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Revisiting the incorporation of Ti(IV) in UiO-type metal-organic frameworks: metal exchange versus grafting and their implications for hydrogen evolution from water

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The inclusion of Ti(IV) in water-stable metal-organic frameworks has been proposed as a strategy for the generation of high surface area heterogeneous photocatalysts, with UiO-66 being a promising candidate. We find that the site of binding of Ti(IV) is at linker defect sites and not incorporated into the inorganic secondary building unit through metal exchange. We also demonstrate the choice of titanium source is critical in the generation of an active hydrogen evolution catalyst, and explain the observed activity using density functional theory calculations, which also enable rational design of future Ti(IV) coordination environments in MOF catalysts.

Introduction

The generation of hydrogen from water (hydrogen evolution reaction – HER) mediated by sunlight is a key challenge in the design of new energy conversion paradigms.[1] While there are many classes of materials that will promote this reaction, metal-organic frameworks (MOFs) have emerged as promising platforms, owing to their high surface area, structural diversity and late-stage tunability.[2] However, most MOFs suffer from hydrolytic instability, limiting their application in aqueous HER photocatalytic systems.[3, 4] MOFs of the UiO series possess good water and thermal stability, and opportunities for post-synthetic modification.[5, 6]

Common strategies for functionalisation of Zr-UiO-type materials include linker modification and metal incorporation.[7-9] The former has been extensively studied in both UiO- and MIL-125-type materials through utilisation of functionalised ligands.[10-12] For example, amination of the terephthalic acid linker in MIL-125 has been shown to close the band gap, redshifting from the UV and thus enabling visible light photocatalysis. In the case of UiO-66, the addition of Ti(IV) has been extensively studied because of its photoaccessible unoccupied Ti(III) state, but nevertheless the

structural characterization of these materials remains largely unknown.[13-18]

The two hypotheses for how incorporation of Ti into UiO-66 occurs are either through metal exchange into the inorganic secondary building unit (SBU), or grafting of the Ti(IV) onto the surface of this node at a linker vacancy site (Figure 1). Metal exchange has been attempted primarily with $TiCl_4 \cdot 2THF$ as a Ti(IV) source, but the nature of this exchange is inconclusive.[9, 14, 19-21]

A major impediment to the understanding of metal inclusion in UiO-type materials, either as ion exchange or metal appendage, is that while Ti(IV) can also be conjectured to occupy linker vacancy sites, until recently the nature of
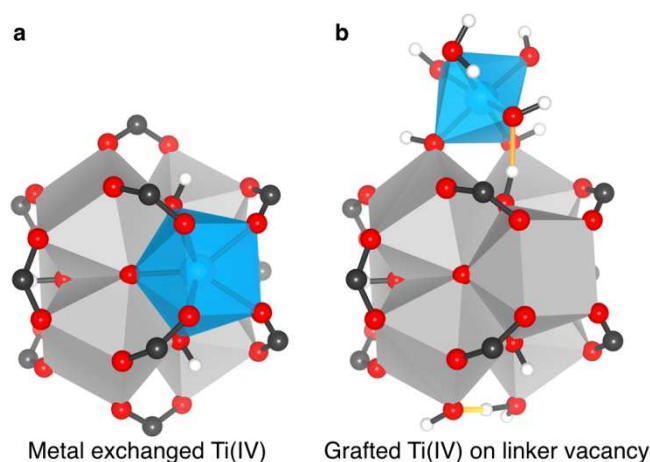
Figure 1. Proposed coordination sites of Ti in UiO-type materials. (a) The inclusion of Ti(IV) in the cluster through metal exchange. (b) The appendage of Ti(IV) to the surface of the cluster at a linker vacancy defect site.

