The Effect of Materials Architecture in TiO₂/MOF Composites on CO₂ Photoreduction and Charge Transfer

Angus Crake^a, Konstantinos C. Christoforidis^{a,1}, Aoife Gregg^a, Benjamin Moss^b, Andreas Kafizas^b,
Camille Petit^{*a}

^a Barrer Centre, Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, UK

^b Department of Chemistry, Imperial College London, South Kensington Campus, London SW7 2AZ, UK

¹Current address: Department of Environmental Engineering, Democritus University of Thrace, Xanthi, Greece

^{*} E-mail: camille.petit@imperial.ac.uk; Phone: +44 (0)20 7594 3182 (Petit C.)

Abstract

CO₂ photoreduction to C₁/C₁₊ energized molecules is a key reaction of solar fuel technologies. Building heterojunctions can enhance photocatalysts performance, by facilitating charge transfer between two heterojunction phases. The material parameters that control this charge transfer remain unclear. Here, we hypothesize that governing factors for CO₂ photoreduction in gas phase are: (i) a large porosity to accumulate CO₂ molecules close to catalytic sites and (ii) a high number of ‘points of contact’ between the heterojunction components to enhance charge transfer. The former requirement can be met by using porous materials, the latter requirement by controlling the morphology of the heterojunction components. Hence, we built composites of titanium oxide or titanate and metal-organic framework (MOF), a highly porous material. TiO₂ or titanate nanofiber were synthesized and MOF particles were grown on the fibers. All composites produced CO under UV-vis light, using H₂ as reducing agent. They are more active than their component materials: ~9 times more active than titanate. The controlled composites morphology is confirmed and transient absorption spectroscopy highlight charge transfer between the composite components. We demonstrate that electrons transfer from TiO₂ into the MOF, and holes from the MOF into TiO₂, as the MOF induces band bending in TiO₂.

Keywords: metal organic frameworks; titanium dioxide; photocatalysis; CO₂ reduction; heterojunction

Graphical abstract

1 Introduction

Driven by strong environmental incentives to diversify our energy portfolio and increase the share of renewables, researchers need to identify efficient routes towards solar fuels production. Solar fuels refer to fuels produced by action of sunlight, particularly H_2 produced from water and C_1 or C_{1+} energized molecules (*i.e.* CO, CH_4 , CH_3OH) produced from CO_2 .^[1] The latter reaction, *i.e.* CO_2 photoreduction, is the focus of this study. Photocatalysis represents one route towards CO_2 photoreduction. In that case, the design and manufacturing of a cost-effective, sustainable, efficient and robust photocatalyst is of paramount importance and remains a highly challenging task combining aspects of materials science, photochemistry and reactor design engineering.

The most widely researched photocatalysts for CO_2 reduction are semiconductors. Of which, TiO_2 has inspired intense research since the first demonstration in 1972,^[2] owing to its high stability, low cost, and non-toxic nature. These studies have shown that the TiO_2 morphology (*e.g.* 1D structures), crystalline form (*e.g.* anatase, rutile, brookite, and titanate), and composition (*e.g.* heterojunction, heterostructure formation) all are critical factors for improved photocatalytic activity.^[3] Another example of semiconductor, considered as a derivative of titania, is titanate. Titanate materials are photocatalytically active, with a crystalline structure similar to anatase TiO_2 and a one-dimensional morphology. Compared to conventional TiO_2 , they 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] Titanates have been used for photocatalysis,^[5] and in particular, we note two studies on CO_2 photoreduction.^[6] Recent photocatalytic improvements routes using titanate – not limited to CO_2 photoreduction – include the formation of composite materials for improved charge separation,^[4b, 5d, 7] and the conversion to a mixed phase anatase/titanate material hydrothermally, whilst retaining the fiber morphology.^[8] Specifically, mixed phase TiO_2 can

enhance charge separation and catalytic activity.^[9] Despite these improvements, the photocatalytic activity of TiO₂ remains below acceptable levels for large scale deployment due to its large bandgap, rapid photogenerated charge recombination, and low CO₂ adsorption capacity.^[10]

Metal organic frameworks (MOFs) have also recently been explored as photocatalysts for CO₂ reduction, with their chemical and structural modularities allowing a systematic and flexible design of the photocatalyst. For details on these studies, we direct the readers towards these reviews: ^[11].

The UiO-66 MOF family has been utilised most widely due to its chemical stability, visible light absorption, and straightforward synthesis.^[12] The formation of MOF composites with other photocatalysts, notably TiO₂, can increase photocatalytic activity owing to a synergistic effect between the coupled materials.^[13] Li et al.^[13a] synthesized TiO₂ nanoparticles onto HKUST-1 to form a TiO₂@HKUST-1 composite with superior photocatalytic activity in CO₂ reduction. We recently showed TiO₂/NH₂-UiO-66 nanocomposites with controlled MOF content can enhance CO₂ adsorption capacity and photocatalytic activity.^[14] In both studies the formation of a heterojunction to facilitate charge separation as evidenced by transient absorption spectroscopy led to higher activity. Taking into account the findings from our previous work, we hypothesised that controlling the interface between titania and MOF particles, and therefore the morphology of the respective particles, would influence the photoreduction of CO₂. In particular, we expect that increasing the number of ‘points of contact’ between the two materials will further improve the charge separation and transfer.

Herein, we report a study dedicated to testing the above hypothesis. Specifically, we synthesized nanocomposites of titanium oxide nanofibers with NH₂-UiO-66 for combined CO₂ capture and photocatalytic conversion. We selected these two materials to couple the high photocatalytic ability of the TiO₂ component with the high CO₂ adsorption capacity of the MOF. Additionally, the MOF

high CO₂ adsorption capacity should increase the CO₂ concentration close to the TiO₂ catalytic sites. To study the TiO₂-MOF interaction for CO₂ conversion, the MOF loading, TiO₂ morphology, and TiO₂ phase were controlled. We selected a 1D nanofibers morphology for the TiO₂ phase, and grew the MOF particles *in-situ* on top of these preformed fibers (Scheme 1) to maximise efficient charge transfer. We used a microwave-antenna synthesis to induce “super-hot” dots on the TiO₂ fibers for TiO₂/MOF composite formation.^[15] We opted for this rapid technique owing to its low energy requirements and its ability to promote MOF formation directly on the fiber leading to strong TiO₂/MOF interactions.^[16] We studied the nanocomposites using various analytical, imaging, and spectroscopic techniques and were evaluated for CO₂ adsorption and photocatalytic reduction. We report for the first time the synthesis and application of these materials for photocatalytic CO₂ reduction using H₂ or H₂O as sacrificial agents in a gas-solid heterogeneous system under UV-visible irradiation.

