



In situ fabrication of Mn₃O₄ decorated graphene oxide as a synergistic catalyst for degradation of methylene blue



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ABSTRACT

Herein we report a one-step approach to the highly efficient synthesis of graphene oxide/Mn₃O₄ (GO/Mn₃O₄) hybrids with superior catalytic activities for decomposition of methylene blue (MB) in water. This method exploits the pristine graphene oxide/manganese sulfate (GO/MnSO₄) suspension produced by the modified Hummers method as the raw materials, in which GO/MnSO₄ has been *in situ* converted into GO/Mn₃O₄ hybrid in combination with KOH and air. This atom-economic reaction produces only K₂SO₄ crystal as the by-product which meets the standard of green chemistry. For catalytic degradation of MB dye at room temperature, the as-prepared GO/Mn₃O₄ catalysts result in a significant enhancement in the reaction rate compared to that of the bare Mn₃O₄ particles with the assistance of H₂O₂. Typically, 50 mL of MB (50 mg L⁻¹) can be 100% decolorized and 77% mineralized with 10 mg of the GO/Mn₃O₄ hybrid. Such excellent catalytic performance of the GO/Mn₃O₄ hybrid is mainly attributed to the synergistic effects of GO, Mn₃O₄, H₂O₂ and MB molecules. Based on the hydroxyl radical experiments, the catalytic activity of GO/Mn₃O₄ hybrids for degradation of MB is closely related with the amount of the reactive •OH species generated from H₂O₂.

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1. Introduction

The increasing amounts of wastewater containing toxic and hazardous organic compounds are generated by various industrial processes, which have caused severe problems to the environment. Tremendous efforts have been dedicated to alleviate the deterioration in water body around the world. Manganese oxide (MnO_x, $x = 2, 3/4$), a non-toxicity and low cost metal oxide has been widely used as a catalyst for oxidation of organic compounds. However, MnO_x particles often suffer from aggregation as well as poor stability, which devastate their catalytic efficiency [1–3]. The combination of MnO_x ($x = 1, 2, 4/3$) and carbon materials should be an alternative way to address above problems. Particularly, graphene with good stability, large surface area and unique electronic property provides a promising candidate [4–6]. Recently, graphene oxide (GO) produced by modified Hummers method has been widely

selected as the precursor to produce graphene/MnO_x composites [7–11]. Typically, GO from Hummers method involves formation of a mixture suspension containing GO, K₂SO₄, MnSO₄ and H₂SO₄ by intercalation and oxidation of graphite with H₂SO₄ and KMnO₄, followed by a fussy process to separate these compounds from GO. This separation process is time consuming and results in the waste of K₂SO₄, MnSO₄ and H₂SO₄. Inspired by the high content of Mn²⁺ in the mixture before separation, a highly atom-economic method has been suggested to produce reduced graphene oxide/MnO₂ from the mixture instead of GO suspension [12]. The obtained materials exhibited ultrafast decomposition of methylene blue (MB) dye at 50 °C in the presence of H₂O₂. In spite of our efforts, a large amount of toxic and highly corrosive H₂SO₄ generated during the synthesis process still represents a menace to the environment. Furthermore, the MB decolorization degree of the RGO/MnO₂ was 100% in 5 min at 50 °C but only 86% in 200 min at room temperature. The low catalytic performance of the RGO/MnO₂ at room temperature was partly ascribed to the irreversible agglomeration of graphene because of its hydrophobic nature in water.

GO, one of the most important derivative of graphene, consists of a hexagonal ring-based carbon network with both

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sp²- and sp³-hybridized carbon atoms. This carbon material has multiple oxygen-containing functional groups, such as hydroxyls and carboxylic acid groups bearing on its basal planes and edges. Previous study has showed that GO sheets are highly negatively charged when dispersed in water, apparently as a result of ionization of the carboxylic acid and phenolic hydroxyl groups [13,14]. Thus electrostatic repulsions between GO sheets eventually facilitate their dispersion in water. Furthermore, the negatively charged surfaces of GO are benefit to remove cationic dyes by electrostatic attraction when it is used as an adsorbent [15]. Except for the charged surfaces, GO is a layered material that can be intercalated or exfoliated by small molecules. These exfoliated GO sheets with suitable surface areas can be used as ideal support materials to load metal or metal oxide particles, resulting in the composites to be good catalysts for the removal of environmental pollutants [7,16–24]. Recently, several groups reported on the synthesis of GO/TiO₂ composites and their application in photocatalytic degradation of various dyes [18,21,25,26]. For instance, Shi et al. demonstrated that GO/Co₃O₄ composite was a synergistic catalyst to degrade Orange II by advanced oxidation technology based on sulfate radicals [27]. GO/CdS composites also showed high efficiency in photodegradation of various water pollutants under visible light irradiation [20]. These studies reveal that the GO may be promising support materials to separate pollutants from wastewater. However, the application of GO as a catalyst support is still scarce, and the synergistic effects between GO, catalyst and dye pollutants are not studied in detail.

