Zinc phthalocyanine coupled with UIO-66 (NH$_2$) via a facile condensation process for enhanced visible-light-driven photocatalysis

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ABSTRACT

Metal-organic frameworks (MOFs) have shown a great potential for water treatment as an environmentally friendly photocatalyst. In this work, a zirconium based MOF, UIO-66 (NH$_2$) covalently coupled with zinc phthalocyanine (ZnTCPc) was prepared via a facile condensation process. Compared with the mixture of ZnTCPc and UIO-66 (Zr) by impregnation, ZnTCPc/UIO-66 (NH$_2$) presented an enhanced photocatalytic activity for the degradation of methylene blue (MB) under visible-light irradiation. The formation of strong covalent bonds and synergistic integration between ZnTCPc and UIO-66 (NH$_2$) was proved by characterization results such as transmission electron microscopy, X-ray photoelectron spectra and Fourier transform infrared spectroscopy. Additionally, ZnTCPc/UIO-66 (NH$_2$) photocatalyst retained excellent stability after five recycles, and the photocatalytic mechanism was investigated systematically. This work demonstrates a high potential of using porous MOFs-based materials not only as supports but as electron acceptors to trigger the reaction for coupling MOFs with dye, fabricating novel MOFs-dye nanocomposite systems and enhancing their photostability and photocatalytic activity.

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1. Introduction

With growing concerns regarding a clean environment and human health, technologies with high efficiency and low cost to reduce the pollutant contents of wastewater are urgently needed [1]. Various homogeneous and heterogeneous photocatalysts systems have been widely studied and employed in the past few decades, including TiO$_2$, g-C$_3$N$_4$, graphene, metal-organic frameworks (MOFs), etc [2–6]. Among the reported photocatalytic materials, MOFs as a new class of porous crystalline networks synthesized by assembling metallic ions with organic ligands attracts more attentions in photocatalysis field [7–12]. Among these MOFs, zirconium based MOFs (UIO-66 (Zr) and UIO-66 analogies), associated with high surface area and superior chemical stability to water, not only possess the cage-like structure and high surface area to accommodate the nanoparticles and disperse the entrapped

nanoparticles, but serve as the semiconductor material itself [13]. Sha et al. reported Ag$_2$CO$_3$/UIO-66 (Zr) could decompose rhodamine B (RhB) under visible-light irradiation [14]. Although UIO-66 series are potential candidates for the photocatalyst, compared with the inorganic photocatalysts and some commercial standards, pristine UIO-66 series failed to achieve satisfactory photocatalytic activities because of the limited light absorption [15,16]. Therefore, it is necessary to develop a high-efficient visible-light driven photocatalyst to extend its spectral response to higher absorption wavelength.

A few attempts have been made to enhance the visible light response of UIO-66 (Zr) and UIO-66 analogies, such as combination with other components, like noble metals, semiconductors and carbon materials [17–19]. Zinc phthalocyanine (ZnPc) and its derivatives as typical organic semiconductors possess wide visible light response, which can be employed to sensitize other semiconductor materials for enhancement of photocatalytic activity [20–23]. However, the traditional ZnPc suffers from the aggregation ascribed to its intrinsic large π-conjugation [24], and therefore, MOFs with the high surface area and desirable porosity can confine the aggregation of ZnPc and maximize the active sites. Based on the properties of UIO-66 and ZnPc, it is worthy to present an efficient

approach to combine UIO-66 with ZnPc for the visible-light-driven photocatalysis. To our knowledge, the photocatalytic properties of UIO-66 incorporated with dyes have remained unexplored.

Herein we prepared composites combining zinc tetracarboxy phthalocyanine (ZnTCPc) with UIO-66 (Zr) and UIO-66 (NH$_2$), respectively. ZnTCPc/UIO-66 (Zr) were obtained by a simple impregnation method, while ZnTCPc was immobilized on UIO-66 (NH$_2$) covalently via N-(3-dimethylaminopropyl)-N'-ethyl-carbodiimide hydrochloride (EDC)/N-hydroxysuccinimide (NHS) activation and amide formation. The photocatalytic performances were evaluated by the degradation of methylene blue (MB) under visible-light irradiation, and the results show that ZnTCPc/UIO-66 (Zr) and ZnTCPc/UIO-66 (NH$_2$) with different interactions have distinct effects on the photocatalytic activity. Compared with ZnTCPc/UIO-66 (Zr), ZnTCPc/UIO-66 (NH$_2$) with stronger covalent bonds and synergistic integration exhibited higher photocatalytic activity. Moreover, the ZnTCPc/UIO-66 (NH$_2$) composite also presents acceptable stability during the degradation experiments. In addition, some typical scavengers were added to identify the active species, and the possible photocatalytic mechanism was investigated systematically.

2. Experimental

2.1. Synthesis of UIO-66 (Zr) and UIO-66 (NH$_2$)

In a typical synthesis, ZrCl$_4$ (0.2332 g, 1.0 mmol) and terephthalic acid (0.1661 g, 1.0 mmol) or 2-NH$_2$-terephthalic acid (0.1812 g, 1.0 mmol) were dissolved in DMF (50 mL), and then the solution was transferred to a 100 mL Teflon-lined stainless steel autoclave [25,26]. The autoclave was sealed and heated in an oven at 120 °C for 40 h under autogenous pressure. After being cooled naturally, the obtained sample was purified with anhydrous ethanol several times to make sure that the DMF molecules were eliminated, and then the off-white UIO-66 (Zr) or yellow UIO-66 (NH$_2$) product was dried at 80 °C for 24 h.

