

Design of a Visible-Light-Responsive Metal–Organic Framework Photocatalyst Containing Pt Complexes as Light Harvesting Units

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1 Introduction

In recent years, metal–organic frameworks (MOFs) also called porous coordination polymers (PCPs) have attracted much attention in the fields of gas storage, molecular sieving, and catalysis owing to their well-ordered porous structures, high specific surface areas, and structure designability. The structure designability that comes from varying combination of constituent organic linkers and metal-oxo clusters allows us to develop novel, rationally-designed materials. In this context, we have developed a visible-light-responsive MOF photocatalyst containing Pt complexes which act as light harvesting units, as its organic linkers. Herein, the detailed structural evaluation of the developed MOF photocatalyst was performed through XRD, UV–vis, and XAFS, and its application to photocatalytic H₂ evolution from aqueous media under visible-light irradiation was studied.

2 Experiment

The visible-light-responsive MOF photocatalyst containing Pt complexes was prepared via a two-step method. Firstly, a MOF consisting of titanium-oxo clusters and 2,2'-bipyridine-5,5'-dicarboxylic acid was prepared by a solvothermal method at 453 K for 48 h (Ti-MOF-bpy). Subsequently, the obtained Ti-MOF-bpy was allowed to react with K₂PtCl₄ in water-acetone solution at 333 K for 5 h, yielding Ti-MOF-Pt(bpy)Cl₂.

Characterizations were conducted by using XRD, UV–vis, and XAFS measurements. Pt L_{III}-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.

For photocatalytic H₂ evolution, Ti-MOF-Pt(bpy)Cl₂ was dispersed in an aqueous solution containing 0.01 M triethanolamine (TEOA) as a sacrificial electron donor and H₂PtCl₆ as a source of Pt co-catalyst (1.0 wt%) and was irradiated with visible light from 500 W Xe lamp fitted with an appropriate cut-off filter. The reactant solution was degassed to remove dissolved O₂ prior to irradiation. The evolved H₂ was analyzed by GC.

3 Results and Discussion

The XRD measurements revealed that the prepared Ti-MOF-bpy possessed a 3D porous network structure and its structure was maintained even after reaction with K₂PtCl₄ to form Pt complexes within the MOF. The formation of Pt complexes was confirmed by UV–vis and XAFS measurements. The UV–vis spectrum of Ti-MOF-bpy showed no absorption band in visible region, while an observable absorption band was seen in the spectrum

of Ti-MOF-Pt(bpy)Cl₂ up to ca. 550 nm. Moreover, the spectral shape of Ti-MOF-Pt(bpy)Cl₂ in visible region was coincident with that of (2,2'-bipyridine)dichloroplatinum(II) complex (Pt(bpy)Cl₂). Pt L_{III}-edge XANES and Fourier transform of EXAFS (FT-EXAFS) spectra of Ti-MOF-Pt(bpy)Cl₂, Pt(bpy)Cl₂, and an aqueous K₂PtCl₄ solution (K₂PtCl₄ aq.) are shown in Fig. 1. Nearly the identical XANES spectra were observed for Ti-MOF-Pt(bpy)Cl₂ and Pt(bpy)Cl₂, which were different from that of K₂PtCl₄ aq. In the FT-EXAFS spectra (without peak shift correction), K₂PtCl₄ aq. exhibited only one peak at 2.0 Å assigned to Pt–Cl bond, whereas Ti-MOF-Pt(bpy)Cl₂ exhibited two peaks at 1.6 and 2.0 Å assigned to Pt–N and Pt–Cl bonds, respectively. These findings suggested that Pt(bpy)Cl₂ complexes are successfully formed within Ti-MOF-bpy through a reaction between bipyridine unit in the MOF framework and K₂PtCl₄.

The potential visible-light-induced photocatalysis of Ti-MOF-Pt(bpy)Cl₂ was evaluated by H₂ evolution from an aqueous medium containing TEOA and H₂PtCl₆. Continuous H₂ evolution occurred under visible-light irradiation ($\lambda > 420$ nm), and the total evolution of H₂ after 3 h irradiation reached 7.2 μ mol. Moreover, the action spectrum measurements revealed that the reaction proceeds via the absorption by the Pt complexes formed within the MOF framework and that the longest wavelength available for the reaction is 550 nm.

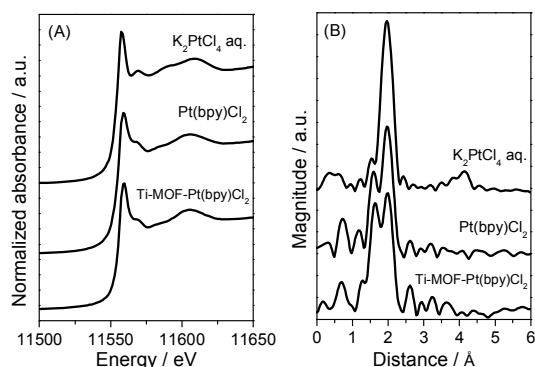


Fig. 1: Pt L_{III}-edge (A) XANES and (B) FT-EXAFS spectra of Ti-MOF-Pt(bpy)Cl₂, Pt(bpy)Cl₂, and K₂PtCl₄ aq.

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