



Fabrication of the magnetic manganese dioxide/graphene nanocomposite and its application in dye removal from the aqueous solution at room temperature



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ABSTRACT

A novel ternary magnetic manganese dioxide/graphene compound (Fe₃O₄/MnO₂@G) was fabricated by a facile and eco-friendly co-blending method with ultrasound assistance. Characterizations show Fe₃O₄ nanoparticles and MnO₂ nano branches were assembled with graphene flakes without any phase change. High degradation activity is observed with a discoloration efficiency of 71.67% after 10 min after using this compound in the degradation of methylene blue dye at room temperature. Furthermore, magnetic property of the compound is helpful in the separation process and recycling of the material.

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1. Introduction

Treatment of the dye wastewater, which is harmful to the environment and the human health, is significantly important [1,2]. Many researchers have been working on the nanoparticles for dye degradation. Among them, the cost-effective and non-toxic MnO₂ nanoparticles, as the catalyst in removing pollutants from the wastewater, have been extensively developed [3–6]. Graphene is a good candidate as a carrier with an impressive surface area and the remarkable electrical properties [7–9]. The development of the fabrication of the graphene–MnO₂ hybrid materials is still in progress. Different morphologies and crystal forms of the MnO₂ nanoparticles have been assembled by using graphene or graphene oxide (GO) [10–13]. The synergistic effect is outstanding, which makes them potential for the substitute of the conventional catalysts.

Conventional methods for synthesis of such compounds involve complex and expensive separation processes such as multiple filtration stages and high-speed centrifugation [14,15]. These are the key obstacles for their practical applications. Therefore, finding an effective approach to separate and recover catalysts for recycling is significantly important. Magnetic separation, an emerging water treatment technology, exhibits high separation

efficiency and relatively low operating costs. Therefore, synthesis of magnetic composite catalysts, such as Fe₃O₄-based materials, is the foundation for separation [16].

In previous studies, graphene/Fe₃O₄ and Fe₃O₄/MnO₂ composites were prepared and used to remove the dye pollutants and the other hazardous substances. Santhosh et al. have synthesized graphene–Fe₃O₄ composites, which can be effectively utilized for the removal of various heavy metal ions and organic dyes [17]. Qin et al. have prepared Fe₃O₄-reduced graphene oxide composite by an *in situ* co-precipitation and investigated Rhodamine B adsorption performance [18]. Zhang et al. have synthesized reduced graphene oxide nanosheets decorated with tunable magnetic nanoparticles for removal of biphenol A [19]. Liu et al. have prepared Fe₃O₄ nanoparticles-decorated reduced graphene oxide magnetic composites as catalysts for methylene blue (MB) degradation [20]. Zhao et al. have reported one pot synthesis of tunable Fe₃O₄–MnO₂ core-shell nanoplates for water purification [21]. However, catalytic efficiency of Fe₃O₄-based nanomaterials is still difficult to be satisfied.

Here, one type of ternary magnetic compounds was fabricated by a co-blending approach with the ultrasound assistance. The Fe₃O₄/MnO₂@graphene nanocomposite (Fe₃O₄/MnO₂@G) was constructed using the graphene flakes as the template and Fe₃O₄/MnO₂ as the blending agents. The new nanocomposite shows a high degradation activity and easy separation and recyclability. These nanocomposites may become promising materials in the dye wastewater treatment.

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2. Experimental

2.1. Materials and reagents

Natural graphite flakes (500 meshes) were purchased from Shanghai Yifan Graphite Ltd., China. Potassium permanganate (KMnO_4), potassium nitrate (KNO_3), ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), polyethylene glycol (PEG200), peroxide (H_2O_2 , 30 wt%), ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28 wt%), concentrated sulfuric acid (H_2SO_4 , 98%), hydrochloric acid (HCl , 1 mol L^{-1}) and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All the chemicals are of analytical grade, which are used without further purification. Water used was distilled and purified by a Milli-Q system.

2.2. Synthesis of GO powder

The GO powder was prepared according to a modified Hummers method [22,23]. Briefly, natural graphite (1.0 g) and KNO_3 (1.2 g) were added into H_2SO_4 (46 mL) and stirred in an ice bath for 10 min. Then, KMnO_4 (6.0 g) was slowly added and maintained at 50 °C for 6 h. Followed by adding 80 mL of water, the reaction was kept at 80 °C for 30 min. Then, 6 mL of H_2O_2 was slowly added and the solution was washed with diluted HCl and water repeatedly. After drying at 60 °C overnight, the brown powder was dispersed in water by ultrasonic method for 90 min to form a homogeneous brown suspension. The GO powder was obtained by freeze-drying for 5 h.

2.3. Synthesis of MnO_2 nano branches

The MnO_2 nano branches were obtained by calcination of the MnOOH precursor [24]. At first, to synthesize MnOOH precursor, 0.050 g of KMnO_4 was dissolved in 25 mL of water and stirred at room temperature. Then, 2 mL of PEG200 was added and stirred for another 30 min. The obtained solution was transferred into a Teflon-lined stainless steel autoclave (30 mL) and heated to 160 °C for 12 h. After cooling to room temperature, the precipitate was filtered, washed with water and ethanol for three times, respectively, and vacuum-dried at 60 °C for 12 h. Finally, the brown MnOOH precursor was turned into black MnO_2 nano branches after heating in a furnace at 350 °C for 240 min.

