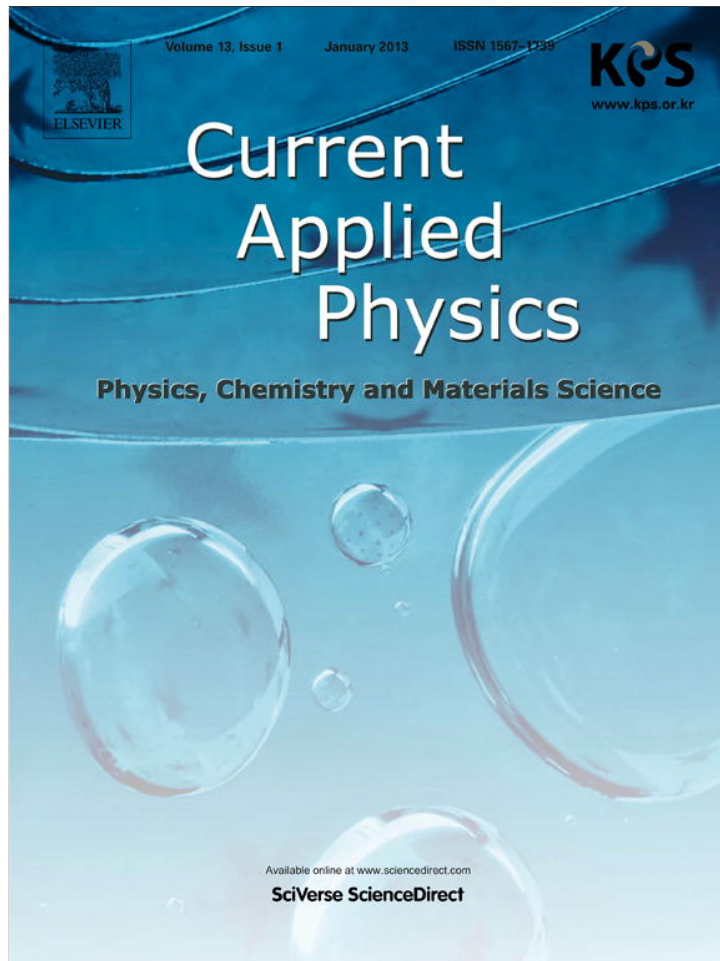


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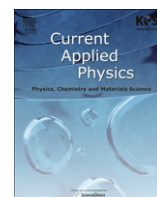
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Corrigendum

Corrigendum to “Preparation of NiO and CoO nanoparticles using M^{2+} -oleate ($M = \text{Ni}, \text{Co}$) as precursor” [Curr. Appl. Phys. 10 (2010) 967–970]Zhongping Chen^{a,b}, Aiqun Xu^c, Yu Zhang^{b,*}, Ning Gu^{b,*}^a State Key Laboratory of Bioelectronics, Jiangsu Key Laboratory for Biomaterials and Devices, Southeast University, Nanjing 210096, China^b School of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, China^c The Analysis and Testing Center, Southeast University, Nanjing 210096, China

The authors regret the mistakes made in Fig. 1, Table 1, and Table 2. In Fig. 1, the order of crystal plane (222) (311) (220) (200) (111) should be (111) (200) (220) (311) (222) from inner to outer of SAED patterns. In Table 1 and Table 2, the second crystal plane should be (200).

The authors would like to thank Dr. Francisco C. Robles Hernandez, Master of Science in Mechanical Engineering Technology, Program Coordinator, University of Houston, College of Technology. His kind enquiry helps us to find this obvious mistake in this paper.

The authors would like to apologise for any inconvenience caused.

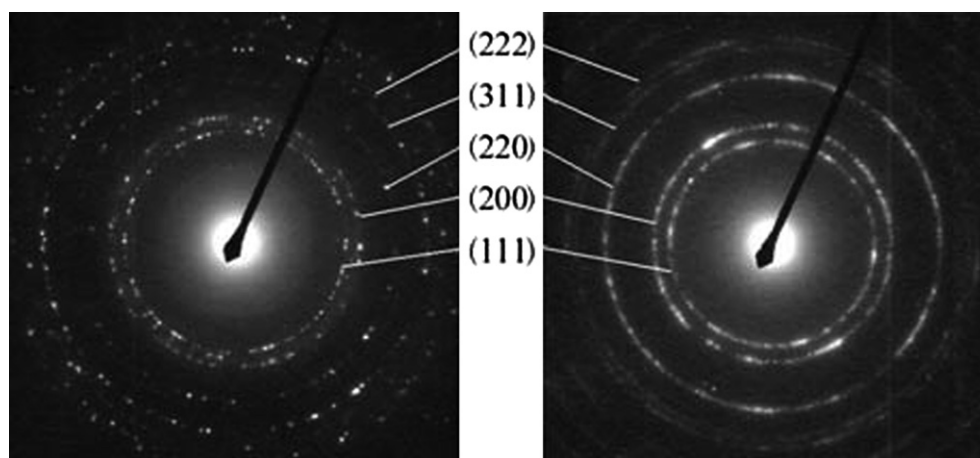


Fig. 1.

