

Synthesis of Manganese Oxide Nanofibers by Self-assembling Hydrothermal Process

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Manganese oxide nanofibers with layered structure and γ -MnOOH structure have been prepared from a layered manganese oxide by using a self-assembling hydrothermal process. This process includes preparation of manganese oxide nanosheets by exfoliating the layered manganese oxide, self-assembling the nanosheets with a cationic surfactant into a nanocomposite, and transforming the nanocomposite into the nanofibers under hydrothermal conditions.

Recently, nanoscale manganese oxides attract much attention in both applied and basic researches because of their semiconducting and magnetic properties.¹⁻³ The manganese oxides have potential applications in ion sieves, molecular sieves, catalysts, cathode materials of secondary rechargeable batteries, and new magnetic materials.^{1,4,5} Stable nanoparticles of manganese oxide are difficult to be prepared because of the strong tendency of manganese oxide to precipitate or coagulate during the synthesis.⁶ Recently, exfoliation behaviors of manganese oxides with layered structure have been investigated, and it has been reported that tetramethylammonium hydroxide solution (TMA^+OH^-) is an excellent exfoliating agent for the layered manganese oxides.^{7,8} TMA^+ ions can be intercalated into the interlayer of manganese oxides, and the intercalated layered manganese oxide can be exfoliated to nanosheets of its elementary layer by swelling in a large amount of water. The exfoliated nanosheet is a new interesting nanomaterial, and this material can also be utilized as a precursor for preparation of other nanomaterials. We have prepared a $\text{MnO}_2/\text{Ni}(\text{OH})_2$ sandwich layered compound by restacking the manganese oxide nanosheets with Ni^{2+} in a solution.⁹ Very recently, Ma et al. have reported that the nanosheets can be rolled into nanotubes.¹⁰

In the present study, we develop a novel self-assembling hydrothermal process for the preparation of manganese oxide nanofibers from a layered manganese oxide. This process includes preparation of manganese oxide nanosheets by exfoliating the layered structure, self-assembling the nanosheets with a cationic surfactant into a nanocomposite, and transforming the nanocomposite into nanofibers by hydrothermal reaction.¹¹

The starting material, a colloidal solution of manganese oxide nanosheet, was prepared by exfoliating a birnessite-type manganese oxide with a layered structure in TMA^+OH^- solution, as described in the literature.⁷ The manganese content in the nanosheet colloidal solution was adjusted to about 0.01 mol/L. A cationic surfactant (*n*-hexadecyltrimethylammonium chloride, CTAC) solution (0.3 M, 10 mL) was added into the nanosheet colloidal solution (100 mL), stirred for 2 h at room temperature, and then hydrothermally treated for 2 days under autogenous pressure in a Teflon-lined stainless steel autoclave.

After the hydrothermal treatment, the product was separated from the solution by centrifuge, then rinsed with distilled water to remove the residual surfactant, and finally dried by a freeze drier.

When the CTAC solution was added into the nanosheet colloidal solution, the exfoliated nanosheets were reassembled into a manganese oxide- CTA^+ nanocomposite precipitate (as-prepared manganese oxide- CTA^+ nanocomposite) immediately, owing to attraction between negatively charged nanosheet and positively charged CTA^+ ion. This sample has a layered structure with a basal spacing of $d = 2.63$ nm (Figure 1A). The basal spacing of 2.63 nm was larger than 0.96 nm for the TMA^+ -birnessite obviously,⁷ indicating CTA^+ ions were intercalated into the layered structure. The structure of the product was dependent on the hydrothermal reaction temperature (Figure 1). The product retained the layered structure up to 130 °C, but the basal spacing of the product increased from 2.63 to 2.80 nm, suggesting that a rearrangement of CTA^+ ions or/and water molecules in the interlayer space enlarged the distance between two neighboring MnO_6 sheets. The diffraction peak of the layered phase became less intense gradually with increasing the reaction temperature up to 130 °C, owing to decrease of the crystallinity of the layered phase. In the temperature range above 140 °C, the sample lost the layered structure completely, and transformed to a γ -MnOOH phase, indicating that the layered phase is unstable under the high temperature conditions. The TG-DTA and FTIR analyses indicated that the elimination of

