



Research paper

Photocatalytic Cr(VI) reduction by mixed metal oxide derived from ZnAl layered double hydroxide



Xiaoya Yuan*, Qiuye Jing, Jingtao Chen, Li Li

College of Materials Science and Engineering, Chongqing Jiaotong University, Chongqing 400074, China

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ABSTRACT

Mixed metal oxide (MMO) is one of the most important photocatalysts intensively investigated for water remediation. In this study, ZnO/ZnAl₂O₄ (ZnAl-MMO) nanocomposite was readily prepared via one-step calcination of ZnAl-layered double hydroxide (ZnAl-LDH) at 900 °C. The obtained MMO composite was thoroughly characterized by powder X-ray diffraction (XRD), Scanning electron microscopy (SEM), High-resolution transmission electron microscopy (HRTEM), UV–Vis diffuse reflectance spectroscopy (DRS). ZnAl-MMO was composed of nano-scaled ZnO and ZnAl₂O₄ crystal grains of high crystallinity and exhibited strong UV light adsorption with a well-developed interface between the two components of the composite. ZnAl-MMO showed high photocatalytic Cr(VI) reduction activity under UV light irradiation and its rate constant was as high as 0.8134 h⁻¹. The photoreduction activity of ZnAl-MMO photocatalyst was ascribed to the synergistic effect between two components of the nanocomposite.

1. Introduction

Layered double hydroxide (LDH) are a class of lamellar two-dimensional anionic clays composing of positively charged brucite-like layers and exchangeable interlayer anions and their basic structure can be described by the general formula $[M_1^{2+}_x M_2^{3+}_x (\text{OH})_2]^{x+} \cdot (A^{n-})_x / n \cdot m\text{H}_2\text{O}$, where M_1^{2+} and M_2^{3+} are di- and trivalent cations, respectively, and A^{n-} is the interlayer anions which balance the positive charges on the layers, x is defined as the molar ratio of $M_1^{2+} / (M_1^{2+} + M_2^{3+})$ (Evans and Slade, 2006). Owing to the unique layered structure, compositional flexibility, low manufacturing cost and ease of synthesis, LDH have been showed promising properties as active materials for a wide range of applications, such as environmental remediation, photocatalytic water splitting and CO₂ photoreduction (Fan et al., 2014; Long et al., 2016; Mohapatra and Parida, 2016; Zhao et al., 2016). Thermal treatment of LDH at moderate temperature (< 650 °C) usually leads to topotactic transformation to mixed metal oxide (MMO) consisting of divalent metal oxide and an amorphous phase (Zhao et al., 2010; Cho and Lee, 2011). The resulting MMO material is capable of reconstructing the original LDH layered structure upon contact with aqueous solution and a variety of anions can be intercalated into the layer of the restored LDH in the rehydration process, which is known now as the memory effect of MMO and thus makes MMO an attractive adsorbents for the removal of anionic pollutants from water (Das et al., 2003; Goh et al., 2008; Li et al., 2014).

Zinc aluminate (ZnAl₂O₄) spinel has gained lots of attention due to its potential applications such as optical coating, host matrix, high temperature ceramic material, catalyst and catalyst support due to its high mechanical and thermal resistance, high chemical and thermal stability, low temperature sinterability and low surface acidity, etc. (Sickfaus and Wills, 1998; Wang et al., 2006). Recently, ZnAl₂O₄ spinel ($E_g \approx 3.8$ eV) has also been intensively investigated as one of promising semiconductor photocatalysts for degradation of organic dyes (Li et al., 2011; Casbeer et al., 2012; Foletto et al., 2012; Battiston et al., 2014). Several methods have been developed for the preparation of ZnAl₂O₄ including solid state reaction, co-precipitation, sol-gel, solvothermal or hydrothermal, combustion and molten salts synthesis, etc. (Kurihara and Suib, 1993; Zawadzki and Wrzyszczyk, 2000; Staszak et al., 2010; Li et al., 2011; Foletto et al., 2012; Battiston et al., 2014). Among them, high temperature decomposition of LDH provides an effective approach for the fabrication of spinel-based materials (Sun et al., 2006; Zhao et al., 2010). Zhao et al. and Cho et al. confirmed that the formation of ZnAl₂O₄ crystal grains started and the amorphous regions could not be found in the final ZnO/ZnAl₂O₄ MMO nanostructures at calcination temperature above 700 °C (Zhao et al., 2010; Cho and Lee, 2011). Meanwhile, the spinel ZnAl₂O₄ phase in the calcined MMO products inhibited reconstruction of MMO to the original hydroxide-like structure during the rehydration process (Kooli et al., 1997; Pfeiffer et al., 2010). To fully exert the photocatalytic performance of the calcined MMO composites, the memory effect of MMO must be

* Corresponding author.

