with H3 hysteresis indicating a mesoporous structure [15, 43]. NH$_2$-UiO-66 exhibited a high surface area (1004 m$^2$g$^{-1}$) due to the presence of micropores [31, 43], similar to those reported using an open vessel [26, 27] and microwave-irradiation induced syntheses [23]. As expected, the composite materials had surface areas and a porous network intermediate to their two components, and proportional to the MOF content measured by TGA. The increase of titanate seeds from 200 mg to 300 mg resulted in the highest composite surface area and MOF loading, a further increase to titanate seeds up to 400 mg lowered to MOF content. This can be explained considering the quantity of titanate, which provides hot spots for MOF formation: low quantities of titanate limit the available sites and results in low MOF formation in the short synthesis period, while excess quantities of titanate reduces the density of induced hot spots so lowers the overall MOF loading. The anatase fibers, T, surface area (113 m$^2$g$^{-1}$) was more than double that of titanate due to increased mesoporosity - aligning with our microscopy observations which showed a rougher surface (Figure 2g-i) and the literature [15, 16]. The MOF composite formed with this material, T-300-MOF, had lower mesoporosity but increased surface area compared to the anatase TiO$_2$ fibers (170 m$^2$g$^{-1}$) due to the formation of microporous MOF particles.

The CO$_2$ adsorption capacity of the photocatalysts was evaluated by measuring sorption isotherms at 25°C up to 1 bara (Figure 6-4a). On average, the CO$_2$ adsorption capacities followed the trend of the BET surface areas. NH$_2$-UiO-66 had a capacity of 1.23 mmol g$^{-1}$, comparable to results reported before [31]. The nanocomposite CO$_2$ adsorption capacities were enhanced considerably compared to titanate, with a 9-fold increase for t-300-MOF. The
thermally treated nanofiber, T, had a higher adsorption capacity than titanate due to the increased surface area. The composite T-300-MOF exhibited slightly lower CO$_2$ adsorption capacity than its TiO$_2$ component. Compared to the TiO$_2$/MOF composite with nanoparticle morphology (TiO$_2$/MOF NP), the composite T-300-MOF had a similar CO$_2$ adsorption capacity [27].

6.4.2 Optical properties and photocatalytic CO$_2$ reduction

6.4.2.1 Light absorption

Diffuse reflectance ultraviolet-visible (DR-UV/Vis) spectroscopy was used to study the light absorption properties of all photocatalysts. The spectra were converted to a Tauc plot presented in Figure 6-A7 in Appendix 6 using the Kubelka-Munk function with TiO$_2$ and NH$_2$-UiO-66 as indirect and direct semiconductors respectively [13, 15, 16, 44-46], the derived bandgaps are presented in Table 6-A2 in Appendix 6. Both titanate and anatase phase TiO$_2$ materials onsets were in the UV region. The titanate bandgap of 3.16 eV was close to values in literature [13, 15, 16], as was the 3.11 eV bandgap of the anatase phase (T) [15, 44]. The red-shift from titanate to anatase phase fibers was expected based on an earlier study [15]. NH$_2$-UiO-66 absorbs in the visible (2.77 eV) [46, 47]. Hence, the composite materials had increased absorption in the visible region compared to their TiO$_2$ components, a desirable feature for photocatalysis due to the increased solar light utilization.

6.4.2.2 Photocatalytic CO$_2$ reduction

The photocatalysts were tested for the reduction of CO$_2$ in a heterogeneous gas/solid photoreactor. The experiments were performed at ambient temperature using H$_2$ as a reducing agent under UV-Vis illumination ($\lambda > 325$ nm, 150 W) without the addition of any co-catalyst or photosensitiser. A gas phase photoreactor was used in this study to evaluate the photocatalysts in an effort to combine CO$_2$ capture and CO$_2$ conversion into a single process
The CO evolution rates of the photocatalysts are presented in Figure 6-4b and Table 6-A3. Titanate (t) was the least active photocatalyst tested and the activity of NH$_2$-UiO-66 was almost 3 times higher.

The composites were all more active than their parent materials showing a synergistic effect between titania and the MOF. Importantly, the composite with the nanoparticle morphology (TiO$_2$/MOF NP) was the less active of all composites of similar composition. This observation supports our initial hypothesis that the optimized mixing and contact between the MOF and titania particles via control of their respective morphology plays a role in the catalytic process. t-300-MOF was the most active composite: it generated 1.8 to 5 times more CO than pure NH$_2$-UiO-66 and titanate, respectively. The anatase fibers (T) were around 6 times more active than titanate fibers, this improvement aligned with other studies [10, 16, 48], and was attributed to the presence of the more active anatase phase. A further increase in CO evolution rate was measured for T-300-MOF, confirming the synergistic effect of forming a composite. The anatase/MOF composite (T-300-MOF) was twice as active as the most active titanate/MOF composite (t-300-MOF), and around 9 times more active than titanate.

