



Recyclable silver-decorated magnetic titania nanocomposite with enhanced visible-light photocatalytic activity



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ABSTRACT

We report a fabrication of rationally-designed multicomponent nanocomposites comprising a magnetite core and an outer silver-decorated anatase shell and their application for visible-light photodegradation of organic compounds. The nanocomposites exhibit a well-defined core-shell structure, superparamagnetic behavior, wide-spectrum photoresponse and markedly enhanced visible-light photocatalytic activity. The enhancement of the photocatalytic activity increases with the density of decorated Ag nanoparticles in the ternary system. More importantly, the obtained nanostructured photocatalysts could be easily collected and separated by applying an external magnetic field and reused at least eight times without any appreciable reduction in photocatalytic efficiency. The enhanced photocatalytic activity and good chemical stability, in combination with the excellent magnetic recyclability, make this multifunctional nanostructure as a promising integrated system for applications in environmental remediation.

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1. Introduction

There is a rapidly-growing demand for the development of materials with high efficiency, good reusability, and low cost to reduce the pollutant content in wastewater. To date, titanium dioxide (TiO₂, titania) has been demonstrated to be a very suitable material in pollutants photodegradation owing to its superior photocatalytic efficiency, biological and chemical inertness, strong oxidizing ability, resistance to photocorrosion, nontoxicity, and low cost [1–6]. It is well recognized that photocatalysis is an integrated process which involves photon-irradiation induced charge carrier generation, surface/interface catalytic reaction, and post-treatment or recycling of the photocatalyst [7]. However, as a single component, titanium dioxide has low capacity to utilize solar energy (no more than 5%) due to its wide band gap and high recombination rate of photogenerated hole–electron pairs. Moreover, the separa-

tion of titanium dioxide from the treated water, especially from a large volume of water, is an expensive process.

To improve the visible-light photocatalytic activity of titanium dioxide, various strategies such as doping with nonmetal and metal [9–12], dye sensitization [13–15], and coupling with other semiconductors [16–19] have been proposed to overcome these problems. In recent years, the formation of TiO₂-based composite with noble metal nanoparticle such as Au, Ag, Pt, and Pd has emerged as an effective way to improve the photocatalytic efficiency [20–22]. The decorated noble metal nanoparticles play a dual role in the photocatalytic process, including (1) the surface plasmon resonance photosensitization caused by noble metal can be utilized to harvest the visible light (accounting for 43% of solar spectrum); and (2) the formation of Schottky barrier between semiconductor and noble metal is beneficial to the separation of electron–hole pairs. Additionally, the synergistic effects induced by the components in the composite also result in an increased photostability and photocatalytic efficiency. Among all the noble metals, Ag is promising for extensive application because of its lower cost, inherent antibacterial activity, and facile preparation [23]. A number of binary Ag–TiO₂ composites have been designed and synthesized [24–27]. However; it is difficult to recycle these

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photocatalysts. Recycling of the photocatalyst is another important task for practical applications in aqueous environments, which allows for multiple reuses, cost reduction and additional contamination prevention.

Recently, magnetic titanium dioxide nanocomposites with core-shell structure have gained increasing attention, as they can integrate both the advantages of magnetic recovery and the superior photocatalysis performance [28]. These materials can be fast and easily removed and recycled with the help of an external magnetic field, thus preventing the loss of the catalysts during recovery and increasing the durability of the catalysts. Fe_3O_4 nanoparticles are often selected in core-shell magnetic titania nanocomposites because of their unique magnetic properties and variable surface properties [29]. To immobilize TiO_2 with Fe_3O_4 nanoparticles, direct way and indirect way with an intermediate layer between them are often used, and high-temperature calcinations are usually applied for further formation of crystalline TiO_2 . However, the magnetic characteristic of the composite catalysts will be significantly influenced by multilayer coating and high temperature calcinations, thus affecting the efficiency of recyclability [30,31]. Therefore, an approachable way to deposit crystalline TiO_2 on to the magnetic nanoparticles at relatively low temperature is highly desired.

Although much effort has been devoted to optimizing the aforementioned concerns, including extension of the light absorption range, increasing charge-separation efficiency, enhancing recyclability, and integration of all these factors [32–34], it still remains a grand challenge to address these problems simultaneously and integrate distinct multiple functional components into one uniform unit at the nanoscale to maximize the photocatalytic efficiency. Herein, we report the design and fabrication of well-defined core-shell silver-decorated magnetic titania nanocomposites as a highly efficient visible-light photocatalysts with excellent magnetic recoverability, which are easy to synthesize at a relatively low temperature. The prepared nanocomposites possess multicomponent structures and multifunctional features. The morphological, structural and physical behaviors of these nanocomposites have been demonstrated and discussed. Their photocatalytic performance and reusability was evaluated using the degradation of Rhodamine B as a model system.

