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Microwave-assisted green synthesis of MnO_2 nanoplates with environmental catalytic activity

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ABSTRACT

In this paper, MnO_2 nanoplates were synthesized in aqueous solution under the microwave irradiation, without using any templates, catalysts, and organic reagents. The as-prepared MnO_2 nanoplates were systematically characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM), high-resolution TEM (HRTEM), Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC) and thermo-gravimetric (TG) analysis, and nitrogen sorption measurements. Microwave irradiation could produce MnO_2 with uniform size and well-defined shape as well as high crystallinity. On the basis of experimental results, a possible formation mechanism of MnO_2 nanoplates was proposed. Furthermore, the resulting MnO_2 nanoplates were found to exhibit remarkable environmental catalytic performance in degradation of Rhodamine B (RhB) in aqueous solution, indicating these MnO_2 nanoplates is very promising for wastewater treatment.

1. Introduction

With the development of cleaner and more benign chemical processes according to green chemistry principles, chemists are challenged to explore environmental-friendly methods to synthesize target materials [1]. Among the 12 principles of green chemistry, "safer solvents" and "higher energy efficiency" were the two key ones considered by synthetic chemists [1–4]. Recently, considerable efforts have been devoted to develop and use nontraditional solvents for synthesis of materials. Such unconventional media include water, supercritical carbon dioxide, ionic liquids, perfluorinated solvents and so on. Among these unconventional solvents, water is the most available and green one. Meanwhile, the application of microwave heating in the materials synthesis is a fast growing research area in recent years [5,6], because the microwave heating has been proved and accepted as a promising method for rapid volumetric heating, high-reaction rate and selectivity, short-reaction time, and high yield as compared to conventional heating methods [7–12]. This opened up the possibility of realizing fast preparation of materials in a very short time with high-energy efficiency [13]. Microwaves are now used routinely in many areas of chemistry ranging from analytical chemistry and liquid-phase organic syntheses to solid-state reactions.

MnO_2 with different phases have attracted much attention because of their particular physical and chemical properties and possess great potential as selective heterogeneous catalysts, adsorbents, and battery materials [14–21]. They have been used for a wide range of industrial catalytic applications, such as ozone decomposition, photocatalytic oxidation of organic pollutants, nitric oxide reduction, selective oxidations of carbon monoxide, decomposition of hydrogen peroxide, and so on [22,23]. A variety of preparation methods for the MnO_2 have been reported in the literatures [24]. For example, it was reported to synthesize MnO_2 by the reduction of $KMnO_4$ using potassium borohydride, sodium dithionate, and sodium hypophosphite [25]. Also, precipitation of MnO_2 from aqueous solutions of $Mn(CH_3COO)_2$ and $KMnO_4$ was also reported [26]. Nanostuctured materials become more and more attractive in recent years, because these materials possess favorable and enhanced physical and chemical properties. Much effort has been made toward the preparation of MnO_2 nanostructures with different morphologies [27–30]. However, few report on the synthesis of MnO_2 nanostructures with microwave irradiation.

In this paper, we report a green method to synthesize MnO_2 nanoplates with uniform size and well-defined shape via a microwave-assisted route in aqueous solution. This method has

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at least two obvious advantages: the process is fast and simple; high-pressure and high-temperature apparatus are not needed. Moreover, we found the as-prepared MnO_2 exhibited remarkable catalytic performance on the Fenton oxidation of Rhodamine B (RhB) in aqueous solution, indicating the MnO_2 nanoplates are promising materials for environment catalysis.

2. Experimental

2.1. Chemicals

All chemicals in this study were of commercially available analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai China). Deionized water was used in all experiments.

2.2. Preparation of the MnO_2 samples

The MnO_2 nanoplates were synthesized in aqueous solution using microwave irradiation. In a typical procedure, 2.0 mmol of $KMnO_4$ and 3.0 mmol of $Mn(NO_3)_2$ were dissolved in 40 mL of distilled water in a flask of 100 mL. Then the resulting aqueous solution was reacted at 160 °C for 30 min under microwave irradiation produced by a microwave oven (MAS-1, Shanghai Xinyi Ltd.). After the reaction was completed, the resulting brownish-black solid product was centrifuged, washed with deionized water to remove ions possibly remaining in the final products, and finally dried at 60 °C in an air oven. For comparison, MnO_2 sample was also prepared by a conventional heating method. In a typical refluxing procedure, 2.0 mmol of $KMnO_4$ and 3.0 mmol of $Mn(NO_3)_2$ were dissolved in 40 mL of distilled water in a flask of 100 mL. The resulting solution was refluxed for 30 min. After being centrifuged, washed with deionized water, and dried at 60 °C in an air oven, a brownish-black precipitate was also finally obtained.

2.3. Characterization of the as-prepared MnO_2 nanoplates

X-ray powder diffraction patterns were obtained on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.54178 Å). Scanning electron microscopy images were performed on a LEO 1450VP scanning electron microscope. Transmission electron microscopy (TEM) study was carried out on a Philips CM-120 electron microscope. The samples for TEM were prepared by dispersing the final powders in ethanol; the dispersion was then dropped on carbon–copper grids. Furthermore, the obtained powders deposited on a copper grid were observed by a high-resolution transmission electron microscope (HRTEM; JEOL JSM-2010 microscope) operating at 200 kV. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Nexus spectrometer with the standard KBr pellet method. Thermal analysis was determined on differential scanning calorimetry–thermo-gravimetric (DSC–TG) analysis at a heating rate of 10 °C min^{-1} under the air atmosphere. The nitrogen adsorption and desorption isotherms at 77 K were measured using a Micrometritics ASAP2010 system after samples were vacuum-dried at 473 K overnight.