2 Results and Discussion

2.1 TiO₂ nanofibers and NH₂-UiO-66 nanocomposites formation

A schematic of the composites synthesis routes is provided in Scheme 1. Overall, we used a microwave-assisted synthesis to form NH₂-UiO-66 particles on the surface of preformed titanate fibers. The temperature was kept relatively low (80°C) to suppress NH₂-UiO-66 formation in the bulk solution. Instead, we grew NH₂-UiO-66 particles directly on the TiO₂ fibers *via* the creation of microwave induced by the “super-hot” dots on the TiO₂^[15a] – Scheme 1 route a. To study and optimise the titanate:NH₂-UiO-66 composites for photocatalytic CO₂ reduction, we varied the quantity of titanate present in the synthesis. The composites are denoted as t-x-MOF, where *x* is the quantity in mg of titanate used and MOF is NH₂-UiO-66. We attempted to improve further the

composite performance by investigating the conversion of the TiO_2 phase, whilst retaining the desirable nanofiber morphology – Scheme 1 route b. The corresponding nanocomposite is labelled T-300-MOF.

Scheme 1. Schematic of the $\text{TiO}_2/\text{NH}_2\text{-UiO-66}$ 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

NH₂-UiO-66 precursors and heated using microwaves to 80°C to form t/NH₂-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/NH₂-UiO-66 composites. The microwave induced hot spots on the TiO₂ promoted direct growth of the MOF on the fibers.

Chemical, physical, structural and morphological properties dictate photocatalytic activity. For this reason, we conducted an in-depth characterization of the materials. XRD confirmed the formation of the titanate structure (t, H₂Ti₂O₅·H₂O) as shown in Figure 1a, with peaks at 11.6° (200), 25.2° (110), and 48.7° (020).^[17] 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.^[7a] NH₂-UiO-66 displayed a diffraction pattern typical for this MOF.^[14, 18] 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 TiO₂ (Figure 1a), with peaks at 25.5° (101), 38.1° (004), 44.3° (003), 48.3° (200), 54.1° (105), and 55.2° (211).^[19] This showed that under hydrothermal conditions at 150 °C, titanate phase was converted to anatase phase TiO₂, as reported by Yu et al.^[8a] The composite T-300-MOF XRD pattern was a combination of the TiO₂ and NH₂-UiO-66 components, confirming the presence of both species.

We then used thermal gravimetric analysis (TGA) to quantify the MOF content of the nanocomposites (Figure S3). Under a nitrogen atmosphere, NH₂-UiO-66 was stable up to around 200 °C when the organic ligands began to decompose.^[14, 18] The titanate remained stable at the

highest temperature tested (900 °C), with a small mass drop from 200-350 °C attributed to removal of interlayer water.^[17] As expected, the composite materials displayed thermal degradation profiles which were a combination of the titanate and NH₂-UiO-66. We used the final masses of the materials (at 900 °C) to quantify the MOF loadings of the composites, shown in Table S1. These loadings ranged from 20-33%wt. The highest loading was obtained for the intermediate TiO₂ seed content in t-300-MOF (33%wt). We give a possible reason for this is below when discussing the surface area (Section 3.2). The anatase nanofiber, T, remained thermally stable at 900 °C (Figure S4), with a similar degradation profile to the untreated titanate. The TiO₂/MOF composite synthesized with the anatase nanofibers, T-300-MOF, contained 15%wt MOF. 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. The reason for this remains unknown at this stage.

We used ATR-FTIR spectroscopy to probe any chemical interaction between the titanate and the organic moieties of the MOF. The spectra are shown in Figure 1b. The NH₂-UiO-66 transmittance spectrum was similar to those reported for that MOF.^[12a, 14] The main titanate bands were H-O-H bending at 1630 cm⁻¹, Ti-O-Ti bending across 1000-400 cm⁻¹, and a broad surface O-H stretching band at 3398 cm⁻¹.^[7a, 8b] 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 bands also confirmed the titanate component in the composites. The thermally treated nanofibers, T, showed ATR-FTIR spectra similar to other anatase (Figure 1b), with an O-H absorption bands at 1653 cm⁻¹ and 3400 cm⁻¹.^[13c, 20] The intensity decrease of the titanate bands across the 1000-1500 cm⁻¹ region further proved the titanate to anatase phase

conversion. The transmission spectrum of T-300-MOF confirmed the presence of both components in the composite, with features of both T and NH₂-UiO-66 visible.

X-ray photoemission spectrum from anatase nanorods (T) also indicated that annealing of titanate (t) produced high purity TiO₂. Indeed, Ti 2*p* core lines (Figure S5a) exhibited a doublet (458.5 eV, 464.3 eV) consistent with a single Ti⁴⁺ environment, split by spin-orbit coupling.^[21] The O 1*s* spectrum confirmed the formation of TiO₂ with the strongest emission peak arising from O²⁻ anions in the TiO₂ lattice (529.8 eV, Figure S5c).^[22] Like for other particulate TiO₂ systems, we observed small amounts of adventitious carbon on the TiO₂ surface (C-C at 284.8 eV, C-O 288.1 eV, Figure S5b; and C-O 532.1 eV, Figure S5c).^[23] NH₂-UiO-66 exhibited core line emission broadly consistent with previous reports of this material.^[14] We observed a single Zr⁴⁺ 3*d* environment (Zr 3*d*_{5/2} at 283 eV)^[24] (Figure S6a). 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 S6b). For the oxygen environment, we observed: a small peak with a binding energy typical of oxide anions in a ZrO₂ environment (*i.e.* a ZrO₆ octahedral environment from the MOF) (530.2 eV)^[25] 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 S7 a-d). Surprisingly, we note a strong shift to higher binding energy (0.6 eV) in all core levels associated with TiO₂ (Figure S8c-d). We attribute this to a shift in the Fermi level of TiO₂ upon forming a junction with NH₂-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.

