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# Microwave-assisted and liquid oxidation combination techniques for the preparation of nickel oxide nanoparticles

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# Abstract

A nickel hydroxide, Ni(OH)<sub>2</sub>, was prepared by microwave-assisted heating technique from nickel nitrate aqueous solution and sodium hydroxide (assigned as PM). Then, the as-prepared PM was oxidized by liquid oxidation with sodium hypochlorite (assigned as PMO). Further, pure nanocrystalline nickel oxide (NiO) particles were obtained from the as-prepared PMO by calcination at 300, 400, 500, 600, 650 and 700 °C (labeled as C300, C400, C500, C600, C650 and C700, respectively). The as-prepared powders (PM and PMO) and the NiO nanoparticles were characterized by X-ray diffraction (XRD), infrared spectroscopy (IR), temperature-programmed reduction (TPR) and scanning electron microscope (SEM). The results indicated that the particle size of nickel oxide was controlled by the calcined temperature. The average crystal size of the NiO nanoparticles ranges from about 5 to 35 nm at 300–700 °C. Mechanism of nickel oxide nanocrystallite growth during thermal treatment was investigated.

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# 1. Introduction

Since the innovation of nanochemistry in past decades, numbers of materials in nano-scale have been synthesized via many methods [1]. Nanomaterials have been widely used in various fields, such as photoelectric, recording materials, catalysts, sensors, ceramic materials, etc., due to their special structures and properties [2–5]. In particular, nanosized nickel oxides exhibit particular catalytic [6,7], anomalous electronic [8,9] and magnetic [10,11] properties. Another important application of NiO is in a battery system [12,13]. Non-stoichiometric nickel oxide is a good P-type semiconductor owing to its defect structure [14],

0925-8388/\$ - see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2006.10.114 a potential gas sensor for  $H_2$  [15] and high active in the degradation of phenol and phenolic derivatives [16]. These applications can be enhanced by decreasing the particle size (preferably to less than 10 nm) and are highly dependent on particle size; the precise control of the size and distribution in a nanometer region is required.

Recently, several methods have been developed to prepare ultrafine nickel oxide powder, including low-pressure apray pyrolysis [17], surfactant-mediated method [18], simple liquidphase process [19] and other techniques [20–22]. The heating effect of high-frequency fields on some materials was recognized even in the 19th century. The mechanism of energy transfer using a microwave field is very different from that of the three well established modes of heat transfer, that is, conduction, radiation and convection [23]. Microwave heating processing has been successfully applied for the preparation of nanosized inorganic materials [24,25]. This work reports the synthesis of nickel oxide nanoparticles by microwave process from an aqueous solution containing nickel nitrated, sodium hydroxide and oxidation process with sodium hypochlorite solution.

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## 2. Experimental

#### 2.1. Preparation of nickel oxide nanoparticles

All the chemical reagents used in this study were analytical grade and used without further purification. 50 ml of  $0.6 \text{ M} \text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution was added to the 100 ml of 3.2 M NaOH solution. The reaction was carried out for 10 min in air in a microwave apparatus (100 W, 2450 MHz, CEM, USA). The obtained as-prepared nickel hydroxide, Ni(OH)<sub>2</sub>, presents a green colloid solution and assigned as PM. Then, the as-prepared PM was oxidized by liquid oxidation with sodium hypochlorite drop by drop under a constant stirring at 0 °C for 2 h. Finally, a kind of black sediment was formed and assigned as PMO. The as-prepared PMO precipitate was thoroughly washed with distilled water six times, respectively, to remove the possible adsorbed ions. After dried at 110 °C for 20 h, the as-prepared PMO powder was calcined under air at 300, 400, 500, 600, 650 and 700 °C, respectively, for 2 h to obtain NiO nanoparticles (labeled as C300, C400, C500, C600, C650 and C700).

## 2.2. Characterization techniques

X-ray diffraction (XRD) measurements were performed using a MAC Science MXP18 diffractometer with Cu K $\alpha_1$  radiation ( $\lambda = 1.5405$  Å) at 40 kV and 30 mA with a scanning speed in 2 $\theta$  of 4° min<sup>-1</sup>. The crystallite sizes of nickel hydroxide and nickel oxide were estimated using the Scherrer equation.

The infrared spectra were obtained by a Perkin-Elmer spectrum GX spectrometer in the range of 500-4000 cm<sup>-1</sup>. One milligram of each powder sample was diluted with 200 mg of vacuum-dried IR-grade KBr and subjected to a pressure of 8 tonnes.

Reduction behavior of nickel hydroxide and nickel oxide was studied by temperature-programmed reduction (TPR). About 50 mg of the sample was heated in a flow of 10%  $H_2/N_2$  gas mixture at a flow rate of 10 ml min<sup>-1</sup>. During TPR, the temperature was increased by 7 °C min<sup>-1</sup> increment from room temperature to 600 °C.

The surface morphology of nickel oxide nanoparticles were observed by means of a scanning electron microscope (JSM-6330TF) operated at 10 kV.

