Controllable Synthesis of Mn₃O₄ Nanowires and Application in the Treatment of Phenol at Room Temperature

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Abstract: Nanosized Mn₃O₄ nanowires are prepared with KMnO₄ and ethanol in mild conditions by facile hydrothermal method. Hydrothermal reaction temperature is optimized to get uniform nanowires. The prepared Mn₃O₄ nanowires exhibit high activity in the treatment of phenol at acid condition and room temperature. The 20 mg Mn₃O₄ nanowires can efficiently dispose of 50 mL phenol solution (0.2 g·L⁻¹) at pH 2 and 25 °C. The nanowires before and after phenol treatment are characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) and the reaction mechanism is discussed.

Keywords: manganese oxide; phenol treatment; nanowire; hydrothermal method; oxidation

1. Introduction

Manganese is one of the most earth-abundant elements and manganese oxides are generally non-toxic. Manganese oxide nanomaterials also show great potential in sustainable nanotechnology. They are widely utilized in catalytic reactions, sensors and batteries because of their low cost and high activity [1,2]. Mn₃O₄, also known as hausmannite, is a mixed valence oxide and a promising candidate for catalysts, microwave absorption materials, sensors and anode materials [3]. It has been used in the catalytic oxidation of methane and reduction of nitrobenzene [4]. Lu et al. prepared the amorphous Mn₃O₄ thin film first then hydrothermally transformed it into Mn₃O₄ nanowires under room temperature in a solution bath of 0.01 M manganese acetate and 0.01 M sodium sulfate mixture [5]. One-dimensional (1D) nanostructures, especially nanowires, are of great importance because of their specific shape and potential applications. Nanowires feature superior functional properties and mechanical strengths which have been used in micro/nanoelectromechanical systems and photovoltaic applications [6]. Veeramani et al. presented a room-temperature synthesis of Mn₃O₄ nanowires solely from water and manganese salt, catalyzed by iron oxide nanocrystals in the presence of piperazine-N,N'-bis(2-ethanesulfonic acid) (PIPES) [7]. Sambasivam et al. synthesized single-crystalline Mn₃O₄ nanowires using solvothermal technique [8].

Tremendous discharge of toxic organic compounds has contributed to serious pollution to our eco-environment and human beings. Phenolic compounds play an important role in the production of pesticides, resins and antioxidants [9]. However, the phenolic waste waters are highly toxic and persistent, and are difficult to treat with traditional biodegradation. Strong oxidants such as H₂O₂ and O₃, without secondary pollution, have been utilized in the treatment of organic compound waste waters. However, the treatment efficiency is relatively low [10,11]. To achieve high mineralization, advanced oxidation processes (AOPs) were proposed to degrade organic pollutants through the
generation of highly reactive hydroxyl radicals [12,13]. The Fenton process combines H₂O₂ and iron as a catalyst to generate hydroxyl radicals, which have strong oxidation capability on the phenol removal [14]. However, the homogeneous Fenton process is limited by its narrow pH range and iron sludge generation [15-17].

In this work, uniform Mn₃O₄ nanowires are fabricated with facile hydrothermal method and common raw materials in mild conditions. They are utilized to deal with phenol solution without extra H₂O₂ or O₃ at room temperature and air condition. The mechanism of the Mn₃O₄ nanowires on the treatment of phenol is also studied with the characterization of scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Preparation and Characterization of Mn₃O₄

The nanosized Mn₃O₄ was provided by US research Nanomaterials, Inc (Houston, TX, USA) for comparison. Analytically pure KMnO₄ and ethanol was used as raw materials. First, 0.2 g KMnO₄ and 20 mL ethanol/water solution were added in a 45 mL Teflon-lined steel autoclave. The ratio of ethanol and reaction temperature in the furnace are investigated to get uniform nanowire and improved performance in phenol treatment. All products were cleaned with deionized water several times and dried in air at 80 °C for 12 h. Then the Mn₃O₄ powder was ground before utilization. The 3Flex Surface Characterization Analyzer (Micromeritics Corporation, Norcross, GA, USA) is able to determine the adsorption–desorption isotherm of nitrogen at 77 K, then, as a function of the kind of isotherm, according to international union of pure and applied chemistry (IUPAC) classification, a mathematical model to find specific surface areas (e.g., Brunauer–Emmett–Teller (BET) adsorption). The prepared Mn₃O₄ and used nanoparticles were tested with SEM (FE-SEM, Hitachi S-4800, Tokyo, Japan), XPS (ThermoESCALAB250Xi, Waltham, MA, USA) and XRD (XRD-7000S, Shimadzu, Tokyo, Japan) to determine the morphology and chemical composition of the material.

