Research Article

Hydrothermal Synthesis of Boron-Doped MnO₂ and Its Decolorization Performance

Ming Sun, Ting Lin, Gao Cheng, Fei Ye, and Lin Yu

School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China

Correspondence should be addressed to Ming Sun; sunmgz@gmail.com

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To functionalize MnO₂ with foreign ions is one of the commonly used methods to improve the adsorption/oxidation properties of MnO₂. Boron-doped MnO₂ was prepared by the reaction of MnSO₄, KMnO₄, and boric acid by a facile hydrothermal method. Boron-MnO₂ was characterized by X-ray diffraction (XRD), Raman spectra, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), selected area electron diffraction pattern (SAED), and X-ray photo-electron spectroscopy (XPS) techniques. The characterization of XPS and EDX confirms that boron has been doped into MnO₂, but the boron dopant has no obvious effect on the crystallization of MnO₂ as shown by the results of XRD and Raman characterization. The boron-doped MnO₂ nanorods display high performance in the methyl orange degradation with a decolorization degree of 90% in 2 min (5% B-MnO₂ dosage, 5 mg; methyl orange concentration, 20 mg L⁻¹).

1. Introduction

Manganese oxides have diverse structures with many derivative compounds [1]. Generally, the valence of Mn in manganese oxides can be +2, +3 or +4, and there may be two or three kinds of valence coexisting in the same crystalline structure. The characteristics in structure make manganese oxides possess unique chemical and physical properties. Thus, research on manganese oxides has received considerable attention in various fields like energy storage/conversion material [2, 3], catalysis material [4], ion-exchange material, and so forth [5]. Of all the applications, the elimination of organic pollutants or heavy metal in water has always been the focus of research from the aspect of environment protection. Manganese oxides are widely used to remove/oxide heavy metal [6, 7], acetaminophen [8], phenol [9], nonylphenol [10], naproxen [11], ciprofloxacin [12], Congo red [13], rhodamine B [14], and so forth.

The adsorption/oxidation properties of manganese oxides are generally influenced by their microstructure, shape, size, and/or composition. Therefore, long-term attention has been paid to the preparation and modification of MnO₂. Generally, there are two ways to improve the adsorption/oxidation properties of MnO₂. One way is to fabricate large-surface-area/mesoporous MnO₂ [15] or loaded MnO₂ with a high-surface-area carrier [16–18], and the other is to functionalize MnO₂ with foreign ions [19, 20]. Compared with the commonly used metal ions, nonmetal elements for MnO₂ are rarely reported [21, 22]. It is notable that nonmetal elements such as B, N, or S have been widely used as dopants for TiO₂ and proved to be very effective for enhancing the photocactivity [23]. The structure of TiO₂ and MnO₂ has somewhat similarity. Inspired by such fact, we tried to synthesis boron-doped MnO₂ via reactions among MnSO₄, KMnO₄, and boric acid under hydrothermal conditions. During the review process of our paper, very recently, Chi et al. [24] reported that boron-doped manganese dioxide showed superior electrochemical performance as supercapacitors and the boron dopant was an effective way to improve and modify the characteristics of manganese oxide. Herein, we systematically characterized the physicochemical properties of the prepared manganese oxide using various techniques. The application in the decolorization of industrial acid dye, methyl orange, was studied as probe reaction to evaluate its activity.
2. Experimental

A group of boron-doped MnO$_2$ were prepared by mixing MnSO$_4$ (22.1 mmol), KMnO$_4$ (16.8 mmol), and different amounts of boric acid with 55 mL H$_2$O under hydrothermal conditions maintained at 160°C for 24 h. The solid precipitate was collected and washed by centrifugation and then dried at 60°C. The products are marked as x% B-MnO$_2$, where x means the theoretical molar ratio of boron to Mn in the raw materials.

X-ray powder diffraction (XRD) was carried out using ULTIMA-III X-ray diffractometer (40 kV, 40 mA, Cu K$_\alpha$ radiation). Scanning electron microscopy and energy dispersive X-ray analysis (SEM-EDX) were performed on a Digital Scanning Microscope S-3400N operated at 15 kV. The transmission electron microscopy (TEM) image, selected area electron diffraction pattern (SAED) and high-resolution transmission electron microscopy (HRTEM) image were obtained on a JEOL JEM-2100HR using an acceleration voltage of 200 kV. Raman spectroscopy was recorded on a dispersive Horiba Yvon LabRam HR800 Microscope, with a 24 mW He-Ne green laser (633 nm). X-ray photo-electron spectroscopy (XPS) was obtained by a Thermo ESCALAB 250 instrument equipped with a monochromatic Al K$_\alpha$ (1486.6 eV) X-ray source. N$_2$ adsorption-desorption isotherms were measured using a Micromeritics ASAP 2020 Analyzer.

The decolorization experiment was performed in a round bottom flask at room temperature. B-MnO$_2$ of 5 mg was added into a solution of methyl orange (20 mg L$^{-1}$, 100 mL) with a pH of 1.7 adjusted by diluted H$_2$SO$_4$. A small quantity of mixture was withdrawn at definite intervals and then centrifuged to remove the sedimentation before UV analysis. The decolorization performance was calculated by UV-visible spectrum (T-245, Shimadzu) by monitoring its characteristic peak at 507 nm.

