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A low temperature composite-hydroxide approach to NiO nanocrystals

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Abstract

Nanocrystalline NiO has been successfully synthesized via a low temperature molten composite hydroxide route using nickel chloride hydrate as nickel source. The as-obtained oxide nanocrystals were characterized by X-ray powder diffraction and transmission electronic microscopy. It is found that the ratio of reagent to molten solvent has a great influence on the quality of the products. The effect of temperature and time was also investigated. The present route may have a good prospect to prepare many functional nanomaterials.

Keywords: A. Oxides; B. Chemical synthesis; C. X-ray diffraction

1. Introduction

Nanomaterials have attracted much attention because of their unusual chemical and physical properties different from those of bulk materials, based on size-quantization effect and extremely large specific surface area [1,2]. In particular, nanosized nickel oxides are of great interest because they exhibit particular catalytic [3], anomalous electronic [4,5] and magnetic [6,7] properties. The characteristic properties of NiO nanoparticles enable one to tailor materials for a variety of applications including catalysis [3], electrochromic windows [8] and sensors [9].

So far, many synthesis methods have been developed for fabricating nickel oxide nanocrystals. For example, Wang and co-workers prepared NiO nanowires by annealing the freshly prepared precursor [10]. Deki et al. prepared highly concentrated nanosized NiO by means of vacuum evaporation of Ni on NH_2-terminated poly(ethylene oxide) film [11]. Qian and co-workers synthesized NiO nanoplatelets by thermal decomposition of the newly prepared nickel hydroxide precursor [12]. Hyeon and co-workers synthesized NiO and Ni nanoparticles by thermal decomposition of Ni-alkylamine complexes in trioctylphosphine (TOP) [13]. However, the existing techniques mainly rely on high pressure, salt–solvent-mediated high temperature, surface-capping agent or organometallic precursor mediated growth process. Seeking a simple approach for low-cost, lower-temperature, large-scale and controlled growth of oxide nanostructures at atmospheric pressure is highly desired.

Molten salts have been well studied and exhibited a wide range of temperatures at which they remain liquid state and thus are appropriate media for synthetic applications [14,15]. NiO nanowires were synthesized by annealing the

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homogeneously grinded the mixture of freshly prepared NiS nanoparticles and NaCl at high temperature (810 °C) [16]. Zheng and Zhang reported a molten-salt synthesis method using NaCl as a flux at 1000 °C to prepare NiO nanoparticles with uniform morphology of hexagon plates [17]. Complex oxides, such as $LiCoO_2$, $LaAlO_3$ and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ powders, were also prepared by a molten-salt method in the temperature range of 700–1000 °C [18–20]. Phase diagram of NaOH–KOH indicates that potassium hydroxide and sodium hydroxide are 323 and 360 °C, respectively [15]. However, the eutectic point at ratio of NaOH:KOH = 51.5:48.5 is only about 165 °C. Therefore, molten solution of mixed KOH/NaOH was adopted as a reaction medium to prepare functional oxides including $BaTiO_3$, $Ba(Sr)TiO_3$ nanocrystals [15]. Herein, we demonstrate an alternative low temperature molten composite hydroxides approach to fabricate nickel oxide nanocrystals in attempting to find new applications or improve the existing performances. The method is based on a reaction between a nickel chloride hydrate and molten solution of mixed potassium hydroxide and sodium hydroxide with the eutectic point at 165 °C and at normal atmosphere without using organic dispersant or capping agent. This methodology may provide a one-step, convenient, nontoxic and mass-production route for the synthesis of nanostructures of functional oxide materials.

2. Experimental

All the chemicals were of analytical grade and used as received without further purification. The synthesis is performed in the following steps: (1) appropriate amount of mixed hydroxides (MHO, NaOH:KOH = 51.5:48.5) and $NiCl_2{\cdot}6H_2O$ was grinded and placed in a 50 mL Teflon-lined autoclave with a cover for preventing dust. (2) The autoclave was put in a furnace, which was preheated to 200–250 °C. (3) After reacting for a period of time, the autoclave was taken out and cooled to room temperature naturally. The product was filtered and washed by deionized water, hot water and ethanol to remove hydroxides on the surface of the particles. The obtained black powders were collected for characterization. It is noted that the molten KOH/NaOH solution is extremely corrosive, and dangerous for operation. When performing experiments, we put on the gloves and protecting-glasses to do manipulation.

X-ray powder diffraction patterns (XRD) of the products were performed on a Japan Rigaku DMax-çA rotation anode X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.54178 Å). Transmission electron microscopy (TEM) and electronic diffraction (ED) were taken on a Hitachi model H-800 transmission electron microscope at an accelerating voltage of 150 kV.

3. Results and discussion

Fig. 1a is the XRD pattern of the as-synthesized product obtained at 200 °C for 24 h with the ratio of 1% of $NiCl_2{\cdot}6H_2O$ to MHO. In the pattern, all the diffraction peaks can be indexed to pure phase of cubic NiO (JCPDS Card 02-1216). The broaden diffraction peaks indicate that the sample is on the nanometer scale. The size estimated from Scherrer equation for the product is about 55 nm. TEM image (Fig. 1b) shows the products consisting of a lot of irregular nanoparticles, and a little amount of small particles exists. The size distribution diagram (Fig. 1c) programmed from 100 nanoparticles, indicated the even diameter of 55 nm, closing to the result from XRD. The standard deviation value is in a range of 55 ± 17 nm.

The initial mass ratio of reagent to MHO was found to have a great effect on the quality of the products. Fig. 2 gives XRD patterns of the as-synthesized products at 250 °C for 2 h with different ratios of reagent to MHO. It can be seen that with the amount of nickel chloride increased, the diffraction peaks became narrower, indicating that the crystallite size became larger. The corresponding TEM images as shown in Fig. 3 demonstrate that the samples are dispersed irregular particles. With the increase of reactants from 2, 10 to 30%, the diameter of the products also increased from 50, 150 to 450 nm, accordingly. The ED pattern shown in Fig. 3d can be assigned to polycrystalline NiO with cubic phase, consisting with the results of XRD. The effect of ratio of reactant to MHO can be explained as follows. When the ratio of nickel chloride to MHO is very little (1–2%), Ni^{2+} would be surrounded by a large amount of OH^- and the nucleation of $Ni(OH)_2$ would be very fast, whereas the particle growth will be restricted by surrounding OH^- to result in small $Ni(OH)_2$ crystallites. The freshly formed $Ni(OH)_2$ would decompose rapidly and thus NiO nanocrystals be produced. If the ratio became larger, the OH^- concentration around Ni^{2+} decreased, the nucleation of $Ni(OH)_2$ became slow. As a result, the produced NiO is more regular in shape and much larger in size.

In the present work, the influence of temperature and time on the formation of the products was also investigated. It can be observed, from Fig. 4 and Table 1, that when the temperature was decreased from 220 to 170 °C, the diffraction