2.4. Environmental catalytic activity of the as-prepared MnO_2 nanoplates

The catalytic reaction was carried out in a 250 mL glass flask, which contained 100 mL of RhB dye solution (5 mg L^{-1}), and 100 mg of prepared MnO_2 nanostructure catalysts without adjusting pH value. The pH of the resulting solution was neutral at about 6.2. After adding 2 mL of 30 wt.% H_2O_2 solution, the mixture was allowed to react at room temperature under continuously stirring. For UV–vis absorption measurements, the solution was immediately centrifuged in order to remove the catalyst particles, which tend to scatter the incident beam. The concentration of RhB was monitored at its maximum absorption wavelength of 555 nm by colorimetry with a U-3310 UV–vis spectrometer (HITACHI) at an interval of 10 min.

3. Results and discussion

3.1. Characterization of the as-prepared MnO_2 nanoplates

The X-ray diffraction was used to characterize the phase structure of the as-prepared MnO_2 samples. Fig. 1 displays the X-ray diffraction (XRD) pattern of the resulting MnO_2 product synthesized in aqueous solution under microwave irradiation. The pattern of the as-prepared sample matches well with the standard patterns of gamma MnO_2 (JCPDS file no. 14-644), where the diffraction peaks at 2θ values of 21.8°, 37.2°, 42.9°, 56.5° and 67.8° can be ascribed to the reflection of (1 2 0), (1 3 1), (3 0 0), (1 6 0) and (0 0 3) planes of the MnO_2, respectively. No peaks for other impurities are observed, indicating the high purity of the as-synthesized product. In addition, the broadening of the XRD peaks reflects the nanocrystalline nature of the resulting material. The XRD pattern suggests that crystalline MnO_2 nanoplates can be easily obtained through this green method.

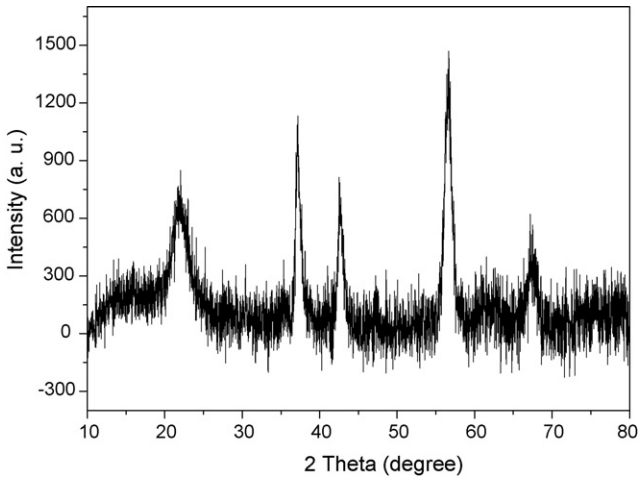

Fig. 1. XRD patterns of the MnO_2 nanoplates prepared under microwave irradiation.

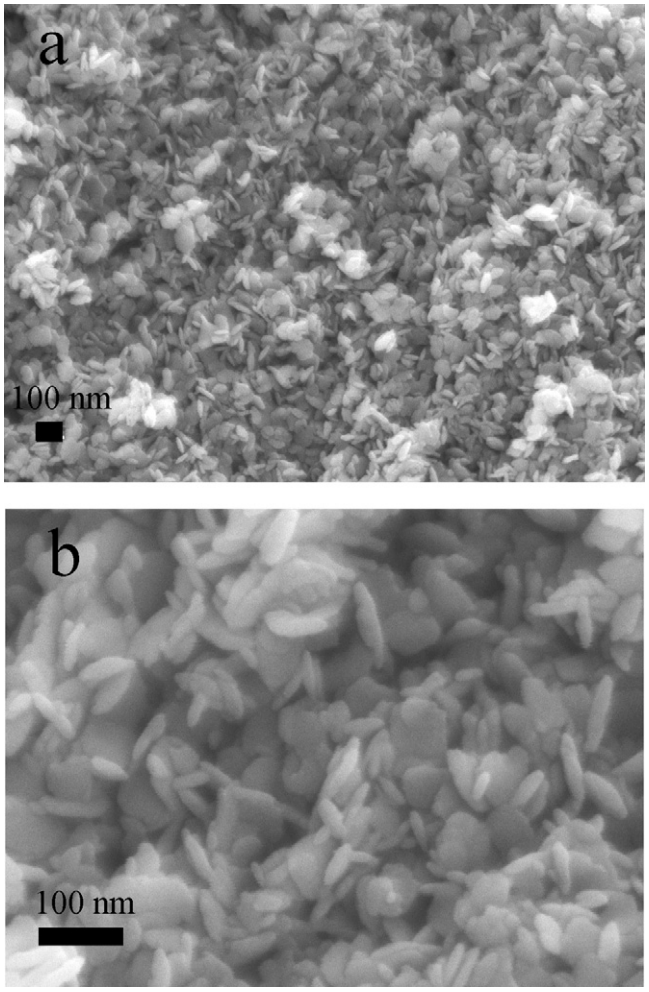

Fig. 2. The SEM images at low magnification (a) and high magnification (b) of the MnO_2 nanoplates prepared under microwave irradiation.