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Synthesis and optical properties of high-purity CoO nanowires prepared by an environmentally friendly molten salt route

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ABSTRACT

CoO nanowires with diameters of 50–80 nm, and lengths of up to more than 5 μm have been successfully synthesized by a simple environmentally friendly molten salt route, in which the precursor $CoCO_3$ nanoparticles are decomposed to form high-purity CoO nanowires in NaCl flux. The structure features and morphology of the as-prepared CoO nanowires were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and selected area electron diffraction (SAED). The chemical composition and oxidation state of the prepared nanowires were systemically studied by X-ray photoelectron spectra (XPS) and laser Raman spectroscopy. The results indicated that the as-prepared CoO nanowires were composed of pure cubic CoO phase. The growth mechanism of the synthesized nanowires was also discussed in detail based on the experimental results.

1. Introduction

The oxides of transition metals, such as copper, iron, nickel, cobalt, and zinc, have received many important applications, including magnetic storage media, solar energy transformation, electronic, semiconductor, varistor, catalysis, and electrical and optical switching devices [1,2]. It is well known that cobalt monoxide (CoO) is low-valence transition-metal oxide with dark yellow color and raw salt *fcc* structure [3,4]. CoO has a very important application in Ni/H_2 and Ni/Cd battery, in which it plays the role of enhancing the discharge deepness and enlarging the current which are the two decisive factors in qualifying the energetic source with huge charge/discharge capacity by greatly decreasing inner resistance of the battery through sediment onto surface of $Ni(OH)_2$ particles, and then transform into β-CoOOH [5]. In order to take full advantages of the energy storage material and to fully realize the promising applications of CoO in the fields of Ni/H_2 and Ni/Cd battery, catalysts, gas sensors, magnetisms, giant magnetoresistance read heads, and tapes [6,7], unique properties such as high purity, high density, high stability, ultrafine diameter, and monodispersion of the as-prepared CoO were required. One can foresee that the requirements would be fulfilled if the CoO could be synthesized in nano-scale size, as many unique properties of nano-scale materials lie just in scope of the aforementioned requirements. For example, It has been reported that the specific capacity of Ni/MH battery with addition of 5% slice CoO nanocrystals at 0.1 C was 318 mAh/g, which was higher than that without CoO (269 mAh/g) [8].

In recent years, several methods have been used to synthesize the CoO nanocrystals with different morphologies [9–13]. For example, tetrahedral CoO nanocrystals with 4–5 nm were synthesized by the oxidation of $Co_2(CO)_8$ in toluene in the presence of the surfactant Na(AOT) at 130 °C [9]. Pure CoO nanoparticles with diameter of 4.5–18 nm were prepared by the decomposition of Co(II) cupferronate in decalin under solvothermal condition [10]. Rod-shaped and cubic CoO nanocrystals were fabricated by the decomposition of cobalt(III) acetylacetonate in oleylamine [11]. Pencil-shaped CoO nanocrystals were obtained by the thermal decomposition of cobalt oleate complex in octadecene [12], and tetrapodal CoO nanocrystals were synthesized by the decomposition of Co(II) oleate complex in non-coordinating solvent octadecene containing dodecanol/oleic acid at 280–320 °C [13]. Although these methods can successfully produce CoO nanocrystals with well-defined shape, an appropriate choice of synthetic organic solvent is sometimes crucial to the synthesis of the CoO nanocrystals, and therefore a complicated process is usually required. In addition, an aggressive chemical reducing agent may be involved in these methods. There is therefore the need to develop environmentally sustainable ("green chemistry") alternatives to the existing methods. Here, we report an

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environmentally friendly molten salt route (MSS) for the synthesis of high-purity CoO nanowires in NaCl flux.

Molten salt synthesis (MSS) is one of the simplest, most versatile, and cost-effective routes for the synthesis of crystalline, chemically purified, single-phase powders at lower temperatures and often overall shorter reaction times [14]. A great advantage of this method is that the reaction takes place inside a molten salt, which is added to the mixture of precursors. The molten medium serves as an inorganic solvent for the reactants. This makes that the kinetics of the reactions in this medium is essentially higher than that in the solid state, resulting in decreasing the temperature and the synthesis duration [15,16]. Recently, the MSS has been developed as one of the simplest techniques for preparing nanomaterials with different morphologies, which needs no expensive synthesis equipments or complex experimental conditions [17,18]. We recently first reported on the growth of the highly quality oxide nanowires with aspect ratios of up to 200 by combining a general molten salt process [19], which is usually used to synthesize micrometer ceramic powder, with room temperature one-step, solid state reaction. The key point of this approach is to prepare nanometer-diameter precursor particles by exploiting one-step, solid-state reaction at room temperature, and subsequently decompose precursor nanoparticles in NaCl flux to fabricate oxide nanowires [19–22]. In this paper, our effort involves taking advantage of the excellence of MSS method to prepare high-purity CoO nanowires by decomposing $CoCO_3$ nanoparticles, which are synthesized by one-step, solid-state reaction between $CoCl_2 \cdot 6H_2O$ and Na_2CO_3 at ambient temperature, in NaCl flux. We chose NaCl as the solvents, because it could provide a favorable growth environment and be easily removed from the final products. Moreover, NaCl is abundant in nature and is also harmless to human beings and the environment. The results indicated that our present method yielded high-purity CoO nanowires, which may find potential applications in the fields of Ni/H_2 and Ni/Cd battery, catalysts, gas sensors, etc.

