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Assembly of highly efficient photocatalytic CO_2 conversion systems with ultrathin two-dimensional metal–organic framework nanosheets

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ABSTRACT

An ultrathin two-dimensional Zn porphyrin-based metal–organic framework (Zn-MOF nanosheets) is developed and used for the first time in photoreduction of CO_2 to CO. Consequently, two novelty noble-metal-free hybrid photocatalytic systems are established and displayed outstanding photocatalytic activity and selectivity for CO evolution under mild photocatalytic reaction conditions. The insight revealed Zn-MOF nanosheets as photosensitizer displays a better charge transport ability and longer lifetime of the photogenerated electron-hole pairs than the Zn-MOF bulk, which are confirmed by photoelectrochemical impedance and photoluminescence (PL) measurements. These studies show that the development of noble-metal-free photocatalytic systems and various MOF-based materials for photocatalytic applications are promising.

1. Introduction

Global climate change and the increasing energy demand have had a serious impact on human society [1–3]. Therefore, mimicking photosynthesis, which converts of CO_2 into fuels and chemical feedstocks using solar energy, would be of great benefit. The photoreduction of CO_2 is extremely difficult because CO_2 is a stable linear molecule, so a large energy is required to change its geometry from linear to bent [4]. Herein, we report on the development of highly efficient and selective photocatalytic systems for the photochemical reduction of CO_2.

So far, photocatalytic systems containing a metal complex as co-catalyst and a dye molecule as photosensitizer have been studied extensively owing to their high selectivity for products [5–10]. However, most of the dye molecules in the system contain a noble metal, such as Ir and Ru [6–9], which hinders their practical applications. In addition, these photocatalytic systems are unstable owing to the photodegradation of the dye molecules under light irradiation [5,7,10]. To solve these problems, the use of stable semiconductors to replace the dye molecules is a promising approach. Ishitani and co-workers have designed a hybrid photocatalytic system containing an homogeneous metal complex and a heterogeneous semiconductor [11–14]. This system was more stable and efficient than the previously reported homogeneous photocatalytic systems; [11–13] however, the efficiency of this system was drastically reduced when a noble-metal-free complex was used as the catalyst instead of the Ru and Re complexes [14]. Therefore, an ideal solution would be to incorporate a highly efficient noble-metal-free co-catalyst together with a photosensitizer that possesses a high light absorption ability and photostability.

Metal – organic frameworks (MOFs), as a new class of hybrid materials that consist of an organic linker and secondary building units, have been extensively researched for decades and have been demonstrated to possess promising applications in various fields [15–18]. Recently, MOFs have been developed as photocatalysts and electrocatalysts to reduce CO_2 to fuels owing to their assistance in CO_2 capture and activation [19–23]. Porphyrin-based MOFs, considered as semiconductors owing to their high light absorption ability, have also been studied for the photochemical reduction of CO_2 [24]. However, the efficiency of bulk porphyrin-based MOFs is too low, mainly as a result of the fast charge recombination of the photogenerated electron-hole pairs [25]. Compared with bulk MOFs, 2D MOF nanosheets possess higher photocatalytic efficiency, because of the synergistic effect of the increased surface area and CO_2 adsorption, enhanced electron-transport properties, and prolonged lifetime of the photogenerated electron-hole pairs. However, without co-catalyst, the efficiency of porphyrin-based MOFs is very low for the photocatalytic CO_2 reduction [26]. Therefore, an attractive approach is to develop a new photocatalytic system which contains a 2D porphyrin-based MOF as photosensitizer and a noble-metal-free complex or ZIF as co-catalysts.

Herein, we report a simple synthetic method for a uniformed ultrathin 2D Zn porphyrin (5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin;

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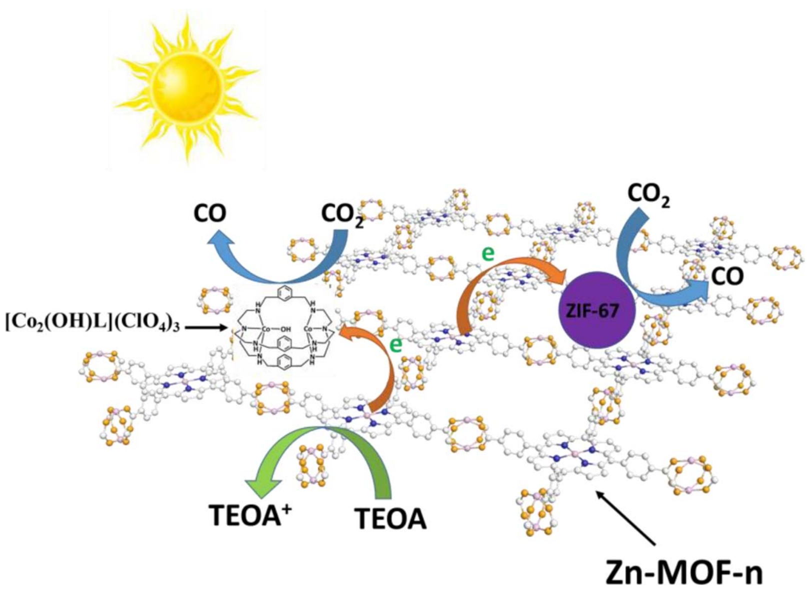

Scheme 1. A MOF/complex or MOF/ZIF system for CO_2 photoreduction with Zn-MOF nanosheets as the photosensitizer.

