Journal of Photochemistry & Photobiology A: Chemistry 364 (2018) 524–533

Contents lists available at ScienceDirect

Journal of Photochemistry & Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Visible-light-driven photocatalytic degradation of pollutants over Cu-doped NH_2-MIL-125(Ti)

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ARTICLE INFO

Keywords:
Metal-Organic framework
Copper
Doping
Photocatalysis
Degradation

ABSTRACT

In our study, we carried out the first synthesis of new copper-doped titanium-based amine-functionalized metal-organic frameworks (Cu-NH_2-MIL-125(Ti)) via an *in situ* doping method. The as-acquired materials were well distinguished by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), inductively coupled plasma (ICP) emission spectroscopy, N_2 adsorption-desorption measurements, UV–vis diffuse reflectance spectroscopy, photoluminescence (PL) spectroscopy, and photoelectrochemical experiments. The Cu-doped NH_2-MIL-125(Ti) exhibited a significant improvement in photocatalytic activity compared to undoped NH_2-MIL-125(Ti). When Cu was 1.5 wt%, the Cu-doped NH_2-MIL-125(Ti) exhibited the greatest photocatalytic activity. The rate constants of the 1.5 wt% Cu-NH_2-MIL-125(Ti) to degrade methyl orange (MO) and phenol were determined as 10.4 and 3.4 times as great as those of undoped NH_2-MIL-125(Ti), respectively. The improved photocatalytic activity of Cu-NH_2-MIL-125(Ti) could be ascribed to the elevated light absorption ability and additional effective charge transportations and separations. Further, the Cu-NH_2-MIL-125(Ti) photocatalysts stayed steady following four consecutive cycles. Additional research proved that the holes and hydroxyl radicals were the primary active species in the degradation procedure.

1. Introduction

Photocatalytic degradation of organic pollutants has garnered a large amount of attention as an encouraging method for resolving environmental issues. In the last several decades, different semiconductor photocatalysts [1–5] have been created for the organic pollutant degradation. However, the photocatalysts' quantum yield and solar energy conversion efficiency remain low, which restricts their use. Therefore, the achievement of new photocatalysts with a high efficiency for the degradation of pollutants is still a great challenge.

Metal-organic frameworks (MOFs) are a version of newly created porous coordination polymers that comprise metal ions/clusters connected via organic ligands [6]. Owing to their unprecedented surface areas, high pore volume, adjustable pore sizes, and tailorable structure, MOFs have garnered a large amount of attention in gas capture and storage [7], catalysis [8], chemical sensing [9], gas separation [10], and drug delivery [11]. Not long ago, MOFs were established as acting as semiconductors when exposed to light, allowing them to be potential photocatalysts for a large range of reactions [12–14]. As the initial demonstration of photocatalytic degradation of phenol on MOF-5 irradiated by UV light [12], the use of MOFs as novel photocatalysts, especially for the removal of dangerous pollutants, has garnered a great amount of interest and is considered a research hotspot [15–20]. As of right now, numerous MOF-based photocatalysts, including UTSA-38 [15], MIL-100(Fe) [16], MIL-53(Fe) [17], MIL-88 A [18], ZIF-8 [19], and NH_2-MIL-125(Ti) [20], have been used in the degradation of organic pollutants. However, the fast recombination of photogenerated electron-hole pairs causes disappointing photocatalytic efficiencies of the documented MOFs. Several strategies, including coupling with noble metals [21,22] and constructing heterojunctions with other semiconductors [23,24], have been used to enhance the photocatalytic activities of MOFs. Besides, metal doping is also a potential route to regulate the electronic structure and improve the photocatalytic activity of a semiconductor. For example, Yang et al. [25] reported the synthesis of Cu-doped ZIF-67 with significantly enhanced photocatalytic activity for degradation of methyl orange (MO). Abdelhameed et al. [26] prepared Cr-doped MIL-125(Ti) by a post-synthetic modification for decomposition of methylene blue. Wang et al. [27] investigated the effect of Ti doping on photocatalytic activity of UiO-66(Zr). Unfortunately, up to today, study on the preparation and photocatalytic properties of metal-ion doped MOFs is still scarce. To the best of our knowledge, no paper has been published on metal-ion doped

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https://doi.org/10.1016/j.jphotochem.2018.06.044
Received 21 April 2018; Received in revised form 27 June 2018; Accepted 28 June 2018

NH_2-MIL-125(Ti).