Figure 1. Structural and chemical characterisation of titanium oxide nanofibers, NH₂-UiO-66, TiO₂/NH₂-UiO-66 composites: a) XRD patterns, b) ATR-FTIR spectra, c) 77 K N₂ sorption isotherms.

2.2 TiO₂ nanofibers and NH₂-UiO-66 nanocomposites morphology and porosity

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, we employed electron microscopy images of the materials to visualise the titanate morphology and to provide direct evidence of titanate/NH₂-UiO-66 composite formation. Figure 2a-b confirmed the nanofiber/nanowire morphology and smooth surface of the titanate material (t). Fibers ranged from 25 to 250 nm in diameter, and up to several microns in length. The titanate interlayer spacing (200) was 0.8 nm.^[8a, 8b, 26] This aligns with the interlayer spacing derived from XRD (Figure 1a). The NH₂-UiO-66 (Figure 2c) formed agglomerated crystals around 25-50 nm in diameter.^[16, 27] Imaging the nanocomposites showed the titanate nanofibers coated in MOF particles (Figure 2e-f). MOF particles grew directly on the titanate nanofibers and did not alter their morphology (Figure 2f). The MOF particles on the titanate were larger than those synthesized in the absence of titanate, supporting the presence of “super-hot” spots on the fiber^[15a] for preferential MOF growth. TEM images of T confirmed that the nanofiber retained their morphology following thermal treatment at 150 °C (Figure 2g-i). However, the fibers were more coarse and porous.^[8a] This conversion of titanate to anatase phase *via* the formation of nanocavities was described as “anti-crystal growth” by Han *et al.*^[28] The lattice spacing was observed to be anatase phase TiO₂ (101).^[29] Again, SEM and TEM images of T-300-MOF (Figure 2j-l) showed

direct growth of $\text{NH}_2\text{-UiO-66}$ on the TiO_2 fibers, confirming the 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 half the size. The MOF formation on the anatase surface was probably less favourable than on titanate, as also suggested by the thermogravimetric analyses. A smaller MOF particle size should absorb light more efficiently and allow better charge separation due to the shortened charge transfer pathway.^[16] We compared the composites morphologies to that of a TiO_2/MOF composite for which the titania particles shape was not controlled ($\text{TiO}_2/\text{MOF NP}$). SEM images of the $\text{TiO}_2/\text{MOF NP}$ composite can be found in Figure S9. Clearly, the latter material exhibited a random structure with no evident particle shape. All the structural and chemical analyses performed on that sample confirmed the formation of the composites with the presence of the two phases (composition: 80.5 %wt TiO_2 , 19.5 %wt MOF).

Figure 2. Electron microscopy images highlighting the well-defined morphology of the materials: of a-b) titanate fibers (t), c) $\text{NH}_2\text{-UiO-66}$, and d-f) t-300-MOF composite, g-i) anatase fibers (T), j-l) T-300-MOF composite.

Not only morphology plays a role in the CO_2 photoreduction, porosity was expected to as well. Hence, we analyzed the textural properties of the materials. The results are presented in Figure 1c

and Table S1. Titanate (t) had a low surface area ($45 \text{ m}^2\text{g}^{-1}$) with a Type IV isotherm with H3 hysteresis indicating a mesoporous structure.^[8a, 30] $\text{NH}_2\text{-UiO-66}$ exhibited a high surface area ($1004 \text{ m}^2\text{g}^{-1}$) due to the presence of micropores,^[12a, 30] similar to those reported using an open vessel^[14, 18] and microwave-irradiation induced syntheses.^[16] As expected, the composites 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 to 400 mg lowered to MOF content. We explain this based on the hot spots created on the surface of titanate 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 ($113 \text{ m}^2\text{g}^{-1}$) doubled compared to titanate. due to an increased mesoporosity. This aligns with the rougher surface observed using electron microscopy (Figure 2g-i) as well as the literature^[8a, 8b]. T-300-MOF had a lower mesoporosity but increased surface area compared to the anatase TiO_2 fibers ($170 \text{ m}^2\text{g}^{-1}$) due to the formation of microporous MOF particles.

3.3. Light absorption

We then evaluated the light absorption of the materials using diffuse reflectance ultraviolet-visible (DR-UV/Vis) spectroscopy. The spectra were converted to a Tauc plot presented in Figure S10 using the Kubelka-Munk function with TiO_2 and $\text{NH}_2\text{-UiO-66}$ as indirect and direct semiconductors, respectively.^[7a, 8a, 8b, 31] The derived bandgaps are presented in Table S3. 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,^[7a, 8a, 8b] as was the 3.11 eV bandgap of the anatase phase (T).^[8a, 31a] The red-shift from titanate to anatase phase fibers was expected, based on an earlier study.^[8a] NH₂-UiO-66 absorbed in the visible (2.77 eV).^[12b, 31c] Hence, the composite materials had increased absorption in the visible region compared to their TiO₂ components, a desirable feature for photocatalysis due to the increased solar light utilization.

3.4. CO₂ adsorption capacity and photocatalytic CO₂ reduction evaluations

One of the first steps towards the photoreduction of CO₂ is the adsorption of the molecules on the surface of the catalyst. An increase in CO₂ adsorption may benefit photocatalysis due to the increased abundance of CO₂ at the catalytic sites.^[13b, 14] To understand how this aspect may impact the reaction, we measured CO₂ adsorption capacity of the photocatalysts at 25°C up to 1 bara (Figure 3a). On average, the CO₂ adsorption capacities followed the trend of the BET surface areas, though this is likely a coincidence given that porosity only plays a minor role at low pressure. NH₂-UiO-66 had a capacity of 1.23 mmol g⁻¹, comparable to results reported before.^[12a] The nanocomposites CO₂ 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. The composite T-300-MOF adsorbed slightly less CO₂ than TiO₂. T-300-MOF adsorbed as much CO₂ as the TiO₂/MOF composite with ‘random’ morphology (TiO₂/MOF NP).^[14] We conducted the CO₂ photoreduction tests in a heterogeneous gas/solid photoreactor, at ambient temperature, using H₂ as a reducing agent under UV-Vis illumination ($\lambda > 325$ nm, 150 W), without the addition of any co-catalyst or photosensitiser. We opted for a gas phase photoreactor in an effort to combine CO₂ capture and CO₂ conversion into a single process.^[14] The CO evolution rates of the