TCPP)-based MOF (denoted as Zn-MOF nanosheets) with a thickness of approximately 4.7 nm. Consequently, a Zn-MOF nanosheets or Zn-MOF bulk was applied as the photosensitizer with a dinuclear cobalt complex $[Co_2(OH)L](ClO_4)_3$($L = N[(CH_2)_2NHCH_2(m\text{-}C_6H_4)CH_2NH(CH_2)]_3N$) or ZIF-67 as co-catalyst in a MOF/complex or MOF/ZIF system for CO_2 photoreduction (Scheme 1). Compared with the Zn-MOF bulk, the Zn-MOF nanosheets displayed a higher photocatalytic activity and selectivity for CO evolution in these systems mainly arising from their better CO_2 adsorption capacity and charge transport ability, as well as the longer lifetime of the photogenerated electron-hole pairs.

2. Experimental

2.1. Synthesis of Zn-MOF nanosheets

$Zn(NO_3)_2{\cdot}6H_2O$ (2.25 mg, 0.0075 mmol), PVP (10.0 mg) and pyrazine (0.4 mg, 0.005 mmol) were dissolved in a solution of DEF/DMF/EtOH (24 mL, v:v:v = 2:1:1). Then TCPP (2.0 mg, 0.0025 mmol) dissolved in 8 mL DMF/EtOH (v:v = 2:1) was added dropwise. The solution was stirred under sonication for 30 min and then heated to 80 °C for 16 h. The reaction mixture was then cooled naturally, the desired purple nanosheets were collected by high speed centrifugalization and washed with DMF and EtOH for several times.

2.2. Characterization

X-ray diffraction (XRD) measurements were carried out by a Rigaku D/MAX2400 diffractometer for the co-planar (out-of-plane, OP) measurement in θ-θ geometry. The XRD data were acquired over a 2θ range of 5–23°. The optical properties were measured by a UV–vis absorption spectroscopy (Agilent 8453). The photoluminescence spectra were measured with a fluorescence spectrophotometer. X-ray photoelectron spectroscopy (XPS) experiments were performed in an ultra-high vacuum system (base pressure 2×10^{-10} mbar) equipped with a non-monochromatic Al Kα X-ray source and a hemispherical energy analyzer (VG-Scienta R4000). The instrumental resolution was less than 500 meV. Atomic force microscopy (AFM) was employed by DI Innova Multimode SPM system. The morphologies and sizes of the Zn-MOF nanosheets and the Zn-MOF bulk were imaged by scanning electron microscopy (SEM) (NOVA NanoSEM 450) and transmission electron microscopy (TEM) (FEI Tecnai G2F20 S-TWIN). Gas adsorption measurement was performed through the ASAP 2020 system. The specific surface area of the photocatalysts was calculated by the Brunauer-Emmett-Teller (BET) method. Thermogravimetric analysis (TGA) was performed in air with a heating rate of 10 °C per minute. Photoelectrochemical properties were measured in a three-electrode system with 0.5 M Na_2SO_4 solution as electrolyte. The Zn-MOF nanosheets or the Zn-MOF bulk was deposited on a FTO conducting glass as working electrode with a working area of 1 cm^2. The suspension for the deposition was 0.2 mL ethanol containing 0.2 mg of the samples. Pt electrode and Ag/AgCl electrode (saturated KCl solution) were used as the counter and reference electrodes.

2.3. Photocatalytic reaction

The photocatalytic reaction was performed in a solution (6 mL, MeCN/MeOH/TEOA = 4:1:1) containing Zn-MOF nanosheets or Zn-MOF bulk (10 mg) as photosensitizer, $[Co_2(OH)L](ClO_4)_3$ or ZIF-67 as co-catalyst and TEOA as electron donor. The photocatalytic system was purged with CO_2 (99.999%) for 30 min and then irradiated for 6 h under a Xe lamp (120 mW cm^{-2}) with a 420 nm cutoff filter. The collected H_2 was analyzed by a gas chromatograph (GC, Techcomp 7890) equipped with thermal conductivity and the CO was test using a GC (Techcomp 7900) equipped with flame ionization detectors. The photocatalytic system with ZIF-67 as co-catalyst was constructed and operated under similar conditions with using $[Co_2(OH)L](ClO_4)_3$ as co-catalyst. Multiple photocatalysis experiments were run at each condition and the average data was calculated.

2.4. Absorption/emission measurements

UV–vis spectroscopy was carried out by a Agilent 8453 diode array spectrophotometer and emission spectroscopy was carried out by a Fluoro Max-4P fluorescence spectrometer, at room temperature using 1 cm quartz cell (light path length = 1 cm).

The quenching rate was determined by the Stern-Volmer equation:

$$\frac{I_0}{I} = 1 + k_q \tau_0 [Q]$$

Where I_0 and I are the fluorescence intensity of the Zn-MOF nanosheets or the Zn-MOF bulk in the absence and presence of the quencher Q. k_q is the quenching rate constant. τ_0 is the fluorescence lifetime of the excited state in the absence of the quencher Q, which was determined to be 0.51 ns (Zn-MOF nanosheets) and 0.33 ns (Zn-MOF bulk) in MeCN/MeOH (v/v, 4:1) solution based on the time-resolved PL spectra. [Q] is the concentration of the quencher Q. In the tests, the concentration of