In this evaluation, the photoactive copper-doped titanium-based amine-functionalized metal-organic frameworks (Cu-NH_2-MIL-125(Ti)) were synthesized successfully using a simple one-step solvothermal technique for the first time. NH_2-MIL-125(Ti) was selected due to its big surface area, high stability, and visible-light responsiveness [28]. Copper provides the advantages of abundance, low cost, no toxicity, and more electronegativity than titanium which can lead to better doping efficiency [29], so copper ion was chosen as a dopant. In order to investigate the versatile photocatalytic degradation abilities of Cu-NH_2-MIL-125(Ti) for wastewater treatment application, we examined the degradation of different organic molecular structures including MO (a color organic pollutant) and phenol (a colorless organic pollutant) under visible light irradiation. As anticipated, the photocatalytic activity of Cu-NH_2-MIL-125(Ti) was substantially greater than that of NH_2-MIL-125(Ti) without Cu doping. No reductions in the activity of the as-prepared Cu-NH_2-MIL-125(Ti) photocatalysts were noted throughout the photocatalytic procedure. The possible photodegradation mechanism of MO and phenol was also investigated and suggested.

2. Experimental section

2.1. Materials

2-Aminoterephthalic acid (NH_2-BDC) was purchased from Chinese J &K Scientific Co., Ltd. Copper nitrate trihydrate ($Cu(NO_3)_2{\bullet}3H_2O$), methanol (MeOH), *N,N*-dimethylformamide (DMF), and tetrabutyl titanate $Ti(OC_4H_9)_4$ were provided by Chinese Sinopharm Chemical Reagent Co., Ltd. All of the chemicals were of analytical grade and utilized without the need for additional purification.

2.2. Synthesis

Cu-NH_2-MIL-125(Ti) was synthesized via an *in situ* doping technique. A suitable amount of $Cu(NO_3)_2{\bullet}3H_2O$, $Ti(OC_4H_9)_4$ (0.52 mL, 1.5 mmol), and NH_2-BDC (1.087 *g*, 6.0 mmol) was added to a solution consisting of DMF (24.3 mL) and MeOH (2.7 mL). The above combination was stirred for 30 min at room temperature, and then it was moved to a Teflon-lined autoclave and left at 150 °C for 24 h. The produced mixture was cooled to room temperature, and the final product was recovered by centrifugation, washed with DMF and MeOH a few times, and dried at 80 °C. The as-synthesized Cu-NH_2-MIL-125(Ti) specimens with 1.0, 1.5, 2.0, and 5.0 wt% Cu, were tagged as CuMIL1.0, CuMIL1.5, CuMIL2.0, and CuMIL5.0, respectively.

To contrast, undoped NH_2-MIL-125(Ti) was also synthesized via the identical technique without using $Cu(NO_3)_2{\bullet}3H_2O$.

