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Shape-controlled synthesis of one-dimensional α-MnO_2 nanocrystals for organic detection and pollutant degradation

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ABSTRACT

Shape control is an important technique for improving the quality and activity of nanomaterials. Two types of one-dimensional manganese dioxide (MnO_2) nanocrystals with different shapes were synthesized by facile hydrothermal methods as the catalyst materials for both sensor fabrication and heterogeneous catalytic reactions. The nanomaterials present an α-crystalline phase (α-MnO_2) in either nanotube or nanowire shapes. The α-MnO_2 nanocrystals were found to have a favorable electrochemical property that can be used to fabricate sensors for rapid detection of hydrogen peroxide and L-ascorbic acid. The α-MnO_2 also functioned well as a catalyst for the oxidation of phenol and chlorophenol by peroxymonosulfate and hydrogen peroxide in an aqueous solution at room temperature. Comparison between the two differently shaped α-MnO_2 catalysts indicated that nanowires performed better than nanotubes in both electrocatalytic detection and catalytic phenol degradation. Compared to α-MnO_2 nanotubes, nanowires have a much greater surface area and lower negative surface charge density, which are probably the main reasons for their higher catalytic activities.

1. Introduction

Manganese dioxide (MnO_2) is one of a group of attractive inorganic materials that can catalyze electrochemical reactions for various environmental applications [1,2]. For example, with its transition to different oxidation states, MnO_2 has been found to be sensitive for the detection of chemical oxidants and reductants, such as hydrogen peroxide (H_2O_2) and L-ascorbic acid (AA), in water [3,4]. Nano-sized MnO_2 particles are also promising catalysts for catalytic degradation of organic pollutants. Ye and coworkers synthesized α-MnO_2 with different shapes for the catalytic oxidation of naproxen [5]. Zhu and coworkers prepared α-, β-, γ- and δ-MnO_2 using a hydrothermal method and evaluated their activities for carbon monoxide oxidation [6]. MnO_2 materials also perform well in Fenton-like reactions, such as β-MnO_2 nanorods for methylene blue oxidation by H_2O_2 [7]. Recently, Wang and coworkers tested various forms of manganese oxides for the catalytic activation of peroxymonosulfate (PMS) and found α-MnO_2 to be the best form for chemical oxidation by PMS [8].

H_2O_2 has been widely applied in industrial processes and domestic uses as a universal oxidant, and it is also a very important intermediate in environmental and biological reactions [9]. AA is known for its antioxidant properties in food and drink and its importance in several human metabolic processes involving oxidations and reductions [10]. Rapid detection of H_2O_2 and AA is therefore of great importance and has attracted research attention for quite some time. It is desirable to develop sensor materials for electrodes that can be readily used to detect H_2O_2, AA and similar chemicals in water.

Water pollution is one of serious environmental problems. Toxic organic pollutants from industrial sources often cause long-term water pollution and threaten ecological systems [11,12]. It is difficult to remove toxic organics from wastewater discharge by conventional biological wastewater treatment methods [13,14]. Adsorption can be effective for chemical separation [15]; however, it cannot degrade organic pollutants and may result in secondary pollution during the processing and disposal of the adsorbents [16,17]. Catalytic oxidation has been promoted as a "green" oxidation technology for wastewater treatment with its advantages of detoxification and organic degradation without generating secondary pollutants [8]. Several oxidants, such as H_2O_2,

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O_2, O_3 or $S_2O_8^{2-}$, may be used for oxidation processes, for which effective catalysts are needed [18–21]. Recently, PMS was proposed as a more effective oxidant for the decomposition of organics [22]. PMS can generate sulfate radicals that non-selectively degrade organics to harmless products such as CO_2, H_2O and inorganic ions [23]. Cobalt ions were first used as a homogenous catalyst for the activation of PMS and the generation of sulfate radicals [22]. Nano-sized heterogeneous catalysts were then developed for more effective activation of PMS, including metal-based materials, such as those involving Co [24] and Ru [25], and graphene-based metal-free catalysts [26].

Shape-controlled synthesis of nanomaterials is an important technique for improving their activity in catalysis reactions. Many materials, including noble metals and metal oxides, have shown shape-related activities. However, the shape effect of α-MnO_2 on sensor fabrication and catalytic activity has not been reported. In this study, we synthesized both α-MnO_2 nanotubes and nanowires using different facile hydrothermal methods. The sensors fabricated by α-MnO_2 nanocrystals were characterized for their electrochemical properties in the detection of H_2O_2 and AA in water. The morphology-dependent activity of α-MnO_2 was also investigated for the catalytic degradation of phenol and chlorophenol by PMS at room temperature. The MnO_2 nanowires were found to be more active than the nanotubes in both electrochemical detection and catalytic oxidation reactions.

2. Experimental materials and methods

2.1. Synthesis of α-MnO_2 materials

α-MnO_2 nanotubes were synthesized following a hydrothermal procedure as follows: [27] 1.35 g of $KMnO_4$ and 3.0 mL of HCl (37 wt%) were added to 120 mL of deionized (DI) water with magnetic stirring to form a precursor solution. After stirring for 20 min, the solution was transferred into a Teflon-lined stainless steel autoclave with a capacity of 150 mL. The autoclave was heated and maintained at 160 °C for 12 h and was then allowed to cool down naturally. The α-MnO_2 precipitate formed in the solution was collected by filtration, washed twice with DI water and ethanol and then thoroughly dried in an oven at 60 °C for 12 h.