# 3. Results and discussion

# 3.1. Characterization of as-prepared materials (PM and PMO)

Fig. 1 shows the XRD patterns of the as-prepared materials, PM and PMO. It indicates that all the major peak positions and relative intensities of the as-prepared PM (Fig. 1(a)) matches the



JCPDS 14-0117 file identifying  $\beta$ -Ni(OH)<sub>2</sub>, with a hexagonal structure. From the disorder broaden of different *h k l* planes, the diffraction peaks can be classified into different families, according to Henn and co-workers [26] suggested: one leading to large dimensions [(1 0 0), (1 1 0)], one leading to small dimensions [(0 0 1), (1 0 2)] and the other peaks belong to intermediate dimensions. This result is typical for anisotropic particles. We used the modified Scherrer equation to calculate the asymmetry sizes that along the (0 0 1) and (1 0 0) directions with Scherrer constant *K* is 0.94 and 1.84, respectively, corresponding to the thickness (*t*) and the diameter (*d*) of the anisotropic Ni(OH)<sub>2</sub> particle [27]. Both *t* and *d* are 2.6 and 21.6 nm, respectively. The XRD pattern of the as-prepared PMO (Fig. 1(b)) has the peaks at ca. 19.0° and 38.4° and these locations are similar with the  $\beta$ -NiOOH with the peaks at (0 0 1) and (1 0 0) planes.

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The infrared spectrum of the as-prepared materials is shown in Fig. 2. The broad absorption bands centered around 3450 and  $1630 \text{ cm}^{-1}$  are assigned to the existence of water. From the strength of absorption, we know that the as-prepared PM (Fig. 2(a)) has stronger absorption ability than the asprepared PMO (Fig. 2(b)) for moisture. The absorption band at  $1530-1320 \text{ cm}^{-1}$  indicates the existence of carbonates. The spectrum (Fig. 2(a)) displays a sharp peak at  $3640 \text{ cm}^{-1}$  and this confirms that the as-prepared PM is  $\beta$ -Ni(OH)<sub>2</sub> [28]. This sharp peak in the OH stretching vibration is shown by  $\beta$ -Ni(OH)<sub>2</sub> because of the absence of hydrogen bonding between hydroxyl groups [29]. The absorption band at  $570 \text{ cm}^{-1}$  (Fig. 2(b)) indicates that the as-prepared PMO is Ni–O stretching vibration mode.

Fig. 3 shows the TPR profile of the as-prepared materials, PM and PMO. The reductive signal of the as-prepared PM (Fig. 3(a)) in TPR proceeded by one step at 236 °C according to Eq. (1).

$$Ni(OH)_2 + H_2 \rightarrow Ni + 2H_2O \tag{1}$$

The ratio of nickel hydroxide species is quantitatively determined from the consumption of hydrogen in TPR traces. The  $N_{H_2}/N_{N_i}$  ratio is 1.02.









Fig. 3. TPR profile of the as-prepared materials: (a) PM and (b) PMO.

Reduction profiles of the as-prepared PMO (Fig. 3(b)) shows two reduction peaks, which are similar to those observed in supported nickel catalysts [30,31]. These profiles point to a two-step reduction process: the first one is of low intensity at 156 °C and the more intense second one whose maximum is occurred at 276 °C according to the following equations:

$$NiO_x + xH_2 \rightarrow NiO + xH_2O$$
(2)

$$NiO + H_2 \rightarrow Ni + H_2O$$
 (3)

The  $N_{H_2}/N_{N_i}$  ratio is determined to be 1.58. This shows that the as-prepared PMO species upon oxidation with NaOCl is  $NiO_x$ , where *x* is larger than 1.

# 3.2. Characterization of nickel oxide

In order to obtain pure nanocrystalline nickel oxide (NiO) particles and understand the thermal characterizations, the asprepared PMO powder is further calcined at 300, 400, 500, 600, 650 and 700 °C, respectively (the calcined temperature assigned as  $T_{\rm C}$ ).

Fig. 4 presents XRD patterns for nickel oxide nanoparticles. The effects of the calcination temperature on the crystallite size of NiO particles can be demonstrated. Traces of NiO crystallite phases (111), (200) and (220) are detected in the XRD pattern for all calcined temperatures and then their intensities increase abruptly when the  $T_{\rm C}$  above 600 °C. In general, the sharpness of the XRD peak (i.e. high crystallinity) is increased as the  $T_{\rm C}$ increases. According to the (200) diffraction pattern of NiO crystalline, the particle size of NiO can be calculated from the full width at half-maximum using the Scherrer equation. Obviously, the particle size of NiO changes as the  $T_{\rm C}$  controlled under 300, 400, 500, 600, 650 and 700 °C; the order is 4.1, 9.4, 12, 14, 32.7 and 34.8 nm, respectively. These indicate that the crystallinity of NiO is accelerated as the  $T_{\rm C}$  above 600 °C. Fig. 5 illustrates the relationship between the annealing temperature and the average crystal size of the NiO nanoparticles. It is obvious that the NiO nanoparticle grows slowly at 300-600 °C and



Fig. 4. XRD patterns for nickel oxide nanoparticles: (a) C300, (b) C400, (c) C500, (d) C600, (e) C650 and (f) C700.