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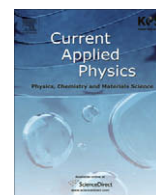
* Corresponding authors. Tel.: +86 25 83794960; fax: +86 25 83792576.

E-mail addresses: zhangyu@seu.edu.cn (Y. Zhang), guning@seu.edu.cn (N. Gu).



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Preparation of NiO and CoO nanoparticles using M^{2+} -oleate ($M = Ni, Co$) as precursor

Zhongping Chen^{a,b}, Aiqun Xu^c, Yu Zhang^{b,*}, Ning Gu^{b,*}

^a State Key Laboratory of Bioelectronics, Jiangsu Key Laboratory for Biomaterials and Devices, Southeast University, Nanjing 210096, China

^b School of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, China

^c The Analysis and Testing Center, Southeast University, Nanjing 210096, China

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ABSTRACT

The preparation of NiO and CoO nanoparticles was reported. The dot-like NiO and flower-like CoO nanoparticles were obtained using M^{2+} -oleate ($M = Ni, Co$) as precursor via thermal decomposition method. Transmission electron microscopic (TEM) images monitored the growth of NiO and CoO nanoparticles. When the reaction complex including M^{2+} -oleate ($M = Ni, Co$) precursor, oleic acid and 1-octadecene was heated to the refluxing temperature (320 °C), the formed NiO and CoO nanoparticles were needle-like and very small, indicating low growth speed. However, when the reaction complex was kept refluxing for 30 min, dot-like NiO and flower-like CoO nanoparticles were observed, suggesting the accelerated growth at this refluxing stage. The difference of the morphology of the resultant NiO and CoO nanoparticles resulted from the difference of their growth mode. Selected-area electron diffraction (SAED) patterns showed the face-centered cubic structures of NiO and CoO nanoparticles. The magnetic property of the nanoparticles was studied using vibrating sample magnetometer (VSM).

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1. Introduction

Transition metal oxides constitute a well-studied class of materials due to their many interesting properties and numerous applications. NiO and CoO nanoparticles are useful in various applications such as electrochemical capacitors [1,2], catalysts [3,4] and solar cells [5]. Therefore, a wide variety of methods have developed to synthesize NiO and CoO nanoparticles such as sol-gel [6,7], thermal decomposition [8–13], electrodeposition [14] and laser vaporization [15]. Among these methods, thermal decomposition methods are widely adopted due to their advantages in controlling the size and morphology of the nanoparticles. Wang et al. synthesized about 9 nm NiO nanoparticles via thermal decomposition of NiC_2O_4 at 450 °C [8]. Liang et al. prepared single-crystalline NiO nanosheets via thermal decomposition of $Ni(OH)_2$ at 400 °C [9]. Similarly, CoO nanoparticles with size ranging in 4.5–18 nm were produced by Ghosh et al. via the decomposition of Co(II) cupferronate in decalin [11]. Pencil-shaped CoO nanorods were synthesized by the thermal decomposition of a Co-oleate [12,16]. Furthermore, Zhang et al. manipulated the morphology of CoO nanoparticles by altering thermal decomposition rate of cobalt oleate with the introduction of activating reagent dodecanol or inhibiting reagent oleic acid into the reaction system [13].

In this work, NiO and CoO nanoparticles were synthesized using M^{2+} -oleate ($M = Ni, Co$) as precursor, oleic acid as surfactant and 1-octadecene as solvent. High-temperature refluxing (320 °C) of 1-octadecene solution containing M^{2+} -oleate ($M = Ni, Co$) and oleic acid generated NiO and CoO nanoparticles. In the beginning of refluxing, the formation of very small NiO and CoO nanoparticles with needle-like morphology was observed; however, after refluxing for 30 min, dot-like NiO nanoparticles and flower-like nanoparticles were observed. This phenomenon implies the different growth modes of NiO and CoO nanoparticles at high temperature.

