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Fabrication of Co_3O_4 nanorods by calcination of precursor powders prepared in a novel inverse microemulsion

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Co_3O_4 nanorods were prepared by improving traditional molten salt synthesis; the length and diameters of the Co_3O_4 nanorods were about 10 μm and 40–100 nm, respectively; the mechanism of formation of the Co_3O_4 nanorods is discussed.

Recently, one-dimensional (1D) nanoscale structures have been an interesting field of research because of their unique chemical and physical properties as a result of their low dimensionality and the quantum confinement effect.[1,2] Therefore, there are many reports on the synthesis of one-dimensional nanomaterials, such as nanorods, nanowires, nanotubes and nanocables,[3–5] including nanorods of WS_2,[6,7] MoS_2,[8] BN,[9] BC_2N,[10] lipids, MCM-41 and peptides.[11] The spinel oxide Co_3O_4 is an important transition metal ceramic oxide (used for electrochemical, magnetic and catalytic applications) traditionally prepared by thermal decomposition of cobalt(II) salts at temperatures of 250–900 °C under oxidizing conditions.[12] Many methods have been developed to prepare the single-phase Co_3O_4 spinel, such as spray pyrolysis, chemical vapor deposition and sol–gel methods[13,14] and other chemical means.[12,15,16] However, there are few reports on the synthesis of Co_3O_4 nanorods. In this communication we report a new method for the preparation of Co_3O_4 nanorods by annealing precursor powders in which cobalt(II) carbonate, formed in the reaction of cobalt(II) chloride and sodium carbonate, is homogeneously mixed with NaCl. The precursors were synthesized in an inverse microemulsion system (IμE). The method is easy to operate and available and does not need any complicated apparatus, as well as being efficient for crystal growth. The approach is similar to that of molten salt synthesis (MSS),[17a] which is one of the simplest techniques for preparing ceramic powders with whiskerlike,[17b] needlelike[17c] and platelike morphology.[17c–f] For the MSS process, however, the resulting diameters range from several to tens of micrometers, and it is difficult to prepare small particles *e.g.* nanoparticles or nanorods. In our work, we prepared nanorods by improving the above-mentioned MSS method.

One of the simple preparation methods to prepare complex oxides is molten salt synthesis, in which molten salts are used as solvents. In our route, the synthesis temperature, IμE and time are decisive factors, leading to controllable results. Changes in the amount and type of salt can induce a huge difference in powder characteristics in that they are responsible for the reaction and growth environments. There are several requirements for the correct selection of salt. First, it must not react with either the reactant or product compounds; *i.e.*, it must be a true solvent. Secondly, the melting point of the salt should be low and appropriate for the synthesis of the required phase. Thirdly, the salt should have sufficient aqueous solubility so that it is eliminated easily by simple washing after synthesis.[18] One ideal system, NaCl–KCl, has been found to satisfy all these requirements. Therefore, NaCl, KCl or NaCl–KCl mixtures are generally chosen to be the salt for MSS.

The starting materials used in the present work include high purity cobalt chloride ($CoCl_2$), sodium carbonate, sodium chloride (NaCl), high purity cyclohexane, and poly(oxyethylene)$_5$ nonyl phenol ether (NP5)–poly(oxyethylene)$_9$ nonyl phenol ether (NP9)–Tween (polysorbate 80) (TW80) (volume ratio 1 : 1 : 1). All chemical reagents were analytical grade. Three IμEs were prepared as follows: **A**: 48 wt% cyclohexane + 48 wt% NP5/NP9/TW80 (hereafter referred to as NPT) + 4 wt% 1 mol l^{-1} $CoCl_2$. **B**; 48 wt% cyclohexane + 48 wt% NPT + 4 wt% 2 mol l^{-1} Na_2CO_3. **C**: 41.7 wt% cyclohexane + 41.7 wt% NPT + 16.6 wt% 2 mol l^{-1} NaCl.

The three IμEs were magnetically stirred until they became homogeneous and transparent. 26 ml of **A** was added to 36 ml of **C** to obtain solution **D** and then 27 ml of **B** was added to **D** to obtain mixture **E** which was poured into a sufficient amount of acetone to produce precipitates. All experimental processes were carried out under magnetic stirring. Finally, the precipitates were repeatedly washed by using anhydrous acetone followed by centrifugation. The precursor powders were then dried in an oven at 80 °C before the annealing of precursor powders was carried out in a conventional furnace with a horizontal quartz tube. The temperature used was 800–815 °C for 2 h and led to Co_3O_4 nanorods.

The microstructures and composition of Co_3O_4 nanorods were investigated by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) (JEM–200CX TEM) with an accelerating voltage of 200 kV and a double-tilt sample holder. Samples for TEM analysis were prepared by dispersing some product in ethanol, immersing in an ultrasonic bath for 30 min, and taking a few drops of the resulting suspension which were placed onto a copper grid coated with a layer of amorphous carbon. Prior to the extraction of sample, the products in ethanol solution were gently shaken several times. IR spectra were measured on KBr disks using a Fourier transform infrared spectrometer (Nexus 870 FT-IR).

