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The synthesis of hierarchical Zn–Ti layered double hydroxide for efficient visible-light photocatalysis

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ARTICLE INFO

Article history:

Received 19 September 2010

Received in revised form

26 December 2010

Accepted 4 January 2011

Keywords:

Layered double hydroxides

Photocatalysis

Visible-light

Methylene blue

ABSTRACT

Zn–Ti layered double hydroxides (LDHs) with different Zn/Ti ratio have been synthesized by co-precipitation of zinc and titanium salts from homogeneous solution, which were demonstrated as efficient visible-light photocatalysts. Powder X-ray diffraction (PXRD), scanning electron microscope (SEM), high-resolution transmission electron microscopy (HRTEM) and Brunauer–Emmett–Teller (BET) revealed that the resulting Zn–Ti LDHs possess high crystallinity, hierarchical structure as well as large specific surface area (91.96–107.9 m² g^{−1}). UV–vis diffuse reflection spectroscopy (DRS) confirmed that Zn–Ti LDHs show a broad absorption in visible light region (400–700 nm). With a low band gap of ~3.06 eV, the as-prepared Zn–Ti LDHs displayed significant photocatalytic activity for the degradation of methylene blue (MB) under visible-light irradiation (~100% of degradation percentage in 100 min), which is much higher than that of commercial product (Degussa P25). Therefore, this work provides a detailed understanding of semiconductor properties of Zn–Ti LDHs which was unrevealed previously, and demonstrates its potential application in the field of photocatalysis.

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1. Introduction

Energy shortage and environmental deterioration have become the major obstacles to the development of economy and society in the past decades. With wide applications in solar energy conversion and environmental remediation (water purification and decontamination, deodorization of air etc.), photocatalysis using semiconductors has been extensively investigated [1]. Many materials including TiO₂ and ZnO, have attracted great interests as promising photocatalysts in areas of environment and energy, due to their high photocatalytic activity, resistance to photocorrosion, photo-stability, low cost and non-toxicity. However, they only can be activated under UV-light irradiation because of large band gap [2], resulting in a low photo-electronic transition efficiency since the ultraviolet light is only 4% in solar spectrum. Therefore, photocatalysts that respond to visible-light are needed to improve the utilization of sunlight for production of hydrogen energy by splitting water [3,4], degradation of organic pollutants [5,6] and other applications. Traditional visible-light photocatalysts are either unstable upon illumination with light (e.g., CdS, CdSe) or have low activity (e.g., WO₃, Fe₂O₃) [7,8]. Visible-light semiconductor photocatalysts consisting of anion doping [9–12] (N, C, S) and

metal doping in MTiO₂ (M = Fe, V, Cr, Mn) [13,14] have attracted much attention, for the purpose of introducing energy levels in the band gap. Recently, Dionysiou et al. synthesized N–F-codoped TiO₂ which showed highly efficient visible light-activated photocatalysis [15]. Intermediate states of the energy levels in the band gap lead to visible light absorption which increases light-harvesting abilities.

Layered double hydroxides (LDHs) are a large class of typical inorganic layered host materials which can be described by the general formula [M^{II}_{1−x}M^{III}_x(OH)₂]^{z+}(A^{n−})_{z/n}·yH₂O (M^{II} and M^{III} are divalent and trivalent metals, respectively; A^{n−} is the interlayer anion compensating for the positive charge of the brucite-like layers). The tunable metal ions in a wide range without altering the structure of the material and anion exchange properties of LDH materials make them attractive candidates as catalysts or catalyst precursors [16–20], ion exchangers [21] and absorbents [22,23]. Furthermore, thermal decomposition of LDH materials at moderate temperature (300–600 °C) leads to the formation of highly active mixed metal oxides (MMOs) nanocomposites with high specific surface area and thermal stability [24–27], which have been used as photocatalysts for the decomposition of dye or phenol in water [24,27,28]. In our previous work, a combined method of atomic layered deposition – *in situ* growth – calcination was reported to fabricate hierarchical MMO framework, which was used as an efficient photocatalyst for the decomposition of sulforhodamine B and an azobenzene-containing polymer [29].

