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Interstratified nanohybrid assembled by alternating cationic layered double hydroxide nanosheets and anionic layered titanate nanosheets with superior photocatalytic activity



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HIGHLIGHTS

GRAPHICAL ABSTRACT

Interstratified nanohvbrid

- Two kinds of nanosheets are well arranged in a layer-by-layer alternating fashion.
- Effective interfacial heterojunction and high specific surface were observed.
- Interstratified nanohybrid exhibits a superior photocatalytic activity.

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ABSTRACT

Trititanate nanosheets

LDH nanosheets

Oppositely charged 2D inorganic nanosheets of ZnAl-layered double hydroxide and layered titanate were successfully assembled into an interstratified nanohybrid through simply mixing the corresponding nanosheet suspensions. Powder X-ray diffraction and high-resolution transmission electron microscope clearly revealed that the component nanosheets in the as-obtained nanohybrid ZnAl–Ti₃O₇ retain the 2D sheet skeletons of the pristine materials and that the two kinds of nanosheets are well arranged in a layer-by-layer alternating fashion with a basal spacing of about 1.3 nm, coincident with the thickness summation of the two component nanosheets. The effective interfacial heterojunction between them and the high specific surface area resulted in that the nanohybrid exhibits a superior photocatalytic activity in the degradation of methylene blue with a reaction constant *k* of 2.81×10^{-2} min⁻¹, which is about 9 and 4 times higher than its precursors H₂Ti₃O₇ and ZnAl-LDH, respectively. Based on UV–vis, XPS and photoelectrochemical measurements, a proposed photoexcitation model was provided to understand its photocatalytic behavior.

H.Ti.O.

nAl-LDI

30 60 90

ZnAl-Ti-O-

Irradiation Time (min)

30

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1. Introduction

The serious environmental problems regarding water pollutants, generated from a number of industrial manufacturing processes such as pesticide, pharmaceutical and textile industries,

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http://dx.doi.org/10.1016/j.jhazmat.2014.07.068 0304-3894/© 2014 Elsevier B.V. All rights reserved. require the development of new, powerful and clean decontamination technology. The semiconductor-based heterogeneous photocatalysis is a promising technique in wastewater treatment [1]. This process can use air to efficiently degrade a variety of toxic organic pollutants in water through photooxidation at ambient temperatures and pressures, and in most cases its final decomposed products are harmless substances such as CO₂, water and mineral salts [1–4]. The photocatalytic process involves the photoactivation of semiconductors and the formation of highly oxidizing radicals. The photocatalytic efficiency depends on the migration process of the photogenerated electrons from the semiconductor inside to the surface and on the recombination process of the photogenerated electron-hole pairs [1].

Many metal oxide semiconductors such as TiO₂ and ZnO are commonly used for photocatalytic applications [1–3]. However, most of them have low photocatalytic efficiency. In order to hasten the migration of the photogenerated electrons, many lowdimensional nanostructured semiconductor materials have been explored [4–9]. Among them, the nonoconjugation of two different semiconductors into a heterojunction structure is an attractive approach [9–14]. The formed heterojunction can further suppress the rapid recombination of the photogenerated carriers. The fabrication of effective heterojunctions is not only strongly dependent on the properties of both semiconductors such as crystal structure, band structures and electron affinity, but also on the interface between the two materials. The intimated interfacial contact between them can allow the prompt migration and the effective separation of photogenerated charge carriers, thus resulting in an efficient photocatalytic reaction.

Nanostructural fabrication using 2D nanosheets is one of the most effective methods for arranging nanosemiconductors on a nanometer scale. It has demonstrated that titanates and other layered semiconductors can be delaminated into 2D individual nanosheets through the liquid exfoliation process [15,16]. One of the most important and attractive aspects of the exfoliated nanosheets is that various nanostructures can be fabricated using them as 2D building blocks. Assembling the 2D exfoliated nanosheets and other species can provide a feasible route to prepare nanostructured hybrids with abundant functionalities [16–22]. Layered titanates ($A_2Ti_nO_{2n+1}$, $A = H^+$ or alkali metal cations, 3 < n < 6) have attracted extensive and increasing interest in recent years due to their excellent photocatalytic and physicochemical properties [22,23]. Exfoliating titanates can produce negatively charged nanosheets [16,17]. In comparison with layered titanates, layered double hydroxides (LDHs) with a general formula of $[M^{2+}_{1-x}M^{3+}_{x}(OH)_{2}](X^{n-})_{x/n} \cdot mH_{2}O$ are less investigated as photocatalysts. But a few ZnM-LDHs (M = Al, Cr, Ti) containing transition metal ions in the octahedral sites have recently been reported to show a fairly high photocatalytic activity [24–27]. The action of formamide on LDHs in nitrate form can induce exfoliation into colloidal unilamellar sheets with positively charge [27,28]. Utilizing the exfoliated nanosheets as the host lattices or the platform supports to couple with other semiconductor nanoparticles for developing highly active photocatalysts has been extensively developed [16-22,29-33]. However, the synthesis of interstratified photocatalysts fabricated by alternating two kinds of nanosheets is underdeveloped. It is due to the difficulties in precisely arranging two kinds of nanosheets in a layer-by-layer alternating fashion. It is notable that the exfoliated LDH and titanate nanosheets possess opposite layer charges, which indicates their interstratified nanohybrid can be prepared by electrostatically derived self-assembly. It is of prime importance that the subnanometer-level thickness of these 2D nanostructured components with unique layered morphologies makes possible to form an effective interfacial contact between them.

