Journal of Alloys and Compounds 654 (2016) 491–497

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Hematite doped magnetic TiO_2 nanocomposites with improved photocatalytic activity

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ARTICLE INFO

Article history:
Received 11 June 2015
Received in revised form
10 September 2015
Accepted 15 September 2015
Available online 16 September 2015

Keywords:
Nanocomposites
Anatase TiO_2
Photocatalytic
α-Fe_2O_3
Self-built electric field

ABSTRACT

A facile approach for the fabrication of magnetic α-Fe_2O_3@TiO_2 nanocomposites has been demonstrated. The obtained composites which were doped by proper amount of hematite exhibited better photocatalytic activity than the samples without α-Fe_2O_3 doping according to the photocatalytic degradation of methyl orange. Moreover, the photocatalytic degradation activity of these nanocomposites is better than P25 at the same photocatalytic experiment conditions. However, when the doping amount of hematite is high, the nanocomposites exhibit poor photocatalytic activity. Because of the self-built electric field formed in the heterojunction of α-Fe_2O_3 and TiO_2, it can be confirmed that of the doping hematite makes a contribution to the ultraviolet–vis light absorption and provides more electrons for the catalysis process. And the combination of two kinds of semiconductor is the key to improve the utilization efficiency of light. Furthermore, that all the samples can be transferred easily by a magnet shows potential application for wastewater treatment.

1. Introduction

Photocatalytic degradation of environmental hazardous substances has attracted much attention for decades. Among various photocatalysts, TiO_2 has been intensively investigated due to its high chemical and thermal stability, nontoxicity, cost effectiveness, and long-term stability against photo corrosion and chemical corrosion [1]. One critical drawback of TiO_2 is that its band energy gap, which is of the magnitude 3.0–3.2 eV, is too large to allow efficient absorption of most sunlight. TiO_2 is active only under the near ultraviolet (UV) irradiation and no visible light response [2]. A proficient way to extend the absorbance of TiO_2 to light is to form a composite of nano-semiconductors, such as α-Fe_2O_3 and TiO_2 [3,4]. Due to the stability under ambient conditions with low cost, the high resistance to corrosion and the environment-friendly features, the hematite (α-Fe_2O_3) can be used as an efficient semiconductor. Hematite has a band gap of 2.2 eV, so it can be considered to be a sensitizer for TiO_2 [5–10]. When the composite is irradiated by light, the electrons in the valence band of α-Fe_2O_3 are excited to the conduction band, leaving holes in the valence band. As a consequence, the electrons in the conduction band of α-Fe_2O_3 are injected to the conduction band of TiO_2 driven by the built-in field in the α-Fe_2O_3–TiO_2 heterojunction. Much effort has been made to prepare α-Fe_2O_3–TiO_2 composites by other researchers [11–18]. However, considering that most photocatalytic processes are conducted in solutions, separating them from a large volume of solution becomes difficult. This is another drawback of the practical use of TiO_2. At this point, magnetic separation provides a convenient approach to introduce magnetic components into TiO_2 particles-based catalysts [19]. Therefore, the obtained magnetic α-Fe_2O_3@TiO_2 particles are both highly photoactive and effective for separation. Recently, Xia et al. synthesized α-Fe_2O_3@TiO_2 nanocomposites with core–shell structure via the hydrothermal reaction route. Using the α-Fe_2O_3 spindle as a hard template displays improved photocatalytic degradation activity for Rhodamine B dye. The as-prepared particles were etched with HCl solution before photocatalytic experiments [20]. Amarjargal et al. prepared a nanosheet-based α-Fe_2O_3 hierarchical structure decorated with TiO_2 nanospheres via post annealing treatment. The samples presented enhancement of photocatalytic activity [21]. It can be seen that this issue has got enough attention by other researchers. On the basis of the above consideration, the obtained composites which were doped by proper amount of hematite (samples A–C) exhibited better photocatalytic activity than P25 at the same photocatalytic experiment conditions. And

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http://dx.doi.org/10.1016/j.jallcom.2015.09.140
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the approach in this paper for the preparation of α-Fe_2O_3@TiO_2 nanocomposites has more advantages in cost, conditions and is more environmental friendly.

2. Materials and methods

2.1. Materials and chemicals

Carbamide ($(NH_2)_2CO$, AR), iron nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, AR), ammonium hydroxide ($NH_3 \cdot H_2O$, 25 wt.%, AR) and citric acid solution ($C_6H_8O_7$, AR) were purchased from Beijing Chemical Works; Titanium sulfate ($Ti(SO_4)_2$, CP) and ferric chloride ($FeCl_3$, CP) were purchased from Sinopharm Chemical Reagent Co., Ltd; Methyl orange ($C_{14}H_{14}N_3NaO_3S$, MO) and ferrous chloride ($FeCl_2 \cdot 4H_2O$, AR) were purchased from Shantou Xilong Chemical Factory, Guangdong; Polypropylene acid (PAA, AR) and absolute ethanol (CH_3CH_2OH, AR) were purchased from Tianjin Tiantai Fine Chemicals Co., Ltd. All the materials were used as received.