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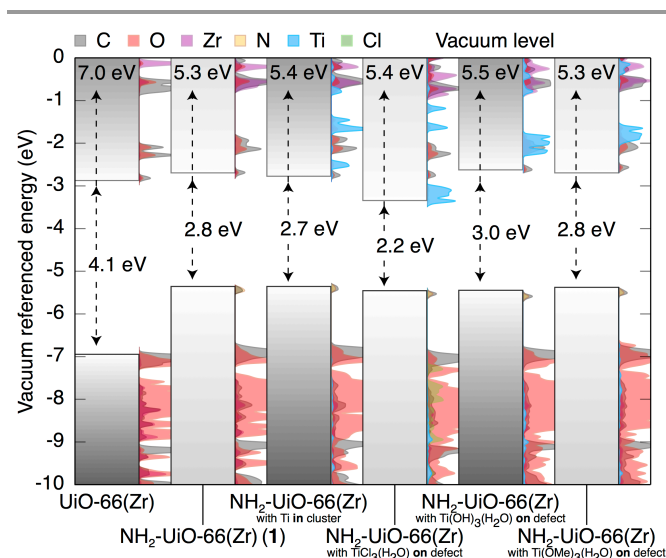c. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, 02139 USA. Email: hendon@mit.edu, murraya@mit.edu
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these vacancies was poorly understood.[22, 23] However, recent advances in the characterisation of UiO defect chemistry has revealed up to 33% linker vacancies,[24-30] and the nature of these vacancies has been systematically explored in the related NU-1000 MOF and the MOF-801 series.[31, 32]
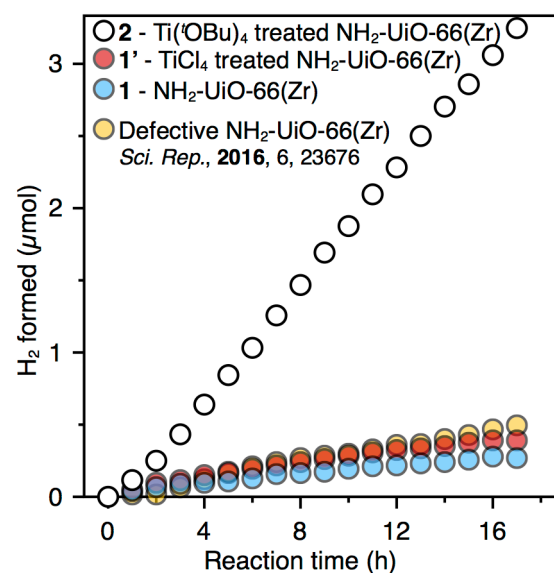
Results and Discussion

An ideal Ti(III) photocatalyst features low energy unoccupied Ti(IV) orbitals that allow facile electron occupation of this state upon photoirradiation, and a local electron rich ligand that can transiently stabilize a proton (*e.g.* a bridging oxo as found in MIL-125, or pendant hydroxy/alkoxy motif).[33, 34] Hence, DFT calculations are able to systematically elucidate the nature of the frontier bands for different Ti coordination environments in UiO-66. The UiO-66 material's frontier orbitals are defined by a ligand-ligand transition (Figure 2).[35] Amination of the linker (*i.e.* NH_2-UiO-66(Zr), **1**) yields an occupied midgap state, albeit still with a ligand-based transition (Figure 2).[36] We then investigated the energies of Ti both in the cluster (metal exchange) and on a defect site (metal appendage), in both the aminated and native frameworks. When Ti is incorporated in the cluster, the valence bands are unaltered and the conduction bands do not feature Ti orbitals at the frontier; rather Ti orbitals are found at marginally higher energies but nevertheless should be photoaccessible. Likewise, with Ti appended on defect sites the conduction band is not defined primarily by Ti orbitals.

These calculations assume that additional ligands on titanium are hydroxyl groups. With a less electronegative ligand such as Cl^- the Ti(IV) unoccupied state is stabilized thus bringing Ti orbitals to the frontier, Figure 2. Therefore, the ligand set as well as the titanium site occupancy should be paramount in generating an active photocatalyst.

As our goal was to generate a visible-light active photocatalyst we used the aminated precursor, **1**. Initially, we attempted to functionalize **1** with $TiCl_4 \cdot 2THF$ using a method previously reported.[9] However, the material formed under these conditions, **1'**, simply featured an increase in linked vacancies as observed by an increase in the BET adsorption isotherm (Figure S1, S2), and increasing infrared O-H stretching anisotropy (Figure S6, S7). Additionally, we see both Ti and Cl inclusion by TEM/EDX (transmission electron microscopy/ energy dispersive X-Ray analysis, Figure S5). Given the propensity of Ti-Cl bonds to hydrolyse under the synthetic conditions (three days in methanol), we instead suspect Cl-termination of zirconium clusters and formation of $Ti(OR)_x$ type materials in the pore. Upon photoexcitation of **1'**, *X/Q*-band EPR (9/34 GHz) indicates electron transfer with a formation of Ti(III) in octahedral coordination environment, similar to MIL-125-NH_2 (Figure 5). However, the observation of sharp peaks with well resolved *g*-tensor components *g*=[1.976 1.945 1.925] is more consistent with a single Ti environment (e.g. $Ti(OR)_x$) rather than with the superposition of environments anticipated if Ti would reside at the defect sites (*vide infra*).

Figure 2. The density of states (DOS) and band alignment of native Zr-UiO-66, the 16%-NH_2-UiO-66(Zr) (**1**), compared to the models with Ti(IV) inside the SBU, or appended to the linker defect site and passivated with Cl^-, ^-OH or ^-OMe. A single H_2O is included to complete the octahedral coordination sphere. DOS at ~5.4 eV and ~2.9 eV have amino-benzene parentage.