Although MMO materials as photocatalysts have been thoroughly studied, the application of LDHs in photocatalysis was rarely

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investigated. Metal hydroxides were seldom applied as photocatalysts, for the photoinduced electron could be easily captured by hydroxyl groups. Recently however, Garcia et al. reported the visible oxygen generation from water with photocatalysis of Zn–M LDH (M=Cr, Ti, Ce), and the results showed that the LDH can be regarded as “doped semiconductors” [30]. This motivates us to further study the semiconductor properties of LDH materials, owing to the low-cost, easy preparation and environmental friendliness.

In this work, the Zn–Ti LDH with hierarchical structure has been synthesized by the co-precipitation method, which exhibited effective photocatalysis for the decomposition of methylene blue (MB) in water. The synthesized Zn–Ti LDH possesses microspheric morphology with diameter of 5–10 μm which consists of two-dimensional thin nanoflakes (width and length: 1–2 μm ; thickness: 80–120 nm). It was found that the Zn–Ti LDH displayed superior photocatalytic activity for the degradation of methylene blue (MB) under visible-light irradiation compared with TiO_2 , ZnO and P25, as a result of its hierarchical structure, high specific surface area (91.96–107.9 $\text{m}^2 \text{g}^{-1}$) as well as low band gap ($\sim 3.06 \text{ eV}$). Moreover, Zn–Ti LDH showed the advantages of low-cost preparation, structural durability and long-term sustainability. Therefore, this work provides a facile approach for the preparation of Zn–Ti LDH with rather high photocatalytic activity in the visible-light region, which can be used in the field of pollutant degradation of water treatment.

2. Experimental

2.1. Materials

Analytical grade chemicals including $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, TiCl_4 , NH_4NO_3 were purchased from the Beijing Chemical Co. Limited and used without further purification. The deionized and decarbonated water was used in all the preparation processes.

2.2. Synthesis

The Zn–Ti LDH was prepared by co-precipitation of zinc and titanium salts from homogeneous solution. A typical synthetic procedure is as follows: 0.22 ml of TiCl_4 , 1.19 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 3.0 g of urea were dissolved in 100 ml of deionized water under vigorous stirring. The resulting reactant was aged in an autoclave at 130°C for 48 h. The precipitate was centrifuged and washed thoroughly with water and finally dried overnight at 60°C . The Zn–Ti LDHs with different molar ratio of $\text{Zn}^{2+}/\text{Ti}^{4+}$ were prepared using the same procedure by varying Ti^{4+} dosage.

2.3. Characterization

Powder X-ray diffraction of Zn–Ti LDH samples were collected on a Shimadzu XRD-6000 diffractometer using a $\text{Cu K}\alpha$ source, with a scan step of 0.02° and a scan range between 3° and 70° . X-ray photoelectron spectra (XPS) were recorded on a Thermo VG ESCALAB250 X-ray photoelectron spectrometer at a pressure of about 2×10^{-9} Pa using $\text{Al K}\alpha$ X-ray as the excitation source. The morphology of the Zn–Ti LDH was investigated using a scanning electron microscopy (SEM; Zeiss Supra 55) with an accelerating voltage of 20 kV, combined with energy dispersive X-ray spectroscopy (EDX) for the determination of metal composition. Transmission electron microscopy (TEM) images were recorded with Philips TECNAI-20 and JEOL JEM-2010 high-resolution transmission electron microscopes. The accelerating voltage was 200 kV. The specific surface area determination and pore volume and size analysis were performed by Brunauer–Emmett–Teller (BET) and Barret–Joyner–Halender (BJH) methods using a Quantachrome

Autosorb-1C-VP Analyzer. Prior to the measurements, the samples were degassed at 120°C for 5 h. Solid-state UV–vis diffuse reflectance spectra were recorded at room temperature in air by means of a Shimadzu UV-3000 spectrometer equipped with an integrating sphere attachment using BaSO_4 as background.

