

Preparation of α -MnO₂ Nanorods and Co₃O₄ Submicrooctahedrons by Molten Salt Route

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α -MnO₂ nanorods and Co₃O₄ submicrooctahedrons have been obtained by simple molten salt preparation route using cheap reagents. Particle size and morphology of the powders were studied by transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM).

Controlling the architecture and morphology of materials at all dimensions from the nanoscale to macroscopic scale has recently attracted much attention because these materials not only have some morphology-induced novel properties but also have potential applications in the design of devices.¹

Manganese dioxide and tricobalt tetraoxide are important inorganic materials for their superior physical and chemical properties. MnO₂ and Co₃O₄ both show potential applications in the fields of catalysts, sensors, magnetic materials, and particularly in energy storage.^{2–6} Recently, MnO₂ and Co₃O₄ powders have been prepared with different morphologies, such as rods,^{7,8} wires,^{9,10} cubes,¹¹ hollow spheres,¹² sea urchin shapes,⁶ etc., using hydrothermal, solvothermal, catalytic, surface-assisted, and electrochemical methods. However, these techniques relied on high pressure, long reaction time, surfactant, organometallic precursor, or catalysts and were not suitable for large-scale production. Therefore, seeking a one-step, convenient, low-cost, mass-production route for the preparation of MnO₂ and Co₃O₄ powders at atmospheric pressure is highly desired.

Molten salt synthesis (MSS) method is one of the simplest techniques to prepare solid inorganic materials.¹³ Up to now, materials with various morphologies have been prepared by the MSS method, including α -Al₂O₃ platelets,¹⁴ BaTiO₃ nanocubes, CoFe₂O₄ nanobelts,¹⁵ BaCeO₃ nanoflowers, and BaMnO₃ nanorods.¹⁶ Although both the preparation of α -MnO₂¹⁷ and Co₃O₄¹⁸ by MSS has been already published, the processes were complex owing to the using of electrolysis and surfactants. In the present work, we report the preparation of α -MnO₂ nanorods and Co₃O₄ submicrooctahedrons by simple molten salt route at normal atmospheric pressure, in the absence of any templates, surfactants or catalysts.

The preparation of the α -MnO₂ follows the following steps. MnSO₄·xH₂O of analytic reagent grade was calcined at 500 °C for 2 h to remove the water of crystallization. 0.01 mol of anhydrous MnSO₄ was mixed with 20 g of KNO₃ by grinding the mixture for 30 min. The above mixture was placed in an alumina crucible and heated at 400 °C for 30 min. After the crucible was cooled to room temperature, deionized water was added to the solid product. The product was filtered, washed by deionized water and absolute ethanol for several times to remove ions possibly remaining in the final products, and finally dried in vacuum at 60 °C for characterization. For the preparation of Co₃O₄, all of the procedures were the same as those stated above except that the raw materials were CoCl₂·6H₂O and

NaNO₃, and the reactive temperature was 350 °C.

The phases of the products were identified by X-ray powder diffraction (XRD, D/MAX-2550V, Rigaku, Tokyo, Japan). High-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction patterns (SAED) were taken with transmission electron microscopy (TEM, JEM-2100F, JEOL, Tokyo, Japan). Scanning electron micrograph was obtained by using field emission scanning electron microscopy (FESEM, JSM-6700F, JEOL, Tokyo, Japan).

Figure 1 shows the X-ray diffraction patterns of the samples. The diffraction peaks of Figure 1a and Figure 1b can be indexed to tetragonal α -MnO₂ phase (JCPDS 44-0141) and cubic Co₃O₄ phase (JCPDS 43-1003), respectively. The XRD patterns indicate that pure α -MnO₂ and Co₃O₄ can be obtained under the current synthetic conditions.

Figure 2a shows the TEM image of the prepared α -MnO₂ powders. The α -MnO₂ powders show nanorod morphology. Figure 2b exhibits a single α -MnO₂ nanorod with a diameter of \approx 6.3 nm. Figure 2c shows the HRTEM image of the single nanorod. The space between the adjacent lattices planes parallel to the growing direction is \approx 0.484 nm, which consistent with the (200) lattice spacing of α -MnO₂.

The morphology of the as-prepared Co₃O₄ powders is characterized by FESEM and TEM. Figure 3 and Figure 4a reveal that the products obtained are octahedrons. Figure 4b and Figure 4c show the TEM images and corresponding electron

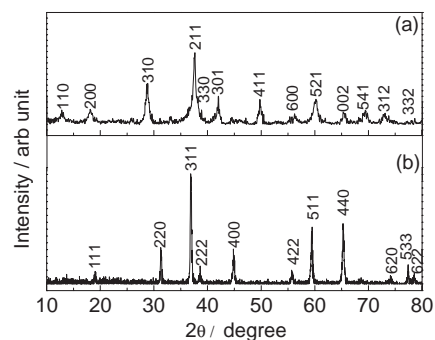


Figure 1. XRD patterns of the prepared (a) α -MnO₂ and (b) Co₃O₄ powders.