2.2. Treatment of Phenol Waste Water at Room Temperature

The phenol was dissolved in de-ionized water with H₂SO₄ to adjust the pH. In a typical procedure, 20 mg Mn₃O₄ was added into a phenol solution (50 mL, 0.2 g L⁻¹ and pH = 2) at room temperature in an air flow. The concentration of phenol is tested with UV-Vis spectrum at 270 nm every 15 min after the reaction solution was filtrated with a 0.1 μm poly tetra fluoroethylene (PTFE) syringe filter (Whatman™, Shanghai, China).

3. Results and Discussion

3.1. Composition and Morphologies of the Prepared Mn₃O₄
Figure 1. X-ray diffraction patterns of prepared particles at various temperatures for 4 h. (From top to bottom: Commercial nanosized Mn3O4; 170; 150; 130; 110 °C).

The effect of hydrothermal temperature on the diffraction patterns are shown in Figure 1. It is obvious that the prepared nanoparticles are all Mn3O4 which are similar with the commercial Mn3O4 nanoparticles. What is more, they are all in accordance with hausmannite type Mn3O4 PDF card (JCPDS no. 24-0734) even though the intensity of some peaks are different which may be induced by the formation of nanowires. When the reaction temperature decreases to 110 °C, the intensity of (211) plane is very high while some other planes such as (101), (220) and (400) planes almost disappeared.

Figure 2. Scanning electron microscopy (SEM) images of Mn3O4 synthesized at different temperatures for 4h (a) commercial Mn3O4; (b) 170; (c) 150; (d) 130; (e) 110 °C.

The SEM images of Mn3O4 prepared at different temperatures are shown in Figure 2. When the hydrothermal temperature is 170 °C, uniform octahedron-like Mn3O4 particles with edge size about
60 nm are observed which are similar with the commercial Mn3O4 nanoparticles. With the decrease of temperature, the uniform Mn3O4 nanowires appear while the blocks disappear gradually. The nanowires with large specific surface area will improve the performance of Mn3O4. According to the data of BET surface area test, the BET surface area of commercial Mn3O4 is 14.48 m²·g⁻¹ while the BET surface area of Mn3O4 (110 °C) and Mn3O4 (130 °C) are 248.8 and 189.69 m²·g⁻¹, respectively, as shown in Table 1. Along with this, the adsorption average pore diameter of Mn3O4 (110 °C) is about 10.6 nm which is positive to the adsorption and reaction activity of the nanowires.

| Table 1. BET surface area of Mn3O4. |
|-------------------------------------|
|                                 | Mn3O4 (commercial) | Mn3O4 (130 °C) | Mn3O4 (110 °C) |
|------------------------------------|--------------------|----------------|----------------|
| BET surface area/(m²·g⁻¹)          | 14.48              | 189.69         | 248.8          |
| Adsorption average pore diameter/nm| 21.5               | 10.3           | 10.6           |

3.2. Treatment of Phenol with Mn3O4 at Room Temperature

Phenol is widely used in the manufacturing of plastics, pesticides and pharmaceuticals. Because of its high toxicity, a lot of method is recommended but still not efficient. In this work, nanosized Mn3O4 (20 mg) was used to deal with the phenol waste water at room temperature in the air condition. As shown in Figure 3, the phenol concentration decreases obviously in 60 min. Especially when the preparation temperature is 110 °C, the performance of the Mn3O4 is the best because the Mn3O4 prepared at 110 °C shows the uniform nanowires and highest specific surface area.

| Table 2. Comparison of phenol removal with different reagents. |
|---------------------------------------------------------------|
| Reagent and content                                           | Phenol concentration | Temperature /°C | Time /h | Conversion /% | References |
| 2.5 g L⁻¹ Au/C + 5 mL H₂O₂                                     | 45 mL (5 g·L⁻¹)      | 80              | 22      | ~100         | [18]       |
| 20 mg CNT/PEG 20 mg Mn3O4 nanowires                            | 50 mL (20 mg·L⁻¹)    | 120             | 0.5     | ~98          | [19]       |

*Figure 3. Effect of preparation temperature on the performance of Mn3O4 (From top to bottom: 170; 150; 130; 110 °C and commercial Mn3O4).*

Effect of pH on the performance of Mn3O4 is studied as shown in Figure 4. At neutral condition, almost no phenol will be consumed at all, which means that Mn3O4 will not react with phenol or adsorb it. With the decrease of pH, the reactivity of Mn3O4 increases obviously. When the pH is below
2, the Mn₃O₄ has good performance on treatment of phenol. However, lower pH will cause serious leaching of Mn₃O₄ because the nanosized Mn₃O₄ can be dissolved in concentrated sulfuric acid and hydrochloric acid.