2.4. Photocatalytic reactions

The photocatalytic activity of Zn–Ti LDH was monitored by degradation of methylene blue (MB) under irradiation with visible-light. Pure ZnO, TiO_2 , Degussa P25 were performed as reference samples, respectively. The visible-light irradiation source was a 300 W xenon lamp equipped with a wavelength pass filter with a length of 420 nm. Running water was circulated through the jacket to ensure constant temperature of the reaction mixture, which was stirred magnetically. Typically, a mixture of 60 ml of MB ($1.6 \times 10^{-5} \text{ M}$) solution and 60 mg of catalyst was vigorously stirred for 30 min to establish an adsorption/desorption equilibrium. Then the reaction solution was stirred under visible-light irradiation. At given time intervals, 3 ml aliquots were sampled and centrifuged to remove the particles. The filtrates were analyzed by measuring the absorption band maximum (664 nm) using a Shimadzu UV-3000 UV–vis spectrophotometer. The blank reaction was carried out following the same procedure without adding catalyst.

3. Results and discussion

3.1. Characterization of Zn–Ti LDHs

Fig. 1A illustrates the powder XRD patterns for Zn–Ti LDHs with $\text{Zn}^{2+}/\text{Ti}^{4+}$ molar ratio of 2:1, 3:1 and 4:1 in the preparation process. A strong reflection (003) was observed for the three samples; XRD patterns also show the reflections of (006), (009), (100), (101), (012), (110) and (113) which can be indexed to typical LDH materials [31]. It was found that the basal reflection ($2\theta \approx 13.2^\circ$, $d_{003} = 0.66 \text{ nm}$) of Zn–Ti LDHs displays a little shift to higher scattering angle compared with natural and synthetic carbonate-containing hydrotalcites with divalent and trivalent cations in the host layers ($2\theta \approx 11.7^\circ$, $d_{003} = 0.76 \text{ nm}$) [32,33], indicating that the basal spacing decreases with the incorporation of tetravalent metal (Ti) in hydrotalcite materials. This is in accordance with the previous report on Ti-containing LDHs [30]. The contraction in the interlayer distance of Zn–Ti- CO_3 LDH is possibly related to the reason that the presence of Ti^{4+} results in a strong electrostatic interaction between host layer and guest carbonate. Several weak reflections at $2\theta = 22^\circ$, 31° and 36° were observed, which can be assigned to small amount of zinc hydroxide impurity (PDF Card No. 20-1437). XPS measurement shows that the surface is essentially dominated by Ti^{4+} (Fig. 1B). The $\text{Ti } 2p_{1/2}$ and $\text{Ti } 2p_{3/2}$ spin-orbital splitting photo-electrons for Zn–Ti LDH are located at binding energies of 463.6 and 458.0 eV, respectively. The peak separation of 5.6 eV between the $\text{Ti } 2p_{1/2}$ and $2p_{3/2}$ signals is in well agreement with the reported value [34]. The FT-IR technique was also used to identify the nature and symmetry of interlayer anions (see Supporting Information Fig. S1). The spectrum showed a broad intense band between 3500 and 3100 cm^{-1} due to the OH stretching mode of hydroxyl groups in host layers and interlayer water molecules. The band at 1503 cm^{-1} together with its accompanying band at 1398 cm^{-1} is attributed to mode ν_3 of interlayer carbonate species [35].

The SEM coupled with EDX and TEM image of the Zn–Ti LDH (molar ratio Zn/Ti of 3:1) are shown in Fig. 2. The synthesized Zn–Ti LDH shows microspheric morphology with a diameter of about 5–10 μm (Fig. 2A). The high-magnification SEM image of an individual microsphere (Fig. 2B) clearly exhibits the pres-

