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Effect of synthesis conditions on the performance of weakly agglomerated nanocrystalline NiO

Xianshuang Xin^a, Zhe Lü^a, Baibin Zhou^b, Xiqiang Huang^a, Ruibin Zhu^a, Xueqing Sha^a, Yaohui Zhang^a, Wenhui Su^{a,c,d,*}

^a Center for Condensed Matter Science and Technology, Harbin Institute of Technology, Harbin 150001, PR China

^b Department of Chemistry, Harbin Normal University, Harbin 150080, PR China

^c Department of Condensed Matter Physics, Jilin University, Changchun 130023, PR China

^d International Center for Materials Physics, Academia Sinica, Shenyang 110015, PR China

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Abstract

Weakly agglomerated nanocrystalline NiO was synthesized by a homogeneous precipitation method in the presence of urea as the precipitation agent. The reaction mechanism about the hydrolyzation of urea, the precipitate process of the as-synthesized precursor, and the decomposition of the precursor during heating treatment was discussed. The effects of the ions concentration and the calcinations temperature on the powder properties were investigated. The as-synthesized precursor was characterized as hydrated basic carbonate by IR spectrum and TG analysis. The results revealed that crystallization started at about 350 °C, and the nanoparticles with the average crystallite size of 5 nm were obtained. With increasing the molar ratio of urea to Ni²⁺ ion, the crystalline size showed a slight increase, and then decrease, however the pH and the yield indicated a pronounced increase. During heating, an enhanced crystallite growth was observed. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

There has been an increasing interest in the applications of nanomaterials during the last two decades. A reduction in particle size to the nanometer scale results in variously special properties such as the quantum size effects, the high surface area and the lower sintering temperature. Nanomaterials exhibit significantly mechanical, electronic, magnetic, optical, thermal and catalytic properties in comparison with their bulk counterparts [1–7]. However, practical methods are still needed for synthesizing high-quality and ultra fine powders with required characteristics in terms of their size, morphology, microstructure, composition purity, crystallizability, etc. These characteristics significantly affect the later-stage processing and sintering properties, and eventually determine the microstructure and performance of the final ceramic materials.

suwenhui@hit.edu.cn (W. Su).

Ultra fine NiO particles with a good dispersion are desirable for many applications such as in the manufacture of electrochromic films, magnetic materials, p-type transparent conducting films, gas sensors, catalyst, alkaline batteries cathode and solid oxide fuel cells (SOFCs) anode [8-12]. Many methods have been used to synthesize NiO nanoparticles [13], nanorods [14], nanoribbons [15] and nanowire [16]. To acquire better applications about NiO, the synthesis conditions must be well controlled to obtain ultra fine powders with a narrow particle size distribution that enhance the performance of materials. Among the diverse synthesis routes of the ultra fine powders, homogeneous precipitation method [17-19] is one of the economically feasible processes to prepare monodisperse metal oxide particles of various shapes and sizes. If the precipitating ligand is added directly by simply pouring one solution into another, then there is little control of the chemistry reaction during precipitation because of the large and inhomogeneous gradients in the solution concentration. However, a better control of the chemical and morphological characteristics can be achieved if the precipitating ligand is generated simultaneously and uniformly

^{*} Corresponding author. Tel.: +86 451 86418570; fax: +86 451 86412828. *E-mail addresses:* xinxianshuang@sohu.com (X. Xin),

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throughout the solution, i.e. a homogeneous precipitation process.

The purpose of this study is to report the synthesis of NiO nanoparticles by the homogeneous precipitation process in the presence of urea. The reaction mechanism was discussed about the process of the urea decomposition and the transformation of the precipitate to nickel oxide under the calcinations condition. The effects of various synthesis parameters such as the concentration of ions and the calcinations temperature, on the powder properties of morphology, crystallite size and degree of agglomeration, were investigated.

2. Experimental

2.1. Preparation of NiO nanoparticles

 $Ni(NO_3)_2 \cdot 6H_2O$ (99.0%) was dissolved into deionized water and mixed with a urea (99.0%) solution, and then stirred uniformly. The stoichiometric solutions were transferred to a Teflon cup, and then put into a stainless steel autoclave. The autoclave was heated to 85 °C for 1 h to form a kind of light green sediment. The precipitated powders were filtered, washed with deionized water to remove the soluble ions and ethanol to reduce agglomeration, and dried in an oven at 85 °C for 2 h in air, finally calcined at different temperatures for 2 h.