![Figure 4. Effect of pH on the performance of Mn₃O₄.](image)

3.3. Analyze of the Function of Mn₃O₄ in the Treatment of Phenol

Different reaction atmosphere is utilized to investigate the mechanism of phenol treatment. As shown in Figure 5, in all the reaction condition, the Mn₃O₄ has the similar performance which means oxygen is not necessary for the treatment of phenol waste water. In the product of the reaction, benzoquinone was detected which means Mn₃O₄ nanowires can oxidize phenol at room temperature.

H₂O₂ is an effective oxygen content with low cost and environmentally friendly nature. The excess H₂O₂ can decompose into safe H₂O and O₂ [20]. However, H₂O₂ (0.1 mol·L⁻¹) cannot oxidize phenol at the same pH in air condition. In contrast, Mn₃O₄ nanowires prepared in this work with large specific area has stronger oxidation reactivity compared with H₂O₂ because it can oxidize H₂O₂. After reaction with H₂O₂, oxygen is formed while Mn₃O₄ is dissolved in the solution. KMnO₄ which is the raw material of Mn₃O₄ nanowires also have strong oxidation ability. In order to completely oxidize phenol, excess dosage of KMnO₄ is needed which will induce secondary pollution to the waste water. Excess Mn₃O₄ nanowires can be easily filtrated and leaching Mn ions can also be removed by neutralization of the acidic waste water.
Benzoquinone and hydroquinone are the common oxidation products of phenol. In this work, pure benzoquinone and hydroquinone solutions are used as the waste water separately, while 20 mg MnO₃ is added in the 50 mL solution (pH = 2, adjusted with H₂SO₄). After 5 min, about 60% hydroquinone is converted to benzoquinone as shown in Figure 6. It was also found that the solution is changed into yellow (the color of benzoquinone) while all MnO₃ nanowires are dissolved which demonstrates that hydroquinone can react with the nanoparticles efficiently. For the benzoquinone solution, the absorbance does not change which means that the MnO₃ nanowires cannot react with stable benzoquinone.

After reaction with phenol, the morphology of MnO₃ changes obviously as shown in Figure 7. The uniform nanowires disappear while a lot of block-shaped particles are formed. After reaction, the reactivity of MnO₃ also disappears because the reaction will not continue after adding extra phenol.
Although the morphology of the Mn₃O₄ particles changes obviously after reaction with phenol, the XRD patterns of Mn₃O₄ after reaction as shown in Figure 8 does not change very much and the characteristic peaks keep similar intensity which means only partial active surface area reacts with phenol. The reacted Mn₃O₄ still has the similar crystal structure with hausmannite.

Figure 7. The morphology changes of Mn₃O₄ before and after reaction with phenol (a) Mn₃O₄ before reaction with magnification of 180,000×; (b) Mn₃O₄ before reaction with magnification of 20,000×; (c) Mn₃O₄ after reaction with magnification of 180,000×; (d) Mn₃O₄ after reaction with magnification of 20,000×.

Figure 8. XRD patterns of Mn₃O₄ before and after reaction with phenol.
The chemical composition and element valence of the materials before and after phenol removal are further examined by XPS (Figure 9). The Mn 2p3/2 peak of the prepared MnO₃ and reacted MnO₃ consisted of three separate peaks at 642.8, 641.6 and 640.6 eV (Figure 5b) which are in accordance with Mn⁴⁺, Mn³⁺ and Mn²⁺, respectively. Before reaction, the relative atomic percentages of Mn⁴⁺, Mn³⁺ and Mn²⁺ are 41.9%, 53.5% and 4.6%, respectively. After reaction with phenol, the relative percentages change into 68.1%, 25.5% and 6.4%. Although the average valence is improved according to the data, the possible reason is the dissolution of Mn with low valence in acid condition because the XPS spectrum of reacted MnO₃ shows obvious noise which indicates pollution of the sample and low content of Mn.

![Figure 9. Mn 2p spectra XPS of MnO₃ before and after reaction with phenol (a) prepared MnO₃; (b) reacted MnO₃.](image)

4. Conclusions

Hydrothermal temperature and ethanol content have a strong effect on the morphology and structure of nanoparticles. Uniform MnO₃ nanowires with high specific surface area (BET surface area, 248.8 m²·g⁻¹) are formed when the hydrothermal temperature is 110 °C and the ethanol content is 10 mL. The MnO₃ nanowires show high efficiency in phenol removal at room temperature and air condition because it has strong oxidation ability compared with H₂O₂. The 20 mg MnO₃ nanowires can efficiently dispose of 50 mL phenol solution (0.2 g·L⁻¹) at pH 2 and 25 °C. According to the SEM, XRD and XPS characterization, the MnO₃ shows strong oxidation capability and reacts with phenol. After reaction, partial Mn with low valence is leaching into the acid solution. Therefore, it is very efficient in the quick removal of phenol in water treatment without special operation parameter. Excess MnO₃ nanowires can be easily filtrated and leaching Mn ions also can be removed by neutralization of the acidic waste water.

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