Contents lists available at ScienceDirect

Catalysis Communications

Short communication

Hydrothermal synthesis and characterization of surface-modified δ-MnO$_2$ with high Fenton-like catalytic activity

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ARTICLE INFO

ABSTRACT

Surface-modified δ-MnO$_2$ with a hierarchical structure was synthesized via a hydrothermal redox reaction between toluene and KMnO$_4$. Toluene is oxidized to produce benzoic acid which rapidly adsorbs onto the surface of δ-MnO$_2$. The δ-MnO$_2$ sample prepared with toluene exhibited a much higher catalytic activity for the Fenton-like oxidation of methylene blue in aqueous solution than that prepared without toluene. The enhanced catalytic activity might be attributed to the surface-bound persistent free radicals produced from the electron transfer from the adsorbed C$_6$H$_5$–COO$^-$ to Mn(IV).

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1. Introduction

Organic pollutants could cause carcinogenic and other deleterious effects on living organisms and are difficult to be degraded. Water pollution with these toxic organic pollutants has become a serious environmental problem in the past decades. The classical Fenton reaction between Fe^{2+} and H$_2$O$_2$ can generate highly potent hydroxyl radical (•OH) for the non-selective oxidation of organic pollutants. However, its application is limited by its narrow working pH range (pH 2–4) and difficult separation and low recovery of the iron species. In recent years, heterogeneous Fenton oxidation process has attracted considerable attention because it can be operated at different pH and the catalyst can be recycled. Significant efforts have also been made on the preparation of highly active heterogeneous Fenton catalysts [1–5].

Manganese dioxide (MnO$_2$) can catalytically decompose H$_2$O$_2$ to •OH for the degradation of refractory organic compounds. It can highly adsorb the organic pollutants and has been widely applied in water treatment [6–9]. The catalytic performance of MnO$_2$ strongly depends on its crystal phase, morphology, particle size, crystallinity and surface composition. Recently, various MnO$_2$ nanostructures have been reported for the highly efficient heterogeneous Fenton-like oxidation of organic pollutants in water. For example, both one-dimensional α-MnO$_2$ and β-MnO$_2$ nanorods show excellent catalytic performance in the Fenton-like reaction [10,11]. In particular, β-MnO$_2$ nanostructures with various morphologies, such as nanopincers, nanorods and hollow octahedra, exhibit high catalytic activity for the dye degradation in the presence of H$_2$O$_2$ [12–15]. δ-MnO$_2$ (birnessite) with layer structures can be readily synthesized at low temperatures and has been widely applied in various fields. However, it has been hardly applied to the Fenton-like oxidation of organic pollutants in water.

In the present work, a surface-modified δ-MnO$_2$ was prepared by a simple hydrothermal method. The effects of toluene on its structure and surface composition were investigated. The as-prepared δ-MnO$_2$ exhibited excellent catalytic performance in the Fenton-like oxidation of methylene blue (MB).

2. Experimental

2.1. Synthesis of δ-MnO$_2$

All chemicals were of analytical grade and used without further purification. Deionized water was used in this study. In a typical procedure, 1.82 g KMnO$_4$ and a certain amount of toluene (0, 1 and 5 mL) were added to 70 mL of deionized water under magnetic stirring. The mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave tube and heated in an oven at 180 °C for 24 h. The as-obtained black solid product was washed with deionized water for several times, dried at 110 °C for several hours and calcined at 300 °C for 7 h. The products prepared with 0, 1 and 5 mL toluene were denoted as Mn-0, Mn-1, and Mn-5, respectively. α-MnO$_2$ was prepared by calcination of Mn-1 in air at 500 °C and denoted as Mn-1-500.

2.2. Characterization

Phase identification was carried out by X-ray diffraction (XRD) with a Bruker D8-Advance using Cu Kα radiation. The morphologies of the products were examined with a Hitachi S-4800 field emission scanning

electron microscopy (FESEM) at an accelerating voltage of 3 kV and a JEM-2100 high-resolution transmission electron microscope (TEM) at an accelerating voltage of 200 kV. Nitrogen adsorption–desorption measurements were performed on a Quantachrome NOVA 4000e surface area and pore size analyzer at 77 K, using the volumetric method. XPS analysis was performed on an AXIS-Ultra instrument (England, Kratos Axis Ultra DLD) using monochromatic Al Kα radiation. Infrared (IR) spectra were recorded on a Nicolet iS 50 Fourier transformation infrared spectrometer with KBr disks in the range of 4000–400 cm^{-1} at room temperature.