photocatalysts are presented in Figure 3b. CO was the only gaseous product detected. Titanate (t) was the least active photocatalyst tested and the activity of NH₂-UiO-66 was almost 3 times higher. This MOF has been recently demonstrated for photocatalytic CO₂ reduction in liquid phase photoreactors.^[12a, 12c] The composites were all more active than their parent materials showing a synergetic effect between titania and the MOF. Importantly, the composite with the ‘random’ morphology (TiO₂/MOF NP) was the least 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 NH₂-UiO-66 and titanate, respectively. The anatase fibers (T) were around 6 times more active than titanate fibers, this improvement aligns with other studies,^[5d, 8b, 32] and is likely due to presence of the more active anatase phase. We measured a further increase in CO evolution rate 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. To allow comparison with other studies on CO₂ photoreduction reported in the literature using a different reaction set-up, we have also measured the performance of titania P25 as it represents the benchmark in the field. Using our set-up, P25 leads to a 1.0 $\mu\text{mol g}^{-1} \text{hr}^{-1}$, which is slightly higher the best performing composite in this study. We note that most studies on CO₂ photoreduction using MOF-based materials are conducted in the liquid phase and hence cannot be compared to the work presented here. Looking at selectivity, we observe 100% selectivity towards CO. Other studies using MOF/TiO₂ composites in the gas phase have reported either pure CH₄ production,^[13a] or a mixture of CH₄ and CO^[13b] or pure CO.^[13b]

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-hour testing period (Figure S11a), indicating a stable CO₂ reduction rate. T-300-MOF remained active over 5 catalytic cycles with no obvious decline in performance (Figure 3c). We observe variations in the performance over these 5 cycles, though no noticeable drop compared to the first run. We formulated two hypotheses for these variations. The first one is that it is experimental error. In fact, if we consider the variations, they are of the same order of the standard deviation for a run. The second hypothesis is that the product remained adsorbed for some time on the material and was desorbed and therefore picked up by the GC only later. Following these experiments, the XRD patterns were unchanged (Figure 3d). In addition, TEM images and XPS spectra of the used samples remained unchanged as well (Figures S12 and S13). A control test under a N₂ and H₂ atmosphere (Table S2, entry 8) yielded no CO. In addition, isotopic tracing experiments using ¹³CO₂ yielded ¹³CO (Figure S11b). These tests proved the photocatalytic origin of the CO in the CO₂ reduction experiments. Water as an alternate reducing agent was also investigated under higher power UV-Vis illumination (300 W), which evolved 1.8 μmol g⁻¹ h⁻¹ CO (Table S2, entry 9).

Figure 3. CO₂ sorption and photoreduction analyses: a) CO₂ sorption isotherms at 25°C 1 bar, and b) photocatalytic CO evolution rates of t, NH₂-UiO-66, t/NH₂-UiO-66 composites, T, and the T/NH₂-UiO-66 composite. c) T-300-MOF CO evolution after repeated photocatalytic experiments, d) T-300-MOF XRD patterns before and after photocatalytic CO₂ reduction experiments. All photocatalytic experiments carried out under UV-Vis illumination (150 W) for 6 hours with H₂ as the reducing agent.

We now turn our attention to the relative contribution of TiO₂ morphology, crystalline phase, and composite heterojunction formation on the performance of the different samples. While a definite quantitative analysis of the different factors remains challenging, a number of insightful observations can be made, especially relating to our previous work on MOF/TiO₂ composites for which the morphology of the composites were not controlled.^[14]

- the formation of a heterojunction allowed an increase between 1.5 and 3 times that obtained for a physical mixture of titanate (or titania) and the MOF, depending on the composites.
- the optimisation of the morphology allows to more than doubled the performance of the composites.
- analysis of the effect of the crystalline phase is more difficult as the titanate/MOF and titania/MOF composites do not have the same composition. Yet comparing the performance of T-400-MOF (titanate phase, 20 wt% MOF) and T-300-MOF (titania phase, 15 wt% MOF), which exhibited the closest composition, we observed an increase of 3.5 in CO production rate.

Hence, overall, the contributions of the three parameters discussed above are of the same order of magnitude.

3.5. Charge carrier dynamics

We used transient absorption spectroscopy (TAS) to measure the charge carrier dynamics in NH₂-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 Figures S12 and S13, respectively. The decay dynamics and spectral changes found in the MOF were analogous to previous work^[14]. However, the decay dynamics found in the anatase TiO₂ powder, T, differed from previous studies^[9c, 33]. In anatase TiO₂ (T), charge carriers were longer lived ($t_{50\%}$ from 10 μ s, $\sim$ 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 $\text{NH}_2\text{-UiO-66}$. The transient absorption spectrum of anatase TiO_2 (T), 10 μs after the laser pulse, showed a broad, flat absorption across the visible (Figure 4). The spectrum of $\text{NH}_2\text{-UiO-66}$ 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 $\text{NH}_2\text{-UiO-66}$ 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 4. Transient absorption spectra, observed 10 μs after a laser pulse, of the innate powders of $\text{NH}_2\text{-UiO-66}$, T and T-300-MOF composite ($\lambda_{\text{exc}} = 355$ nm, ~ 1.5 $\text{mJ}\cdot\text{cm}^{-2}$, 6 ns pulse width, 0.65 Hz).

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.^[33] 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 S14). With methanol, significant hole scavenging occurred from ~1 ms resulting in a plateau in the decay dynamics (Figure S14a). We attribute this plateau to the formation of long-lived electrons, which absorb more strongly in the blue (Figure S14b). The anatase TiO₂ sample, T, showed a scavenging effect in both methanol (Figure S15) and silver nitrate solution (Figure S16). In methanol, holes were scavenged on the pre-μs timescale, giving rise to long-lived electrons (Figure S15a); an effect previously observed in mesoporous anatase TiO₂.^[33] These electrons absorb more strongly in the red, at ~900 nm (Figure S15b). Electron scavenging in silver nitrate solution was less pronounced (Figure S16). From the decay dynamics, electron scavenging occurred from ~1 ms (Figure S16a), where the concomitant holes gave rise to a strong absorption in the blue (Figure S16b). The locations of electron and holes signals in T were analogous to previous studies of anatase TiO₂.^[9c]

In summary, our scavenging studies showed that photogenerated electrons in NH₂-UiO-66, and holes in anatase TiO₂, 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 NH₂-UiO-66 to T, (ii) electron transfer from T to NH₂-UiO-66 or (iii) a combination of these two effects.