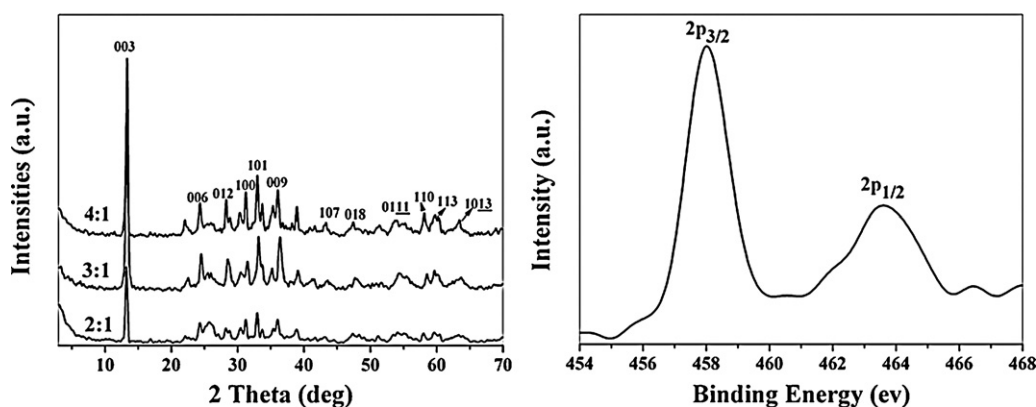


Fig. 1. (A) Powder XRD patterns for Zn–Ti LDHs with different molar ratio of $\text{Zn}^{2+}/\text{Ti}^{4+}$: 2:1, 3:1 and 4:1, respectively; (B) XPS spectrum of the Ti 2p line.

ence of hierarchical structure consisting of two-dimensional thin nanoflakes with 1–2 μm in width and length and 80–120 nm in thickness. More importantly, these nanoflakes form a 3D architecture involving macropores with different size, which may serve as paths for transportation of species. The energy dispersive X-ray spectrometry (EDX) analysis of the Zn–Ti LDH (Fig. 2C) shows the presence of Zn, Ti and O with a Zn/Ti molar ratio of ~ 3.2 , approximately matching with the nominal ratio ($\text{Zn}/\text{Ti} = 3.0$). The structure of Zn–Ti LDH material was further characterized by HR-TEM image (Fig. 2D). The pattern of individual nanoflake of Zn–Ti LDH exhibits hexagonally arranged spots (Fig. 2D, inset), confirming the single-crystal nature [36]. The lattice with a d spacing of 0.15 nm was observed, corresponding to the (1 1 3) plane of the Zn–Ti LDH phase. This value is in accordance with the in-plane structural parameter of Zn–Ti LDH crystal determined from the XRD characterization ($d_{113} = 0.155 \text{ nm}$).

To give a further insight on the specific surface area and porosity of the as-prepared Zn–Ti LDH, nitrogen sorption measurement was carried out. Fig. 3 displays the N_2 adsorption–desorption isotherm

and the corresponding pore size distribution curve for the Zn–Ti LDH samples with different molar ratios. The Zn–Ti LDH material exhibits a typical IV isotherm with a H3-type hysteresis loop ($P/P_0 > 0.4$), indicating the presence of mesopores. Furthermore, any limiting adsorption at higher P/P_0 was not observed, indicative of the existence of macropores [37]. This is in accordance with the SEM observations (Fig. 2B). This result is further confirmed by the corresponding wide distribution of pore size in Fig. 3B (15–100 nm, maximum at 65 nm), resulting from the hierarchical structure stacking of LDH nanoflakes. A high specific surface area ($91.96\text{--}107.88 \text{ m}^2 \text{ g}^{-1}$) was obtained for the three Zn–Ti LDHs owing to the hierarchical structure.

3.2. Photocatalytic activities

To demonstrate the potential applicability of Zn–Ti LDH in photocatalysis, the photodegradation of MB was carried out under irradiation with visible-light ($\lambda > 420 \text{ nm}$). 60 mg of catalyst was added into a 60 ml of MB ($1.6 \times 10^{-5} \text{ M}$) solution and stirred vig-