2.3. Catalytic activity of δ-MnO₂

The heterogeneous Fenton-like oxidation of MB was carried out by adding 10 mg catalyst to 85 mL 50 mg L^{-1} MB solution in a glass beaker. The suspension was vigorously stirred for 40 min in the dark to achieve adsorption/desorption equilibrium. Fifteen milliliters of H_2O_2 was added to the suspension and the reaction mixture was continuously stirred at room temperature. Samples were filtered through a Millipore filter and measured at 665 nm on a UV–vis spectroscope to monitor the concentration change of MB during the reaction.

3. Results and discussion

Fig. 1a, b and c shows the XRD patterns of the resultant MnO_2 products prepared with 0, 1 and 5 mL of toluene, respectively. All the diffraction peaks can be indexed to δ-MnO₂ (JCPDS 80-1098). The most intensive peak at ~12.4° can be assigned to the (001) reflection. All the δ-MnO₂ samples are poorly ordered. The peaks of Mn-1 and Mn-5 are weaker than those of Mn-0, indicating that toluene can decrease the crystallinity of the δ-MnO₂ product. The diffraction peaks of Mn-1-500 (Fig. 1d) match well with the standard pattern of α-MnO₂ (JCPDS 44-0141), demonstrating that the poorly ordered δ-MnO₂ can convert to well-crystallized α-MnO₂ at a high temperature.

Mn-0 and Mn-1 were further characterized to investigate the effect of toluene on the structure of δ-MnO₂ products. SEM images of Mn-0 and Mn-1 reveal that both of them possess a hierarchical complex architecture (Fig. 1S). Uniform flowerlike microspheres with diameters in the range of 1–2 μm were obtained in the absence of toluene. These microspheres are composed of numerous thin nanosheets. Irregular hierarchical assemblies with smaller sizes were obtained in the presence of toluene. These assemblies are composed of nanosheets and nanorods (Fig. 2S(a)). The d-spacing of the lattice fringes of Mn-1 is 0.69 nm (Fig. 2S(b)), consistent with the spacing between (001) planes of δ-MnO₂. The SAED pattern of a single nanoparticle demonstrates that

Mn-1 is polycrystalline (inset in Fig. 2S(b)). In addition, the specific surface areas and pore volumes of Mn-1 and Mn-5 are much larger than those of Mn-0 and Mn-1-500 (Table 1S).

The surface composition of Mn-0 and Mn-1 was examined with FTIR and XPS. As shown in Fig. 2, five absorption bands at 526, 436, 1048, 1638 and 3438 cm^{-1} were observed in the IR spectra of Mn-0. Characteristic bands of birnessite at 526 and 436 cm^{-1} can be assigned to the Mn–O stretching modes of the octahedral layers. The wide band at 3438 cm^{-1} was attributed to the stretching and bending vibrations of water molecules and hydroxyl groups in the interlayer [16]. The band at 1638 cm^{-1} was assigned to the bending vibration of the O–H bonded with Mn atoms [17]. The absorption peak at 1048 cm^{-1} can be possibly assigned to Mn^{3+}–O vibration [18]. Two new peaks at 1541 and 735 cm^{-1} were observed in the spectra of Mn-1, which were assigned to the asymmetric stretching vibration of the carboxylate group and the stretching vibration of Mn–O, respectively. This can be explained that the redox reaction between toluene and $KMnO_4$ occurred during the hydrothermal synthesis process. Toluene was oxidized to benzoic acid (C_6H_5–COOH) by $KMnO_4$ and C_6H_5–COO$^-$ was rapidly adsorbed onto the surface of the in situ formed δ-MnO₂ [19]. The formation of δ-MnO₂ with this hydrothermal synthesis route can be expressed as the following:

$$2KMnO_4 + C_6H_5-CH_3 = 2\delta-MnO_2 + C_6H_5-COOK + H_2O + KOH. \quad (1)$$
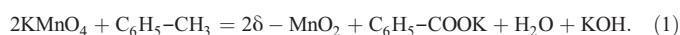
The binding energies (BEs) of Mn 2p3/2 and Mn 2p1/2 of Mn-0 are 642.6 and 653.2 eV, respectively and its 2p3/2–2p1/2 spin orbit splitting is 11.6 eV (Fig. 3S), indicating that the oxidation state of Mn is +4 [20]. The Mn $2p_{3/2}$ BE of Mn-1 (642.7 eV) is slightly higher than that of Mn-0, which may be attributed to the coordination of C_6H_5–COO$^-$ to Mn. Three surface oxygen species were identified through deconvolution of the O 1s spectra of Mn-0 and Mn-1 (Fig. 3). These three oxygen species in manganese oxides can be assigned to lattice oxygen (O^{2-}), hydroxide oxygen (OH$^-$), and oxygen in water molecules (i.e., physisorbed, chemisorbed and structural H_2O and the H_2O in poor electrical contact with the mineral surface) [21,22]. The relative contents of lattice oxygen (529.3 eV), hydroxide oxygen (531.7 eV), and oxygen in water molecule (533.1 eV) of Mn-0 are ~10%, 47% and 43%, respectively. Those of Mn-1 are 14%, 46% and 40%, respectively. The lower contents of hydroxide oxygen and oxygen in the water molecule in Mn-1 might be attributed to the adsorption of C_6H_5–COO$^-$ on the surface of δ-MnO₂, which is consistent with the FTIR results. In all, surface-modified δ-MnO₂ can be synthesized in the presence of toluene by a simple hydrothermal synthesis method.

The catalytic performance of the surface-modified δ-MnO₂ was evaluated by its catalytic activity in the degradation of MB by H_2O_2. As
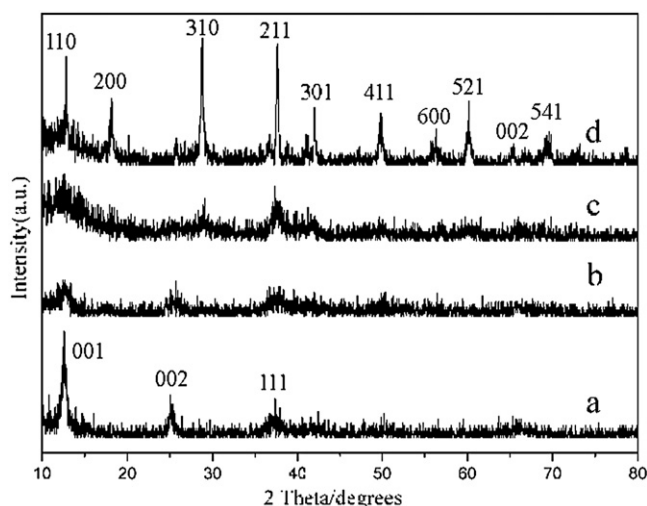

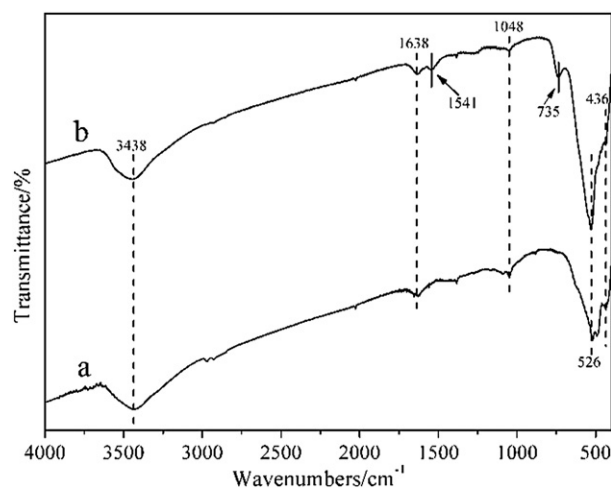**Fig. 1.** XRD patterns of (a) Mn-0, (b) Mn-1, (c) Mn-5, and (d) MnO₂-1-500.

Fig. 2. FTIR spectra of (a) Mn-0 and (b) Mn-1.