2.2. Preparation of magnetic Fe_3O_4 and α-Fe_2O_3

The coprecipitation method was chosen to prepare magnetic Fe_3O_4 particles. Typically, 1215 mg of $FeCl_3$ and 745 mg of $FeCl_2 \cdot 4H_2O$ were dissolved in 200 mL of distilled water with vigorous stirring. The color of the solution immediately turned black after 10 mL of ammonium hydroxide was added rapidly into the mixture solution. Then 5 mL of citric acid solution (2 mg/mL) was added rapidly into the solution. The temperature of the mixture solution was increased and kept at 80 °C for 30 min, and finally, the solution was naturally cooled. The whole process was under nitrogen atmosphere. Then the obtained black Fe_3O_4 powders were separated by a magnet and washed with distilled water and ethanol, followed by drying in oven at 60 °C. Synthesis of the α-Fe_2O_3 particles was as follows. PAA colloidal aggregates were prepared firstly. Typically, 360 mg of PAA was dissolved in 12 mL of ammonia hydroxide and mixed with 180 mL of absolute ethanol at room temperature. Then 2018 mg of iron nitrate was added into the PAA colloidal solution with vigorous stirring. After 4 h, composites were collected by suction filtration and dried at 60 °C. Composites were heated at 400 °C for 3 h subsequently in order to remove the polymeric templates and obtain α-Fe_2O_3 particles.

2.3. Preparation of magnetic α-Fe_2O_3@TiO_2 composites

Magnetic α-Fe_2O_3@TiO_2 composites were synthesized by the following method. Firstly, $Ti(SO_4)_2$ was dispersed in 120 mL of distilled water with ultrasonic stirring. Secondly, $(NH_2)_2CO$ was added into the solution, followed by the addition of 80 mL of distilled H_2O. The concentration of the titanium source was 20 mmol/L. The relative molar ratio (Mr) of $(NH_2)_2CO$ to $Ti(SO_4)_2$ was always 16. Thirdly, 100 mg of Fe_3O_4 was added into the mixed solution under stirring in the air. After 4 h, different amounts of α-Fe_2O_3 particles were added into the mixed solution. At last, the mixture solution was maintained at 90 °C for 2 h under stirring in the air. Afterwards, the products were collected by a permanent magnet and washed with distilled water and ethanol. Samples with different amount of α-Fe_2O_3 were named as samples A–E, namely, 1%, 5%, 10%, 15%, and 0% respectively. The percentage was the mass percentage which was the mass of α-Fe_2O_3 relative to the total quality of Fe_3O_4 and TiO_2. Preparation conditions of the samples are listed in Table 1.

2.4. Photocatalytic experiments

The photocatalytic activity of the sample was investigated by monitoring the degradation of methyl orange (MO) in the liquid phase. In a typical procedure, 100 mg of samples was dispersed in an MO aqueous solution (150 mL, 10 mg/L). Then the photocatalytic reaction was induced by a 500 W mercury lamp. The luminous range of the lamp includes the UV light region and the visible light region. At given irradiation time intervals (10 min), a series of aqueous solution (2 mL) were sampled. Then the UV–vis absorption spectrum of the solution was measured to evaluate the concentration of MO. The whole experiment time was 90 min. The final degradation rates were obtained afterwards (in Table 1). The calculation method of the final degradation rate was with reference to other researchers' work [22]. Specifically speaking, first, align the absorption spectra according to baseline. Second, measure the intensity of the characteristic peak at given time points (every 10 min). Finally, calculate the final degradation rate of methyl orange by the samples according to the formula. The formula is $C = (1-B/A)^*100\%$, where A represents the initial intensity of the characteristic peak. B is the intensity of the characteristic peak at subsequent time points. C represents the final degradation rate of methyl orange by samples at time points in correspondence with B.

2.5. Characterization apparatus and methods

The phases of the specimens were identified by X-ray diffraction (XRD) using Cu Kα radiation (Rigaku-D-Max νA; $\lambda = 0.15418$ nm) within an angular range of 10°~90° with an increment of 0.02° on the 2θ scale at room temperature. Transmission Electron Microscopy (TEM) images were taken on JEM-2200FS transmission electron microscope. The valence states of Fe and Ti in the samples were obtained by X-ray Photoelectron Spectroscopy (XPS). XPS was performed on thermo ESCALAB *250* with an Al Kα (1486.6 eV) radiation source. Fiber optic spectrometer (AvaSpec–2048, Netherlands) was used for testing the UV–vis absorption spectrum. The magnetic properties were measured by vibrating sample magnetometer (VSM), which was calibrated by a pure nickel sphere under a maximum applied field of 20 kOe.

3. Results and discussion

3.1. XRD analysis of α-Fe_2O_3 and Fe_3O_4

Fig. 1 (a) presents the XRD patterns of Fe_3O_4, with diffraction

Table 1
Preparation conditions, the Ms and the final photocatalytic degradation rates of the samples.

Samples	$Ti(SO_4)_2$/mg	$(NH_2)_2CO$/g	Fe_3O_4/mg	H_2O/mL	α-Fe_2O_3 (%)	Ms (emu/g)	Final photocatalytic degradation rate (%)
A	600	2.4	100	200	1	23.78	99.75
B	600	2.4	100	200	5	23.98	98.91
C	600	2.4	100	200	10	35.02	91.86
D	600	2.4	100	200	15	33.79	34.28
E	600	2.4	100	200	0	43.66	68.56
P25	–	–	–	–	–		53.79