2.2. Characterization

Infrared (IR) spectra were obtained with an IFS 66 v/S Fourier transform infrared (FT-IR) spectrometer. Samples were prepared by mixing the powders with potassium bromide (1:300 by weight ratio) in a steel die. Thermogravimetric analysis (TGA) was measured between room temperature and 800 °C (heating rate $10 \,^{\circ}$ C min⁻¹) by a TA SDT2960 (operated in air, flow rate 100 ml min⁻¹).

The crystalline structure was identified by powder X-ray diffractometer (Bede Scientific D¹, operated at 40 kV, 45 mA), employing Cu K α radiation ($\lambda = 1.5418$ Å). The average crystalline size was estimated according to the Scherrer equation [20]. The grain size and morphology of the samples were taken by transmission electron microscopy (TEM JEOL JEM-1200EX working at 100 kV).

3. Results and discussion

3.1. FT-IR study

The as-synthesized precursor and the powders calcined at different temperatures were investigated by IR spectroscopy. The IR spectrum of the as-synthesized precursor (Fig. 1a) exhibits extensive absorption peaks. The broad absorption band centered at $3400 \,\mathrm{cm}^{-1}$ is attributable to the band O–H stretching vibrations, and the band near $1650 \,\mathrm{cm}^{-1}$ (H–O–H bending mode) provides the evidence for the water of hydration in the structure. The bands at 831, 912, 1157 and 1384 cm^{-1} are primarily due to the banding vibration of ionic CO_3^{2-} . The IR spectrum of the as-synthesized precursor is characteristic of hydrated basic carbonates [17]. It is interesting to note that the bands near both 640 and 2250 cm⁻¹ confirm the presence of the –NCO species produced by the urea decomposition. After the sample was heated to $350 \circ C$ (Fig. 1b), the broad OH⁻ and CO₃²⁻ bands are reduced, which implies a cleavage of the hydroxyl and CO_3^{2-} ligands, and the band of -NCO disappears. After the sample was heated to 600 °C (Fig. 1c), the bands of CO_3^{2-} are further reduced. The strong band at 440 cm^{-1} is observed, corresponding to the



Fig. 1. FT-IR spectra of the as-synthesized NiO precursor (a), and the calcined powders at 350 °C (b) and 600 °C (c).

banding vibration of NiO. The weak band near 3400 cm^{-1} and the bands in the region of $831-1384 \text{ cm}^{-1}$ (Fig. 1b and c) are due to the fact that ultra fine powers tend to physically absorb H₂O and CO₂.

3.2. Chemical considerations and TG analysis

In this study, heating the solutions of nickel salts in the presence of urea forms the precursor precipitate by the homogeneous precipitation method. Urea produces ammonium and cyanate ions:

$$H_2N - CO - NH_2 \xrightarrow{k} NH_3 + HOCN \Leftrightarrow NH_4^+ + OCN^-$$
(1)

The rates of urea decomposition at elevated temperatures $(k=3.3 \times 10^{-6} \text{ and } 1.1 \times 10^{-5} \text{ s}^{-1} \text{ at } 80 \text{ and } 90 \,^{\circ}\text{C}$, respectively) are quite slow [17].

In an acidic solution, cyanate ions react rapidly according to

$$OCN^- + 2H^+ + H_2O \rightarrow CO_2 + NH_4^+$$
⁽²⁾

whereas, in neutral or basic solutions, carbonate and ammonium ions or ammonia are formed

$$\mathrm{OCN}^{-} + 2\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{CO}_3^{2-} + \mathrm{NH}_4^{+} \tag{3}$$

$$OCN^{-} + OH^{-} + H_2O \rightarrow CO_3^{2-} + NH_3$$
 (4)

The presence of metal salts can accelerate urea decomposition. The nickel ion, Ni^{2+} , is slightly hydrolyzed in water. The hydrated Ni^{2+} ions can form complexes with H₂O molecules or OH⁻ ions

$$[\text{Ni}(\text{H}_2\text{O})_n]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Ni}(\text{OH})(\text{H}_2\text{O})_{n-1}]^+ + \text{H}_3\text{O}^+$$
 (5)

With increasing the number of nickel ions, the equilibrium shifts to the right. The precipitation of the basic carbonates proceeds then according to the overall mass balance equation:

$$2[\text{Ni}(\text{OH})(\text{H}_2\text{O})_{n-1}]^+ + \text{CO}_3^{2-}$$

$$\rightarrow [\text{Ni}_2(\text{CO}_3)(\text{OH})_2] \cdot x \text{H}_2\text{O} \downarrow + (2n - x - 2)\text{H}_2\text{O}$$
(6)



Fig. 2. TG curves for the as-synthesized NiO precursor.