As the most active photocatalyst in this study, further investigations were made into the photocatalytic properties of the anatase fiber MOF composite (T-300-MOF). The CO evolution was linear over a 6 h testing period (Figure 6-5a), indicating a stable CO$_2$ reduction rate. Repeated photocatalytic tests showed CO evolution from T-300-MOF remained active and relatively constant throughout 5 catalytic cycles (Figure 6-4c). Following these experiments, the XRD pattern was unchanged (Figure 6-4d), further confirming the robustness of the material. A control test under a N$_2$ and H$_2$ atmosphere (Table 6-A3, entry 8) yielded no CO. In addition, isotopic tracing experiments using $^{13}$CO$_2$ yielded $^{13}$CO (Figure 6-5b). These tests proved the photocatalytic origin of the CO in the CO$_2$ reduction experiments. Water as an
alternate reducing agent was also investigated under higher power UV-Vis illumination (300 W), which evolved 1.8 \mu\text{mol g}^{-1} \text{h}^{-1} \text{CO} (Table 6-A3, entry 9).

**Figure 6-4.** a) \text{CO}_2\text{ sorption isotherms at 25°C 1 bar, and b) photocatalytic CO evolution rates of t, NH}_2\text{-UiO-66, t/NH}_2\text{-UiO-66 composites, T, and the T/NH}_2\text{-UiO-66 composite. c) T-300-MOF CO evolution after repeated photocatalytic experiments, d) T-300-MOF XRD patterns before and after photocatalytic CO}_2\text{ reduction experiments. All photocatalytic}
experiments carried out under UV-Vis illumination (150 W) for 6 hours with \( \text{H}_2 \) as the reducing agent.

**Figure 6-5.** T-300-MOF photocatalytic \( \text{CO}_2 \) reduction experiment under UV-Vis illumination with \( \text{H}_2 \) as a reducing agent a) CO evolution over the 6 h experiment, b) mass spectrometer chromatographs (full scan) of evolved gases using \( ^{13}\text{CO}_2 \).

6.4.2.3 *Transient light absorption*

Transient absorption spectroscopy (TAS) in this section were carried out and analysed by Dr. Andreas Kafizas at Imperial College London.
We used TAS to measure the charge carrier dynamics in NH$_2$-UiO-66, T, as well as infer the direction of charge transfer in the best performing composite, T-300-MOF. The decay dynamics and spectral changes are provided in Figure 6-A8 and Figure 6-A9, respectively. The decay dynamics and spectral changes found in the MOF were analogous to previous work [27]. However, the decay dynamics found in the anatase TiO$_2$ powder, T, differed from previous studies [20, 49]. In anatase TiO$_2$ (T), charge carriers were longer lived ($t_{50\%}$ from 10 µs, ~10 ms) compared to what has been previously observed in mesoporous and dense thin films of anatase ($t_{50\%}$ from 10 µs, ~0.5 ms). In the T-300-MOF composite, charge carriers recombined at a similar rate to that in NH$_2$-UiO-66. The transient absorption spectrum of anatase TiO$_2$ (T), 10 µs after the laser pulse, showed a broad, flat absorption across the visible range (Figure 6-6). The spectrum of NH$_2$-UiO-66 peaked at ~650 nm and decreased into the red. However, the spectrum of the composite differed from those of the parent materials. We could not simply attribute the spectral shape to the sum of both NH$_2$-UiO-66 and TiO$_2$ powders, as this would have given rise to a flat absorption across the visible. This indicated that charge transfer process occurred in the composite.
Figure 6-6. Transient absorption spectra, observed 10 µs after a laser pulse, of the innate powders of NH$_2$-UiO-66, T and T-300-MOF composite ($\lambda_{\text{exc}} = 355$ nm, $\sim$1.5 mJ.cm$^{-2}$, 6 ns pulse width, 0.65 Hz. Transient absorption spectroscopy was performed by Dr. Andreas Kafizas at Imperial College London.

We then carried out chemical scavenger studies to determine the direction of charge transfer using methanol as a hole scavenger and silver nitrate$_{aq}$ as an electron scavenger.$^{[49]}$ We did not observe any effect on the charge carrier dynamics in the MOF when dispersed in a silver nitrate solution, unlike in the case of methanol (Figure 6-A10). With methanol, significant hole scavenging occurred from $\sim$1 ms resulting in a plateau in the decay dynamics (Figure 6-A10a). We attribute this plateau to the formation of long-lived electrons, which absorb more strongly in the blue (Figure 6-A10b). The anatase TiO$_2$ sample, T, showed a scavenging effect in both methanol (Figure 6-A11) and silver nitrate solution (Figure 6-A12). In methanol, holes were scavenged on the pre-µs timescale, giving rise to long-lived electrons (Figure 6-A11a); an effect previously observed in mesoporous anatase TiO$_2$.$^{[49]}$ These electrons absorb more strongly in the red, at $\sim$900 nm (Figure 6-A11b). Electron scavenging in silver nitrate solution was less pronounced (Figure 6-A12). From the decay dynamics, electron scavenging occurred
Results and Discussion

from \(\sim 1\) ms (Figure 6-A12a), where the concomitant holes gave rise to a strong absorption in the blue (Figure 6-A12b). The locations of electron and holes signals in T were analogous to previous studies of anatase TiO\(_2\).\(^{[20]}\)