3.6. Mode of charge transfer in the TiO₂/NH₂-UiO-66 composites

To identify the mode of charge in the composites from the three options listed above, we investigated the relative band energy diagram of TiO₂ and NH₂-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 5). Peaks in all core levels associated with NH₂-UiO-66 in the composite appeared at commensurate binding energies to those of the parent material (Figure S6a-c). However, as mentioned earlier, a large shift (0.6 eV) to higher binding energy was observed in peaks attributed to TiO₂. O 1s peaks from transition metal oxides are broadly insensitive to changes in metal redox state.^[25] 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 TiO₂). Rather, the shifts are attributed to a 0.6 eV increase in the Fermi level (the reference/zero level in XPS) of TiO₂ upon forming a junction with NH₂-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 5. 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.

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 S8). 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-UiO66 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 (TiO₂) moves up to meet the material with higher donor density (UiO-66-NH₂). 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 S8b). 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 S8c) demonstrates that the valence 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 (Figures S5 – S8 and Figure 5) and the optical band gaps of the materials (Figure S11), a band energy diagram was constructed (Figure 6).^[34] This formed a type II staggered gap, in which the valence and conduction bands of anatase lay above the valence and conduction bands of $\text{NH}_2\text{-UiO-66}$, 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 $\text{NH}_2\text{-UiO-66}$ 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. Overview of the mode of charge transfer with visualization of the band energy alignment in the MOF/TiO₂ 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 (NH₂-UiO-66).

3 Conclusions

Composites of titanate or titania and metal-organic framework were produced and tested for CO₂ photoreduction. Of particular importance was the control of the morphology of the composites, which was hypothesised to impact charge transfer. We achieved this morphology control by: (i) forming nanofibers of titanate or titania (anatase) and (ii) growing *in-situ* MOF particles on the surface of the nanofibers. We evaluated the CO₂ adsorption of the composites along with their ability to photocatalyse CO₂ reduction in a gas/solid heterogeneous system under UV-Vis illumination with H₂ as a reducing agent.

All materials photocatalytically converted CO₂ to CO. The composites performed better than 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 TiO₂ phase was also studied by converting the titanate nanofibers to anatase nanofibers to further improve the photocatalytic

activity. The titania/MOF composite exhibited a further increase in photocatalytic activity, 9 times more when compared to titanate.

The in-depth study of the composites morphology, light absorption and charge carrier dynamics allowed to confirm: (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 (type II) in the materials. We demonstrate that the MOF induces strong band bending in anatase. 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. The contributions of each of these factors seem to be of the same order of magnitude.

4 Experimental Section

4.1 Material synthesis

All reagents used in this study were of analytical grade and used without further purification.

Titanium oxide P25 ($\geq 99.5\%$ trace metals), sodium hydroxide ($\geq 98\%$), zirconium chloride ($\geq 99.5\%$ trace metals), polyvinylpyrrolidone (PVP, average molecular weight 10,000), N,N-Dimethyl Formamide (99.9%), hydrochloric acid (37%wt), and acetic acid ($\geq 99.7\%$) were purchased from Sigma-Aldrich.

4.1.1 Synthesis of titanium dioxide nanofibers

We produced TiO₂ nanofibers (NF) *via* a hydrothermal synthesis, following a previously reported method.^[35] 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”.

We initiated for phase conversion of the TiO₂ nanofibers – from titanate to titania via a thermal treatment (Scheme 1 route b).^[36] “t” (600 mg), 30 mL deionised, 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”.

4.1.2 Synthesis of NH₂-UiO-66 and TiO₂/NH₂-UiO-66 nanocomposites

We employed an *in-situ* growth method to synthesize NH₂-UiO-66 on the as-synthesized TiO₂ nanofibers – Scheme 1 route a. The formation of the NH₂-UiO-66 particles was based on a previously reported method,^[18] 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-aminoterephthalic 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/TiO₂ 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 NH₂-UiO-66. NH₂-UiO-66 was synthesized using the same procedure above but with no titanate present.

The thermally treated titanate, T, was also used for the synthesis of a TiO₂/MOF nanocomposites using the same procedure as above. This composite was labelled T-300-MOF to identify its thermally treated TiO₂ component (T), and the quantity of TiO₂ present during synthesis (300 mg).

To assess the role of the composites morphology on the photoreduction process, we compared the composites in the present study to a composite of the same materials in a previous study in which the morphology of the titania and the MOF synthesis sites were not controlled.^[14] In brief, for this synthesis 0.147 g of zirconium (IV) chloride, 17.63 mL N,N-Dimethyl Formamide, 1.18 mL concentrated hydrochloric acid (37 %), 0.158 g of 2-aminoterephthalic acid (99%) and 0.5 g of TiO₂ nanosheets were combined, sonicated, transferred to a round bottom flask, and then heated under stirring to 150 °C for 24 h. This *in-situ* approach was adopted for the development of NH₂-UiO-66 in the presence of pre-synthesized TiO₂ nanosheets. The TiO₂/NH₂-UiO-66 nanocomposite formed had a MOF content of 19.5%wt and was the most photocatalytically active for CO₂ to CO conversion in that previous study. Herein, we refer to that sample as TiO₂/MOF composite with “random” nanoparticle (NP) morphology, denoted “TiO₂/MOF NP”.

