



Copper(II) imidazolate frameworks as highly efficient photocatalysts for reduction of CO₂ into methanol under visible light irradiation

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ABSTRACT

Three copper(II) imidazolate frameworks were synthesized by a hydrothermal (or precipitation) reaction. The catalysts were characterized by X-ray diffraction (XRD), nitrogen adsorption, transmission electron microscopy (TEM), ultraviolet–visible spectroscopy (UV–vis), Fourier transform infrared spectra (FTIR), thermogravimetry (TG). Meanwhile, the photocatalytic activities of the samples for reduction of CO₂ into methanol and degradation of methylene blue (MB) under visible light irradiation were also investigated. The results show that the as-prepared samples exhibit better photocatalytic activities for the reduction of carbon dioxide into methanol with water and degradation of MB under visible light irradiation. The orthorhombic copper(II) imidazolate frameworks with a band gap of 2.49 eV and green (G) color has the best photocatalytic activity for reduction of CO₂ into methanol, 1712.7 μmol/g over 5 h, which is about three times as large as that of monoclinic copper(II) imidazolate frameworks with a band gap 2.70 eV and blue (J) color. The degradation kinetics of MB over three photocatalysts fitted well to the apparent first-order rate equation and the apparent rate constants for the degradation of MB over G, J and P (with pink color) are 0.0038, 0.0013 and 0.0016 min⁻¹, respectively. The synergistic effects of smallest band gap and orthorhombic crystal phase structure are the critical factors for the better photocatalytic activities of G. Moreover, three frameworks can also be stable up to 250 °C. The investigation of Cu-based zeolitic imidazolate frameworks maybe provide a design strategy for a new class of photocatalysts applied in degradation of contaminations, reduction of CO₂, and even water splitting into hydrogen and oxygen under visible light.

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1. Introduction

Porous metal–organic frameworks (MOFs) have been extensively investigated since 1990 [1,2]. Zeolitic imidazolate frameworks (ZIFs) are a new class of nanoporous compounds with tetrahedral networks that resemble those of zeolites: transition metals (Co, Cu, Zn, etc.) replace tetrahedrally coordinated atoms (for example, Si), and imidazolate links replace oxygen bridges [3,4]. As a subfamily of MOFs, ZIFs exhibit the tunable pore size and chemical functionality of classical MOFs [5]. Meanwhile, they are chemically and thermally stable, yet have the long-sought-after design flexibility offered by functionalized organic links and a high density of transition metal ions [3]. Because of these combined features, ZIFs have very promising applications in catalysis [6–8], gas storage [3,9,10], chemical separation [11,12], molecular recognition [13] and optical [14], electronic [15,16], photoluminescence and magnetic materials [17], and consequently have drawn considerable attention from chemists around the

world nowadays. Recently, Zifs have also been used in the photocatalytic degradation of organic dye, Isimjan et al. [7] loaded Pt/ZIF-8 nano-crystallites onto the surfaces of TiO₂ nanotubes and observed increase in photocatalytic properties of ZIF-8 loaded TiO₂ nanotubes by photodegradation of phenol. Yang et al. [18] doped copper into ZIF-67 and found that the Cu-doped ZIF-67 showed high gas uptake capacity and highly efficient visible-light-driven photocatalytic property on the degradation of methyl orange.

The energy shortages and the environmental pollution causing by the depletion of fossil fuels and the gradual increase of atmospheric carbon dioxide (CO₂) concentration are two main challenges in today's society. The artificial photosynthesis, converting CO₂ and water into valuable energy-bearing compounds (such as CO, methane, and methanol) by means of solar energy, is one of the most attractive methods to overcome both global warming and energy crisis. Since photocatalytic reduction of CO₂ to formic acid, formaldehyde, methanol, and methane over TiO₂ under UV light was discovered by Fujishima and Inoue [19], a number of semiconductors such as TiO₂ nanoparticles or nanotubes [20–26], CaFe₂O₄ [27], ZnGa₂O₄ [28], ZnGe₂O₄ [29,30], Bi₂WO₆ [31], HNb₃O₈ [32], InTaO₄ [33], Zn–Cu–Ga photocatalyst [34], and GaP [35] have been reported to be available for CO₂

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conversion under light illumination. However, the efficiency attained by these studies has been very low due to the large band gaps or the photocorrosion process. In order to make full use of solar energy, it is of great importance to develop new visible light photocatalysts with high activities. Moreover, it is well known that copper has good selectivities for photo-reduction CO₂ into methanol [22,36–38] and that the metal free polymer containing C=N band have good photocatalytic activities for hydrogen produced from water [39,40] and photocatalytic reduction of CO₂ [41]. In particular, to our knowledge, the directly photocatalytic reduction of CO₂ on the photocatalysts of copper-based MOFs or imidazolate frameworks containing C=N band under visible light has not been reported yet until now.

Therefore, the synergistic effects of copper and C=N band in imidazolate frameworks on the photocatalytic activities of semiconductors are very interesting research topics. Herein, we reported for the first time the photocatalytic reduction of CO₂ into methanol on three copper(II) Imidazolate Frameworks, which named green (G), blue (J) and pink (P), respectively. The photocatalytic activities of the photocatalysts were studied in a continuous-flow reactor system under visible light irradiation. The relations between the structures, visible light absorption capabilities and the CO₂ conversion efficiency under visible light irradiation were reported.