E-mail address: yuanxy@cqjtu.edu.cn (X. Yuan).

hindered. To verify this concept, the ZnO/ZnAl₂O₄ MMO nanocomposite was prepared via one-step calcination of ZnAl-LDH at 900 °C because ZnO ($E_g \approx 3.2$ eV) is also a well-established promising photocatalyst for environmental remediation. The structures of the resulting MMO were characterized in detail and its photocatalytic activity was evaluated by photoreduction of aqueous hexavalent chromium(VI).

Aqueous Cr(VI) is the most toxic of the chromium species and has been listed as one of the priority pollutants by the US Environmental Protection Agency due to its notoriously toxic, mutagenic and carcinogenic activity to human beings (Katz and Salem, 1993). Photocatalytic reduction is an efficient, active, and clean technology for Cr(VI) removal because of its acceptable cost and easy operation as well as the inexhaustible solar energy (Wang et al., 2013; Padhi et al., 2014; Mishra et al., 2016; Nanda et al., 2017). Although several papers about the photooxidation of organic pollutants using MMO calcined at low temperature were disclosed (Fan et al., 2011; Zhao et al., 2012; Liang et al., 2014; Prince et al., 2015; Zhang et al., 2016), to the best of our knowledge, there are few reports about the use of MMO in the photocatalytic reduction of aqueous Chromium(VI) (Alanis et al., 2013).

2. Experimental

2.1. Synthesis of ZnAl-MMO nanocomposite

All chemicals used in this study were of analytical grade and used as received without any further purifications. ZnAl-LDH precursor was prepared by the co-precipitation method with Zn/Al molar ratio of 3 (Zhao et al., 2012). An aqueous solution (150 mL) of Zn(NO₃)₂·6H₂O (0.9 mol/L) and Al(NO₃)₃·9H₂O (0.3 mol/L) and another solution containing 1.92 mol/L NaOH and 0.6 mol/L Na₂CO₃ was simultaneously added into 100 mL deionized water with vigorous mechanic stirring and the pH of the mixed solution was maintained at about 10. Afterwards, the resulting slurry was aged at 80 °C for 24 h, then filtered and washed thoroughly with water until pH = 7. After drying in vacuum at 60 °C for 12 h, the solid was gently ground and finally annealed at 900 °C for 4 h to give ZnAl-MMO.

2.2. Characterization

SEM images were obtained with a Hitachi SU8020 scanning electron microscope with acceleration voltage of 20 kV. HRTEM were performed on a FEI Tecnai G2 F20 field-emission transmission electron microscopy at an accelerating voltage of 200 kV. XRD patterns were recorded on a PANalytical X'pert Pro powder diffractometer with Cu-K α radiation ($\lambda = 1.5418$ Å) with a scan step of 0.013°. DRS was carried out on a Hitachi U-4100 UV-vis spectrophotometer using BaSO₄ as the reference sample.

2.3. Photocatalytic tests

The photocatalytic property of ZnAl-MMO towards photoreduction of aqueous Cr(VI) was performed with a 500 W high-pressure Hg lamp with maximum wavelength emission at 365 nm (8.85 mW/cm², Shanghai Jiguang Special Lighting Factory, Shanghai, China). The lamp was placed in a trap with a running-water circulating through a jacket in order to maintain a constant temperature in the reaction system and the distance between the light source and the tube containing the reaction mixture was set to be 15 cm. Stock solution (1000 mg/L) of Cr(VI) was prepared by dissolving K₂Cr₂O₇ into distilled water. In each experiment, 100 mg photocatalyst was dispersed in 50 mL aqueous Cr(VI) solutions of different concentrations. The solution pH was adjusted by 0.1 mol/L aqueous HCl or NaOH solution. Prior to irradiation, the mixture solution was magnetically stirred for 60 min in the dark to establish the adsorption-desorption equilibrium. During the irradiation, 4 mL of the reaction aliquots was withdrawn at certain time intervals