4.2 Materials characterization methods

X-ray diffraction measurements were performed with a PANalytical X'Pert PRO instrument at room temperature (reflection mode at 40 kV and 40 mA using Cu K α radiation ($\alpha_1 = 1.54057 \text{ \AA}$, $\alpha_2 =$

1.54433 Å, weighted average = 1.54178 Å). The interplanar spacing was calculated using Bragg's law:

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

Attenuated total reflection Fourier transform-infrared (ATR-FTIR) spectra was collected using a Perkin-Elmer Spectrum 100 Spectrometer equipped with an ATR cell at room temperature. The spectra was generated, collected 8 times, and corrected for the background noise. The experiments were performed using powdered samples, without KBr addition. Scanning electron microscopy (SEM) images were taken using a high resolution LEO Gemini 1525 microscope in secondary electron mode at 5 kV (InLens detector). Prior to imaging, the samples were mounted on carbon tape and coated with 10 nm chromium. Transmission electron microscope (TEM) images were taken by a JEOL 2100Plus instrument at an acceleration voltage of 200 kV. Before imaging, the samples were sonicated in ethanol and then drop casted on a carbon coated copper grid. Nitrogen adsorption and desorption isotherms at -196 °C were measured using a Micrometrics 3Flex sorption analyzer. The surface area was calculated from the Brunauer-Emmett-Teller method.^[37] The total volume of pore was calculated from the volume adsorbed at P/P₀=0.97. The volume of micropores was determined using the Dubinin-Radushkevich method.^[38] The volume of mesopores was calculated as the difference between the total pore volume and the volume of micropores. CO₂ sorption isotherms at 25°C were measured up to 1 bara using the same instrument. Prior to all sorption measurements the samples were degassed at 0.2 mTorr, 120 °C for 24 hours. Diffuse reflectance ultraviolet-visible (DR-UV/Vis) spectra were obtained using an 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. Spectra were treated using Kubelka-Munk function^[39] to eliminate any tailing contribution from the DR-UV-vis spectra. The following equation was applied:

$$F(R) = \frac{(1 - R)^2}{2R}$$

where R is the reflectance. The band-gap (E_g) values were estimated from the plot of $F(R)h\nu^{1/n}$ versus energy by extrapolating the linear section.

X-ray photoemission spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha spectrometer equipped with an Al K α X-Ray source (1486.6 eV) and an 180° double focusing hemispherical analyzer with a 2D detector at an operating pressure of 1×10^{-8} mbar and a flood gun to minimise charging from photoemission. Powders were mounted onto conductive carbon tape adhered to a sample holder. To further correct for charging, all core lines were referenced against the C 1s (C-C) core line at 284.8 eV. Data was then processed and analyzed in the Avantage software package.

4.3 Photocatalytic CO₂ reduction

A gas-solid reactor setup was assembled as illustrated in Figure S1.^[14] The photocatalysts (25 mg) were deposited on a stainless steel metal disc with a fixed area of 9.6 cm². Research grade (99.999%) CO₂ and H₂ (99.9995%, Peak Scientific PH200 hydrogen generator) were flowed at controlled rates using mass flow controllers (Omega Engineering, 0-50 mL/min). For experiments requiring water vapour, this was generated from a saturator at room temperature (20 °C). The photoreactor (35 cm³) was vacuumed and replenished with reactant gases five times. Then the reactor was purged with the reactant gases for 15 residence times before it was sealed at 1.25 bara. A CO₂/H₂ ratio of 1.5 (vol/vol) was used for experiments using both these gases. A xenon arc lamp (150 W and 300 W, $\lambda > 325$ nm – see Figure S2 for full spectra, LOT Quantum Design), equipped with a water filter was used as the irradiation source. Evolved gases were detected by a gas chromatograph (GC, Agilent Technologies) with hayesep and mol sieve columns in series, thermal

conductivity (TCD) and flame ionisation (FID) detectors. The stability of the photocatalysts was tested by repeating process above after each 6 h illumination without opening the photoreactor. Isotopic tracing experiments were performed with $^{13}\text{CO}_2$ (BOC, >98% atom $^{13}\text{CO}_2$ compared to $^{12}\text{CO}_2$, >99%).

4.4 Transient absorption spectroscopy (TAS)

We studied the charge carrier dynamics of the materials using transient absorption spectroscopy, from the microsecond to second timescale, measured in diffuse reflection mode. We used a WeNd:YAG laser (OPOTEK Opolette 355 II, ~6 ns pulse width) as the excitation source, generating 355 nm light from the third harmonic transmitted to the sample through a light guide. The laser was fired at the sample at a rate of 0.65 Hz with a power density of $\sim 1.5 \text{ mJ.cm}^{-2}$. As the photo-induced changes in reflectance were low (< 1%), we assumed that the transient signal was directly proportional to the concentration of excited species. The probe light was a 100 W Bentham IL1 quartz halogen lamp. Long pass filter (Comar Instruments) were placed between the lamp and sample to minimize short wavelength irradiation of the sample. Diffuse reflectance from the sample was collected by a 2" diameter, 2" focal length lens and relayed to a monochromator (Oriel Cornerstone 130) to select the probe wavelength. Time-resolved intensity data was collected with a Si photodiode (Hamamatsu S3071). Data at times faster than 3.6 ms was recorded by an oscilloscope (Tektronics DPO3012) after passing through an amplifier box (Costronics), whereas data slower than 3.6 ms was simultaneously recorded on a National Instrument DAQ card (NI USB-6251). Each kinetic trace was obtained from the average of between 100 and 250 laser pulses. Acquisitions were triggered by a photodiode (Thorlabs DET10A) exposed to laser scatter. Data was acquired and processed using home-built software written in Labview.

Experiments were carried out in diffuse reflectance, since the materials were highly light scattering. Two types of experiment were conducted: (i) analysis of the innate powder and (ii) chemical scavenger experiments in which ~10 mg of the powder was dissolved in a chemical scavenger solution (0.6 mL of either pure methanol, a well-known hole scavenger, or an aqueous solution of silver nitrate [2 mM], a well-known electron scavenger).^[33] Solutions were sonicated for 15 minutes to achieve good dispersion (VWR ultra-sonic cleaner, 30 W, 45 kHz). Transient changes in diffuse reflectance were then measured in the visible region between 500 and 1000 nm.

5 Acknowledgements

This work was supported by the Engineering and Physical Science Research Council through the First Grant scheme (EP/N024206/1). A.C. and B.M thank Imperial College London and the Engineering and Physical Sciences Research Council for Doctoral Training Partnerships. A.K. thanks Imperial College London for a Junior Research Fellowship and the Royal Society for a Research Grant (RSG\R1\180434). A.G. thank the Royal Society of Chemistry for the Undergraduate Research Bursary.