In summary, our scavenging studies showed that photogenerated electrons in NH\(_2\)-UiO-66, and holes in anatase TiO\(_2\), both absorb more strongly in the blue. Given the composite material showed a stronger absorption in the blue, with respect to its parent materials, we attribute this rise in absorption to either: (i) hole transfer from NH\(_2\)-UiO-66 to T, (ii) electron transfer from T to NH\(_2\)-UiO-66 or (iii) a combination of these two effects.

6.4.3 Proposed Reaction Mechanism

X-ray photoemission spectroscopy in the section below was performed and analysed by Mr Benjamin Moss at Imperial College London.

To identify the mode of charge in the composites from the three options listed above, we investigated the relative band energy diagram of TiO\(_2\) and NH\(_2\)-UiO-66 in the composites using XPS. The O 1s and Ti 2p core emission spectra of the composite exhibited the same number of chemical environments as the parent materials (Figure 6-7). Peaks in all core levels associated with NH\(_2\)-UiO-66 in the composite appeared at commensurate binding energies to those of the parent material (Figure 6-A4a-c). However, as mentioned earlier, a large shift (0.6 eV) to higher binding energy was observed in peaks attributed to TiO\(_2\). O 1s peaks from transition metal oxides are broadly insensitive to changes in metal redox state.\(^{[38]}\) Consequently, the positive binding energy shift observed cannot be attributed to the formation of more oxidised states upon composite formation (which is unlikely in an already oxidised material such as TiO\(_2\)). Rather, the shifts are attributed to a 0.6 eV increase in the Fermi level (the reference/zero level in XPS) of TiO\(_2\) upon forming a junction with NH\(_2\)-UiO-66. As peaks
attributed to the NH2-UiO-66 did not shift significantly upon composite formation, it is likely that Fermi level of the MOF did not shift substantially. This implies that the donor density of the MOF greatly exceeded that of the anatase nanofibers.

Figure 6-7. Comparison of the (a) Ti 2p and (b) O 1s core levels in the T-300-MOF composite with the anatase nanorods nanofibers and NH2-UiO-66 parent materials. X-ray photoemission spectroscopy was performed by Mr Benjamin Moss at Imperial College London.

To further test this hypothesis, we compared the valence band photoemission spectra of TiO2 and NH2-UiO-66 to that of the T-300-MOF composite (Figure 6-A6). The Fermi level of anatase falls approximately 2.58 eV above the valence band edge making the material moderately n-type. In contrast, the Fermi level of NH2-UiO-66 falls 3.29 eV above the valence band edge. This would make NH2-UiO-66 either a very strongly n-type semiconductor or a degenerate semiconductor. This conclusion ($N_D^{MOF} \gg N_D^{T-300}$, where $N_D^i$ is the donor density of species $i$) is consistent with the large positive shift in binding energies attributed to TiO2 in the T-300-MOF composite (with respect to TiO2) and the relative invariance of MOF peaks.
upon composite formation, as under such conditions, the Fermi level of the high donor density material would be expected to be invariant. Equilibrium is therefore achieved when the Fermi level of the material with lower donor density (TiO$_2$) moves up to meet the material with higher donor density (NH$_2$-UiO-66). This information is consistent with the valence band spectrum of the composite, which is aligned with that of the MOF, implying that the Fermi Level of the composite is determined by the MOF (Figure 6-A6b). The shape of the valence band spectrum of the T-300-MOF composite is distinct from that of the MOF. However, applying Fermi level shift of +0.6 eV to the valence band spectrum of anatase (Figure 6-A6c) demonstrates that the valance band of the T-300-MOF composite matches that of anatase. This implies that in the composite, the highest energy (valence) states are mainly TiO$_2$ valence states. This is likely a result of anatase making up most of the composite.