2. Experimental

2.1. Preparation of copper(II) imidazolate frameworks

The crystal of P was synthesized according to the procedure reported previously [42], whereas the crystal of G and J were synthesized by a modified procedure reported previously [42]. Briefly, For P, NaOH (0.1 M) was added to a 50 ml of mixture of imidazole (2 g, 29.4 mmol) and Cu(NO₃)₂ · 3H₂O (2.50 mmol), the obtained reddish-purple powder was washed with ethanol and dried in vacuo at 80 °C for J, after 12.5 ml of CuSO₄ · 5H₂O solution (0.8 M) was added dropwise to a 50 ml of mixture of imidazole and NaHCO₃ at 80 °C, the mixture was left under room temperature for 2 h. Then, the blue compound was filtered off, washed with water, and dried at 80 °C overnight in an oven. For G, after 15 ml of imidazole solution (0.245 M) was added to the 25 ml of mixture of CuSO₄ · 5H₂O and NH₄OH, the mixture was hydrothermally treated at 110 °C in a Teflon-lined stainless steel autoclave for 48 h. After reaction, the product was collected by filtration and then washed 3–4 times with distilled water. Finally, the samples were dried at 80 °C overnight in an oven.

2.2. Characterization

Nitrogen adsorption measurements were carried out at 77 K by using an accelerated surface area and porosimetry system (ASAP 2010, Micromeritics) equipped with commercial software of calculation and analysis for determination of the textural properties of the photocatalyst studied [24,43–45]. The UV–Vis spectroscopy in the 200–800 nm was measured with a Shimadzu UV-2550PC diffuse reflectance spectroscopy. The transmission electron microscopy (TEM) was performed on a JEM-2100HR (200 kV, Japan) operated at 120 kV. The scanning electron microscope (SEM) was done on a LEO 1530VP field emission scanning electron microscope (LEO Electron Microscopy Inc., Germany). The XRD patterns were obtained at room temperature using a MSAL-XD2 diffractometer with CuK α radiation (operated at 36 kV and 30 mA, λ =0.15406 nm). The Fourier transform infrared spectra (FTIR) of the samples were recorded using a Nicolet 510 P spectrometer.

2.3. Photocatalytic reduction of CO₂

The photocatalytic reduction of CO₂ was performed in a continuous-flow reactor system as shown in our previous study [24]. A 500 W Xe lamp located in the quartz cool trap was the irradiation source and the UV light below 400 nm was removed by a 2.0 M sodium nitrite solution [24,46]. Prior to experiments, sodium hydroxide (0.80 g) and absolute sodium sulfite (2.52 g) were dissolved in 200 ml distilled water. This solution was then put into a photochemical reaction instrument. Before irradiation, ultrapure CO₂ was bubbled through the solution in the reactor for at least 30 min to ensure that all dissolved oxygen was eliminated, then, 200 mg of catalyst powder was added into above solution, and the irradiation lamp was turned on to start the photoreaction. Ultrapure CO₂ was continuously bubbled through the above solution in the reactor during the whole irradiation. The radiation time was 5 h. A needle-type probe was inserted into the solution in the reactor to withdraw a small liquid sample at 1, 2, 2.5, 3, 3.5, 4, 4.5 and 5 h, respectively. The concentration of methanol in the samples was analyzed using a GC9560 gas chromatograph equipped with a flame ionization detector and a stainless steel packed column (Porapak-Q, 2 mm × 3 m). The blank test was performed in the dark with the catalyst and CO₂ or in the light without CO₂ under the same other experimental conditions. The methanol has not been detected.

2.4. Photocatalytic activity for the degradation of methylene blue.

Visible light photocatalytic activities of G, J, and P were also evaluated through the degradation of methylene blue (MB) solution with an initial MB concentration of 10 mg/l. A 500 W Xe lamp located in the quartz cool trap was the irradiation source, and the UV light below 400 nm was removed by a 2.0 M sodium nitrite solution [24,46]. In a typical run, aqueous slurries were prepared by adding 0.2 g photocatalyst to 600 ml methyl orange aqueous solution. After that, the suspension was stirred for 30 min in the dark to ensure adsorption/desorption equilibrium before light illumination. During the irradiation procedure, the reaction sample was collected at 20-min intervals and centrifuged to remove photocatalyst particles. The filtrates were analyzed with a spectrophotometer by measuring its absorbance at 662 nm.

3. Results and discussion

3.1. XRD analysis

All three as-prepared samples were studied by powder XRD to identify the phase structures. Fig. 1 shows the XRD patterns of different samples. As observed in Fig. 1, all the diffraction peaks of G and J matches well with those of G (green) and J (blue) simulated from the single-crystal structure reported in Ref. [42], and no other crystallite phases were observed. Thus, it is easy to find that the G shows orthorhombic structure with distorted square-planar coordination (trans N–Cu–N angles of 154° for Cu₁ and 142° and 138° for Cu₂), and the room temperature lattice parameters are a =21.139 Å, b =19.080 Å and c =9.2843 Å; whereas, the results also revealed that the as-synthesized sample J was monoclinic phase with the unit cell parameters, a = 11.75 Å, b = 14.07 Å and c = 8.77 Å. Moreover, although P does not match well with any structural model due to its complexity and broad peak features, the XRD patterns of P are consistent with the observed one of the P phase in Ref [42]. In conclusion, the above analyses and XRD patterns evidence further confirm that three different phase structures of G, J and P were successfully prepared.

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