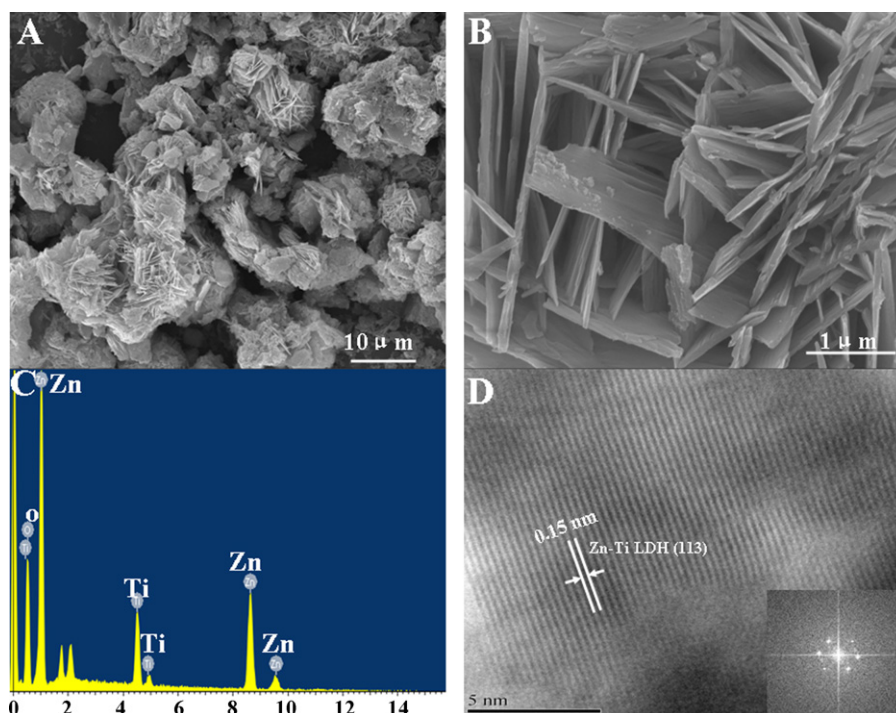


Fig. 2. (A) SEM images of Zn–Ti LDH with $\text{Zn}^{2+}/\text{Ti}^{4+}$ molar ratio of 3:1. (B) High-magnification SEM image of individual spherical structure. (C) The corresponding EDX spectrum of the Zn–Ti LDH. (D) HR-TEM image and SAED pattern (inset in panel D) of the Zn–Ti LDH.

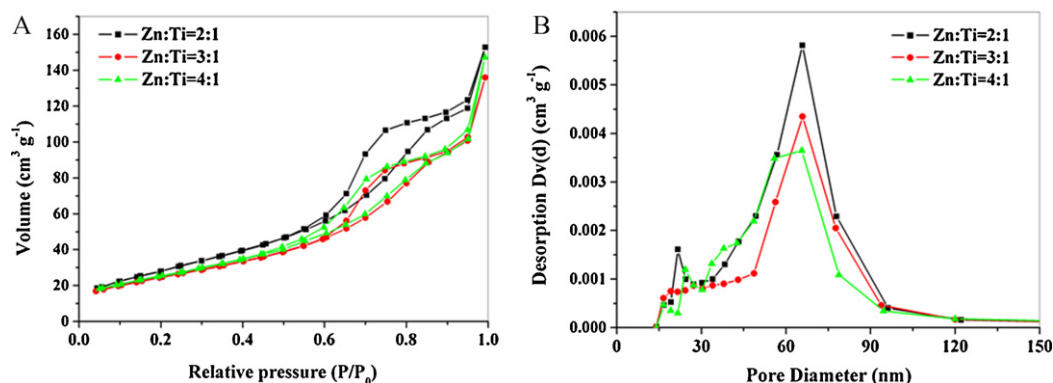


Fig. 3. (A) N₂ sorption isotherms and (B) pore size distribution of the Zn-Ti LDH with different molar ratios.

ously for 30 min in dark to establish an adsorption/desorption equilibrium. Then the solution was stirred under visible-light irradiation for photocatalytic reaction. The Zn-Ti LDH photocatalyst was dispersed in MB solution under irradiation of visible-light, and the absorption spectra of the solution as a function of irradiation time were recorded by using a UV-vis spectrometer. The decomposed percentage of MB was calculated by C/C_0 , where C and C_0 are the absorbance intensity of the sample at time intervals and initial state, respectively. The strong absorption bands of MB located at $\lambda = 292$ nm and $\lambda = 664$ nm decreased gradually upon increasing irradiation time and the absorbance of dye solution was close to zero after 100 min of irradiation for Zn/Ti = 3:1 LDH catalyst (Fig. 4). In addition, the solution color changed from an initial deep blue to nearly transparent during the degradation process of MB. Taking into account the important role of Ti in the photocatalysis, the influence of molar ratio of Zn/Ti on its photocatalytic activity was also studied, which are shown in Fig. S2. It was found that all the Zn-Ti LDHs with 2:1, 3:1 and 4:1 displayed high photocatalytic activity under visible-light irradiation. The decomposition of MB by the Zn-Ti LDH (Zn/Ti = 3:1) reaches ~100% over 100 min, comparative to ~95% and ~96% by the samples with Zn/Ti = 2:1 and 4:1, respectively. The Zn-Ti LDH (Zn/Ti = 3:1) shows the strongest absorption in the visible light region among the three samples (shown in Fig. S3), accounting for the highest photocatalytic activity.