2. Experimental section

2.1. Materials

Nickel (II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, 98%), cobalt (II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, 99%) and sodium oleate (98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Oleic acid (99%) was purchased from Shanghai Chemical Reagent Co., Ltd. 1-Octadecene (Tech. 90%) was purchased from Alfa Aesar. All chemicals were used as received without further purification.

2.2. Synthesis of NiO and CoO nanoparticles

The nanoparticles were synthesis in two steps: first to prepare an M^{2+} -oleate ($M = Ni, Co$) precursor and second to decompose the precursor. To prepare M^{2+} -oleate ($M = Ni, Co$), the reported work was followed [16]. Typically, 1.18 g of $NiCl_2 \cdot 6H_2O$ (5 mM)

* Corresponding authors. Tel.: +86 25 83794960; fax: +86 25 83792576.

E-mail addresses: zhangyu@seu.edu.cn (Y. Zhang), guning@seu.edu.cn (N. Gu).

and 1.18 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (5 mM) were dissolved in a mixture solution containing 6 ml of water, 8 ml of ethanol and 14 ml of hexane, respectively. Each resulting solution was added by 3.04 g sodium oleate (10 mM) under vigorous stirring for 4 h at 70 °C. The precipitate was separated in a separatory funnel and washed three times with 3 ml of water. Then, the aqua Ni-oleate and wine Co-oleate were dried under vacuum condition overnight. To synthesize NiO nanoparticles, about 5 mM Ni-oleate and 2 mM oleic acid were dissolved in 15 ml of 1-octadecene. The mixture was heated to 320 °C with a constant heating rate of 3.3 °C/min and kept at that temperature for 30 min. After the resulting solution was cooled, NiO nanoparticles were collected by addition of excess ethanol. The synthesis of CoO nanoparticles was the same with that of NiO nanoparticles.

2.3. Characterization

The size and morphology of the particles were determined by transmission electronic microscopy (TEM, JEOL, JEM-200EX) operating at 120.0 kV. Samples were dropped from hexane onto a carbon-coated copper grid and dried under room temperature. Magnetic measurements were carried out with a Lakeshore 7470 vibrating sample magnetometer (VSM).

3. Results and discussion

Selected-area electron diffraction (SAED) measurements were performed to confirm the crystallinity of as-prepared nanoparticles. Fig. 1 show SAED patterns of NiO (Fig. 1, left) and CoO nanoparticles (Fig. 1, right). The respective hkl planes were (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2). According to the SAED pattern, the d -spacing can be calculated in the following equation:

$$L\lambda = dR$$

where L is the distance between the test sample and the film ($L = 137$ cm), λ is the wavelength of electron beam ($\lambda = 0.0251$ Å), R is the radius of the diffraction ring. The calculated d -spacing for hkl planes were 2.3 (1 1 1), 1.96 (2 0 0), 1.38 (2 2 0), 1.27 (3 1 1) and 1.21 (2 2 2) for NiO nanoparticles, and 2.41 (1 1 1), 2.08 (2 0 0), 1.46 (2 2 0), 1.25 (3 1 1) and 1.17 (2 2 2) for CoO nanoparticles. These calculated results were well-accorded with theoretical d -spacing values of NiO (JCPDS card No. 75-0269) and CoO (JCPDS card No. 78-0431), which were shown in Tables 1 and 2, respectively.

To follow the temporal evolution of the size and morphology of NiO and CoO nanoparticles, the reaction was monitored by taking TEM measurements at different refluxing intervals. When the

Table 1

The d -spacing calculated based on SAED pattern of NiO nanoparticles in comparison with theoretical values.

	1	2	3	4	5
R (cm)	1.50	1.74	2.51	2.77	3.00
ED results- d (Å)	2.3	1.96	1.38	1.27	1.10
Theory values- d (Å)	2.40	2.08	1.47	1.25	1.14
Crystalline lane (hkl)	(1 1 1)	(2 2 0)	(2 2 0)	(3 1 1)	(2 2 2)

Table 2

The d -spacing calculated based on SAED pattern of CoO nanoparticles in comparison with theoretical values.