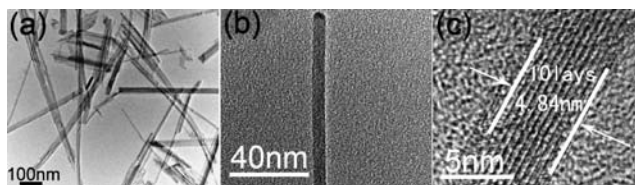


Figure 2. (a) TEM image of prepared α -MnO₂ powders; (b) Typical TEM image of a single nanorod and (c) its corresponding HRTEM image.

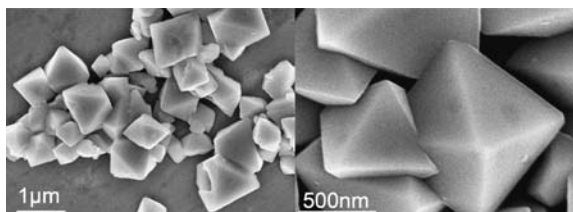


Figure 3. FESEM images of the prepared Co_3O_4 powders.

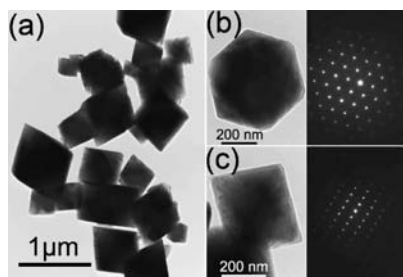
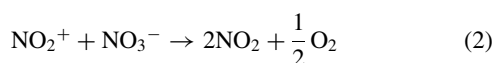
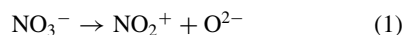


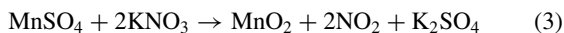
Figure 4. (a) TEM image of prepared Co_3O_4 powders. (b) and (c) Typical TEM images and corresponding SAED patterns.

diffraction patterns of the octahedrons when the electron beams are parallel to the $\langle 111 \rangle$ and $\langle 013 \rangle$, respectively. These typical TEM images further demonstrate their octahedral geometries.

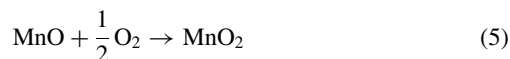
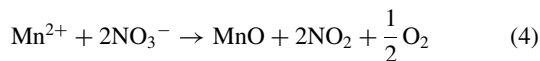
The mechanism for the preparation of MnO_2 and Co_3O_4 is suggested as follows. Acid–base-type reactions occurring in molten oxosalts were classified as Lux–Flood (L–F) acid–base reactions, oxide donors and acceptors were defined as L–F bases and acids, respectively. In molten nitrates, the nitrate anion acted as an oxygen anion donor, or an oxygen atom donor. The following equations have been proposed to describe L–F interaction of molten nitrates with appropriate ionic or neutral oxoacids:¹³



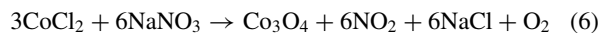
According to the experimental results and the above equations, a possible chemical reaction equation for the preparation of $\alpha\text{-MnO}_2$ is suggested as



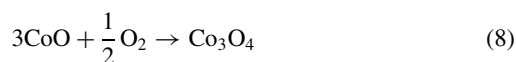
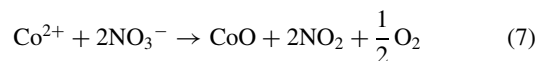
which comprises two reaction processes



For the preparation of Co_3O_4 , the chemical reaction can be formulated as



which comprises two reaction processes



Similar chemical equations have been used to explain the mechanism for preparation of Al_2O_3 ¹⁹ and CeO_2 ²⁰ from the reactions of anhydrous sulphate or chloride with molten nitrates.

The formation of $\alpha\text{-MnO}_2$ nanorods could be explained by the anisotropic growth habit of $\alpha\text{-MnO}_2$ owing to the markedly different lattice parameters of a_0 (9.784 nm) and c_0 (2.863 nm). Three same lattice parameters of Co_3O_4 result in its octahedral morphology. In the reaction process, molten salt not only serves as reactant but also provides fluid phases which accelerate the reaction, lower the reaction temperature, and penetrate among the solid particles as well as prevent the agglomeration of particles.¹⁸

In summary, we successfully prepared $\alpha\text{-MnO}_2$ nanorods and Co_3O_4 submicrooctahedrons by molten salt preparation method using inexpensive sulphate, chloride and nitrate as raw materials. Molten salt synthesis method is a simple, low cost and especially mass-production technique for the preparation of inorganic materials.

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