3. Results and Discussion

The structure of the B-doped MnO$_2$ was characterized by XRD and Raman spectroscopy as displayed in Figures 1 and 2, respectively. Figure 1 shows the XRD patterns with peaks located at 2$\theta$ = 12.6°, 17.8°, 28.5°, 37.3°, 41.8°, 49.7°, and 60.0°, which match well with the standard patterns of α-MnO$_2$ (JCPDS 44-0141). With boron dopant increasing, no vital difference for the XRD peaks is observed. Besides, the peaks belonging to borate impurities are not detected.

The Raman spectra (Figure 2) are almost identical for all the samples, indicating that the amount of boron dopant had no effect on the structure of MnO$_2$. The Raman spectra feature four main bands at 187, 392, 582, and 647 cm$^{-1}$. The two Raman bands at 582 and 647 cm$^{-1}$ are indicative of the vibration modes of MnO$_6$ octahedron [25]. No peaks at around 770 cm$^{-1}$ and 805 cm$^{-1}$, corresponding to [BO$_3$] tetrahedron and B$_2$O$_3$, are found [26], and this observation proves that no isolate boron exists.

Figure 3 shows one-dimensional stacked rod-like morphologies of B-MnO$_2$ with the length of hundreds of nanometers, and this result is in agreement with that observed by Ma et al. [13]. No vital difference can be found with the rise of boron doping. The TEM image in Figure 4(a) clearly shows 5% B-MnO$_2$ is in a typical nanorod shape with various lengths and a diameter of about 35 nm. The representative HRTEM is given in Figure 4(b). The separated spacing of 0.49 nm corresponds to (200) plane in the α-MnO$_2$ crystal structure. The single crystal feature of B-MnO$_2$ is proved by the inset electron diffraction image, which shows the B-MnO$_2$ nanorod grows along the [001] crystal direction. The SAED pattern also confirms the single crystal feature of the B-MnO$_2$. The TEM and HRTEM results are consistent with the XRD and Raman data, verifying the good crystallinity of the B-MnO$_2$. Elementary composition analysis by EDX and XPS confirms the presence of boron (Figures 4(c) and 4(d)). The EDX spectrum demonstrates peaks of O, K, Mn, and B. The binding energy located at around 198 eV for B is different from the B is of H$_3$BO$_3$ or B$_2$O$_3$ located at 192–193 eV [27].

Figure 5 shows the nitrogen adsorption-desorption isotherms. The B-MnO$_2$ nanorod possesses a typical type II
Figure 3: SEM images of x% B-MnO$_2$.

Figure 4: TEM and HRTEM image, EDX, and XPS of 5% B-MnO$_2$ sample.

isotherm with an H3-type hysteresis loop, which is indicative of slit-like pores. The BET surface area of the B-MnO$_2$ materials is also listed in the figure, ranging from 37 to 54 m$^2$/g.

Methyl orange (MO) decolorization is selected to study the decomposition properties of B-MnO$_2$ (Figure 6).

The degree of decolorization is expressed as $(A_0 - A)/A_0$, where $A_0$ is the initial absorption of peak wavelength (507 nm) and $A$ is the absorption after decolorization in different reaction time. Blank test is done in a solution of methyl orange (20 mg L$^{-1}$, 100 mL) without B-MnO$_2$, and no color change is observed at room temperature. The B-MnO$_2$
Figure 5: Nitrogen adsorption/desorption isotherms of x% B-MnO₂ nanorods.

It is interesting that even when the concentration of MO is increased from 20 mg L⁻¹ to 40 mg L⁻¹, the used B-MnO₂ is still capable of decolorizing MO efficiently. As for such a high concentration of MO, apparently, pure adsorption is not enough to explain the decolorizing ability. Kuan and Chan [28] pointed out that methyl blue could be adsorbed or oxidized by tunneled manganese oxide. Similarly, MO can also be oxidized by B-MnO₂. Figure 5 shows that a new peak at around 250 nm appeared after 2 min, inferring an intermediate produced by the oxidation of MO. The oxidation ability may come from the excess surface oxygen of B-MnO₂ [19, 28]. Based on the above analysis, we can say that both adsorption and oxidation degradation play a role in the decolorizing of MO. Zhang et al. [29] also reported that the mechanism for decoloration of methyl blue can be attributed to oxidation degradation as well as adsorption. However, one thing to point out is that, under the acid conditions, the B-MnO₂ can dissolve slowly into the solvent. After the decolorization test over 5%B-MnO₂, we have detected about 20 ppm Mn²⁺ using atomic absorption spectrometry. Hydrogen peroxide or tert-butyl hydroperoxide was used in some reported decolorization reactions [14, 19, 30]. However, in this study, the addition of H₂O₂ caused large amount of gas bubble, and the color of the solution did not change at all after 50 min. This is because MnO₂ is consumed preferentially by the decomposition of H₂O₂, thus leading to the failure of decolorization. Therefore, H₂O₂ is not necessary in our case.

4. Conclusions

In summary, different amounts of boron-doped α-MnO₂ nanostructures have been prepared by hydrothermal route. The dopant boron has no effect on the structure of MnO₂. The B-MnO₂ showed nanorods morphology with length of few
hundred nanometers. The 5% B-MnO$_2$ exhibited the highest efficiency in the MO decolorization without the assistance of H$_2$O$_2$. The prepared B-MnO$_2$ is promising to be used in degradation of other organic pollutants.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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