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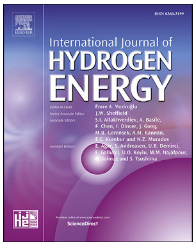

Tunable conduction band energy and metal-to-ligand charge transfer for wide-spectrum photocatalytic H_2 evolution and stability from isostructural metal-organic frameworks

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ABSTRACT

Metal-organic framework (MOF) materials with their synthetic tunability and structural regularity offer an interesting platform to achieve photocatalytic H_2 production. To determine whether metal ions in MOF materials affect the photocatalytic hydrogen (H_2) evolution activity, very few studies investigated MOF materials having the same crystal structures and ligands. In this study, we describe the synthesis of isostructural MOF materials. Cadmium (II) or copper (II) were linked with the 4′-(2,4-disulfophenyl)-3,2′:6′,3″-terpyridine (H_2DSPTP) organic ligand to form Cd-MOFs and Cu-MOFs, respectively. Although Cd-MOFs and Cu-MOFs had the same valence band (VB) energy, the conduction band (CB) level of Cu-MOFs was more negative than that of Cd-MOFs. Therefore, the reduction ability of Cu-MOFs was greater than that of Cd-MOFs. Moreover, Cu-MOFs showed excellent absorption of visible and even near-infrared (NIR) radiation, because it has strong metal-to-ligand charge transfer (MLCT) character. Interestingly, the rate of photocatalytic H_2 generation was 18.96 μmol h^{-1} in the presence of Cu-MOFs, which were irradiated with NIR light; however, Cd-MOFs did not report any such activity. Moreover, the performance and stability of Cd-MOFs were different from that of Cu-MOFs. In this study, the proof of knowledge for rational photocatalyst design introduced here furnishes the notional framework for constructing high-activity MOF materials.

Introduction

To compensate the continuous depletion of fossil fuels, scientists are tapping the potential of renewable sources of energy. Solar energy was recently used to carry out photocatalytic water splitting, resulting in the evolution of hydrogen (H_2) fuel. Because H_2 fuel is a clean and renewable energy source, the reaction has attracted the attention of several scientists [1–4]. Fujishima and Honda first performed

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photocatalytic water splitting by using TiO_2. Thereafter, various materials were used to carry out photocatalytic H_2 evolution, but none of them could be scaled further for commercial applications [5,6]. In photocatalytic H_2 evolution, idea photocatalyst has to fulfill the following properties: suitable band gap (ca. 2.0 eV), reasonable band edge alignment with thermodynamic requirements, and long-term stability in water [7–9]. Compared to several other semiconductor catalysts, metal-organic framework (MOF) materials can be reliably synthesized as extended hierarchical structures [10]. Crystal engineering is used to synthesize MOF materials from well-defined molecular building blocks. In light harvesting and photocatalytic H_2 evolution, MOF materials have become promising candidates because of their tunable band gaps, large surface areas, and small clusters of metal oxides [11,12]. To perform photocatalytic H_2 evolution from water, Mori's group used MOF materials as photocatalysts for the first time [13]. Thereafter, many research studies have investigated whether MOF can be used as photocatalysts. Presently, the following MOF materials are used as photocatalysts: NH_2-UiO-66 [14], UiO-66 [15], NH_2-MIL-125(Ti) [16], Ti-MOF-Ru$(tpy)_2$ [17], and MIL-125 [18]. To improve H_2 evolution, scientists used modified MOF materials that included various functional substances, such as metal nanoparticles, hydrogenase, and complex [19,20]. Recently, fluorescein and eosinY dye were used to sensitize MOF materials; these dye-sensitized MOF materials improved photocatalytic H_2 evolution from water [21,22]. There has been tremendous improvement in solar-driven H_2 evolution due to advancements in MOF materials; however, these MOF materials still exhibit low photocatalytic activity because of problems, such as limited light harvesting, speedy recombination of charges, and poor stabilities [23–25].

