

Design and Characterization of Visible Light-Responsive Ti-Based Metal–Organic Frameworks for the Application to Photocatalytic Hydrogen Evolution

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1 Introduction

There has been much attention to H₂ evolution from water under sunlight in the context of clean energy production. H₂ is a promising energy source because it does not emit greenhouse gases upon combustion. In order to utilize solar light effectively the development of photocatalysts efficiently operating under visible light is urgently needed. Metal–organic frameworks (MOFs) referred to as porous coordination polymers (PCPs) are favorable candidate materials because of their diversity of chemical and structure features. The various combinations of organic linkers and metal-oxo clusters allow for accurate material design. The present study focuses on the development of an amino-functionalized Ti-based MOF (Ti-MOF-NH₂) that can absorb visible light due to the chromophore in their organic linkers and its application to visible-light-promoted H₂ evolution from aqueous media.

2 Experiment

Ti-MOF-NH₂ was prepared based on previously reported method [1]. A mixture of tetrapropyl orthotitanate, 2-amino-terephthalic acid, N,N-dimethylformamide (DMF), and methanol was subject to solvothermal conditions in a Teflon-lined stainless steel autoclave for 48 h at 423 K under autogenous pressure. The formed precipitate was separated by filtration, washed repeatedly with DMF and dried at room temperature overnight, followed by drying under vacuum for 1 h, yielding Ti-MOF-NH₂ as yellow powder.

Characterizations were conducted by using UV–vis, XRD, and XAFS measurements. Ti K-edge XAFS spectra were measured in the fluorescence mode at the BL-7C facilities of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba.

Photocatalytic H₂ evolution was performed under visible-light irradiation ($\lambda > 420$ nm) from 500 W Xe lamp fitted with an appropriate cut-off filter. Ti-MOF-NH₂ was dispersed in an aqueous solution containing 0.01 M triethanolamine (TEOA) as a sacrificial electron donor. The reactant solution was degassed to remove air prior to irradiation. The evolved H₂ was analyzed by GC.

3 Results and Discussion

The UV–vis spectrum of Ti-MOF-NH₂ showed an observable band in the visible-light region up to around 500 nm. XRD measurements revealed that the synthesized Ti-MOF-NH₂ possesses a 3-D network structure coincident with conventional Ti-MOF prepared using terephthalic acid [1]. To elucidate the local

structure around Ti center in Ti-MOF-NH₂ Ti K-edge XAFS analyses were performed. Fig. 1 shows Ti K-edge XANES spectra of Ti-MOF-NH₂ and titanium dioxides (anatase and rutile). Ti-MOF-NH₂ exhibited completely different spectrum from titanium dioxides, indicating that bulky titanium dioxide does not form in Ti-MOF-NH₂. Moreover the Ti-MOF-NH₂ spectrum resembles that of an intermediate titanium cluster formed during the formation of titanium dioxide nanoparticles, reported by J. Stötzel *et al* [2].

Following the confirmation of the formation of a visible light-responsive Ti-MOF, the H₂ evolution reaction from aqueous solution containing TEOA as a sacrificial electron donor was performed by using the Ti-MOF-NH₂ photocatalyst under visible-light irradiation ($\lambda > 420$ nm). Continuous H₂ evolution occurs from the beginning of the irradiation period, and the total evolution of H₂ after 3 h irradiation reaches 5.0 μ mol. Thus the Ti-MOF-NH₂ was found to act as an efficient visible light-responsive photocatalyst.

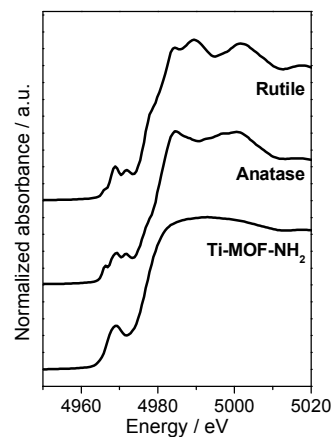


Fig. 1: Ti K-edge XANES spectra of Ti-MOF-NH₂, anatase, and rutile.

Acknowledgement

XAFS spectra were recorded at the beamline BL-7C facility of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba, Japan (2011G556).

References

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- [2] J. Stötzel *et al.*, *J. Phys. Chem. C* **114** (2010) 6228.

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