Thermogravimetric (TG) analysis was conducted for the assynthesized precursor to examine the conversion process during calcinations. Fig. 2 shows the thermal decomposition result of the precursor precipitate from room temperature to 800 °C in air atmosphere. The weight loss (24.0%) before 200 °C may be attributed to the thermal dehydration and the evaporation of the physically absorbed matter including absorbed water. There is a weight loss of 29.2% between 200 and 350 °C, which is very close to the theoretically stoichiometric weight loss, 29.3%, calculated from reaction (7). This can be connected with the decomposition of nickel basic carbonates, corroborating the results of the IR spectrum about the as-synthesized precursor being the hydrated basic carbonates. So the following decomposition reaction can be deduced from the weight losses evaluated from the TG curve:

Table 1

Effects of urea and Ni²⁺ concentrations on the pH of the solutions, the average crystalline size, and the yields (the samples calcined at $350 \,^{\circ}$ C)

[Urea] (mol dm ⁻³)	$[Ni^{2+}]$ (mol dm ⁻³)	[Urea]/[Ni ²⁺]	pН	Crystalline size (nm)	Yield (%)
0.4	0.2	2	6.4	6.8	41.8
0.8	0.2	4	7.0	6.7	45.0
1.6	0.2	8	7.2	6.3	69.2
3.2	0.2	16	8.0	7.7	88.4
3.2	0.1	32	8.5	5.8	84.4

of all the samples. The average crystallite sizes were calculated from the full-width at half maximum (FWHM) of the reflections using the Scherrer equation:

$$D = \frac{0.89\lambda}{\beta\cos\theta} \tag{8}$$

where *D* is the average crystalline size, β the full-width at halfheight of the peak, λ the wavelength of X-ray and θ is the diffraction angle of the peak.

Table 1 indicates that at a constant concentration of Ni²⁺, with increasing the urea concentration, the average crystalline size slightly decreases and then increases. However, at a constant concentration of urea, compared with the molar ratios of 16, the solution of rather high molar ratios of [Urea]/[Ni²⁺] (\sim 32) indicate the minimum of the crystalline size. This result suggests the significance of the molar ratio of [Urea]/[Ni²⁺] on the generation of the resulting nanoparticles. Fig. 4 shows the TEM micrograph of the as-synthesized precursor (prepared from the solutions of the molar ratios [Urea]/[Ni²⁺] = 32). The micrograph shows

$$[\text{Ni}_{2}(\text{CO}_{3})(\text{OH})_{2}] \cdot x\text{H}_{2}\text{O} + \text{absorbed matter} \xrightarrow{-24.0\%(35-200\,^{\circ}\text{C})} \text{Ni}_{2}(\text{CO}_{3})(\text{OH})_{2} \xrightarrow{-29.2\%(200-350\,^{\circ}\text{C})} 2\text{NiO} + \text{CO}_{2} \uparrow + \text{H}_{2}\text{O} \uparrow \tag{7}$$

3.3. Effect of the concentration

Fig. 3 shows the XRD patterns of NiO samples (calcined at $350 \,^{\circ}$ C) synthesized from the different molar ratios of urea to Ni²⁺ ion, [Urea]/[Ni²⁺]. Good crystalline states are observed



Fig. 3. XRD patterns of nanocrystalline NiO (calcined at $350 \,^{\circ}$ C) synthesized from the different molar ratios of urea to Ni²⁺ ion: (a) 2, (b) 4, (c) 8, (d) 16 and (e) 32.

similarity to the other as-synthesized precursor samples from the different molar ratios. Namely there are no regular shape and size, and there seems to be a flocculent structure observed of all the samples. As analyzed from Eq. (1) and the IR result, $OCN^$ or HNCO species exists at the as-synthesized precursor. The absorbed matter as Eq. (7) may include not only the absorbed water, but also the species of HNCO or OCN^- which is easy to form a complex compound to Ni²⁺, so the organic network whose structure is flocculent may be formed.

The precipitation process requires, first of all, the formation of stable nuclei, after which particle growth can take place. The controlled release of CO_3^{2-} and OH^- ions by urea decomposition causes precipitation once the critical supersaturation in terms of reaction components is achieved. At lower urea contents ([Urea]/[Ni²⁺] < 8) the precipitation process is slow, or even incomplete, as shown by the lower pH from the mother liquor of the corresponding precipitation (Table 1). Under such conditions, small crystalline sizes are initially formed, and the low conversion ratios appear. The yields increase with increasing the urea concentration. At the larger urea contents ([Urea]/[Ni²⁺] ~ 16) the process is faster, resulting in large particles at the same reaction time. However, the urea itself appears to affect the number of original nuclei, and the number increases in



Fig. 4. TEM micrograph of the as-synthesized NiO precursor.

the presence of a still larger excess of urea ($[Urea]/[Ni^{2+}] \sim 32$). This process gives a single burst of nuclei with consequent dispersions of narrow size distribution, and represents a higher nuclei concentration, resulting again in smaller final crystalline size. During a homogenous precipitation only a short time interval passes during which the concentration is high enough to nucleate particles. Further material precipitates by enlarging the existing nuclei. This works because the precipitation agent will be produced only slowly by the precursor, in this case urea. Increasing the urea concentration protracts the nucleation interval. Much more particles will be nucleated which finally will have a smaller grain size, despite of the higher yield.