To the best of our knowledge, no previous study has investigated the effect of metal ions on the photocatalytic activity of MOF materials till date. Metal ions are chemically bonded to O^{2-} ions in metal oxides. The role of organic ligands in MOF materials is analogous to the role of O^{2-} ions in metal oxides. Therefore, the valence band (VB) of MOF material is primarily formed by the outer orbitals of organic ligands. Meanwhile, the conduction band (CB) is formed by the empty outer orbitals of the central metal ion [26]. During the process of electron transfer from the ligand to the metal-oxide cluster, different metal ions in MOF materials would affect the transmission efficiency of photogenerated electrons when the same crystal structure of MOF is formed with the same ligand. The efficiency of hydrogen production would depend on the transmission efficiency of photogenerated electrons. Therefore, it is necessary to determine the function of metal ions in the electron transfer mechanism of MOF system. To avoid the effect of metal ions with different valencies, we chose divalent metal ions in our experiment. Cadmium (II) has been extensively used in various inorganic materials, such as $CdWO_4$ [27], CdS [28], and $Zn_xCd_{1-x}S$ [29] etc. On the other hand, copper (II) is a relatively cheap metal that is abundantly available on earth. For example, copper (II) plays an important role in respiration and photosynthesis [30]. However, MOF materials containing cadmium (II) and copper (II) are rarely used in photocatalytic H_2 production.

In this study, we carried out the syntheses and characterization of an isostructural pair: Cd-MOFs ($C_{21}H_{21}CdN_3O_{10}S_2$) and Cu-MOFs ($C_{21}H_{21}CuN_3O_{10}S_2$). Although the ligand ($H_2$DSPTP) and crystal structure (the monoclinic space group $P2_1/n$) were the same in the aforementioned isostructural pair, the photocatalytic H_2 evolution rates of Cd-MOFs and Cu-MOFs were significantly different under visible light ($\lambda > 420$ nm) and near-infrared light ($\lambda > 800$ nm) illumination. Both Cd-MOFs and Cu-MOFs had the same VB energy (+0.90 eV). The reduction ability of Cu-MOFs was greater because the negative potential of CB level in Cu-MOFs (−1.49 eV) was greater than that of Cd-MOFs (−0.96 eV). Furthermore, the metal-to-ligand charge transfer (MLCT) process typically produced low-energy absorption bands. A series of experiments were performed to determine the light-harvesting capacity, stability, charge transfer, and charge separation efficiency of Cd-MOFs and Cu-MOFs.

Experimental

Reagents

Copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, 99.0%), cadmium carbonate ($CdCO_3$, 99.9%), triethanolamine ($C_6H_{15}NO_3$, 99.0%), and ammonia (NH_3, 25.0–28.0%) were purchased from Aladdin Co. Ltd. Hydrochloric acid (HCl) was purchased from Guangzhou Guoling Instrument Co. Ltd. The ligand H_2DSPTP was obtained from Jinan Camolai Trading Company. The materials were all utilized without furthermore purification and were all analytically pure. Deionized water was utilized throughout the experimental part.

Synthesis of Cd-MOFs

$CdCO_3$ (36.76 mg, 0.21 mmol), H_2DSPTP (10 mg, 0.02 mmol), and H_2O (1.0 mL) were all mixed and put in hydrothermal cell (12 mL) and pH regulated to 7.0 with HCl (0.4 M) and ethylenediamine (0.5 M), and heated for 72 h at 120 °C in the oven. Finally, the hydrothermal cell was cooled slowly (2 °C/h) to air temperature, affording as dark yellow block crystals. The opaque crystals were respectively washed by ethanol and deionized water. The yield was 82% based on the H_2DSPTP organic ligand. Elemental analysis (%) calcd for Cd-MOFs: C, 38.69, N, 6.45, H, 3.25. Found: C, 38.72, N, 6.48, H, 3.22%. Crystal structure data for Cd-MOFs are given in from by single-crystal diffraction.

Synthesis of Cu-MOFs

$CuSO_4 \cdot 5H_2O$ (2.67 mg, 0.01 mmol), H_2DSPTP (5 mg, 0.01 mmol), and H_2O (1.5 mL) were mixed and put in hydrothermal cell (20 mL) and pH regulated to 5.0 with NH_3 (0.25 mol/L), and heated for 48 h at 120 °C in the oven. Finally, the hydrothermal cell was cooled slowly (2 °C/h) to air temperature, affording as blue block crystals. The opaque crystals were respectively washed by ethanol and deionized water. The yield was 67% based on the H_2DSPTP organic ligand. Elemental analysis (%) calcd for Cu-MOFs: C, 43.11, N, 7.18, H, 3.27. Found: C, 43.14, N, 7.16, H, 3.29%. Crystal structure data for Cu-MOFs are given in from by single-crystal diffraction.

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