Figure 3. Photocatalytic activity of native NH_2-UiO-66(Zr) (**1**, *blue*) and a deliberately defective analogue (*yellow*) compared to the $TiCl_4$-loaded NH_2-UiO-66(Zr) (**1'**, *red*)**,** and Ti(^tOBu)$_4$-treated NH_2-UiO-66(Zr) (**2**, *white*). Deliberately defective NH_2-UiO-66 was synthesized using the method presented in Ref 35.
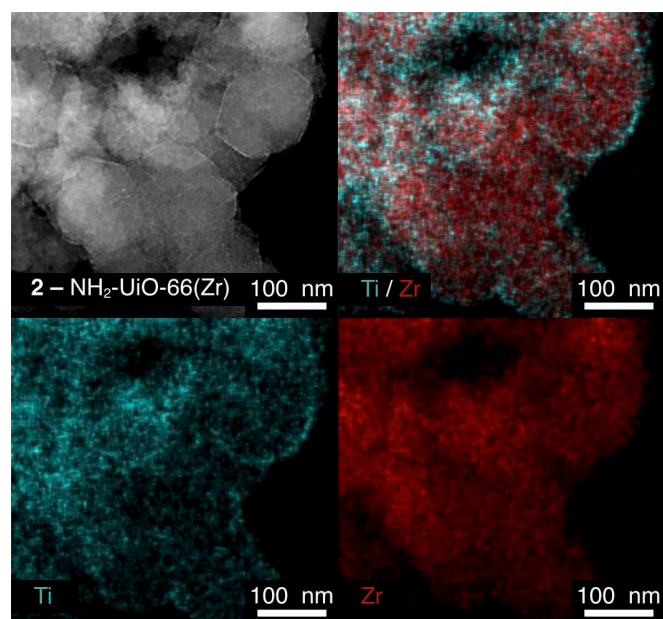
Figure 4. Transmission electron microscopy / energy dispersive X-ray spectroscopy images of NH₂-UiO-66(Zr) (**2**). Ti(IV) is present throughout the crystal, with highest concentrations found on the crystal edges.

The photocatalytic hydrogen evolution activity of **1'** was found to be 1.5x greater than native **1** (Figure 3). Indeed, this HER activity is in line with previously reported results for the defect-laden version of this material (data of the deliberately defective NH₂-UiO-66(Zr) showed a 1.7x increase in photocatalytic activity, with approximately 30% linker vacancies).[36] From this data, we propose that Ti is not primarily responsible for catalytic activity in this case. Therefore, we developed a new synthetic route to minimize new linker vacancies formed during the metal inclusion.

The most frequently proposed defect passivation of the zirconia SBUs is through termination with pendant –OH groups, that share a third proton in a bridging H-bond (depicted at the bottom of Figure 1b). We propose that use of a more basic Ti salt could deprotonate the defect site and thus enhance grafting of Ti onto the inorganic SBU. Thus, we selected Ti(OⁿBu)₄ as the Ti(IV) source for post-synthetic modification of **1** to form a postulated Ti-grafted product referred to as **2** (depicted in Figure 1b). Given the reaction conditions, a representative model of the Ti-coordination sphere is likely either octahedral Ti(IV) with either associated hydroxides or alkoxides. The electronic structure of both systems is presented in Figure 2. **2** demonstrates the expected decrease in BET area (associated with the grafting of the Ti(IV) to the surface of the SBU, a single IR O-H stretching resonance, and a higher proportion of remaining residues of metal oxides observed by TGA (Figure S1, S4, S6) corresponding to the appendage of a metal with no concurrent increase in site vacancies. Importantly, if metal exchange were occurring into the SBU, we would expect no decrease in the surface area.

TEM/EDS mapping of Ti shows good dispersion of Ti(IV) (Figure 4), with some preference for surface functionalization. EPR of the photoexcited material (X- and Q-band) in this case shows a more diffuse Tiᴵᴵᴵ signal relative to **1'** (Figure 5), indicative of a broader distribution of g-tensor components and suggesting a number of possible combinations of Ti-containing linker defects on Zr SBUs. Noteworthy, measurements of the T1 and T2 relaxation times of **2** are in good agreement for highly dispersed Ti(IV) through the UiO-66 lattice (Figure S11) and suggest that Ti is atomically dispersed. Long-range crystallinity appeared to be maintained as observed by PXRD (Figure S3).