2. Experimental details

2.1. Materials

Iron (III) chloride hexhydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), anhydrous sodium acetate (NaAc), ethylene glycol, trisodium citrate dehydrate, silver nitrate, sodium borohydride, and titanium (IV) *n*-butoxide (TBOT, $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$) were purchased from Sigma-Aldrich. Rhodamine B (RhB) was purchased from Alfa Aesar. Anhydrous ethanol was purchased from International Scientific Pte Ltd. Aqueous ammonia solution (28 wt.%) was purchased from Emsure. Acetonitrile was purchased from TEDIA. Analytical grade solvents and compounds were used without further purifications for preparation. Deionized water was used for all experiments.

2.2. Synthesis of magnetic nanoparticles (Fe_3O_4)

The spherical magnetic particles were prepared through a solvothermal reaction. Typically, 1.35 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 3.6 g of NaAc, and 0.40 g of sodium citrate were dissolved in 40 mL of ethylene glycol. The mixture were stirred vigorously for 30 min to form a homogeneous yellow solution and then transferred into a 50 mL Teflon-lined stainless-steel autoclave. The autoclave was heated at 200 °C and maintained for 16 h; then it was cooled to room tem-

perature. The product was centrifuged, washed repeatedly with ethanol and distilled water, and then dried in vacuum at 60 °C overnight.

2.3. Synthesis of magnetic titania nanocomposites (MTN)

The MTN was synthesized following the procedure in the literature with some modifications [35]. Briefly, 0.05 g of the as-prepared magnetite nanoparticles were well dispersed in a mixed solvent containing ethanol (75 mL), acetonitrile (25 mL), and concentrated ammonia solution (0.5 mL, 28 wt%). Then a solution of TBOT (1 mL) in ethanol (15 mL) and acetonitrile (5 mL) was added dropwise to the solution under vigorous stirring. After reaction for 1.5 h, the products were centrifuged, washed repeatedly with ethanol and acetonitrile and dried in vacuum at 60 °C overnight, denoted as $\text{Fe}_3\text{O}_4@ \text{TiO}_2$. Next, the obtained $\text{Fe}_3\text{O}_4@ \text{TiO}_2$ nanocomposites were redispersed in a mixed solvent containing ethanol (40 mL) and deionized water (20 mL). The mixture was then transferred to a Teflon-lined stainless-steel autoclave (capacity of 100 mL). The autoclave was heated at 160 °C and maintained for 20 h. Finally, the mixture was cooled to room temperature, and the products were centrifuged, washed repeated with ethanol, and dried in vacuum at 60 °C overnight.

2.4. Synthesis of silver-coated magnetic titania nanocomposites (SMTN)

The SMTN was synthesized by using NaBH_4 as the inducer. First, MTN (0.1 g) was well-dispersed into an aqueous solution (20 mL) containing AgNO_3 and trisodium citrate ($C/C = 1:1$) and stirred vigorously for 30 min. Then a 0.01 M solution of NaBH_4 (0.6 mL) was added dropwise into the above solution and mechanically stirred for 24 h. The SMTN were obtained by centrifugation (8000 r/min) for 10 min, rinsed with water twice, and dried in vacuum at 60 °C for 24 h. A series samples with different Ag loadings (0.2, 0.4, 0.8, 1, 1.2, 1.4 wt.%) were prepared, denoted as SMTN-X ($X = 0.2, 0.4, 0.8, 1, 1.2, \text{ and } 1.4$).

2.5. Characterization

Transmission electron microscopy (TEM) images were taken with a JEM-2010 transmission electron microscope made by Japanese JEOL Company. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker on a Rigaku D/MAX 2500 diffractometer with Ni-filtered Cu K radiation (40 kV, 40 mA). Energy-dispersive X-ray spectroscopy (EDX) was used for analysis of the element distribution. The nitrogen adsorption and desorption isotherms were measured by a Nova 2200 analyzer. Before measurements, the samples were degassed in a vacuum at 150 °C for 4 h. Surface areas were calculated by the Brunauer–Emmett–Teller (BET) method, and the pore volume and pore size distributions were calculated using the Barrett–Joyner–Halenda (BJH) model. Magnetization measurements were performed on a MPM5-XL-5 superconducting quantum interference device (SQUID) magnetometer at 300 K. The content of Ag in SMTN was measured using an inductively coupled plasma (ICP) spectrometer (Perkin-Elmer). The optical properties of the samples were measured with a Shi-madzu UV-2600 UV-vis spectrophotometer. All spectroscopic measurements were performed in at least triplicate.

2.6. Measurement of photocatalytic activity

The photocatalytic activity was tested by examining the degradation of RhB in an aqueous solution. Ultraviolet (UV) light was illuminated by a 50W high-pressure mercury lamp. Visible light and simulated solar light were illuminated by a Xe lamp with a

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