The photocatalytic behavior of Zn-Ti LDH was further evaluated by a comparison study with the performance of TiO₂, ZnO as well as P25. As shown in Fig. 5, MB degraded ~40% under

light exposure without catalyst, indicating that photolysis reaction also contributes to the degradation of the dye. However, the photodegradation of MB was enhanced remarkably with the presence of Zn-Ti LDH (Zn/Ti = 3:1). Especially, the photocatalytic activity of the Zn-Ti LDH (Zn/Ti = 3:1) was significantly higher than that of commercial P25. As shown in Fig. S4, the plots of $\ln(C_0/C)$ vs irradiation time suggest that the photodegradation of MB follows the pseudo-first-order rate law. The rate constant was calculated to be 0.0407 min^{-1} ($t_{1/2} = 50$ min) with Zn-Ti LDH (Zn/Ti = 3:1) as the photocatalyst, much larger than that of TiO₂, ZnO as well as P25. In order to give a further understanding of the high photocatalytic performance of the Zn-Ti LDH, measurements of the optical properties were also performed. Fig. 6 shows the UV-vis absorption spectra of Zn-Ti LDH and other reference samples using the diffuse reflection method. A comparison of the corresponding absorption spectra between Zn-Ti LDH and ZnO, TiO₂ and P25 clearly shows that the Zn-Ti LDH exhibits enhanced absorption in the visible-light region (400–700 nm). In addition, the absorbance of Zn-Ti LDH in the region 200–400 nm indicates the octahedral coordination of Ti atoms in the brucite-like sheets. It is well-known that light absorption by the material and the migration of the light-induced electrons and holes are the most key factors controlling a photocatalytic reaction, which is relevant to the electronic structure characteristics of the material [38]. Moreover, UV-vis diffuse reflectance spectra of the samples was also used to determine the band gap (Fig. 6, inset), from which a band gap of ~3.06 eV for Zn-Ti LDH was obtained. This value is smaller than that of P25 (~3.19 eV), pure ZnO (~3.21 eV) and TiO₂ (~3.22 eV). The lower

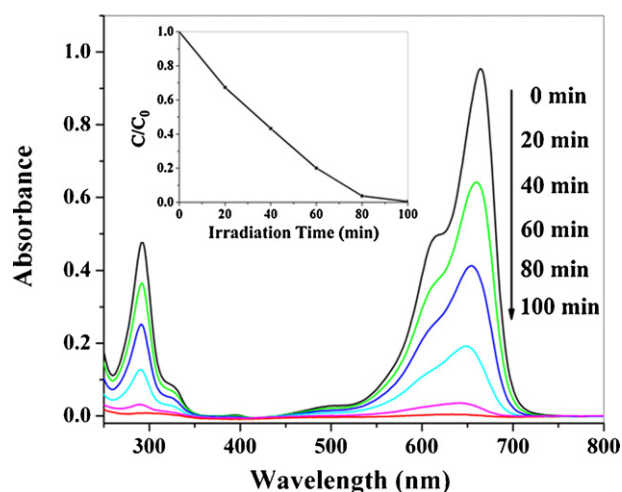


Fig. 4. Absorption changes of MB solution during the photodegradation process over sample Zn-Ti LDH (Zn/Ti = 3:1) under visible-light irradiation ($\lambda > 420$ nm). Inset shows the plot of degradation $\ln(C/C_0)$ as a function of irradiation time.