Fig. 1 shows the microstructure of the powders after calcination at 800 °C for 2.5 h. The nanorods are straight with uniform diameters in the range 40–100 nm and lengths up to tens of micrometers and the aspect ratio reaches up to 250. SAED patterns were measured from a single crystalline nanorod of 40 nm diameter. The SAED pattern can be indexed to the

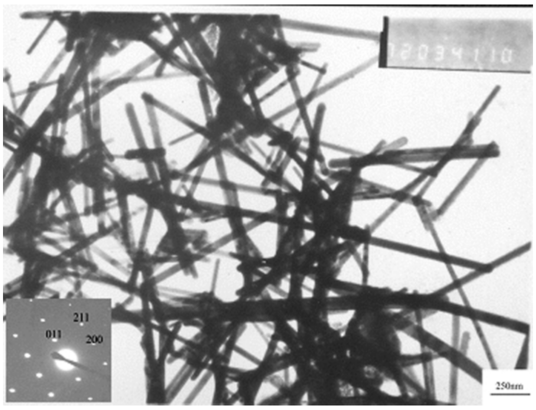

Fig. 1 TEM images of Co_3O_4 nanorods.

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cubic Co_3O_4 structure with $a = 0.8084$ nm. The analysis of the SAED of a single nanorod shows that the growth direction of the Co_3O_4 nanorod is [111].

Fig. 2 shows the XRD pattern of Co_3O_4 nanorods. All peaks are assigned to cubic lattice of Co_3O_4 (*hkl* indices are indicated). The diffraction data are consistent with JCPDS file No. 9-418 with no CoO or other impurities detected.

IR spectra of the as-prepared sample (not shown here) shows a band at 545.6 cm^{-1} resulting from the v_4 modes (F_{2g} species),[19,20] which is shifted 15.6 cm^{-1} to higher wavenumber relative to bulk Co_3O_4. The bands at 567.6, 662.4 cm^{-1} are derived from the v_7 and v_7 polar modes (F_{1u} species). Compared to the results of Shirai and coworkers and others,[19–21] all peaks are shifted to higher wavenumber.

In addition, we have investigated the influence of surfactants on the synthesis of Co_3O_4 nanorods. Under the same conditions, in the absence of NP5/NP9 or TW80, only Co_3O_4 particles were observed. The composition of the IμE plays an important role in the morphology of the products. There is a strong correlation between the synthesis of nanorods and the presence of NP5/NP9 and TW80 and further studies are underway. It appears that the mechanism for Co_3O_4 nanorod formation is similar to that of molten salt synthesis.[17,18] The growth of whiskers or rods require a fluid phase in which elements of the crystal phase can easily move long distances.[22] The precursors are fired at a temperature above the melting point of the salt to form a flux in which the oxides can diffuse rapidly.[17,18] With further heating, the Co_3O_4 nanorods are formed through a nucleation and growth process. One of effects of molten salt is that it may accelerate the reaction, lower the reaction temperature and penetrate among the solid particles as well as preventing the agglomeration of particles. The liquid environment can also promote whisker or nanorod formation. Additionally, the molten salt may also play a role in separating the Co_3O_4 particles and promoting their diffusion. This liquid environment also leads to a homogeneous distribution of the prepared material.

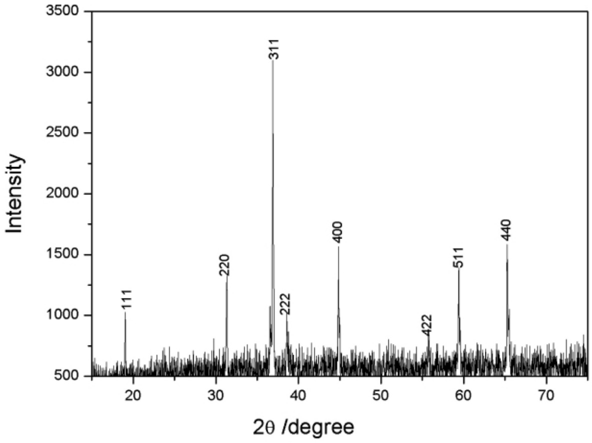

Fig. 2 XRD pattern of Co_3O_4 nanorods.

In summary, well crystallized Co_3O_4 nanorods with diameters of 40–100 nm and lengths ranging up to tens of micrometers have been successfully prepared by calcining the precursors prepared in an inverse microemulsion. The IR spectrum peaks of the as-prepared Co_3O_4 nanorods are shifted to higher wavenumbers than found for bulk Co_3O_4. The Co_3O_4 nanorods form through nucleation and growth processes.

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