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Microwave-assisted hydrothermal synthesis of Mn_3O_4/reduced graphene oxide composites for efficiently catalytic reduction of 4-nitrophenol in wastewater

Hong Huang[a], Zhiyuan Zhao[a], Wenxin Hu[a], Chunyan Liu[a], Xiang Wang[a], Ziyu Zhao[a], Weichun Ye[a,b,*]

[a] *Department of Chemistry, Lanzhou University, Lanzhou 730000, China*
[b] *Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, Lanzhou University, Lanzhou 730000, China*

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ABSTRACT

We designed a microwave-assisted hydrothermal method to synthesize Mn_3O_4/reduced graphene oxide (Mn_3O_4/RGO) composites for catalytic reduction of 4-nitrophenol (4-NP), in which Mn_3O_4 nanoparticles were uniformly anchored on the surface of RGO. The catalytic activity for 4-NP reduction was directly dependent on the RGO-to-Mn_3O_4 mass ratio and the amount of the catalyst. With RGO-to-Mn_3O_4 ratio of 3/1 (G3M1), significantly enhanced activity of the Mn_3O_4/RGO composites was achieved in comparison to their individual components, which could be attributed to the synergistic effect between Mn_3O_4 and RGO. As the amount of G3M1 was 19 µg/ml, the normalized rate constant reached 556/s/g, which could be compatible to some noble metal catalysts. Considering 4-NP as a serious pollutant in industrial wastewater, the effects of various inorganic and organic compounds were further tested. It was found that these compounds had an inessential impact on the catalytic activity. Also, the composites could be conveniently handled for filtering and catalyzing and recycling with an excellent catalytic stability even in stimulated wastewater, which was of practical value for achieving regioselective oxidation into useful products.

1. Introduction

4-Nitrophenol (4-NP), as one important kind of nitrophenols, is categorized as a serious pollutant in industrial and agricultural wastewater [1,2]. A trace amount of 4-NP may cause serious health threats to human and aquatic lives due to its high toxicity and refractoriness [3]. Accordingly, United State Environmental Protection Agency (USEPA) has set the concentration of nitrophenols in natural water as less than 10 ng/L [4]. To effectively control the 4-NP pollution from effluents before its entering into surface waters, one desirable method is to convert 4-NP into useful compounds with low or no toxicity like 4-aminophenol (4-AP) in aqueous medium under mild conditions. Specifically, the reduction of 4-NP in the presence of $NaBH_4$ has been mostly studied in the manufacture of 4-AP [5,6]. 4-AP is considered as an essential intermediate compound for synthesizing various kinds of pharmaceutical and plastic product [7]. Therefore, the transformation of toxic 4-NP into beneficial 4-AP by a reduction reaction is of great significance, which can not only eliminate pollution but also produce considerable economic benefits.

Up to date, efficient reduction of 4-NP to 4-AP by $NaBH_4$ is typically based on expensive and rare noble metal nanocatalysts (Ag, Au, Pt, Pd) [8–10], which is limited for practical applications. Considerable efforts have been devoted to develop high-performance, cost-effective, eco-friendly, and noble-metal-free catalysts. For this reason, transitional metal oxides are attractive materials due to their low cost and facile preparation [11,12]. Particularly, Mn_3O_4 with the spine structure and active chemical character is widely used in field of catalytic [13]. Nowadays, various synthetic methods like chemical precipitation [14], sol–gel [15] and conventional hydrothermal synthesis [16,17] have been successfully used to prepare Mn_3O_4 nanoparticles. However, conventional heating approach is time consuming during the hydrothermal and hydrolysis process. By contrast, microwave heating can provide rapid heating rates and give the synthesized materials with homogeneous particle size distributions [18]. Furthermore, to improve the catalytic properties, attempts have been made to decorate Mn_3O_4 on carbon materials, such as graphene (or reduced graphene oxide, RGO), carbon nanotubes and active carbon. Graphene as a 2D material is a perfect support used for carrier owing to large surface

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* Corresponding author at: Department of Chemistry, Lanzhou University, Lanzhou 730000, China.
E-mail address: yewch@lzu.edu.cn (W. Ye).

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area, good electrical conductivity and mechanical stability. Simultaneously, the combination of graphene with metal oxides can prevent the agglomeration of graphene and supply more active sites for metal oxides [12,19]. In view of the advantages of Mn_3O_4 and graphene, excellent catalytic performance of the Mn_3O_4/RGO composite is expected.

In this work, the $Mn_3O_{4/}$RGO composites were synthesized *via* a microwave-assisted hydrothermal method to obtain a particle size distribution. The as-prepared composites were characterized in detail. The mass ratio of Mn_3O_4 and RGO was adjusted by changing the ratio of manganese precursor and graphene oxide (GO). The catalytic activity and stability of the Mn_3O_4/RGO composites were estimated for the reduction of 4-NP in the presence of $NaBH_4$. The effects of chemical composition and the catalyst amount on the catalytic performance were discussed. Considering the raw source of 4-NP from wastewater, we investigated the effects of interferent including inorganic and organic compounds on the catalytic activity. Even in stimulated wastewater, the Mn_3O_4/RGO composites still demonstrated excellent catalytic efficiency and stability for 4-NP reduction.

2. Experimental section

2.1. Chemicals

All reagents were of analytical grade and purchased from Sinopharm Chemical Reagent Co., China. $MnC_4H_6O_4{\bullet}4H_2O$ was purchased from Macklin Biochemical. GO was obtained from XF NANO Company (China). All the chemicals were used without further purification. Water used throughout the experiments was purified with the Millipore system (Millipore Inc., 18.2 MΩ cm).