6 Supporting Information

Supplementary data is available containing: Photocatalytic reactor set-up, lamps emission spectra, thermogravimetric analysis, N₂ isotherms, X-ray Photoelectron Spectra, ¹³C analyses, SEM images, DR-UV-Vis, and transient absorption spectroscopy spectra.

7 References

- [1] a) Y. Izumi, *Coordination Chemistry Reviews* **2013**, 257, 171; b) M. Mikkelsen, M. Jorgensen, F. C. Krebs, *Energy & Environmental Science* **2010**, 3, 43.
- [2] A. Fujishima, K. Honda, *Nature* **1972**, 238, 37.
- [3] a) H. Xu, S. Ouyang, L. Liu, P. Reunchan, N. Umezawa, J. Ye, *Journal of Materials Chemistry A* **2014**, 2, 12642; b) B. Wang, W. Chen, Y. Song, G. Li, W. Wei, J. Fang, Y. Sun, *Catalysis Today* **2018**, 311, 23.
- [4] a) V. Bem, M. C. Neves, M. R. Nunes, A. J. Silvestre, O. C. Monteiro, *Journal of Photochemistry and Photobiology A: Chemistry* **2012**, 232, 50; b) B. Barrocas, T. J. Entradas, C. D. Nunes, O. C. Monteiro, *Applied Catalysis B: Environmental* **2017**, 218, 709; c) S. Thennarasu, K. Rajasekar, K. Balkis Ameen, *Journal of Molecular Structure* **2013**, 1049, 446.
- [5] a) H.-H. Ou, S.-L. Lo, *Separation and Purification Technology* **2007**, 58, 179; b) D. V. Bavykin, F. C. Walsh, *European Journal of Inorganic Chemistry* **2009**, 2009, 977; c) Y. Zhang, Z. Jiang, J. Huang, L. Y. Lim, W. Li, J. Deng, D. Gong, Y. Tang, Y. Lai, Z. Chen, *RSC Advances* **2015**, 5, 79479; d) K. C. Christoforidis, A. Sengele, V. Keller, N. Keller, *ACS Applied Materials & Interfaces* **2015**, 7, 19324.
- [6] a) S. K. Parayil, A. Razzaq, S.-M. Park, H. R. Kim, C. A. Grimes, S.-I. In, *Applied Catalysis A: General* **2015**, 498, 205; b) H. Park, H.-H. Ou, A. J. Colussi, M. R. Hoffmann, *The Journal of Physical Chemistry A* **2015**, 119, 4658.
- [7] a) T. A. Silva, J. Diniz, L. Paixão, B. Vieira, B. Barrocas, C. D. Nunes, O. C. Monteiro, *Solid State Sciences* **2017**, 63, 30; b) Z. Xiong, X. S. Zhao, *Journal of the American Chemical Society* **2012**, 134, 5754.
- [8] a) H. Yu, J. Yu, B. Cheng, M. Zhou, *Journal of Solid State Chemistry* **2006**, 179, 349; b) E. Ylhäinen, M. Nunes, A. Silvestre, O. Monteiro, *Journal of Materials Science* **2012**, 47, 4305; c) H. Y. Zhu, Y. Lan, X. P. Gao, S. P. Ringer, Z. F. Zheng, D. Y. Song, J. C. Zhao, *Journal of the American Chemical Society* **2005**, 127, 6730.
- [9] a) D. C. Hurum, A. G. Agrios, K. A. Gray, T. Rajh, M. C. Thurnauer, *The Journal of Physical Chemistry B* **2003**, 107, 4545; b) S.-G. Kim, L. K. Dhandole, J.-M. Lim, W.-S. Chae, H.-S. Chung, B.-T. Oh, J. S. Jang, *Applied Catalysis B: Environmental* **2018**, 224, 791; c) A. Kafizas, X. Wang, S. R. Pendlebury, P. Barnes, M. Ling, C. Sotelo-Vazquez, R. Quesada-Cabrera, C. Li, I. P. Parkin, J. R. Durrant, *The Journal of Physical Chemistry A* **2016**, 120, 715.
- [10] a) C. Han, Y. Wang, Y. Lei, B. Wang, N. Wu, Q. Shi, Q. Li, *Nano Research* **2015**, 8, 1199; b) K. Li, T. Peng, Z. Ying, S. Song, J. Zhang, *Applied Catalysis B: Environmental* **2016**, 180, 130.
- [11] a) C. Wang, Z. Xie, K. E. deKrafft, W. Lin, *Journal of the American Chemical Society* **2011**, 133, 13445; b) Y. Fu, D. Sun, Y. Chen, R. Huang, Z. Ding, X. Fu, Z. Li, *Angewandte Chemie* **2012**, 124, 3420; c) H. Zhang, J. Wei, J. Dong, G. Liu, L. Shi, P. An, G. Zhao, J. Kong, X. Wang, X. Meng, J. Zhang, J. Ye, *Angew Chem Int Ed Engl* **2016**, 55, 14310; d) T. Zhang, W. Lin, *Chemical Society Reviews* **2014**, 43, 5982; e) A. Crake, *Materials Science and Technology* **2017**, 33, 1737; f) S. Wang, X. Wang, *Small* **2015**, 11, 3098; g) R. Li, W. Zhang, K. Zhou, *Advanced Materials* **2018**, 30, 1705512.