	1	2	3	4	5
R (cm)	1.42	1.65	2.35	2.75	2.95
ED results- d (Å)	2.41	2.08	1.46	1.25	1.17
Theory values- d (Å)	2.46	2.13	1.50	1.28	1.23
Crystalline lane (hkl)	(1 1 1)	(2 2 0)	(2 2 0)	(3 1 1)	(2 2 2)

temperature was up 80 °C, the reaction complex turned to a clear solution. After continuously heating, the clear solution became turbid, but the formation of nanoparticles was not observed below 250 °C. When reaction complex was heated to refluxing temperature, very small and needle-like NiO (Fig. 2a) and CoO nanoparticles (Fig. 2c) were observed, indicating the low growth speed of the nanoparticles before refluxing. However, after refluxing the growth accelerated and the dramatic changes of the size and morphology of the nanoparticles occurred. The very small and needle-like NiO and CoO nanoparticles changed to dot-like NiO nanoparticles (Fig. 2b) and flower-like CoO nanoparticles (Fig. 2d and e), and their sizes changed from several nanometers to about 20 and 50 nm, respectively. From TEM results, it could be concluded that the growth of these very small nanoparticles resulted in the formation of dot-like NiO and flower-like CoO nanoparticles; however, the growth modes of NiO and CoO nanoparticles were different.

The growth mechanism of nanostructures remained an intricate and challenging question despite great achievements in the preparation of nanostructures. Although there were numerous examples for the synthesis of diverse nanostructures, morphology was still not easy to predict. In terms of the knowledge from colloidal chemistry, the formation of nanocrystals could be divided into nucleation and growth processes: (i) nucleation initiated by a sudden increase of monomer concentration up to supersaturation levels, and (ii) subsequent growth of the seeds formed in the nucleation stage. Generally speaking, the crystalline phase of the seeds formed at the nucleating stage was crucial for the subsequent nanoparticles shapes. In this work, the formation of dot-like NiO and

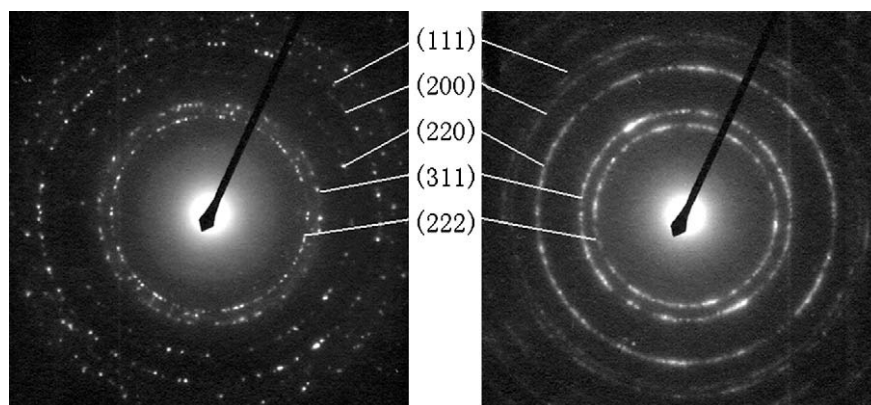


Fig. 1. SAED patterns of NiO (left) and CoO nanoparticles (right). The respective hkl planes were (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2).