2.4. Synthesis of Fe_3O_4 nanoparticles

The Fe_3O_4 nanoparticles were prepared by a coprecipitation method [25]. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.20 g) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.08 g) were dissolved in water (100 mL). Then the mixture was heated to 50 °C and ultrasound for 60 min by addition of 10 mL of ammonia under N_2 flow. The obtained black solid were separated by a magnet, washed with water for three times, and dried at 30 °C for 12 h under vacuum state.

2.5. Synthesis of $\text{Fe}_3\text{O}_4/\text{MnO}_2@G$ nanocomposite

In a typical reaction, the as-prepared GO powder (0.04 g) was re-dispersed in water (50 mL) using ultrasonic agitation for 90 min. Then, Fe_3O_4 (0.04 g) and MnO_2 powder (0.015 g) were added to the dispersion and the system was agitated by ultrasonic method for another 70 min. The as-prepared mixture was then transferred to a Teflon-lined autoclave (80 mL) and maintained at 100 °C for 5 h. After cooling to room temperature, the solid was obtained by filtration, and was washed and then was dried in a vacuum oven at 35 °C for 12 h.

2.6. Characterization

The morphologies the as-prepared samples were characterized by field-emission transmission electron microscopy (TEM, Tecnai G2 F20, FEI). All samples were dispersed in ethanol by an ultrasonic bath for 15 min and were dropped onto the carbon holey grid for tests. X-ray powder diffraction (XRD) was conducted on D/max-2500 (Rigaku, Japan) using $\text{Cu K}\alpha$ radiation ($\lambda = 0.1542$ nm) with a scanning speed of 2° min^{-1} , operating at 40 kV and a cathode current of 30 mA. X-ray photoelectron spectroscopy (XPS) patterns were obtained on a Thermo Escalab 250 with a monochromatic $\text{AlK}\alpha$ source. All the binding energies were referenced to the C1s peak at 284.8 eV. The magnetization curves were recorded on a magnetometer (MPMS XL-7, Quantum Design) with a magnetic field of ± 20 KOe at room temperature.

2.7. Application in dye removal from the aqueous solution

In a typical reaction, the as-synthesized $\text{Fe}_3\text{O}_4/\text{MnO}_2@G$ nanocomposite (40 mg) and H_2O_2 (20 mL) were added into the methylene blue (MB) dye solution (100 mL, 65 mg L^{-1}) at room temperature under continuous ultrasonic vibration (420 W). At different time intervals, 5 mL aliquots of the suspension were taken out and diluted with water and the solid catalyst was removed by a magnet. The absorbance intensities at the maximum absorption wavelength (664 nm) were recorded on a UV-vis spectrophotometer (UV, 1901, Youke, China). The discoloration efficiency of MB dye solution was calculated from the following equation:

$$\eta (\%) = (A_0 - A_t) / A_0 \times 100$$

where η , A_0 and A_t represent the discoloration efficiency in %, the initial concentration and the concentration at different time intervals, respectively.

3. Results and discussion

Fig. 1 shows the three stages that are included in the process: (1) preparation, (2) catalytic reactions and (3) separation and regeneration of $\text{Fe}_3\text{O}_4/\text{MnO}_2@G$ nanocomposite. The magnetic and highly efficient nanocomposite was obtained by a simple co-blending process. The separation of the catalyst from the reaction systems can be easily performed by a magnet. In the novel nanocomposite, the Fe_3O_4 nanoparticles act as the magnetic source, MnO_2 nano branches act as the main catalyst and the graphene flakes act as the main adsorbent. More importantly, the synergistic effect is remarkable. The combination of the Fe_3O_4 nanoparticles and the MnO_2 nano branches prevents the graphene flakes from agglomeration. Moreover, the Fe_3O_4 nanoparticles act as the co-catalyst to accelerate the reaction rates and the MnO_2 nano branches act as the co-adsorbent to improve the adsorption capacity. Graphene flakes provide more electron channels over the whole composite to enhance the electrical conductivity. Therefore, it demonstrates high catalytic activity for the removal of the MB dye from aqueous solution.

TEM studies were used to reveal the morphology of the materials, Fig. 2. It is shown that the three-dimensional branched-shape structure of the MnO_2 (Fig. 2(a) and (b)) has different number of branches with a branch ranging from 500 nm to several microns, which is effective for agglomeration prevention of graphene. Combined HRTEM and SEAD patterns (Fig. 2(c) and (d)), the dispersed Fe_3O_4 nanoparticles (~ 20 nm on an average) have a good crystal structure and a tendency for agglomeration. In as-synthesized $\text{Fe}_3\text{O}_4/\text{MnO}_2@G$ nanocomposite (Fig. 2(e)), the Fe_3O_4 nanoparticles and the MnO_2 nano branches are assembled with the graphene flakes randomly. The graphene flakes was self-assembled in a layered structure with MnO_2 nano branches embedded between

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