Herein, we present a one-step method to fabricate GO/Mn₃O₄ composites which can highly effective decomposition of MB with the assistance of H₂O₂. GO/MnSO₄ suspension produced by the modified Hummers method has been converted into GO/Mn₃O₄ hybrid *in situ* in combination with KOH and air. Compared with our previous report about RGO/MnO₂ catalysts [12], we get more advantages in this work as followed: (1) toxic and highly corrosive H₂SO₄ produced from Hummers method is eliminated during the atom-economic synthesis of GO/Mn₃O₄ composites; (2) the chemical reduction of GO into graphene is avoided; (3) Mn₃O₄ nanoparticles are distributed on GO sheets to avoid the restacking of GO as well as the agglomeration of Mn₃O₄; (4) good hydrophilicity of GO toward aqueous solution and electrostatic attractions existed in between GO and MB are favorable to the catalytic reaction; (5) MB dye is decomposed at room temperature; (6) excellent contact between Mn₃O₄ nanoparticles and GO sheets enhances the durability of GO/Mn₃O₄ composites. As expected, the resulting GO/Mn₃O₄ composites exhibit higher catalytic efficiency than that of bare Mn₃O₄ when MB dye is used as a test probe.

2. Experimental

2.1. Synthesis of GO/Mn₃O₄ composites

The pristine GO/MnSO₄ suspension was synthesized from natural graphite powder based on a modified Hummers method according to our previous work [28]. Typically, 10 mL of the homogeneous GO/MnSO₄ suspension was diluted to 100 mL and then sonicated for 1 h. An aqueous solution of KOH (2 mol L⁻¹) was added dropwise into the above solution under bubbling air and stirring until the pH value of solution reached 12. After exposure in air for 6 h, the sediment composed of GO/Mn₃O₄ was harvested by several rinse–centrifugation cycles with deionized water until the solution became neutral. The collected precipitate was fully dried at 80 °C overnight to get GO/Mn₃O₄ composites.

Composites with different mass percentages of Mn₃O₄ were synthesized as below. Two test tubes, each containing 10 mL of homogeneous pristine GO/MnSO₄ suspension, were labeled as A and B. The suspension in tube A was centrifuged at 8000 rpm for 10 min to spin down GO as precipitate and to get supernatant liquid (including MnSO₄, H₂SO₄, K₂SO₄). And diverse amount of supernatant liquid in tube A was transferred to tube B. So the GO/MnSO₄ suspensions with the different mass ratios of GO to MnSO₄ were obtained. The following processes were similar to those of GO/Mn₃O₄ synthesis. The as-synthesized samples were denoted as GO/Mn₃O₄-X, where X represented the mass percentages of Mn₃O₄ in GO/Mn₃O₄ composites. For comparison, bare Mn₃O₄ particles or GO was synthesized by a similar procedure in the absence of GO or Mn₃O₄. Furthermore, GO/Mn₃O₄-74 was reduced by glucose to produce RGO/Mn₃O₄ according to the reference [12].

2.2. Test of the catalytic activity

The catalytic performances of as-synthesized GO/Mn₃O₄ composites were evaluated with GO and Mn₃O₄ particles as the reference. The catalytic reaction was performed in a 100 mL glass beaker containing 50 mL of MB dye solution (50 mg L⁻¹), 10 mg of catalysts and 10 mL of 30 wt% H₂O₂ solution. The mixture was stirred at room temperature. For a given time interval, 4 mL of the mixture solution was centrifuged at 10,000 rpm for 10 min to get a supernatant liquid, leaving the catalysts as the precipitate. The dye concentration was determined by the peak intensity at 664 nm by UV–vis spectroscopy. Furthermore, in the stability tests of GO/Mn₃O₄-74 composite, the catalyst was gathered after completion of the reaction, washed, dried, and reused in a fresh solution of MB and H₂O₂. After reaction, the sample, named as GO/Mn₃O₄-74-used, was gathered for further characterization.

2.3. Analysis of hydroxyl radical (•OH)

The measurement of •OH was carried out by a similar procedure described in Ref. [29,30]. Typically, 10 mg of a certain kind of as-synthesized catalysts was dispersed in a 50 mL aqueous solution involved 5 × 10⁻⁴ mol L⁻¹ of terephthalic acid (TA) and 2 × 10⁻³ mol L⁻¹ of NaOH. Subsequently, 10 mL of 30 wt% H₂O₂ solution was added. The reactions were performed under continuous stirring at room temperature. A sample (5 mL) was removed in 5 min interval, and the catalyst was separated from the solution with centrifugation. The remaining clear liquid was used for fluorescence spectrum measurements. PL spectra of generated 2-hydroxyterephthalic acid were measured at 446 nm excited by 325 nm light.

The morphologies and structures of the as-obtained products were examined using transmission electron microscopy (TEM, Philips Tecnai G2 20), field emission scanning electron microscopy (SEM, Hitachi Ltd SU8010), powder X-ray diffraction (XRD, Rigaku D/max-2500 diffractometer with Cu K α radiation), Raman spectroscopy (JY Lab-Ram HR800), X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific Sigma Probe spectrometer), thermogravimetric analyses (TGA, Perkin-Elmer Diamond TG analyzer), UV–vis spectroscopy (Shimadzu UV-3150 spectroscope), ion chromatograph (Shimadzu, LC-10ADsp Ion Chromatograph), inductively coupled plasma emission spectroscopy (ICP, Perkin Elmer, Optima 2000DV) and photoluminescence spectra (PL, Hitachi, F-7000 fluorescence spectrophotometer), H₂ temperature-programmed reduction (H₂-TPR, Micromeritics, ChemiSorb 2720). The Brunauer–Emmett–Teller (BET) surface area of as-synthesized samples was determined by physisorption of N₂ at 77 K using a Micromeritics ASAP 2020 analyzer.

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