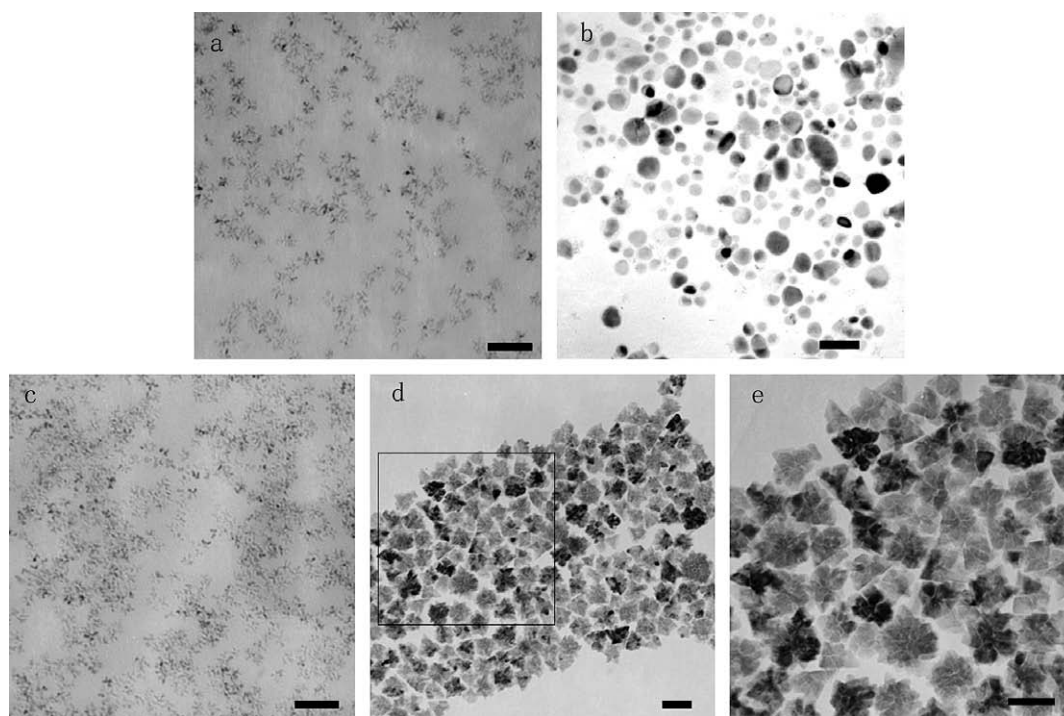


Fig. 2. TEM images of NiO and CoO nanoparticles taken at different reaction times. In the beginning of refluxing, the formed NiO (a) and CoO (c) nanoparticles are very small and needle-like. After refluxing for 30 min, dot-like NiO (b) and flower-like CoO nanoparticles (d) are observed. (e) The enlarged image of the region marked with the square in (d). All bars are 50 nm.

flower-like CoO nanoparticles indicated the difference of the crystalline phase of their seeds. The CoO nanoparticles could be the result of growth of the seeds along [11] direction in a dendritic fashion, resulting in the highly anisotropic flower-like shape [13]. Compared to CoO nanoparticles, the non-anisotropic growth of NiO nanoparticles led to dot-like shape.

As described above, we synthesized flower-like CoO nanoparticles via thermal decomposition of Co-oleate at 320 °C refluxing temperature by exactly controlling heating rate (3.3 °C/min) and without stirring. However, under the condition of vigorously stirring An et al. synthesized pencil-shaped CoO nanorods [12]. Moreover, Lee et al. prepared Co nanoparticles at 286 °C refluxing temperature using the same method [17], indicating that CoO nanoparticles might originate from the oxidation of Co nanoparticles at high temperature under oxygen-sufficient condition. These results revealed that many parameters should be taken into account in synthesizing metal or metal oxide nanoparticles via thermal decomposition of metal-oleate.

Magnetic properties of NiO and CoO nanoparticles are shown in Fig. 3. From the magnetization curve as a function of an external magnetic field at room temperature (RT), it could be concluded that the saturation magnetization (M_s) of NiO and CoO nanoparticles were comparatively low. NiO nanoparticles were superparamagnetic and the M_s was about 0.8 emu/g. For antiferromagnetic CoO nanoparticles, the M_s was 6.3 emu/g; the coercivity was 390 Oe and the remanence magnetization was 2.2 emu/g. The M_s of both NiO and CoO nanoparticles were smaller than that of bulk NiO and CoO particles, due to their small size and non-magnetic surfactant coated on the surface of NiO and CoO nanoparticles.

4. Conclusions

A general method was reported to synthesize dot-like NiO and flower-like nanoparticles via the thermal decomposition of M^{2+} -oleate ($M = \text{Ni, Co}$) precursor. The crystallinity of as-prepared

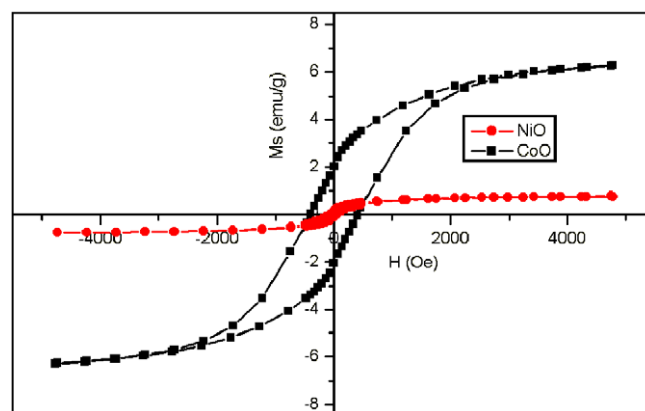


Fig. 3. Hysteresis loops for NiO and CoO nanoparticles at room temperature.

nanoparticles was confirmed by SAED. The growth of NiO and CoO nanoparticles was monitored, revealing their different growth modes at refluxing temperature. The results were compared to the reported work, indicating the importance of controlling reaction parameters to the synthesis of nanoparticles via metal-oleate decomposition method. This work could be applied to the synthesis of other metal oxides.

Acknowledgments

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