- [12] a) D. Sun, Y. Fu, W. Liu, L. Ye, D. Wang, L. Yang, X. Fu, Z. Li, *Chemistry – A European Journal* **2013**, 19, 14279; b) D. Sun, W. Liu, M. Qiu, Y. Zhang, Z. Li, *Chemical Communications* **2015**, 51, 2056; c) Y. Lee, S. Kim, J. K. Kang, S. M. Cohen, *Chem Commun (Camb)* **2015**, 51, 5735.
- [13] a) R. Li, J. Hu, M. Deng, H. Wang, X. Wang, Y. Hu, H.-L. Jiang, J. Jiang, Q. Zhang, Y. Xie, Y. Xiong, *Advanced Materials* **2014**, 26, 4783; b) M. Wang, D. Wang, Z. Li, *Applied Catalysis B: Environmental* **2016**, 183, 47; c) S. S. Yan, S. X. Ouyang, H. Xu, M. Zhao, X. L. Zhang, J. H. Ye, *Journal of Materials Chemistry A* **2016**, 4, 15126; d) L. Liu, F. Zhang, J. Zhang, X. Tan, B. Zhang, J. Shi, D. Shao, D. Tan, B. Han, G. Yang, *Soft Matter* **2017**, 13, 9174; e) J. C. Cardoso, S. Stulp, J. F. de Brito, J. B. S. Flor, R. C. G. Frem, M. V. B. Zanoni, *Applied Catalysis B: Environmental* **2018**, 225, 563; f) Z. Huang, P. Dong, Y. Zhang, X. Nie, X. Wang, X. Zhang, *Journal of CO2 Utilization* **2018**, 24, 369.
- [14] A. Crake, K. C. Christoforidis, A. Kafizas, S. Zafeiratos, C. Petit, *Applied Catalysis B: Environmental* **2017**, 210, 131.
- [15] a) D. Zhang, P. Liu, S. Xiao, X. Qian, H. Zhang, M. Wen, Y. Kuwahara, K. Mori, H. Li, H. Yamashita, *Nanoscale* **2016**, 8, 7749; b) S. Xiao, P. Liu, W. Zhu, G. Li, D. Zhang, H. Li, *Nano Letters* **2015**, 15, 4853.
- [16] X. Wang, X. Zhao, D. Zhang, G. Li, H. Li, *Applied Catalysis B: Environmental* **2018**, 228, 47.
- [17] F. Jiang, S. Zheng, L. An, H. Chen, *Applied Surface Science* **2012**, 258, 7188.
- [18] M. J. Katz, Z. J. Brown, Y. J. Colon, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp, O. K. Farha, *Chemical Communications* **2013**, 49, 9449.
- [19] a) K. C. Christoforidis, M. Fernandez-Garcia, *Catalysis Science & Technology* **2016**, 6, 1094; b) J. Cui, D. Sun, W. Zhou, H. Liu, P. Hu, N. Ren, H. Qin, Z. Huang, J. Lin, H. Ma, *Physical Chemistry Chemical Physics* **2011**, 13, 9232.
- [20] M. Mehta, N. Kodan, S. Kumar, A. Kaushal, L. Mayrhofer, M. Walter, M. Moseler, A. Dey, S. Krishnamurthy, S. Basu, A. P. Singh, *Journal of Materials Chemistry A* **2016**, 4, 2670.
- [21] D. Courcot, L. Gengembre, M. Guelton, Y. Barbaux, B. Grzybowska, *Journal of the Chemical Society, Faraday Transactions* **1994**, 90, 895.
- [22] J. L. Ong, L. C. Lucas, G. N. Raikar, J. C. Gregory, *Applied Surface Science* **1993**, 72, 7.
- [23] B. Moss, K. K. Lim, A. Beltram, S. Moniz, J. Tang, P. Fornasiero, P. Barnes, J. Durrant, A. Kafizas, *Scientific Reports* **2017**, 7, 2938.
- [24] A. E. Hughes, B. A. Sexton, *Journal of Electron Spectroscopy and Related Phenomena* **1990**, 50, C15.
- [25] E. N. K. Glover, S. G. Ellington, G. Sankar, R. G. Palgrave, *Journal of Materials Chemistry A* **2016**, 4, 6946.
- [26] C. Huang, X. Liu, L. Kong, W. Lan, Q. Su, Y. Wang, *Applied Physics A* **2007**, 87, 781.
- [27] N. Yin, K. Wang, L. Wang, Z. Li, *Chemical Engineering Journal* **2016**, 306, 619.
- [28] W. Q. Han, L. J. Wu, R. F. Klie, Y. M. Zhu, *Advanced Materials* **2007**, 19, 2525.
- [29] Q. Xiang, K. Lv, J. Yu, *Applied Catalysis B: Environmental* **2010**, 96, 557.
- [30] K. S. W. Sing, in *Adsorption by Powders and Porous Solids (Second Edition)* (Ed: F. R. R. S. W. S. L. Maurin), Academic Press, Oxford **2014**, p. 237.

- [31] a) K. C. Christoforidis, A. Iglesias-Juez, S. J. A. Figueroa, M. Di Michiel, M. A. Newton, M. Fernandez-Garcia, *Catalysis Science & Technology* **2013**, 3, 626; b) L. Valenzano, B. Civalieri, S. Chavan, S. Bordiga, M. H. Nilsen, S. Jakobsen, K. P. Lillerud, C. Lamberti, *Chemistry of Materials* **2011**, 23, 1700; c) Y. Su, Z. Zhang, H. Liu, Y. Wang, *Applied Catalysis B: Environmental* **2017**, 200, 448.
- [32] X. Zhang, J. Yuan, Y. Yu, Q. Dong, Z. Xiong, H. Yu, X. Zhu, H. Shen, Y. Xie, *Journal of Alloys and Compounds* **2017**, 712, 549.
- [33] X. Wang, A. Kafizas, X. Li, S. J. Moniz, P. J. Reardon, J. Tang, I. P. Parkin, J. R. Durrant, *The Journal of Physical Chemistry C* **2015**, 119, 10439.
- [34] D. O. Scanlon, C. W. Dunnill, J. Buckeridge, S. A. Shevlin, A. J. Logsdail, S. M. Woodley, C. R. A. Catlow, M. J. Powell, R. G. Palgrave, I. P. Parkin, G. W. Watson, T. W. Keal, P. Sherwood, A. Walsh, A. A. Sokol, *Nat Mater* **2013**, 12, 798.
- [35] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, *Langmuir* **1998**, 14, 3160.
- [36] M. Chaudhary, S.-m. Chang, R.-a. Doong, H.-m. Tsai, *The Journal of Physical Chemistry C* **2016**, 120, 21381.
- [37] S. Brunauer, P. H. Emmett, E. Teller, *Journal of the American Chemical Society* **1938**, 60, 309.
- [38] S. G. Chen, R. T. Yang, *Langmuir* **1994**, 10, 4244.
- [39] P. C. Rao, A. K. S, S. Mandal, *CrystEngComm* **2014**, 16, 9320.