



In-situ fabrication of ZIF-8 decorated layered double oxides for adsorption and photocatalytic degradation of methylene blue

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ABSTRACT

Combining metal-organic frameworks (MOFs) with a variety of functional materials have received considerable attention recently due to their enhanced performances and widespread applications. In this work, ZIF-8/Zn-Al Layered double oxides (LDO) composite was synthesized via in-situ growth method without adding any zinc source. Hierarchical porous structure was formed by the growth of ZIF-8 onto LDO surface, and the resulted composite exhibited high adsorption capacity and good photocatalytic degradation activity for methylene blue (MB). More than 58% of the initial concentration of MB could be adsorbed and degraded within 180 min of UV irradiation, which was significant higher than that of ZIF-8 and LDO, suggesting a synergy of adsorption and photocatalysis between ZIF-8 and LDO. Moreover, ZIF-8/LDO could be easily regenerated and reused at least 4 times without loss of its degradation ability.

1. Introduction

Water pollution has become a worldwide issue as more and more waste is being disposed of in our oceans, rivers and lakes. Organic dye is a typical water pollutant, which has received great attention due to its toxic nature and adverse effect on all forms of life [1]. Therefore, exploring efficient and environment-friendly methods to remove dye pollutants from wastewater has become an urgent need [2–4].

Photocatalysis is an important and widely used process for water treatment [5]. The design of photo catalysts with high efficiency has always attracted extensive studies as catalyst plays a vital role in photocatalytic degradation reaction [6,7]. Layered double hydroxides (LDHs) are a class of anionic clays, which can be expressed by the general formula $[M_1^{2+} M_x^{3+} (OH)_2]^{x+} (A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal ions, respectively, and A^{n-} is an intercalate anion [8]. After being calcined under high temperature, the LDH can be converted into a bimetallic oxide, in which the second metal could be in a highly dispersed state. Due to its anion exchangeability and compositional flexibility, calcined LDH (LDO) has attracted great attention to be one of the most potential materials for photocatalytic degradation of organic in wastewater recently [9,10].

Zeolitic imidazolate frameworks (ZIFs) is a subclass of MOFs formed by inorganic connectors and imidazolate organic linkers [11,12]. Compared with other conventional inorganic porous materials, its high

porosity and good stability makes it desirable for potential application in gas storage and adsorption separation [13–15]. Recently, the use of ZIFs as photocatalyst for wastewater treatment has also been reported [16,17]; however, the application of ZIFs in water treatment is often limited owing to the difficulty in recycling and separating nanosized ZIFs particles from aqueous solution. Therefore, it is assumed that enhanced particle size and photocatalytic performance could be achieved by preparing LDO and ZIF-8 composite structures.

Herein, ZIF-8 covered Zn-Al LDO was successfully synthesized via an in-situ growth method without adding extra zinc source. The as-synthesized ZIF-8/LDO was characterized by different technics and used as adsorbent and photo-catalyst to remove methylene blue (MB) from water.

2. Experimental

2.1. Materials

$Zn(NO_3)_2 \cdot 6H_2O$ ($\geq 99.0\%$), $Al(NO_3)_3 \cdot 9H_2O$ ($\geq 99.0\%$), $HCOONa$ ($\geq 99.0\%$), urea ($\geq 99.0\%$), MB ($\geq 98.0\%$) and methanol ($\geq 99.7\%$) were purchased from Sinoreagent company (Shanghai, China). 2-methylimidazole ($\geq 98.0\%$) was obtained from Adamas Reagent Co., Ltd (Shanghai, China). All chemicals were used as received without any purification.

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2.2. Synthesis of LDO

In a typical procedure, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and urea at the molar ratios of $\text{Zn}^{2+}/\text{Al}^{3+}/\text{urea} = 2:1:10$ were added into 100 mL of deionized water (total metal ions concentration of 0.3 mol/L), the solution was stirred continuously for 8 h at 100 °C. After that, the mixture was filtrated and washed with deionized water and ethanol for several times. LDH powder was then obtained by drying the above sample at 50 °C in air. Finally, the as-prepared LDH was calcined at 600 °C for 6 h in air, resulting in transformation of the structure into layered double oxides (LDO).

2.3. Synthesis of ZIF-8/LDO

ZIF-8/LDO sample was synthesized by in situ growth of ZIF-8 on LDO. Typically, 0.75 g of 2-methylimidazole and 0.405 g of HCOONa were added into 60 mL of methanol under string. Then, 0.36 g of pre-dried LDO powder was added to the above solution and stirred continuously for 4 h at 60 °C in a water bath. The white product was collected by centrifugation (3000 rpm, 3 min), washed three times by methanol, and dried at 50 °C for 24 h. The prepared sample was marked as ZIF-8/LDO.

2.4. Characterization

X-ray diffraction patterns (XRD) were performed on a Bruker D8 ADVANCE diffractometer with $\text{Cu K}\alpha$ radiation (40 KV, 30 mA). The morphology of the samples was taken with a FEI Quanta 400 FEG scanning electron microscope (SEM) and transmission electron microscope (TEM) (FEI Tecnai G2 F20). N_2 adsorption-desorption isotherms were measured after sample degassing at 100 °C overnight in a Quantachrome iQ2 porosimeter. The Brunauer-Emmet-Teller (BET) method was used to calculate the specific surface area. Total pore volume was determined by the volume of liquid nitrogen adsorbed at a relative pressure of 0.99. The micropore volume (V_{micro}) was calculated using t-plot method and mesopore volume was obtained by subtracting V_{micro} from the total pore volume. Thermogravimetric analysis (TGA, Netzsch STA 449 F5) measurement was performed under Ar gas at a flow rate of 100 cm^3/min . The sample was heated from 20 °C to 800 °C with a temperature ramp rate of 10 °C/min. X-ray photoelectron spectroscopy (XPS) data were obtained on Thermo Scientific Escalab 250 Xi spectrometer equipped with an Al $\text{K}\alpha$ radiation source. FT-IR spectra were measured with a Thermo Nicolet iS5 spectrometer in transmission mode in the range of 4000–400 cm^{-1} .