α-MnO_2 nanowires were synthesized following a modified hydrothermal procedure [5]. Typically, 60 mL of 0.2 M $KMnO_4$ was mixed with 50 mL of 0.125 M $MnSO_4$, and the solution was stirred for 30 min. The mixture was then transferred into a 150 mL Teflon-lined stainless steel autoclave, which was heated and maintained at 160 °C for 12 h. After it cooled down to room temperature, the brown MnO_2 precipitate was collected from the solution by filtration and washed with DI water and ethanol, followed by thorough drying in an oven at 60 °C for 12 h.

2.2. Material characterizations

The crystal forms of MnO_2 were analyzed by the X-ray diffraction (XRD) technique using a Bruker D8 Advance X-ray powder diffractometer. The structure and morphology of the materials were examined using scanning electron microscopy (SEM, Hitachi S-4800 FEG), transmission electron microscopy (TEM, Philips Tecnai G220 S-TWIN), high-resolution TEM (HRTEM) and selected area electron diffraction (SAED). The surface area and pore distributions of the material samples were determined by a Beckman Coulter SA3100 surface area analyzer based on the nitrogen adsorption–desorption isotherm at the temperature of liquid nitrogen (−196 °C), and the ζ-potential of the MnO_2 particles was also measured in water using a ζ-potential analyzer (Delsa Nano, Beckman Coulter).

2.3. Sensor fabrication and detections

To make a working electrode for chemical determinations, 10 mg of the MnO_2 synthesized and 0.5 mg polyvinylidene difluoride (PVDF) were first mixed into 4 mL N,N-dimethylmethanamide (DMF). The mixture was dispersed by ultrasonication for 60 min, and 10 μL of the suspension was then dropped using a micropipette onto the surface of a bare glass carbon electrode (GCE) of 3 mm in diameter. After evaporation of the DMF at 60 °C, solids were left that adhered firmly to the GCE surface to form a sensor electrode. A platinum film (2 × 1 cm) served as the counter electrode, and an Ag/AgCl electrode was used as the reference electrode. Before each electrochemical measurement, the buffer solution and the chemical solution were purged for 20 min with nitrogen. A computer-controlled potentiostat (Princeton VersaSTAT 4) was used to test the sensor electrode on its cyclic voltammetric (CV) behavior for H_2O_2 and AA in 0.02 M phosphate buffer solution (PBS, pH = 7.2) or 0.1 M NaOH solution, respectively.

2.4. Catalytic phenol degradation

The tests on phenol, 2-chlorophenol and 2,4-dichlorophenol degradation were carried out in 500-mL glass beakers at room temperature (25 °C). First, 10 mg of MnO_2 as the catalyst was dispersed into DI water of a pre-determined volume, then 0.1 g PMS ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) was added as an oxidant into the solution with constant magnetic stirring for 10 min. A model chemical solution (1 mg/mL of phenol, 2-chlorophenol or 2,4-dichlorophenol) was then added to make an initial phenolic concentration at 10 mg/L for the catalytic degradation test. The solution was sampled after pre-determined time intervals for analysis by high-performance liquid chromatography (HPLC). The samples were filtered, and 0.5 mL of each filtered sample was injected into an HPLC vial that contained 0.5 mL of pure methanol to quench the reaction. The concentrations of phenolic compounds were measured by an HPLC (Waters 2695 with a photodiode array detector). A C-18 column was used for organic separation while the mobile phase consisting of 40% CH_3CN and 60% water was injected at a flow rate of 1.0 mL/min.

3. Results and discussion

3.1. Characterization of the α-MnO_2 nanocrystals

The XRD patterns of the MnO_2 nanocrystals synthesized following the two different hydrothermal procedures are shown in Fig. 1a. Both XRD profiles appear rather similar, indicating the same crystallographic structure of the two MnO_2 products. All diffraction peaks could be readily indexed to a pure tetragonal phase of α-MnO_2 with lattice constants of $a = 9.7847$ Å and $c = 2.8630$ Å (JCPDS 44-0141), and no impurities were detected.

The SEM images of the MnO_2 samples are shown in Fig. 2. The α-MnO_2 synthesized by the hydrothermal treatment of $KMnO_4$ and HCl is found to have a nanotube structure (Fig. 2a and b). The magnified SEM image (Fig. 2b) reveals that the nanotubes have a tetragonal open end, with an outside dimension of ~150 nm and a wall thickness of ~40 nm. The α-MnO_2 synthesized from the hydrothermal treatment of $KMnO_4$ and $MnSO_4$ exhibits a nanowire structure (Fig. 2c and d). The magnified SEM image (Fig. 2d) shows a diameter of only ~50 nm for the nanowires.

Fig. 3a presents the TEM image of a typical MnO_2 nanotube, while the SAED pattern for a single nanotube is given in the inset of Fig. 3a. A lattice spacing of about 0.50 nm for (200) planes of the tetragonal α-MnO_2 across the nanotubes can be readily resolved (Fig. 3b). The SAED pattern and HRTEM analysis reveal that the nanotube axis is along the (001) direction (c axis). These