Considering the Fermi Level energy alignment determined from our XPS studies (Figure 6-A5 to Figure 6-A6 in Appendix 6 and Figure 6-7) and the optical band gaps of the materials (Figure 6-A7), a band energy diagram was constructed (Figure 6-8). This formed a type II staggered gap, in which the valence and conduction bands of anatase lay above the valence and conduction bands of NH$_2$-UiO-66, respectively. This type of alignment promotes electron transfer from anatase into the MOF, and hole transfer from the MOF into anatase. It is consistent with the results of our transient spectroscopy studies. Given the higher donor density present in the MOF, we conclude that NH$_2$-UiO-66 improves performance in the composite by inducing strong band bending in anatase, which in turn improves charge separation by driving electrons into the MOF and holes away from the MOF/TiO$_2$ interface.
Figure 6-8. Overview of the mode of charge transfer with visualisation of the band energy alignment in the MOF/TiO$_2$ composite (T-300-MOF), as determined from XPS analysis and optical spectroscopy. Zero on the energy axis is set to the Fermi level of MOF (NH$_2$-UiO-66).

6.5 Conclusions

Titanate nanofibers synthesised hydrothermally from TiO$_2$ powder (P25). A microwave assisted synthesis was used to induce “super-hot” dots on the titanate fibers for synthesis of the metal organic framework (MOF) NH$_2$-UiO-66 directly on the fiber, to form titanate/MOF composites confirmed by various analytical techniques. The composites CO$_2$ adsorption capacities were measured and they were evaluated for photocatalytic conversion of CO$_2$ in a gas/solid heterogenous system under UV-Vis illumination with H$_2$ as a reducing agent.

All materials photocatalytically converted CO$_2$ to CO, the composites had enhanced activity compared to their component materials. The titanate/MOF composite with the highest MOF content was the most catalytically active, around 5 times more than titanate. The effect of TiO$_2$ phase was also studied by converting the titanate nanofibers to anatase nanofibers to further
improve the photocatalytic activity. An anatase fiber/MOF composite exhibited a further increase in photocatalytic activity, 9 times more when compared to titanate.

The study of the composites morphology, light absorption and charge carrier dynamics confirmed: (i) the positive effect of the morphology control on the charge separation, (ii) the beneficial red shift toward lower energy absorption compared to the parent materials and (iii) the interfacial charge transfer across the heterojunction in the materials. This leads to an improved charge separation as electrons transfer from TiO$_2$ to the MOF.

Overall, the study shows that the control of the TiO$_2$ morphology, crystalline phase, and composite heterojunction formation can lead to significant increase in photocatalytic activity for CO$_2$ reduction.

In relation to the research objectives the above study addressed each by the following findings:

**RO 1: To design and synthesise bifunctional photocatalysts for improved CO$_2$ adsorption capacity and photocatalytic reduction of CO$_2$ and investigate their morphology, textural properties and light utilization properties.**

- The TiO$_2$/MOF composite materials were bifunctional materials capable of combined CO$_2$ adsorption and CO$_2$ photoreduction.
- The TiO$_2$/MOF materials had increased CO$_2$ adsorption capacity compared to the titanate fibers by a factor 8 and increase CO$_2$ reduction by a 40% when compared to TiO$_2$ anatase nanofibers.
The formation of titanate/MOF composites with MOF coating the titanate nanofibers was confirmed and they had increased surface area and CO$_2$ adsorption capacity compared to theoretical mixture of these materials.

The conversion of titanate nanofibers to anatase phase TiO$_2$ nanofibers was confirmed. This resulted in increased surface area, CO$_2$ adsorption capacity, and higher photocatalytic activity when compared to titanate.

The anatase phase TiO$_2$ nanofiber/MOF composite had a lower CO$_2$ adsorption capacity but higher photocatalytic activity than the anatase phase TiO$_2$ nanoparticle/MOF composites synthesised in Chapter 5. This showed the further control of heterojunction formation can further increase material performance.

Overall the improved morphology compared to the morphologies explored in Chapter 5 were shown to have contributed to the increased photoreduction rates.

**RO 2: To investigate the photocatalysts robustness and recyclability for photocatalytic CO$_2$ reduction.**

The anatase TiO$_2$ nanofiber/MOF composite photocatalytically reduced CO$_2$ at a stable rate over the 6 h testing period.

Repeated photocatalytic tests with no regeneration step showed no significant decrease in activity and the materials crystallinity was unchanged after 5 experiments.
6.6 References


[46] Y. Su, Z. Zhang, H. Liu, Y. Wang, Cd0.2Zn0.8S@UiO-66-NH2 nanocomposites as efficient and stable visible-light-driven photocatalyst for H2 evolution and CO2 reduction, Applied Catalysis B: Environmental, 200 (2017) 448-457.


Chapter 7  Conclusions and outlook

7.1  Conclusions

This thesis presents the development and applications of bifunctional materials for CO\textsubscript{2} capture and photocatalytic conversion. To achieve this, solid sorbent and TiO\textsubscript{2} composites were investigated to form materials capable of both CO\textsubscript{2} capture by adsorption and CO\textsubscript{2} conversion by photocatalysis. From reviewing previously published works, carbon nitride and metal organic frameworks (MOFs) were identified as promising materials for these applications.

