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Improvement of photocatalytic activity of TiO_2 nanoparticles on selectively reconstructed layered double hydroxide

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ABSTRACT

Supported TiO_2 nanoparticles have been successfully fabricated by selective reconstruction of a Cu^{2+}, Mg^{2+}, Al^{3+}, Ti^{4+}-containing layered double hydroxide (CuMgAlTi-LDH) precursor, synthesized by coprecipitation, through calcination and rehydration process. A systematic investigation of the structural characterization and the photodegradation tests of methylene blue (MB) dye molecules from solution under both UV and visible light irradiation for the resulting TiO_2/CuMgAl-RLDH sample were carried out. Anatase-type TiO_2 nanoparticles are found to be homogeneously distributed on the surface of the selectively reconstructed CuMgAl-RLDH support. And the direct evidence for the surface TiO_2/LDH heterojunction formed on CuMgAl-RLDH is presented. For MB photodegradation under UV light or visible light illumination, TiO_2/CuMgAl-RLDH sample has superior photocatalytic properties to the rehydrated single phase R-TiO_2, the physical mixture of R-TiO_2 and CuMgAl-RLDH, the composite CuTi/MgAl-RLDH synthesized by the rehydration of mixture of MgAl-MMO and CuTi-MMO, and the TiO_2/MgAl-RLDH prepared under the same procedure as TiO_2/CuMgAl-RLDH without containing Cu ions. The skeleton Cu^{2+} ions dispersed in the mainlayer of CuMgAl-RLDH support can enable the photocatalytic activity for MB photodegradation. The TiO_2/LDH heterojunction nanostructure is proposed to contribute the efficient spatial separation between the photogenerated electrons and holes, which can concomitantly improve the photocatalytic activity. Our method provides a novel approach to fabricate new modes of load-type doped semiconductor photocatalysts which are both active under illumination by UV and visible light.

1. Introduction

Semiconducting photocatalysts have attracted extensive attention due to their potential industrial applications such as environmental purification and solar energy cell [1–4]. Although the remarkable progress has been made in the synthesis of new types of photocatalysts working in the ultraviolet or visible light regions, titanium dioxide-based semiconductor materials are still considered to be one of the superior candidates for their many desirable properties. Taking into account the large band gap of TiO_2 semiconductor, which requires UV light for excitation and thus limits the efficient utilization of solar energy, the improving of photoefficiency of the electronic process as well as the extending of absorption into the visible part of the spectrum plays an important role for the technical applications of TiO_2 in the future [5].

The use of supported TiO_2 has allowed the enhancement of photocatalysis rates in comparison with neat TiO_2. Active carbon [6] and molecular sieves [7,8] have been reported to be adopted as the supports. It was shown that such arrangements (highly adsorptive supports and nanosized TiO_2) produced higher quantum yields. Reddy et al. [9] attempted to use a transition metal modified MCM-41 for supporting TiO_2 and found that some metals, such as Cu and Cr, can enhance the performance of the photocatalysts. However, because the supported particulate catalysts are hard to be homogeneously dispersed and unstable during the course of photocatalytic reactions, it is possible to lead to the reduced photocatalytic activity and lost in the reaction to a great extent. Development of new approach for preparation of supported TiO_2-based photocatalysts with improved activity and stability working in visible light region is thus highly valued.

As one member of clay family, layered double hydroxides (LDHs, also known as hydrotalcite-like materials) are one such potential inorganic support. They can be described by the general formula $[M_{1-x}{}^{2+}M_x{}^{3+}(OH)_2]^{x+}A^{n-}{}_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are di-and tri-valent cations, respectively; the value of the coefficient x is equal to the molar ratio of $M^{3+}/(M^{2+}+M^{3+})$; and A^{n-} is an anion [10–12]. This flexibility in composition allows LDHs with a wide variety of properties to be prepared [13]. One of the most attractive features of LDHs materials is the so called "reconstruction effect" [14]: calcination of MgAl-LDH at moderate temperatures leads to the formation of magnesium aluminum mixed metal oxides (MMO), and rehydration of MMO results in spontaneous structural reconstruction of