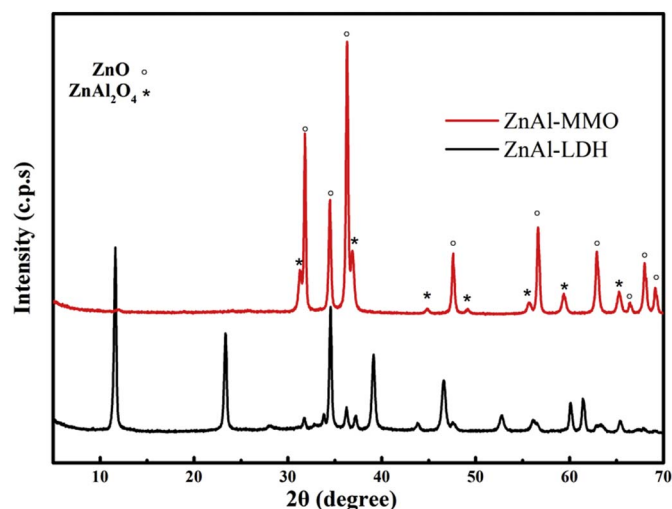


Fig. 1. XRD patterns of ZnAl-LDH precursor and ZnAl-MMO nanocomposite.

and centrifuged to separate the photocatalyst from the solution. The Cr(VI) concentrations were determined by 1,5-diphenylcarbazide method at a wavelength of 540 nm using Evolution 600 UV-Vis spectrophotometer (Carriazo et al., 2011). For comparison, the blank experiments to test the Cr(VI) stability under UV irradiation and the dark experiments to test the physical adsorption capacity of ZnAl-MMO material were conducted under the identical conditions.

3. Results and discussion

3.1. Characterization of ZnAl-LDH precursor and ZnAl-MMO nanocomposite

Fig. 1 shows the XRD patterns of ZnAl-LDH precursor and ZnAl-MMO nanocomposite. For ZnAl-LDH, the characteristic reflections at $2\theta = 11.6^\circ, 23.4^\circ, 34.5^\circ, 39.1^\circ, 46.6^\circ, 60.1^\circ$ and 61.5° were observed, which were attributed to (003), (006), (009), (015), (018), (110) and (113) planes of the typical well-crystallized hydrotalcite-like LDH materials (JCPDS no. 38-0486) (Zhao et al., 2012; Zhang et al., 2014). Upon calcination, the lamellar structure of ZnAl-LDH collapsed and thus these characteristic peaks fully disappeared. New strong reflections were discerned in the XRD pattern of ZnAl-MMO nanocomposite. The reflections at $31.8^\circ(100), 34.4^\circ(002), 36.2^\circ(010), 47.4^\circ(102), 56.5^\circ(110), 62.8^\circ(103)$ and $67.9^\circ(112)$ matched well with the standard data of the ZnO hexagonal wurtzite phase (JCPDS No. 36-1451) (Sun et al., 2012) and the diffraction reflections at $31.4^\circ, 36.9^\circ, 44.8^\circ, 49.1^\circ, 55.6^\circ, 65.2^\circ$ could be indexed to the (220), (311), (400), (331), (422) and (440) planes of cubic ZnAl₂O₄ (Li et al., 2011; Battiston et al., 2014) respectively, which confirmed the ZnO and ZnAl₂O₄ phases in ZnAl-MMO nanocomposite. Meanwhile, the diffraction reflections of ZnO phase were much sharper and intense than those of ZnAl₂O₄, indicating that ZnO phase of high crystallinity was the dominant phase in MMO and thus favored its photocatalytic activity in photoreduction of Chromium(VI).

Fig. 2 presents the representative SEM images of ZnAl-LDH and ZnAl-MMO nanocomposite. ZnAl-LDH exhibited a typical platelet-like morphology with hundreds of nanometers (Fig. 2a–b). Fig. 2c indicated that ZnAl-MMO nanoplates seemed smaller than ZnAl-LDH due to the collapse of the brucite-like layer. Fig. 2d clearly showed that ZnAl-MMO exhibited more irregular flake-morphology and many aggregates composed of round-edged nanoparticles on their surfaces were observed. Zhao et al. proposed the transformation mechanism of the structure evolution of ZnAl-LDH precursor to MMO and suggested the aggregates covering the resulting MMO surface was the nano-sized ZnO particles (Zhao et al., 2010).

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