Magnetic nanocomposite based on titania–silica/cobalt ferrite for photocatalytic degradation of methylene blue dye

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Abstract

Magnetic photocatalysts were successfully prepared by coating titania–silica (TiO_2–SiO_2) on cobalt ferrite ($CoFe_2O_4$) nanoparticles. A simple organic acid precursor method was employed to prepare the magnetic part, while the TiO_2–SiO_2 was synthesized and coated onto $CoFe_2O_4$ by the sol–gel technique. Controlling the modification process of TiO_2–SiO_2 with $CoFe_2O_4$ nanoparticles is a key factor for obtaining appropriate catalytic performance. Under optimized conditions, a core–shell structure could be obtained in which $CoFe_2O_4$ is a core while TiO_2–SiO_2 forms a shell. The current photocatalyst exhibits remarkable catalytic activity for the degradation of methylene blue dye in water under UV irradiation. It was demonstrated that the catalyst could remove as high as 98.3% of the organic dye in just 40 min. The degradation efficiency was found to depend essentially on initial dye concentration, solution pH and the catalyst loading. The as-synthesized catalyst was characterized by different techniques including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy and N_2 adsorption–desorption isotherm. The photocatalyst could be removed from the reaction mixture and its recyclability remains effective and active after six cycles.
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Keywords: A. Sol–gel processes; B. Nanocomposites; C. Magnetic properties; D. TiO_2

1. Introduction

Surface coating of nanoparticles with various materials to form core–shell morphologies is often used for development of catalysts and the optoelectronic devices [1–3]. Core–shell structures have been used as precursors to prepare hollow structures by the complete removal of core materials through chemical etching or combustion, and partial elimination of the core have enabled preparation of novel nanostructures inside the shell [4–6]. However, semiconductor photocatalysts have

recently attracted much interest due to the potential applications of detoxification of environmental pollutants [7,8]. Particularly, the importance of degradation of organic contaminations using semiconductors photocatalysts has stimulated wide efforts to develop methods for their synthesis and characterization, making this area of study an integral part of photocatalysis [9–12].

Among the photocatalysts, titania (TiO_2) is the widely used semiconductor material because of its superior photoreactivity, nontoxicity, long-term stability, and low price. The photocatalytic activity of TiO_2 depends on various parameters, including crystallinity, impurities, surface area, and density of surface hydroxyl groups. Generally, TiO_2 could be used as a photocatalyst in both anatase and rutile crystal structures. Anatase phase has a much higher activity than rutile [13]. Nanocrystalline anatase has been used for degradation of

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undesirable organics in air or liquid phase [14,15]. Further, TiO_2 slurry is the frequently applied method to deal with pollutants in water due to its high specific surface area and good dispersion [16]. However, the use of TiO_2 slurry is still limited due to the difficulty to separate TiO_2 particles from the treated water [17]. One way to enhance the separation of catalyst is mixing TiO_2 with silica (SiO_2) as a support to increase the surface area, improve the photocatalytic activity and facilitate the separation and recovery of the catalyst [18]. Another strategy to overcome the separation limitation of catalyst is to modify the TiO_2 surface by depositing them onto magnetic nanoparticles [19–22].

Among the magnetic particles, spinel ferrite structures (AFe_2O_4) (where A is a divalent cation: Mn, Cu, Co, Mg, Co, Ni, Fe …etc.) have been coated with TiO_2 to synthesize magnetic nanocomposites to enhance the recovery of the catalyst and re-use it for several times from the treated water by applying an external magnetic field [23–25]. The popular magnetic material is the ferrite, because of its strong ferromagnetism and ease of preparation [26–28]. Chung et al. [29] synthesized a magnetic photocatalyst of nickel ferrite ($NiFe_2O_4$) coated with TiO_2 or TiO_2–SiO_2, by a multi-step ultrasonic spray pyrolysis with an aim to obtain a core–shell structure. However, a non-uniform coating on the surface of the magnetic cores was obtained; instead they formed patches on the surface, which resulted in decreasing the recycling of the magnetic photocatalyst. Zhang et al. [30] prepared a magnetic photocatalyst of titania coating on silica and modified with cobalt ferrite. They prepared the photocatalyst via hydrolysis and condensation of water-soluble titanium bis-ammonium lactato dihydroxide at low temperature and employed the catalyst for the degradation of methyl orange. However, neither the factors affecting the photodegradation process nor the recyclability of the photocatalyst was investigated.