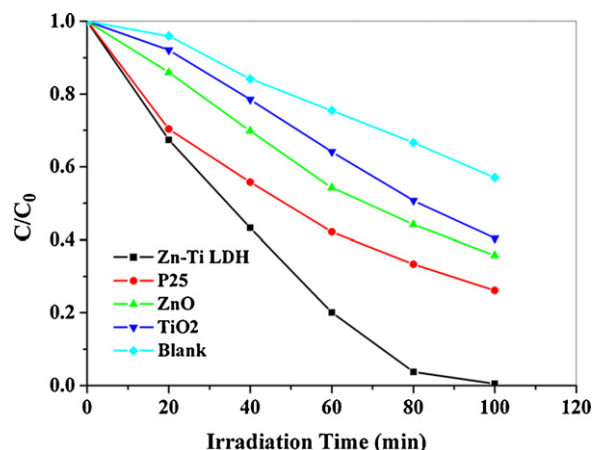


Fig. 5. Photodegradation of MB monitored as the normalized concentration vs irradiation time under visible-light irradiation ($\lambda > 420$ nm) with the presence of different photocatalysts.

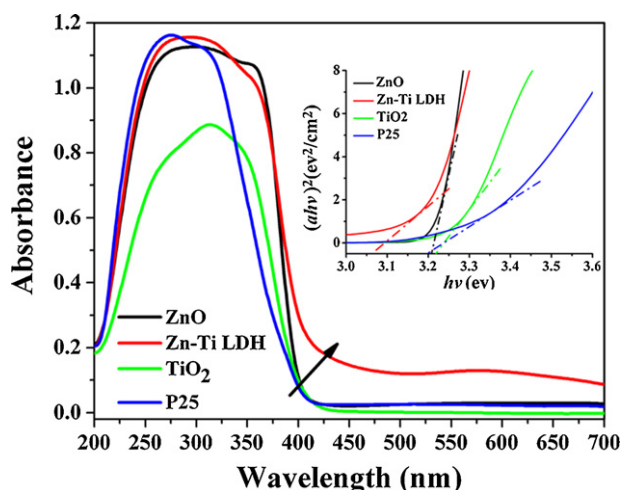


Fig. 6. UV-vis diffuse reflectance spectra of the as-synthesized Zn-Ti LDH and comparison samples: ZnO, TiO₂, P25. The inset shows their corresponding plots of $(\alpha h\nu)^2$ vs $h\nu$ for the determination of the direct band gap.

band gap of Zn-Ti LDH in this work accounts for its high visible-light photocatalytic activity. In addition, the high photocatalytic activity of Zn-Ti LDH is also attributed to its hierarchical structure and high specific surface ($91.96\text{--}107.88\text{ m}^2\text{ g}^{-1}$). The high specific surface area is responsible for providing strong adsorption ability toward target molecules and thus the generation of photoinduced electron-hole pairs of active sites [39,40]. A wide distribution of macropores of Zn-Ti LDH is favorable for the transportation and diffusion of species.

The long-period performance of the Zn-Ti LDH (Zn/Ti = 3:1) was also tested. As shown in Fig. S5, the photocatalyst is stable under five repeated application cycles with nearly constant photodecomposition percentage, indicating that Zn-Ti LDH does not deactivate during the photocatalytic process of the pollutant molecules. Moreover, this material can be easily separated from the reaction system due to the microscopic particle size of Zn-Ti LDH. The results thus indicate that the Zn-Ti LDH can be used as an attractive photocatalyst for large-scale environmental purification with high photocatalytic activity, long-term sustainability and excellent recyclability.

4. Conclusion

In summary, the Zn-Ti LDH was prepared with the method of co-precipitation, which displayed superior photocatalytic activity in the visible part of the solar spectrum for the degradation of MB compared with TiO₂, ZnO as well as P25. The remarkable visible-light photocatalytic activity of Zn-Ti LDH is attribute to its lower band gap ($\sim 3.06\text{ eV}$), hierarchical microsphere structure as well as high specific surface ($91.96\text{--}107.88\text{ m}^2\text{ g}^{-1}$). In addition, Zn-Ti LDH retained its activity after several recycles of the MB photodegradation. Therefore, it is expected that the Zn-Ti LDH with hierarchical structure in this work can be potentially used as an effective and recyclable visible-light photocatalyst for large-scale environmental purification.

Acknowledgment

This project was supported by the National Natural Science Foundation of China, the 111 Project (Grant No. B07004) and the 973 Program (Grant No. 2011CBA00504).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2011.01.016.

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