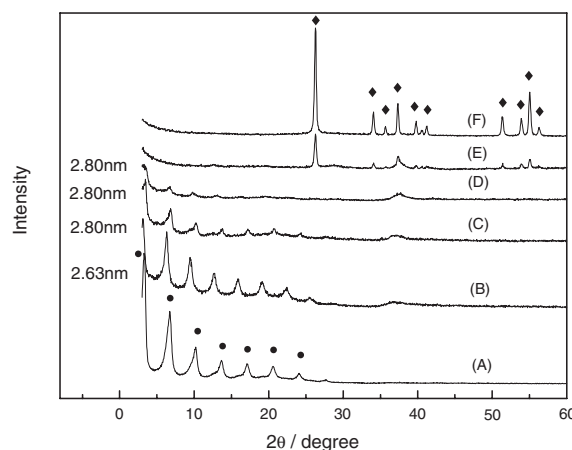


Figure 1. XRD patterns of (A) as-prepared manganese oxide- CTA^+ nanocomposite, and samples obtained by hydrothermal treatment of the nanocomposite at (B) 110 °C, (C) 120 °C, (D) 130 °C, (E) 140 °C and (F) 150 °C, respectively. ●: layered phase; ◆: γ -MnOOH phase (JCPDS No. 41-1379).

CTA⁺ ions from the solid phase to the solution was accompanied by the structural transformation, and no CTA⁺ ion was detected in the γ -MnOOH samples.

Particle morphology of the sample changed dramatically with increasing the hydrothermal reaction temperature (Figure 2). The as-prepared manganese oxide-CTA⁺ nanocomposite has sheet-like particle morphology. The sample prepared at 120 °C shows needle-like morphology, and the samples prepared above 130 °C show fibrous particle morphology. These fibrous particles have dimensions of about tens of nanometer in diameter and tens of micrometers in length. These results indicate that the layered manganese oxide nanofibers can be obtained at 130 °C, and the γ -MnOOH nanofibers can be obtained at higher temperatures.

A TEM analysis on the morphology transformation process suggested that the nanofibers were formed by split of the sheet-like particles of the as-prepared nanocomposite under hydrothermal conditions. The sample obtained at 110 °C shows fringe-like particle morphology with alternating dark and bright contrast (Figure 2E), revealing that the sheet-like particles begin to be

split into the fibrous particles. After hydrothermally treated at 130 °C, fibrous particles were formed, but some fibrous particles still linked together. Above 140 °C, completely individual fibers were obtained. The high-resolution TEM images for the individual fibers show clear interplanar lattice fringes (Figure 2F), indicating each fiber is a single crystal, and the fibrous axis is parallel to the (100) plane of γ -MnOOH phase.

On the basis of the experiment results, we suggest a transformation mechanism from the sheet-like particles to the nanofibers. The CTA⁺ ions in the interlayer spaces of the as-prepared nanocomposite tend to self-assemble together to form rod micelles. As the result of this tendency, the sheet-like particles are split into the nanofibers, and form the layered manganese oxide nanofibers in the low temperature range. The dissolution reaction of the manganese oxide under the hydrothermal conditions promotes the split of the sheet-like particles. Above 140 °C, the layered structure transforms to the γ -MnOOH structure and releases CTA⁺ ions without changing the morphology of the nanofibers.

In summary, we succeed in the preparation of the layered manganese oxide and γ -MnOOH nanofibers by using the self-assembling hydrothermal process. The surfactant ions play an important role in the formation of the nanofibers. We believe that the process developed here has potential applications for the preparations of other metal oxide nanofibers from their nanosheets.

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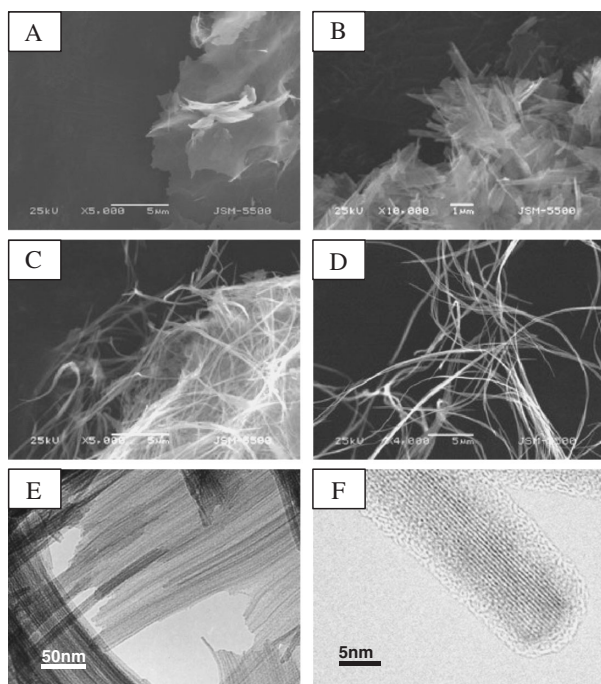


Figure 2. SEM images of (A) as-prepared manganese oxide-CTA⁺ nanocomposites, and samples obtained by hydrothermal treatment of the nanocomposite at (B) 120 °C, (C) 130 °C, and (D) 140 °C, respectively, and TEM images of samples obtained at (E) 110 °C, and (F) 150 °C.