2. Experimental procedure

All of the chemical reagents used in this experiment were of analytical grade as received. In a typical CoO nanowires synthesis, 4.486 g of $CoCl_2 \cdot 6H_2O$ and 2.000 g of Na_2CO_3 were ground for 5 min each before mixing together. After 15 min of grinding, the product was washed several times with distilled water to remove unreacted reactants and by-product. Finally, the product was dried in an oven at 60 °C for 5 h. The obtained product was collected for the preparation of the CoO nanowires.

Of about 0.2 g of the as-prepared precursor particles was mixed with 0.8 g of NaCl and 3 mL of nonyl pheyl ether (9) (NP-9) with an agate mortar, and then the mixture was ground for 5 min. The mixed sample was heated in a porcelain crucible that was placed in the middle of an alumina tube with a horizontal tube electric furnace at 850 °C for 2 h, the heat treatment sample was cooled gradually to room temperature in air, washed several times with distilled water to remove NaCl flux, filtered, and then dried in an oven at 80 °C for 5 h.

X-ray powder diffraction (XRD) pattern was obtained on a Rigaku (Japan) $D_{max}\gamma_A$ rotation anode X-ray diffractometer equipped with the graphite monochromatized Cu K_α radiation ($\lambda = 1.54178$ Å), employing a scanning rate of $0.02^\circ s^{-1}$ in the 2θ range from 10° to 75°. Transmission electron microscopy (TEM) images were taken with a JEM-200 CX transmission electron microscope, using an accelerating voltage of 200 kV. High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) pattern were carried out on a JEOL-2010 transmission electron microscope, using an accelerating voltage of 200 kV. The composition and oxidation state of the as-prepared CoO nanowires were further analyzed by the X-ray photoelectron spectra (XPS), which were collected on an ESCALAB M K_αX-ray photoelectron spectrometer, using Mg-K_α X-ray as the excitation sources. The binding energies obtained in the XPS analysis were corrected with reference to C_{1s} (284.6 eV). Laser Raman spectroscopy was obtained using a LABRAM-HR Confocal Laser MicroRaman spectrometer from 1000 to 0 cm^{-1} at room temperature. The 514.5 nm line of the laser was used as the excitation source, with the capability of supplying 250 mW.

3. Results and discussion

Fig. 1a shows the TME images of the precursor sample prepared via one-step, solid-state reaction between $CoCl_2 \cdot 6H_2O$ and Na_2CO_3 at room temperature, indicating that the nanoparticles have spherical morphology. Because of the small dimensions and high surface energy of the particles, it is easy for them to aggregate as seen in Fig. 1a. We also can find from this figure that the morphology of the particles is almost homogeneous. TEM observations reveal that the diameter distribution of the as-prepared nanoparticles is in the range of

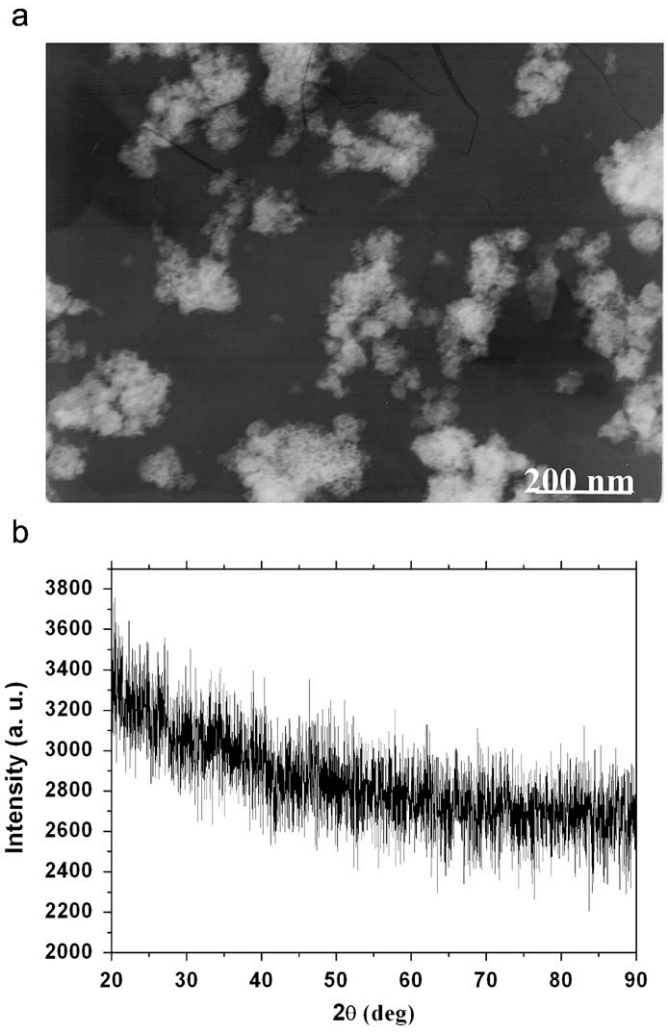

Fig. 1. (a) TEM images and (b) XRD pattern of the precursor $CoCO_3$ nanoparticles prepared by one-step, solid-state reaction between $CoCl_2 \cdot 6H_2O$ and Na_2CO_3 at ambient temperature.