2.5. Photocatalytic degradation

The photocatalytic performances of samples were evaluated by photo reduction of MB under 70 W ultraviolet lamp irradiation with wavelength of 365 nm in open air at room temperature. The distance between the light source and the beaker containing reaction mixture was fixed at 5 cm.

Typically, 20 mg of sample was put into 50 mL of MB solution with a concentration of 10 mg/L. Before irradiation, the suspension was stirred in dark for 1 h to ensure the adsorption reached equilibrium. The mixture was drawn at regular intervals and filtered by a 0.45 μm filter membrane for analysis. The concentration of MB was measured with a UV-Vis spectrophotometer (TU-1810, Persee Co., China) based on the absorbance at 665 nm.

3. Results and discussion

XRD patterns of LDH, LDO and ZIF-8/LDO samples are shown in Fig. 1. Pure LDH showed diffraction peaks at $2\theta = \sim 11.7^\circ, 23.5^\circ, 34.7^\circ, 39.2^\circ$ and 46.7° , representing (003), (006), (009), (012), (015) and (018) planes of the layered hydroxalate-like material, respectively

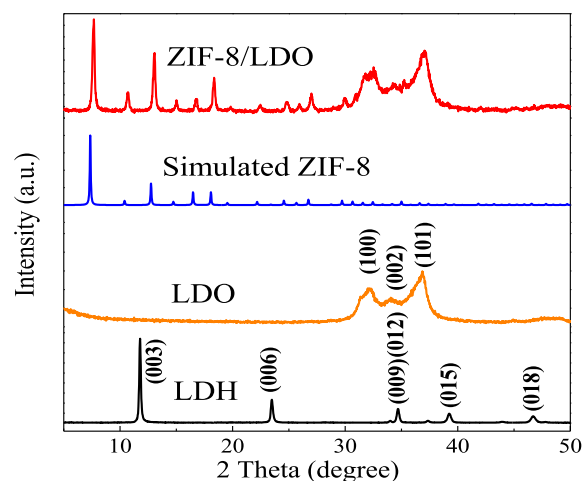


Fig. 1. XRD patterns of LDH, LDO and ZIF-8/LDO sample.

[18–20]. Usually, the (009) reflection overlaps with the (012) to form a broad peak. The basal spacing distanced (003) of LDH is estimated to be 0.751 nm, which is consistent with the reported value [19,21]. After calcined at 600 °C, the XRD peaks of LDO agree well with the typical peaks characteristic of ZnO with hexagonal wurtzite structure [19]. There is no diffraction peak of aluminum species observed, due to the formation of amorphous aluminum. With in situ synthesis of ZIF-8 onto LDO, peaks representing the superimposition of LDO phase and simulated ZIF-8 phase could be found in the ZIF-8/LDO composite, indicating effective formation of the ZIF-8/LDO composite.

Fig. 2 shows the TEM and SEM micrographs of ZIF-8, LDH, LDO and ZIF-8/LDO samples. The morphology of pure ZIF-8 shows the aggregation of uniform nanoparticles (Fig. 2a). Lamellar particles with hexagonal layer structure is observed for LDH (Fig. 2b), which is a common structure for hydroxalate-like material [22,23]. After calcination, the sheet-like structure of LDH has been well maintained but became more densely packed (Fig. 2c). A rough surface with small particles could be clearly observed for ZIF-8/LDO (Fig. 2d), suggesting the formation of ZIF-8 onto the surface of LDO. Moreover, the surface of LDO was not fully covered by ZIF-8 particles, as part of bare surface could also be seen. As shown in Fig. 2e–j, a homogeneous Zn and N distribution could be observed, revealing that ZIF-8 particles were uniformly spread on the LDO surface.

The porosity of LDH, LDO, ZIF-8/LDO and ZIF-8 samples was evaluated by nitrogen adsorption-desorption method. The results are shown in Fig. 3 and Table 1. Pure ZIF-8 exhibits a type I isotherm, which is characteristic of microporous materials. The LDH and LDO samples show a typical IV adsorption isotherm with a H3-type hysteresis loop, which is an indication of the existence of mesoporous structure. Moreover, there is no plateau at the relative pressure near to 1, revealing the coexistence of macropores. Unlike LDH and LDO, a combination of type I and type IV isotherm with a significant hysteresis is displayed by ZIF-8/LDO composite, which suggests coexistence of microporous and mesoporous structure in the composite. The micropore is convinced from the inheritance of porous ZIF-8. The surface area of LDH and LDO is only 16.6 and 55.9 m^2/g , respectively. However, ZIF-8/LDO composite is much superior in surface area, with a value of 471.2 m^2/g , which is still lower than the ZIF-8/LDH sample ($\sim 1320 \text{m}^2/\text{g}$) that we synthesized previously [24]. This should be attributed to the lower content of ZIF-8 in ZIF-8/LDO, as confirmed by SEM images. Moreover, the curves displayed in Fig. 3b demonstrate that LDO has a narrower pore size distribution, and a coexistence of micropore and mesopore structure in ZIF-8/LDO was further confirmed.

The TG curves of all samples are shown in Fig. S1. It can be clearly seen that there are several stages involved during the decomposition of LDH: the first one is associated with evaporation of weakly adsorbed

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