The aim of the present work is to provide a solid base of knowledge for the synthesis of well defined nanocomposites based on TiO_2–SiO_2/$CoFe_2O_4$ that have remarkable photocatalytic activity together with superior magnetic properties. The as-synthesized magnetic photocatalyst is applied for the degradation of methylene blue (MB) dye in aqueous solutions as a model pollutant. Results of catalyst synthesis and characterization and its catalytic performance evaluation are thoroughly addressed and discussed in this paper.

2. Experimental

2.1. Catalyst synthesis

The applied procedure for the synthesis of TiO_2–SiO_2/$CoFe_2O_4$ magnetic photocatalyst is schematically depicted in the flowchart of Fig. 1. Cobalt ferrite nanoparticles were firstly prepared using aqueous solutions of $FeCl_3 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ with a molar ratio $Fe^{3+}:Co^{2+}=2:1$ in presence of oxalic acid according to our earlier work [31]. The solution was stirred and evaporated at 80 °C until a clear, viscous gel was obtained, and then dried at 110 °C for 24 h. The powder was then calcined in air at 1000 °C for 2 h. Synthesis of $CoFe_2O_4/TiO_2$–SiO_2 nanocomposites were
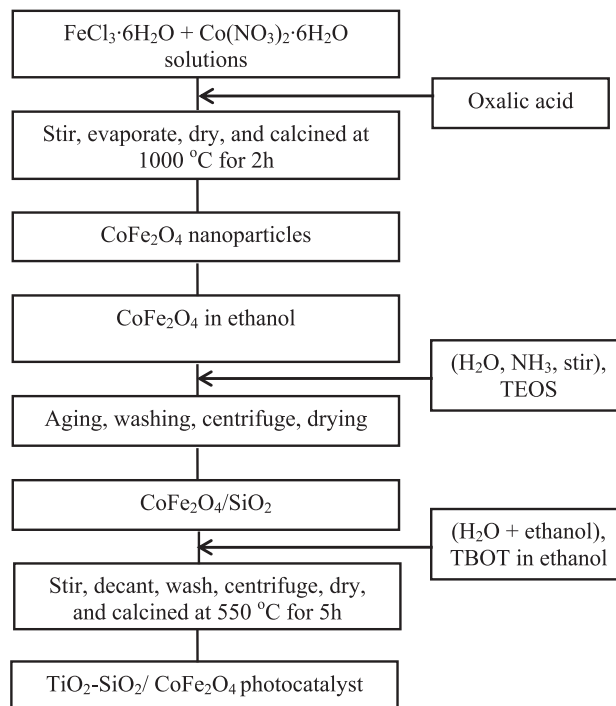
Fig. 1. Schematic flowchart for the preparation of TiO_2–SiO_2/$CoFe_2O_4$ magnetic photocatalyst.

then conducted via a two steps as follows. *First step*: coating of $CoFe_2O_4$ with silica via dispersing $CoFe_2O_4$ powder in absolute ethanol followed by adding the amount of H_2O required for the hydrolysis process and stirring for 10 min. Ammonia solution was then added to the mixture under vigorous stirring for another 10 min. A stoichoimetric ratio from tetraethyl orthosilicate TEOS ($Si(OC_2H_5)_4$) was dropped into the above solution. The solution was consequently aged for 5 h for a complete precipitation of silica. The product was washed using water and ethanol, then centrifuged and dried at 60 °C for 24 h in an oven. *Second step*: coating the Co-ferrite/SiO_2 with TiO_2. The product of first step (0.125 g) was dispersed in 25 ml ethanol in an ultrasonic bath for 30 min. at a temperature 20 °C, transferred the dispersion to a mixture of ethanol and water, 35 ml+25 ml, respectively. An amount of TBOT (titanium (IV) butoxide, $C_{16}H_{36}O_4Ti$) in 40 ml of ethanol is then transferred dropwise to the above mixture. The solution was kept under vigorous stirring for 3 h at room temperature, followed by a decantation overnight. The final product was then washed by water and ethanol, centrifuged and dried for 2 days at 60 °C in an oven, followed by calcination at 550 °C for 5 h. The choice of calcination temperature and time is selected accordingly to our previous report [32].

2.2. Catalyst characterization

The as-produced catalysts were evaluated and characterized using different techniques. The phase and crystal structure of the catalysts were obtained using X-ray powder diffraction (XRD) using a model Bruker axis diffractometer (D8-ADVANCE) with Cu Kα radiation, operating at 40 kV and 30 mA with a rate of 2°/min. X-ray photoelectron spectroscopy