ZnAl-LDH and $H_2Ti_3O_7$ are two typical layered semiconductors with good photocatalytic activity [34,35]. In the present work, derived from the electrostatic interaction, a new interstratified nanohybrid ZnAl–Ti₃O₇ has been successfully prepared using the positively charged ZnAl-LDH nanosheets and the negatively charged trititanate nanosheets as 2D building blocks. The synergistic effects between the two kinds of nanosheets on its physicochemical properties were investigated. Methylene blue (MB), one of the most used organic dyes, was used as the typical organic pollutant to evaluate its photocatalytic activity.

2. Experimental

2.1. Materials

All reagents were of analytical grade; titanium dioxide was purchased from Jiujiang Tanbre Co., Ltd., and others supplied by Sinopharm Chemical Reagent Co., Ltd. They were used without further purification. Deionized and decarbonated water (DDW) was used throughout the experiments.

2.2. Preparation of interstratified nanohybrid

The pristine ZnAl-LDH precursor was synthesized by the hydrothermal method reported previously [18]. The pH of aqueous solution (100 mL) containing 3 moles of Zn(NO₃)₂·6H₂O and 1 mol Al(NO₃)₃·9H₂O was adjusted to 8 with a 1 M NaOH solution under vigorous agitation, followed stirring for 1 h under a N₂ atmosphere. The resulting slurry was centrifuged and washed with DDW for three times. Afterwards, it was manually redispersed in 60 mL of DDW, and then hydrothermally treated in a Teflonlined stainless autoclave at 100 °C for 24 h. Based on the results of ICP-OES, TG and CHN elemental analysis, the composition of the resultant ZnAl-LDH was carbonate-free and determined to be $[Zn_{0.75}Al_{0.25}(OH)_2](NO_3)_{0.25} \cdot 0.57H_2O$. The Zn/Al ratio of 3.0 is the same as the initial reaction mixture. The exfoliation of ZnAl-LDH was achieved by ultrasonicating a LDH sample (1 g/L) in formamide at room temperature for 6 h under N₂ bubbling to avoid carbonate contamination, and centrifugating at 6000 rpm for 5 min, similar to the reported procedure [28].

The Na₂Ti₃O₇ precursor was prepared by a solid-state reaction with a mixture of TiO₂ and Na₂CO₃ in a molar ratio of 3:1 at 800 °C for 24 h and another 24 h at 800 °C after grinding [17]. The protonated trititanate, H₂Ti₃O₇, was obtained by an ion-exchange reaction in 1.5 M hydrochloric acid at 60 °C for 3 days, in which the acid solution was replaced with a fresh one every day. The exfoliation of the trititanate nanosheets was achieved by the reaction of H₂Ti₃O₇ with methylamine/propylamine solution in a molar ratio of 1:20/30, the mixture was placed into an autoclave and heated to 80 °C for 4 h. After the reaction, the resultant colloidal suspension of trititanate nanosheets was further dispersed in water to be a concentration of 2.5 g/L under ultrasonication at room temperature for 6 h.

The ZnAl–Ti₃O₇ nanohybrid was synthesized by slowly adding the trititanate nanosheets into the formamide suspensions of LDH in a molar ratio of 1:1 under vigorous stirring at room temperature for 4 h in N₂ atmosphere. Before mixing, the two nanosheet suspensions were adjusted to pH $6.5 \sim 7$ by a diluted HNO₃ solution. Flocculation occurred immediately after mixing these suspensions, as a result of the hybridization between the negatively charged trititanate nanosheets and the positively charged LDH nanosheets. The obtained material was separated by centrifugation, washed thoroughly with ethanol/water mixed solvent (1:1, v/v), and finally dried under vacuum at 80 °C for 24 h.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were collected at room temperature on a Rigaku SmartLab 3 kW diffractometer using Cu K α radiation (λ = 0.15418 nm). Field emission scanning electron microscope (SEM) images were observed with a Hitachi S-4800 microscope, combined with energy dispersive X-ray spectroscopy (EDX, Oxford 7021) for determination of metal composition. Highresolution transmission electron microscope (HRTEM) images were taken using a Tecnai F30 with an accelerating voltage of 300 kV. The samples were suspended in ethanol and sonicated over 10 min. Subsequently, a drop of the supernatant dispersion was placed onto Download English Version:

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