Most importantly the grafted material, **2**, demonstrates significantly improved photocatalysis compared to the other materials considered here. Upon irradiation in CH₃CN/Et₃N/H₂O, hydrogen was evolved from water with a rate of 0.2 μmol h⁻¹, attributed to photocatalysis occurring at the Ti(III) sites, (Figure 3). This corresponds to a rate 14x greater than either native NH₂-UiO-66(Zr) (**1**) or the material formed by Ti incorporation through treatment of **1** with TiCl₄.2THF (**1'**). Indeed, upon photoirradiation of **2** at 370 nm, a new transient absorption band centred at around 750 nm was observed (Figure S9), which, in agreement with EPR, likely corresponds to a Ti(III) excitation.[37-40]
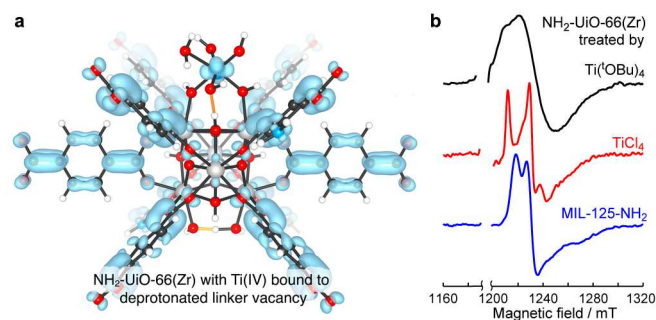
Figure 5. (**a**) The spin density of the pseudoexcited state of 16%-NH₂-UiO-66(Zr)-Ti(OH)₃(H₂O), **2** shows a majority of spin contribution on the organic linker but, importantly a minor contribution from a Ti(III) d-orbital. The Ti(III) density should increase proportionally with loading on the framework. (**b**) Q-band continuous wave EPR spectra (≈33.5 GHz) of photoexcited MIL-125-NH₂, **1'** and **2** in the reaction mixture of CH₃CN/Et₃N/H₂O.

From direct comparison of the **2**–Ti–Cl, –Ti–OH and –Ti–OMe structures we see that the electron density of the ligand determines the extent of Ti contribution to the conduction band. Whilst –Cl termination is electronically the most favourable, it is unlikely that such ligand environments persist under relevant reaction conditions. Despite both –OH and –OMe terminated models suggesting minimal Ti d orbital contributions to their conduction band minima, the ground state DFT calculation is not the most informative representation of the orbital density upon photoexcitation. Thus, we constructed a model of triple–OH terminated **2** and find that indeed most of the band is defined by the ligands, but there is additional highly localized titanium d character as a minor component (emphasized in Figure 5a). Two conclusions can be drawn from this calculation: i) the titanium density of states will increase proportionally with the increased loading of Ti in the MOF, and ii) titanium density will increase with proportionally to linker vacancies (either by increased loading of Ti-sites, or by decreased linker contribution to the frontier bands).

Conclusion

We have found that upon titanium incorporation into the MOF UiO-66, the type of Ti binding is through appendage of Ti to a linker vacancy rather than replacement of zirconium in the SBU. Careful choice of titanium source in the post-synthetic modification of this MOF determines the extent of covalent interaction between the MOF and Ti. Furthermore, the appendage of Ti(IV) to the surface of the MOF yields a moderately active HER photocatalyst. More active catalysts will likely spawn from the engineering the Ti-bound ligand set to achieve persistence in reaction conditions whilst being weakly electron donating (to lower the Ti(III) band deeper into the electronic band gap). Therefore, we have shown that in MOF catalyst design both the defect environment and external ligand field are equally important in the further improvement of activity in photocatalysis for this class of materials.

Experimental Methods

Comprehensive experimental details of PXRD, EPR, TEM/EDX, gas sorption isotherms, DRIFTS, diffuse reflectance UV-Vis, DTAS, and computational methods are included in the Supporting Information.

Acknowledgements

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Broader Context

Much of the interest in mitigating the rise in atmospheric CO_2 levels has focussed on the use of H_2 as the energy source in both convectional engines and fuel cell applications. However, the formation of H_2 from H_2O using a sustainable energy source remains one of the key challenges impeding the transition to a hydrogen economy. Use of sunlight is arguably the ideal energy source for this transformation, and thus a suitable catalyst is needed to harness this resource into chemical bonds. Metal-organic frameworks (MOFs) offer both compositional diversity and extremely high surface area, enabling them as unique scaffolds for a suite of catalytic processes. A paradigm in the photocatalytic transformation of H_2O to H_2 is through the use of photoexcited Ti(IV) reagents, and incorporation of analogous Ti(IV) compounds into/onto MOFs provides an avenue to the realisation of high surface area catalysts with ample active heterogenous sites. We report that the incorporation of Ti(IV) into/onto water stable MOFs is indeed a viable strategy for the generation of novel photocatalysts, however the activity is highly dependent on the nature of the Ti(IV) incorporation. Thus, we provide a roadmap to the development of highly active MOF-based water-stable Ti(IV) catalysts for hydrogen evolution from water, using visible light.

TOC graphic