650–750 °C, respectively, while the nanoparticle grow rapidly at 600–650 °C.

Under the condition that the nanocrystallites grow homogeneously, a straight line of  $\ln(d)$  against 1/T can be plotted in Fig. 6 according to below equation [32], which approximately describes the nanocrystallite growth during annealing:

$$d = C \, \exp\left(-\frac{E}{RT}\right) \tag{4}$$

where *d* is the XRD measured average crystal size, *C* a constant, *E* the activation energy for nanocrystallite growth, *R* the ideal gas constant and *T* is the absolute temperature of heat treatment. The activation energy for NiO nanocrystallite growth during calcinations is calculated to be 23.2 kJ mol<sup>-1</sup>. It indicates that the  $T_C$ has a more remarkable effect on the growth of NiO nanocrystallite during annealing. The crystal size increases gradually with the  $T_C$ , and especially becomes more quickly larger in the range of 600–650 °C, as can be observed from Fig. 5. Generally, it can be considered that the agglomeration of NiO nanoparticle



Fig. 5. Effect of annealing temperature on the crystal size of nickel oxide nanoparticle.



Fig. 6. Plot of ln (*d*) against 1/T for the equation  $d = C \exp(-E/RT)$ .



Fig. 7. TPR profiles for nickel oxide nanoparticles: (a) C300, (b) C400, (c) C500, (d) C600, (e) C650 and (f) C700.



Fig. 8. SEM images of the as-prepared PMO and heat-treated nickel oxide nanoparticles: (a) PMO, (b) C300, (c) C600 and (d) C700.

comes from the interfacial reaction. Evidently, in the case of low  $T_{\rm C}$  (<600 °C), the porosity is quite high and most pores are interconnected to maintain smaller crystal sizes. For the specimens calcined at higher temperatures (>600 °C), continuous grain boundary networks have been formed due to the bridging of fine particles to increase the crystal sizes. The agglomeration and densification processes continue with the  $T_{\rm C}$  also can be seen in the SEM images (see Fig. 8).

Moreover, the reducibility of the calcination temperature on the crystallite size of NiO particles is obtained with the qualitative and quantitative TPR technique. Fig. 7 displays the TPR profiles of the calcined product, NiO, at different temperatures. All the samples show a similar TPR profile. A qualitative analysis of the TPR profile shows that the reduction peak  $(T_{red})$ appears shifted to higher temperatures as the  $T_{\rm C}$  increased (as can be seen in Fig. 7(a–d)), i.e., the  $T_{red}$  of sample C300 is 361 °C (Fig. 7(a)). While, the  $T_{\rm red}$  of sample C600 is 394 °C (Fig. 7(d)). According to the calculated particle sizes of nickel oxide from XRD, we know that the shift in the  $T_{red}$  toward higher temperature is marked more as the particle size increases. The more reducible nickel oxide is located mainly in the small pores with a mean diameter of  $\sim$ 4 nm and the less reducible oxide is located in the larger pores with a mean diameter larger than 10 nm. But, the reductive temperature is decreased as the nanoparticle secondary agglomerates abruptly into bulk structure at 650 °C. Also, the ratio of nickel oxide species for the calcined product, NiO, at different temperature is quantitatively determined from the consumption of hydrogen in TPR traces. The  $N_{H_2}/N_{N_i}$  ratio is determined to be 1.09, 1.11, 1.11, 1.10, 1.08 and 1.13, respectively, for C300, C400, C500, C600, C650 and C700. This shows that the dominant species upon calcination at 300-700 °C is NiO, where x approaches 1.

The SEM images of the as-prepared PMO and heat-treated nickel oxide nanoparticles (C300, C600 and C700) are show in Fig. 8. It can be observed that the as-prepared PMO has assembled-rod morphology with a length of ca. 10 nm (shown in Fig. 8(a)). As the PMO is annealed, moderately agglomerated particles seem to be present (Fig. 8(b–d)). The assembled-rod NiO<sub>x</sub> nanoparticle can completely change to roundel-like nanoparticle with narrow size distribution by conventional thermal treatment. Apparently, the C700 sample (shown in Fig. 8(d)) processes the secondary aggregated roundel particles through densification process to obtain about 50–60 nm particles. This possibly results from an orientation growth of present, which is greatly related to the large surface energy of the nanoparticle [20].

# 4. Conclusion

Nanocrystalline NiO particles have been successfully prepared by combination of microwave-assisted and liquid oxidation, then subsequent thermal treatment. It has found that the assembled-rod  $NiO_x$  nanoparticle can completely change to roundel-like nanoparticle with narrow size distribution by conventional thermal treatment. The average crystal size of the NiO nanoparticles ranges from about 4.1 to 34.8 nm under 300–700 °C. Nanocrystallite NiO particles grow rapidly through densification process in the range of 600–650 °C to increase the rate of bridging of fine particles. The calculation of the activation energy ( $E = 23.2 \text{ kJ mol}^{-1}$ ) indicates that NiO nanocrystallite grows during annealing by means of an interfacial reaction.

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