2.3. Characterization

The crystal structure of the acquired specimens was determined via X-ray diffraction (XRD, D/MAX-2550, Cu Kα radiation). Fourier transform infrared (FT-IR) spectra were documented on a Nicolet 6700 infrared spectrophotometer in the range of 4000–400 cm^{-1}. Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS) examinations were conducted on a JEOS JSM 6510. Photoluminescence (PL) spectra were documented on a Hitachi F-7000 fluorescence spectrophotometer at room temperature. X-ray photoelectron spectroscopy (XPS) examinations were conducted on an ESCALab250 spectrometer. UV–vis diffuse reflectance spectra (DRS) were documented on a Hitachi U-3010 UV–vis spectrophotometer. Brunauer-Emmett-Teller (BET)-specific surface areas of the specimens were examined via N_2 adsorption with a Micromeritics ASAP 2460 adsorption apparatus. The precise concentration of Cu in the as-prepared MOFs was measured via inductively coupled plasma emission spectroscopy (ICP, PERKINE 7300DV). The electron spin resonance (ESR) signals of superoxide radicals (${\bullet}O_2^-$) and hydroxyl radicals (•OH) trapped with 5,5-dimethylpyrroline-*N*-oxide (DMPO) were investigated on a Bruker model ESR JES-FA200 spectrometer.

2.4. Photocatalytic evaluation

Photocatalytic activities of the as-prepared specimens were assessed via the photocatalytic decomposition of MO and phenol beneath visible light illumination. A 500-W Xe lamp (BL-GHX-V, Shanghai Bilon Instruments Co., Ltd., China) together with a 420-nm cut-off filter was the light source. In every investigation, a 0.02-g photocatalyst specimen was placed into 50 mL MO or phenol aqueous solution (10 mg L^{-1}) in a reaction cell. Before irradiation, the suspension was stirred in the dark for 30 min with a magnetic stir bar to reach an adsorption-desorption equilibrium between photocatalyst and pollutants. After that, the suspension was irradiated with visible light. At particular intervals of time, 5 mL of each of the suspensions was sampled and centrifuged (10,000 rpm, 10 min) to eliminate the residue photocatalysts. The pollutant concentration that remained in the solution was determined using a UV–vis spectrophotometer (Hitachi, U-3310) by observing the absorbance at 464 nm (for MO) and 270 nm (for phenol). The total organic carbon (TOC) of the solution was determined by a TOC analyzer (Multi N/C 2100). To detect the species that are active in the process of photocatalytic degradation, the active species trapping investigations were examined via disodium ethylenediamine tetraacetate (EDTA-2Na, 1 mM), isopropyl alcohol (IPA, 1 mM), and *p*-benzoquinone (BQ, 1 mM) as the scavengers for hole (h^+), •OH, and ${\bullet}O_2^-$, respectively.

2.5. Photoelectrochemical measurements

Photocurrent density was conducted in a CHI660E electrochemical station (Shanghai Chenhua Instrument Co. Ltd., China) based on the conventional three-electrode system. All of the measurements were performed in an electrolyte solution of 0.5 M Na_2SO_4. The light source was a 300-W Xe lamp. An Ag/AgCl electrode and a Pt foil acted respectively as the reference and counter electrode. The working electrodes were fabricated via a dip-coating technique: 10 mg of the as-prepared photocatalyst was placed in 1 mL ethanol to generate a homogeneous suspension. The produced suspension was then dip-coated onto an indium tin oxide (ITO) glass electrode (effective area ~0.3 $cm^{2)}$. The ITO glass was air-dried and then annealed at 120 °C for 6 h.

3. Results and discussion

3.1. Characterization of materials

The actual contents of Cu ions in the as-synthesized Cu-NH_2-MIL-125(Ti) samples were determined by ICP and the data are shown in Table 1. One can see that the real Cu amounts are almost congruent with theoretical values.

The XRD patterns of the as-prepared NH_2-MIL-125(Ti) and Cu-doped MOFs can be seen in Fig. 1a. The pattern of NH_2-MIL-125(Ti) is in agreement with that documented in the literature [30–32],

Table 1
Cu contents and textural properties of the as-prepared samples.

Samples	Cu contents (wt%)	Surface area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	Average pore size (nm)
NH_2-MIL-125(Ti)	0	1338.0	0.4112	0.66
CuMIL1.0	0.95	1265.9	0.3871	0.65
CuMIL1.5	1.46	1219.3	0.3768	0.64
CuMIL2.0	1.97	1196.1	0.3547	0.62
CuMIL5.0	4.81	1084.6	0.3089	0.62