2.2. Synthesis of ZnTCPc

ZnSO$_4$·7H$_2$O (0.048 mol), trimellitic anhydride (0.176 mol), ammonium chloride (0.085 mol) and urea (1 mol) were mixed with ammonium molybdate tetrahydrate (0.004 mol). The mixture was dissolved in 10 mL nitrobenzene and then refluxed at 185 °C during 4 h. The dark blue solid obtained was purified with 0.1 M NaOH and 1 M HCl solution, respectively.

2.3. Synthesis of ZnTCPc/UIO-66 (Zr)

ZnTCPc sensitized UIO-66 (Zr) was prepared by an impregnation method. Typically, UIO-66 (Zr) (100 mg) was first dispersed in deionized water by ultrasonic treatment for 30 min to give an off-white solution. ZnTCPc (10 mg) dissolved in DMF (5 mL) was added into UIO-66 (Zr) solution drop by drop, and the mixture was stirred for 6 h. The obtained sample was purified with deionized water and ethanol several times, and dried at 80 °C for 12 h. The nominal weight ratio of ZnTCPc to UIO-66 (Zr) was 10 wt %, and the actual content of zinc was shown in Table S1.

2.4. Synthesis of ZnTCPc/UIO-66 (NH$_2$)

Fig. 1 shows the preparation process of ZnTCPc/UIO-66 (NH$_2$). UIO-66 (NH$_2$) (100 mg) was dispersed in deionized water, and was subjected to sonication (100 W, 40 kHz) at 25 °C for 3 h. ZnTCPc (10 mg) was dissolved in DMF (5 mL) by ultrasonic treatment for 3 h to give a green solution. EDC (0.1 M) and NHS (0.1 M) were

dissolved in deionized water, and then added into ZnTCPc solution [27,28]. The ZnTCPc solution was added dropwise to the ultrasonic UIO-66 (NH$_2$) dispersion. After reacting for 6 h, the mixture was filtered and washed with deionized water and ethanol several times. The obtained ZnTCPc/UIO-66 (NH$_2$) was dried at 80 °C for 12 h. The nominal weight ratio of ZnTCPc to UIO-66 (NH$_2$) was 10 wt %, and the content of zinc was shown in Table S1.

2.5. Characterization

Powder X-ray diffraction (PXRD) patterns were recorded with a Shimadzu XRD 6000 X-ray diffractometer using Cu Kα (λ = 0.15406 nm) radiation with a nickel filter operating at 40 kV and 10 mA. The patterns were compared with JCPDS reference data for phase identification. The surface morphology of the catalyst was observed by field emission scanning electron microscopy (FESEM) on a Quanta 200F instrument using accelerating voltages of 5 kV. Samples for SEM were dusted on an adhesive conductive carbon belt attached to a copper disk, coated with 10 nm Au prior to measurement. The TEM images were carried out using a JEOL JEM 2100 electron microscope equipped with a field emission source at an accelerating voltage of 200 kV. Fourier transform infrared spectroscopy (FT-IR) spectra were obtained on an FTS-3000 spectrophotometer manufactured by American Digilab Company. The measured wafer was prepared as KBr pellet with the weight ratio of sample to KBr, 1/100. Raman spectra were measured at room temperature using a LabRAM XploRA Raman spectrometer (Horiba Jobin Yvon France) with a 532 nm laser focused on a spot about 3 nm diameter. Specific surface area was measured by adsorption-desorption of N$_2$ gas at 77 K with a Micromeritics ASAP 2000 gas sorption analyzer. Before the measurements, the samples were outgassed at 160 °C for 10 h. X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer PHI-1600 ESCA spectrometer using Mg Kα (hν = 1253.6 eV) X-ray source. TGA data were obtained using a Perker Elmer TGA6 instrument under N$_2$ flow. Electron paramagnetic resonance (EPR) measurements were carried out on a Bruker model A300 spectrometer. UV−Vis diffused reflectance spectra (DRS) experiments were performed on a UV−Vis spectrophotometer (Hitachi U-4100) with the integration sphere diffuse reflectance attachment. ^{1}H NMR spectrum was recorded on a Bruker AV-300 spectrometer.

2.6. Evaluation of the photocatalytic activity

The photocatalytic activity was evaluated by the degradation of MB under visible light irradiation. A 500 W Xe arc lamp with an UV cut-off filter (λ ≥ 420 nm) was used as a visible light source. A suspension containing a powdered catalyst (20 mg) and a fresh aqueous solution of MB (100 mL, 15 mg/L) were magnetically stirred in the dark for about 20 min to establish an adsorption-desorption equilibrium of MB species. To measure the dye degradation, a 1.5 mL sample of the reaction suspension was collected after irradiation for a certain period, and the photocatalyst was removed by centrifugation (5000 rpm for 20 min) before the absorption spectroscopy measurements. The filtrate was analyzed by a 759 UV−vis spectrophotometer (Shanghai Precision & Scientific Instrument Co., Ltd.). To evaluate the photostability of the photocatalysts, samples were separated from the suspension after photocatalytic degradation reaction for 120 min, and then collected by centrifugation and dried at 50 °C overnight. The recovered photocatalysts were reused for subsequent cycles of photocatalytic degradation under the same conditions. The photocatalytic mechanism was investigated by different scavengers to compete with the potential active species that may be involved in the degradation process of MB. Benzoquinone (BQ), ethylenediaminetetraacetic acid