The reaction temperature of ~85 °C, which was found to be critical, is determined by the necessity not only to achieve a single burst of nuclei but also to control the uniform growth of particles as studied in literature [17]. At the reaction temperatures >100 °C, the rate of the urea decomposition is rather fast so as to produce broad size distributions. At temperatures <70 °C the urea decomposition is exceedingly slow and almost no precipitation occurs.

3.4. Effect of the calcinations temperature

The XRD patterns of the as-synthesized precursor (prepared from the solutions of the molar ratios [Urea]/[Ni²⁺] = 32), as well as of the nickel oxide powders produced by heating the precursor at different temperatures are shown in Fig. 5. The as-synthesized precursor and the powders calcined at 200 °C show no detectable X-ray diffraction peak, indicating the amorphous nature of the powders. The weak peaks appear after the



Fig. 5. XRD patterns of the as-synthesized NiO precursor and the powders calcined at different temperatures.

powders were calcined at 300 °C, indicating that the reaction as Eq. (7) starts but it is not completed to form good crystalline state. A well-crystallized state is observed at 350 °C. During heating, a simultaneous growing and narrowing of the peaks is observed due to the enhanced crystalline growth. The crystalline growth is the process that the average crystalline size of the nanomaterial increases continuously during heating treatment in order to minimize interfacial surface energy [21]. All the diffraction peaks can be perfectly indexed to the cubic structure NiO.

The evolution of the average crystallite sizes (Fig. 6) was investigated during heating treatment. The results show that the average crystalline size is about 5 nm at 350 °C. The crystalline size increases with increasing the calcinations temperature, and increases to an average crystalline size of 38 nm at 650 °C. Smaller crystalline sizes result from the powders synthesized in the presence of the concentrated precipitation agent solutions. The crystalline sizes of NiO are affected, in fact, by the nucleation rate, which is in turn proportional to the concentration of the precipitation agent. Thus, the higher the precipitation agent will be, and then the smaller particle sizes result.



Fig. 6. Effect of the calcinations temperature on the crystalline sizes of nanocrystalline NiO.



Fig. 7. TEM micrographs (the magnificated micrograph of the corresponding sample as an inset) of nanocrystalline NiO at different calcined temperatures.

3.5. TEM results

TEM analysis provides information on the size and morphology of primary particles and their state of agglomeration. The particles obtained by homogeneous precipitation ([Urea]/[Ni²⁺] = 32) clearly exhibit well-crystallized nanocrystalline of homogeneous and weakly agglomerated assembly with the primary particle size of about 5 nm (Fig. 6 350 °C). This is in good agreement with the powder X-ray diffraction result. The results also suggest that the crystallites have nearly spherical morphology.

From the TEM micrographs, it can be seen that as the calcinations temperature increase (Fig. 7), the primary particle sizes of NiO nanoparticles increase (10 and 22 nm for 400 and 500 °C, respectively.). A magnification micrograph of the corresponding power sample as an inset shows that there is no further aggregation observed with increasing the calcinations temperature. The formation of NiO particles in the calcinations process undergoes the procedure from nuclei formation to particles growth. With increasing the calcinations temperature, the growth rate of the particles increases more rapidly than the nucleation rate does. Therefore, the average size of NiO nanoparticles increases with the increase of the calcinations temperature.

4. Conclusion

By the homogeneous precipitation method, well-crystallized, narrow-sized and weakly agglomerated nanocrystalline NiO was synthesized. The reaction mechanism was investigated. The IR spectrum and TG curve confirmed that the as-synthesized precursor was hydrated nickel basic carbonates. With the increase of the calcinations temperature, a simultaneous growing and narrowing of the peaks was observed due to the enhanced crystalline growth. At lower urea contents ([Urea]/[Ni²⁺] < 8), the precipitation process was incomplete, which showed a lower pH and yields. At a constant concentration of Ni²⁺, with increasing the urea concentration, a slight decrease and then increase in the crystalline size was observed, and the enhanced pH and yields were obtained. The higher molar ratio of [Urea]/[Ni²⁺] (\sim 32)

represented the minimum of the crystalline size, indicating that the nucleation rate increases more rapidly than the crystalline growth rate does.

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