A gas/solid heterogeneous photoreactor system was designed, constructed, and calibrated for the photocatalytic CO\textsubscript{2} reduction experiments. A versatile system was designed to allow various experiments to be performed: CO\textsubscript{2}, N\textsubscript{2}, H\textsubscript{2} and H\textsubscript{2}O gas inlets, batch or continuous operation, UV-Vis irradiation sources with UV and IR filters, gas quantification and analysis by on-line GC for detection of various gases using TCD, FID and MS detectors.

From the materials designed, synthesised, characterised and evaluated for photocatalytic CO\textsubscript{2} reduction, the following main conclusions are made.

In Chapter 4, nanocomposites of TiO\textsubscript{2} and carbon nitride nanosheets (CNNS) were studied. Successful composite formation with control of the TiO\textsubscript{2} morphology was confirmed and this study demonstrated photocatalytic CO\textsubscript{2} reduction using TiO\textsubscript{2}/CNNS composites for the first time. The composite with more \{001\} TiO\textsubscript{2} facets exposed showed a 3-fold increase in CO\textsubscript{2} adsorption capacity and 10-fold increase in photocatalytic conversion of CO\textsubscript{2} to CO when compared to TiO\textsubscript{2}. Investigations into the light absorption of the materials showed control of TiO\textsubscript{2} facets facilitated TiO\textsubscript{2}-CNNS charge transfer for this composite only. The robustness and
recyclability of this composite showed stability over one experiment and stabilisation after an initial drop for repeated catalytic cycles. This study demonstrated TiO₂-CNNS composites can have increase material performance and that further enhancement can be made through control of the exposed crystal facets.

TiO₂ and MOF (NH₂-UiO-66) nanocomposites were first explored in Chapter 5. Confirmation of the composites was made, showing nanoparticle (NP) morphologies of the TiO₂ and MOF forming heterostructures. This study showed photocatalytic CO₂ reduction using TiO₂/MOF (NH₂-UiO-66) composites for the first time, and that variation of the material composition was important in optimising photocatalytic activity, additionally gas/solid heterogeneous systems had rarely been applied for MOF photocatalysts. The optimum TiO₂/MOF composite maintained the high CO₂ adsorption capacity from the MOF component and had 1.5 times higher photocatalytic conversion of CO₂ to CO than TiO₂. Analysis of the light absorption dynamics showed TiO₂-MOF charge transfer for this composite and it was observed to reduce CO₂ at a constant rate from repeated catalytic experiments.

Further development of TiO₂/MOF (NH₂-UiO-66) composites are presented in Chapter 6 with greater control of the TiO₂-MOF interfaces using TiO₂ nanofibers (NF) achieved using a novel synthesis method. Composite formation was confirmed by observation of the MOF on the TiO₂ nanofibers. The study showed application of these materials for photocatalytic CO₂ reduction for the first time and provided further evidence that the control of the TiO₂-MOF interfaces was key for improved photocatalytic performance - the TiO₂ NF/MOF activity was 2.5 times greater than the TiO₂ NP/MOF composite in Chapter 5. Studies into the charge dynamics showed that electrons transfer from TiO₂ into the MOF, and holes from the MOF into anatase TiO₂. The robustness of the TiO₂ NF/MOF composite was evidenced by maintained CO₂ to CO production over 5 catalytic cycles.
Overall the thesis presents the development of bifunctional materials for applications in CO₂ capture and photocatalytic conversion. It has been demonstrated the combination of these processes can be achieved using composite materials of CO₂ adsorbent and photocatalytic functions for improved performance. From the composite materials studied in this thesis, the TiO₂ and CNNS with nanosheet TiO₂ morphology was the most active material for photocatalytic CO₂ reduction. Investigations into charge dynamics of these materials showed that the formation of heterojunctions to facilitate charge transfer was crucial in the improved photocatalytic performance. These heterojunctions were governed by control of exposed facets, composite composition and composite morphologies as shown from Chapter 4 through to Chapter 6.
7.2 Future Work

Photocatalytic CO$_2$ reduction is a very challenging process and despite advances conversion rates remain low, it therefore requires continued development of new materials for increased photocatalytic activity. From the development of a photoreactor system and the design of novel photocatalysts there are potential improvements to made in both aspects.

In terms for the photoreactor system, future developments could incorporate *in-situ* degassing with a more powerful vacuum pump and heating of the catalyst bed. For highly porous materials this is relevant as material activation may influence catalytic activity. Additionally, this would reduce contamination risks form using a shared vacuum oven. The potential formation of liquid products (e.g. formate) on the catalyst could also be investigated with this feature, which could explain the instability and decreases in CO evolution observed over this project. Automated photoreactor sampling values could further automate photocatalytic CO$_2$ reduction experiments, allowing increased screening of catalysts. Modification of the catalyst support from a flat circular plate to increase the exposed catalyst surface to illumination could also increase the rate of CO$_2$ conversion.