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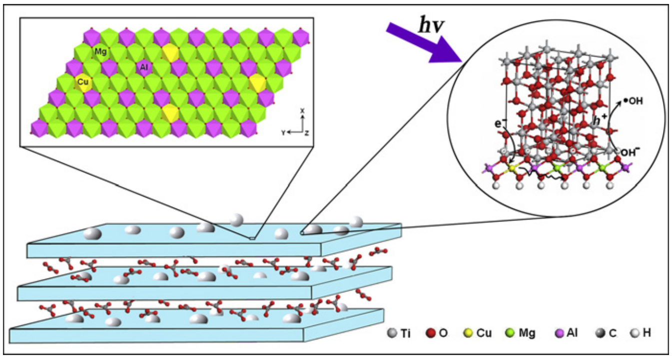

Fig. 1. Schematic illustration of the resulting TiO_2/CuMgAl-RLDH sample and the proposed photocatalytic mechanism.

LDH. The reconstructed LDHs have been reported to be used as solid base catalysts [15], for sensing water uptake in organic coatings [16], and even for fabrication of erasable nanoporous antireflection coatings [17].

In the present work, by taking advantage of the characteristic "reconstruction effect" of LDH materials, we describe the fabrication of surface-doped TiO_2 semiconductor supported on LDH with high dispersion. Cu^{2+}, Mg^{2+}, Al^{3+}, Ti^{4+}-containing LDH was first synthesized by coprecipitation. Then, CuMgAlTi-MMO was obtained after calcination of the LDH precursor in air at 400 °C. By subsequent rehydration in deionized water at room temperature, LDH structure with Cu^{2+}, Mg^{2+}, Al^{3+} in mainlayers (CuMgAl-RLDH) was selectively reconstructed producing the TiO_2 nanoparticles supported on the LDH surface (Fig. 1). Substituting part magnesium with copper ions in the framework during synthesis of LDH makes it possible to improve the photoefficiency. The resulting samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), ultraviolet–visible spectroscopy (UV–vis), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and electron paramagnetic resonance spectroscopy (EPR). The photocatalytic performance of the resulting sample was investigated using the degradation of MB dye molecules under both UV and visible light irradiation as a probe reaction. It is demonstrated that the resulting sample exhibit excellent photocatalytic efficiencies.

2. Experimental

2.1. Materials preparation

The carbonate-intercalated CuMgAlTi-LDH precursor was synthesized by the coprecipitation method. All reagents were commercially available and used as received without further purification. For the synthesis of CuMgAlTi-LDH with Cu/Mg/Al/Ti molar ratio of 1/30/10/9, a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.002 mol), $Mg(NO_3)_2 \cdot 6H_2O$ (0.06 mol), $Al(NO_3)_3 \cdot 9H_2O$ (0.02 mol), and $TiCl_4$ (0.018 mol) were dissolved in 100 mL of deionized water (solution *A*). NaOH (0.16 mol) and Na_2CO_3 (0.016 mol) were dissolved in 100 mL of deionized water (solution *B*). Solution *B* was added dropwise to solution *A* until a pH of 8.5 was attained, and the system was then aged at 60 °C for 18 h. The solid product was collected by centrifugation, washed with deionized water and alcohol separately, and finally dried at 90 °C overnight. The dried LDH precursor was further calcined in air at 400 °C for 5 h, with a heating rate of 2 °C/min, in order to transform the LDH precursor into CuMgAlTi-MMO. For comparison, samples of MgAl-MMO, CuMgAl-MMO, CuTi-MMO, and MgAlTi-MMO with Mg/Al molar ratios of 3/1, Cu/Mg/Al molar ratios of 1/30/10, Cu/Ti molar ratios of 1/9, and Mg/Al/Ti molar ratios of 30/10/19, respectively, as well as a single metal oxide TiO_2, were synthesized under the same reaction conditions.