2.2. Characterization

The samples were characterized with transmission electron microscopy (TEM TecnaiG2 F30, FEI, USA) and X-ray diffraction (XRD, Rigaku D/max-2400). X-ray photoelectron spectroscopy (XPS) was performed on a multifunctional spectrometer (Thermon Scientific) using Al K radiation. Raman spectrum was obtained on a Raman system (Zolix Finder Vista-HiR; laser excitation at 532 nm with a power of 1 mW). UV–vis absorption spectra were recorded using a UV-2102C model spectrometer.

2.3. Synthesis process of RGO/Mn_3O_4 composites

In a typical procedure, 8 ml of GO dispersion (2.0 mg/ml) was firstly added to 10 ml ethanol to acquire an optically well-dispersed solution *via* ultrasonic dispersion for 30 min. Then, different amount of $MnC_4H_6O_4{\bullet}4H_2O$ was dissolved in water. And the solution of manganese salt was slowly added into the as-obtained GO dispersion to form a uniform black solution under magnetic stirring. Additionally, 3.5 ml of ammonia (33 wt%) was dropwise added into the black solution. The mixture was transferred to a microwave reaction vessel and kept at 180 °C for 3 h (Preekem NOVA-2S). The resulting Mn_3O_4/RGO composites were collected by centrifugation and washed several times with water and dried at 80 °C overnight. Here, the RGO-to-Mn_3O_4 mass ratios were adjusted as 4/0, 3/1, 1/1, 1/3 and 0/4, respectively. The corresponding samples were donated as G, G3M1, G1M1, G1M3 and M (respectively).

2.4. Catalytic process for 4-NP reduction

The experimental process of 4-NP reduction was carried out at room temperature in a standard quartz cell with a path length of 1 cm. The aqueous solution of $NaBH_4$ (0.1 M) was freshly prepared. First, 0.4 ml of a $NaBH_4$ solution was mixed with 2.6 ml of 0.1 mM 4-NP in the quartz cell. Then, different volume of the catalysts (2 mg/ml) was added in the mixture. Immediately after that, the UV–vis absorption spectra were recorded with a time interval over the scanning range of 250–500 nm.

For the study of effect of the composition, the final concentration of the catalysts in the cell kept at 75 µg/ml; for the study of effect of the catalyst amount, the final concentration of the catalyst in the cell kept at 19, 37.5, 75 and 150 µg/ml, respectively.

For the study on the effect of interferents, a series of inorganic and organic compounds (10 mg) were added into the reaction cell. After 10 min of reaction, the reaction solution was measured at 400 nm. The catalyst was G3M1 with 75 µg/ml in the reaction cell.

The reusability of G3M1 was tested in stimulated wastewater. The stimulated wastewater is the aqueous solution containing $CaCl_2$, $MnSO_4$, $ZnSO_4$, $FeSO_4$, KH_2PO_4, $(NH_4)_2SO_4$ and glucose (0.1 mg/ml for each). The reaction solution was composed of 0.4 ml $NaBH_4$ (0.1 M), 0.3 ml 4-NP (1 mM), G3M1 as the catalyst and 2.3 ml stimulated wastewater. The final concentration of G3M1 was 75 µg/ml in the cell. After 10 min, the reaction solution was collected by centrifugation before measuring the absorbance at 400 nm. The recycled catalyst was washed several times with water and was re-dispersed in the above reaction solution for the next cycle. Here, ten successive repeated cycles for the reduction of 4-NP were performed.

2.5. Filtering and catalyzing of 4-NP based on catalytic reduction

1.0 mg G3M1 was first dispersed in 3 ml water under ultrasonication to form a uniform dispersion solution. Then, the dispersion solution was injected into a funnel to make the catalyst be loaded on a filter film. The filter film was dried in air. Finally, 30 ml of stimulated wastewater containing 0.1 mM 4-NP + 0.1 M $NaBH_4$ was slowly adding into the filter head. The wastewater passed through the filter film followed by vacuum filtering for 10 min.

3. Results and discussion

3.1. Characterization

The morphology of the Mn_3O_4/RGO composites was characterized by SEM. Pure Mn_3O_4 exhibits spherical structure while there are some agglomeration (Fig. 1A). With the increase of the RGO amount, we observed the layered graphene with the loading of Mn_3O_4 nanoparticles (Fig. 1B–D). Due to the negative charge of the GO surface, Mn^{2+} ions are easily anchored on the GO surface *via* the electrostatic interaction [20]. Thus, Mn_3O_4 with good crystallinity are successfully loaded on the surface of RGO. It can be seen that with the addition of graphene, Mn_3O_4 is well dispersed. To confirm the dispersion of Mn_3O_4 nanoparticles on graphene, TEM was further used to characterize the morphology of G3M1. It is found from Fig. 1E that small Mn_3O_4 nanoparticles with the diameter of ~40 nm grow on the flexible graphene. From high-resolution TEM (HRTEM) image (Fig. 1F), the fringe spacing of 0.309 nm is observed, which corresponds to the (112) plane of Mn_3O_4 [21]. The particles sizes of Mn_3O_4 become smaller in M. G1M3, G1M1, G3M1, which is 670, 430, 220, 76 nm, respectively. It can be seen that with the addition of graphene Mn_3O_4 is well dispersed. The crystalline structure of Mn_3O_4/RGO composites was characterized by XRD. In Fig. 2A, the diffraction peaks corresponding to the tetragonal hausmannite structure of Mn_3O_4 (JCPDS card no. 01-089-4837) can be clearly seen in the samples of pure Mn_3O_4 and Mn_3O_4/RGO composites. As the RGO amount increased, the diffraction peak appeared at 23.6°, which indicates that GO was converted to RGO, and the conjugated graphene network (sp^2 carbon) was re-established during the reduction process [22].

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