More advanced reactor designs could incorporate *in-situ* analysis of photocatalytic CO$_2$ reduction. For example, specific to MOFs, *in-situ* characterisation of adsorbed CO$_2$ by XRD, XPS or FTIR could light on the interactions between CO$_2$ and the physical and chemical attributes of the MOF. This knowledge can be used to for targeted synthesis of higher performing new materials.

In terms of future catalyst design there are of course a vast array of materials currently being investigated for improved photocatalyst CO$_2$ reduction. From the findings of this thesis it was seen that porous materials can provide increased CO$_2$ affinity and surfaces to increase exposed
catalytic sites to illumination and facilitate charge transfer, so these should be investigated further. MOFs in particular are promising as they are a versatile class of materials and their tunability allows other MOFs to be explored for photocatalytic reduction either as a standalone or as composite materials. MOFs with high CO$_2$ adsorption capacity should be considered. The TiO$_2$/CNNS composite with nanosheet TiO$_2$ morphology in Chapter 4 showed the use of CNNS as a substrate for TiO$_2$ crystal growth can enhance exposure of TiO$_2$, which had the most active sites for photocatalysis. It was shown in Chapter 5 and 6 that the TiO$_2$/MOF material the MOF was able act as a CO$_2$ adsorbent and photocatalyst, with the both the MOF and TiO$_2$ providing active sites for photocatalysis. These findings were made from photocatalytic CO$_2$ reduction experiments and light absorption properties, more detailed studies in composites could reveal more information about the active sites and reaction mechanisms. As reviewed in Chapter 2, further improvements could be made in by investigation of morphology, linker functionalisation, metal ion exchange, and formation of composites with MOFs. As certain MOFs absorb visible light, the development of more visible light active photocatalyst would result in improved performance under solar radiation as part of an industrial scale CO$_2$ utilization process.

In terms of material robustness, further experiments could be made into the mechanical stability, as at high pressure MOFs have been observed to collapse, thus eradicating their crystallinity and lowering the specific surface area. This is importance for the application of MOF catalysts in the form of pellets. Further work could also test the catalytic activity under different atmospheres akin to a flue gas stream (for a CCUS process) with species present such as N$_2$, H$_2$O, O$_2$, and traces amounts of NO$_x$ and SO$_x$. These are significant challenges, as these have the potential to suppress photocatalytic ability greatly, but they are required to make direct CO$_2$ reduction processes from flue gas streams feasible.
Appendix 1

Appendix 2

Appendix 3


Appendices
Appendix 4

Figure 4-A1. a) XPS Survey spectra of the prepared materials, b) core level XPS spectra of the pure prepared materials in the N 1s region. XPS was performed by Dr Spyridon Zafeiratos in the University of Strasbourg.

Figure 4-A2. Kubelka-Munk UV-Vis light absorption plot of the g-C₃N₄, CNNS, TiO₂, and TiO₂/CNNS composites.
Figure 4-A3. a) XRD patterns, b) nitrogen adsorption-desorption isotherms at -196 °C, c) Kubelka-Munk UV-Vis light absorption plots, d) ATR-FTIR spectra of Ti-NS/CN before and after 3 photocatalytic CO$_2$ reduction testing cycles
Figure 4-A4. TAS spectra of powdered at different delay times following 355 nm photoexcitation of a) Ti-NS/CN composite, b) CNNS, c) Ti-ISO/CN. TAS was carried out Dr. Robert Godin at Imperial College London.

<table>
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<th>Final mass (% mass)</th>
<th>Δmass loss$^a$ (% mass)</th>
<th>$x_{\text{TiO}_2}$ (%)</th>
<th>$x_{\text{NH}_2\text{-UiO-66}}$</th>
<th>$x_{\text{TiO}_2\text{ Theo}}$ (%)</th>
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<td>35.3%</td>
<td>80.5</td>
<td>18.5</td>
<td>70.0</td>
</tr>
<tr>
<td>3-TiMOF</td>
<td>86.6</td>
<td>32.7%</td>
<td>75.5</td>
<td>24.5</td>
<td>60.0</td>
</tr>
<tr>
<td>4-TiMOF</td>
<td>81.3</td>
<td>27.4%</td>
<td>63.2</td>
<td>16.8</td>
<td>45.0</td>
</tr>
<tr>
<td>NH$_2$-UiO-66</td>
<td>53.9</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>

$^a$. Calculated: Δmass loss = TiO$_2$ Final mass – Final mass. $^b$. Calculated: $x_{\text{TiO}_2} = (\Delta \text{mass loss})/(\text{TiO}_2 \ Final mass – \text{NH}_2\text{-UiO-66 Final mass})$. $^c$. $x_{\text{NH}_2\text{-UiO-66}} = 1 - x_{\text{TiO}_2}$. $^d$. $x_{\text{TiO}_2\text{ Theo}}$ is the expected TiO$_2$ content base on the unmodified NH$_2$-UiO-66 synthesize yield.
Figure 5-A1. XPS survey spectra of the pure NH$_2$-UiO-66 and TiO$_2$ and the 2-TiMOF nanocomposite. XPS was performed by Dr Spyridon Zafeiratos in the University of Strasbourg.