The CuMgAlTi-MMO powder (1 g) was placed into 100 mL deionized water, and then stirred for 24 h at room temperature. The resulting TiO_2/CuMgAl-RLDH was collected by centrifugation, washed several times with deionized water, and dried at 60 °C overnight. For comparison, after the rehydration of MgAlTi-MMO under the same conditions we got TiO_2/MgAl-RLDH. CuTi/MgAl-RLDH was synthesized by the rehydration of the mixture of MgAl-MMO and CuTi-MMO. Additionally, R-TiO_2/CuMgAl-RLDH was a mechanical mixture of the rehydrated TiO_2 and rehydrated CuMgAl-MMO (denoted R-TiO_2 and CuMgAl-RLDH, respectively).

2.2. Characterization

XRD patterns of the products were recorded on a Shimadzu XRD-6000 diffractometer, using Cu Kα radiation ($\lambda = 0.15418$ nm) at 40 kV and 30 mA. FT-IR spectra were recorded using KBr discs in the region 400–4000 cm^{-1} with a Bruker Vector 22 spectrometer. SEM images were obtained using a Hitachi S-4700 field emission SEM at 20 kV, with the surface of the samples coated with a thin platinum layer to avoid a charging effect. TEM images were recorded on a JEOL JEM-2010 high-resolution transmission electron microscope at an accelerating voltage of 200 kV. The sample was ultrasonically dispersed in ethanol, and then the suspension was deposited on a microgrid coated with a holey carbon film. UV–vis diffuse reflectance spectra were recorded at room temperature in air on a Shimadzu UV-2501PC spectrometer equipped with an integrating sphere attachment using $BaSO_4$ as background. Elemental analyses for metals were performed with a Shimadzu ICPS-7500 inductively coupled plasma emission spectrometer (ICP-ES) on solutions prepared by dissolving the samples in dilute HCl. XPS were recorded with a PHIQ2000 X-ray photoelectron spectrometer equipped with a monochromatized Al Kα X-ray source. An operating power of 25 W was used with a spot diameter of 100 μm. EPR spectra of paramagnetic species were recorded with a Bruker EPR 300E spectrometer, the irradiation source ($\lambda = 355$ nm) was a Quanta-Ray Nd:YAG pulsed (10 pulses/s) laser system.

2.3. Photocatalytic activity measurements

Photocatalytic activities of the TiO_2-based samples were evaluated using the photodegradation of MB under UV and visible light irradiation as the model reaction. Under visible light irradiation, a quartz beaker (capacity 150 mL) was used as the photoreaction vessel. Typically, the reaction system containing MB (aqueous solution, 1×10^{-5} M) and catalyst sample (0.3 g/L) was magnetically stirred in the dark for 30 min to reach the adsorption equilibrium of MB with the catalyst and was then exposed to light from a 300 W Xe lamp equipped with a UV cutoff filter ($\lambda \geq 420$ nm). At specific time intervals, 3 mL of the reaction solution was withdrawn by a syringe. The solution was centrifuged to remove the catalyst sample before being analyzed by UV–vis absorption spectroscopy. A blank reaction was carried out under the same reaction conditions without adding any catalyst. For UV light irradiation, the procedure is the same, excepting for using a 500-W high-pressure mercury lamp equipped with a double-walled quartz glass cooling tube and a quartz reactor (capacity 250 mL) as the reaction equipment.

3. Results and discussion

Fig. 2 illustrates the XRD patterns of the samples of carbonate-intercalated CuMgAlTi-LDH precursor, CuMgAlTi-MMO, and TiO_2/CuMgAl-RLDH. The patterns of the LDH precursor exhibit the characteristic reflections of a well-ordered layer structure, with