Figure 5-A2. High resolution XPS spectra in the region of: a) C1s, b) N1s and c) O 1s. XPS was performed by Dr Spyridon Zafeiratos in the University of Strasbourg.
Figure 5-A3. N$_2$ adsorption-desorption isotherms at -196 °C.
Figure 5-A3. Transient absorption spectroscopy of pure TiO$_2$ (A & D), NH$_2$-UiO-66 MOF (B & E) and a composite 2-TiMOF (C & F) showing the transient absorption spectra at select times from 10 µs to 900 ms after a laser pulse (A-C) and the kinetics of charge carrier recombination at numerous wavelengths from 500 – 900 nm (D-F), [\lambda_{exc} = 355 \text{ nm}, \sim 2 \text{ mJ.cm}^{-2}, 6 \text{ ns pulse width, 0.6 Hz}]. TAS was carried out Dr. Andreas Kafizas at Imperial College London.
**Figure 6-A1.** Thermogravimetric analysis of titanate (t), NH$_2$-UiO-66, and titante/NH$_2$-UiO-66 composites.

**Figure 6-A2.** Thermogravimetric analysis of T, NH$_2$-UiO-66, and T-300-MOF.
Figure 6-A3. X-ray photoelectron spectroscopy of the (a) Ti 2p, (b) C 1s and (c) O 1s core lines in the anatase nanorods (T). X-ray photoemission spectroscopy was performed by Mr Benjamin Moss at Imperial College London.
Figure 6-A4. X-ray photoelectron spectroscopy of the (a) Zr 3d, (b) C 1s and (c) O 1s core lines in the NH$_2$-UiO-66 MOF. X-ray photoemission spectroscopy was performed by Mr Benjamin Moss at Imperial College London.
Figure 6-A5. X-ray photoelectron spectroscopy of the (a) C 1s, (b) O 1s, (c) Ti 2p and (d) Zr 3d core lines in the T/NH$_2$-UiO-66 composite (T-300-MOF). X-ray photoemission spectroscopy was performed by Mr Benjamin Moss at Imperial College London.
Figure 6-A6. Valance band photoemission of (a) anatase nanorods (T), (b) NH₂-Uio-66 and (c) the T/NH₂-Uio-66 composite (T-300-MOF). X-ray photoemission spectroscopy was performed by Mr Benjamin Moss at Imperial College London.
Figure 6-A7. Tauc plot of all photocatalysts.
Table 6-A1. Textural parameters derived from N\textsubscript{2} sorption isotherms, CO\textsubscript{2} adsorption capacity at 1 bar 25°C of titanate, NH\textsubscript{2}-UiO-66, t/NH\textsubscript{2}-UiO-66 composites, thermally treated titanate (T), and the T/NH\textsubscript{2}-UiO-66 composite. With the composite MOF loadings (%wt) calculated from TGA.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>BET Surface area (m\textsuperscript{2}/g)</th>
<th>Calc</th>
<th>BET V\textsubscript{Tot} (cm\textsuperscript{3}/g)</th>
<th>V\textsubscript{Meso\textsuperscript{a}} (cm\textsuperscript{3}/g)</th>
<th>V\textsubscript{Micro\textsuperscript{b}} (cm\textsuperscript{3}/g)</th>
<th>CO\textsubscript{2} ad. \textsuperscript{c} (mmol/g)</th>
<th>MOF (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t</td>
<td>45</td>
<td></td>
<td>0.103</td>
<td>0.103</td>
<td>-</td>
<td>0.06</td>
<td>-</td>
</tr>
<tr>
<td>t-400-MOF</td>
<td>240</td>
<td>237</td>
<td>0.195</td>
<td>0.131</td>
<td>0.064</td>
<td>0.41</td>
<td>20</td>
</tr>
<tr>
<td>t-300-MOF</td>
<td>394</td>
<td>362</td>
<td>0.279</td>
<td>0.201</td>
<td>0.078</td>
<td>0.53</td>
<td>33</td>
</tr>
<tr>
<td>t-200-MOF</td>
<td>354</td>
<td>307</td>
<td>0.290</td>
<td>0.194</td>
<td>0.096</td>
<td>0.53</td>
<td>27</td>
</tr>
<tr>
<td>NH\textsubscript{2}-UiO-66</td>
<td>1004</td>
<td></td>
<td>0.933</td>
<td>0.704</td>
<td>0.229</td>
<td>1.23</td>
<td>100</td>
</tr>
<tr>
<td>T</td>
<td>113</td>
<td></td>
<td>0.338</td>
<td>0.338</td>
<td>-</td>
<td>0.41</td>
<td>-</td>
</tr>
<tr>
<td>T-300-MOF</td>
<td>170</td>
<td>249</td>
<td>0.230</td>
<td>0.206</td>
<td>0.024</td>
<td>0.36</td>
<td>15</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Calculated from V\textsubscript{meso} = V\textsubscript{total} - V\textsubscript{micro}, \textsuperscript{b} Micropore volume from t-plot, \textsuperscript{c} CO\textsubscript{2} adsorption capacity measured at 25 °C.

Table 6-A2. Photocatalyst bandgaps derived from Tuac plots.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Bandgap (nm)</th>
<th>Bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t</td>
<td>392</td>
<td>3.16</td>
</tr>
<tr>
<td>T</td>
<td>399</td>
<td>3.11</td>
</tr>
<tr>
<td>NH\textsubscript{2}-UiO-66</td>
<td>448</td>
<td>2.77</td>
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</table>
Table 6-A3. Photocatalytic CO evolution rates of titanate, NH$_2$-UiO-66, titanate/NH$_2$-UiO-66 composites, thermally treated titanate (Ti$_{150}$), and the Ti$_{150}$/NH$_2$-UiO-66 composite under UV-vis illumination (150 W) with H$_2$ as the reducing agent unless stated otherwise.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Photocatalyst</th>
<th>CO gen (µmol/gcath)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>t</td>
<td>0.09±0.04</td>
</tr>
<tr>
<td>2</td>
<td>t-400-MOF</td>
<td>0.31±0.05</td>
</tr>
<tr>
<td>3</td>
<td>t-300-MOF</td>
<td>0.44±0.09</td>
</tr>
<tr>
<td>4</td>
<td>t-200-MOF</td>
<td>0.24±0.03</td>
</tr>
<tr>
<td>5</td>
<td>NH$_2$-UiO-66</td>
<td>0.24±0.03</td>
</tr>
<tr>
<td>6</td>
<td>T</td>
<td>0.59±0.08</td>
</tr>
<tr>
<td>7</td>
<td>T-300-MOF</td>
<td>0.84±0.26</td>
</tr>
<tr>
<td>8</td>
<td>T-300-MOFa.</td>
<td>n.d</td>
</tr>
<tr>
<td>9</td>
<td>T-300-MOFb.</td>
<td>1.8</td>
</tr>
</tbody>
</table>

$^a$N$_2$ and H$_2$ atmosphere control test, $^b$H$_2$O as sacrificial agent and 300 W illumination
Figure 6-A8. Transient absorption decay dynamics of innate powders of (a) NH$_2$-UiO-66, (b) the T/NH$_2$-UiO-66 composite (T-300-MOF), and (c) T, from 10 µs after a laser pulse ($\lambda_{exc}$ = 355 nm, $\sim$1.5 mJ.cm$^{-2}$, 6 ns pulse width, 0.65 Hz). Transient absorption spectroscopy was performed by Dr. Andreas Kafizas at Imperial College London.
Figure 6-A9. Spectral decay dynamics of innate powders of (a) NH$_2$-UiO-66, (b) the T/NH$_2$-UiO-66 composite (T-300-MOF) and (c) T, from 10 µs after a laser pulse ($\lambda_{\text{exc}} =$ 355 nm, $\sim$1.5 mJ.cm$^{-2}$, 6 ns pulse width, 0.65 Hz). Transient absorption spectroscopy was performed by Dr. Andreas Kafizas at Imperial College London.
Figure 6-A10. (a) Transient absorption and (b) spectral decay dynamics of NH$_2$-UiO-66 in methanol (~10 mg of the powder in 0.6 ml), from 10 µs after a laser pulse ($\lambda_{\text{exc}} = 355$ nm, $\sim 1.5$ mJ.cm$^{-2}$, 6 ns pulse width, 0.65 Hz). Transient absorption spectroscopy was performed by Dr. Andreas Kafizas at Imperial College London.
Figure 6-A11. (a) Transient absorption and (b) spectral decay dynamics of T in methanol (~10 mg of the powder in 0.6 ml), from 10 µs after a laser pulse (λ_{exc} = 355 nm, ∼1.5 mJ.cm^{-2}, 6 ns pulse width, 0.65 Hz). Transient absorption spectroscopy was performed by Dr. Andreas Kafizas at Imperial College London.
Figure 6-A12. (a) Transient absorption and (b) spectral decay dynamics of T in an aqueous solution of silver nitrate [2 mM] (~10 mg of the powder in 0.6 ml), from 10 µs after a laser pulse ($\lambda_{\text{exc}} = 355$ nm, $\sim 1.5$ mJ.cm$^{-2}$, 6 ns pulse width, 0.65 Hz). Transient absorption spectroscopy was performed by Dr. Andreas Kafizas at Imperial College London.