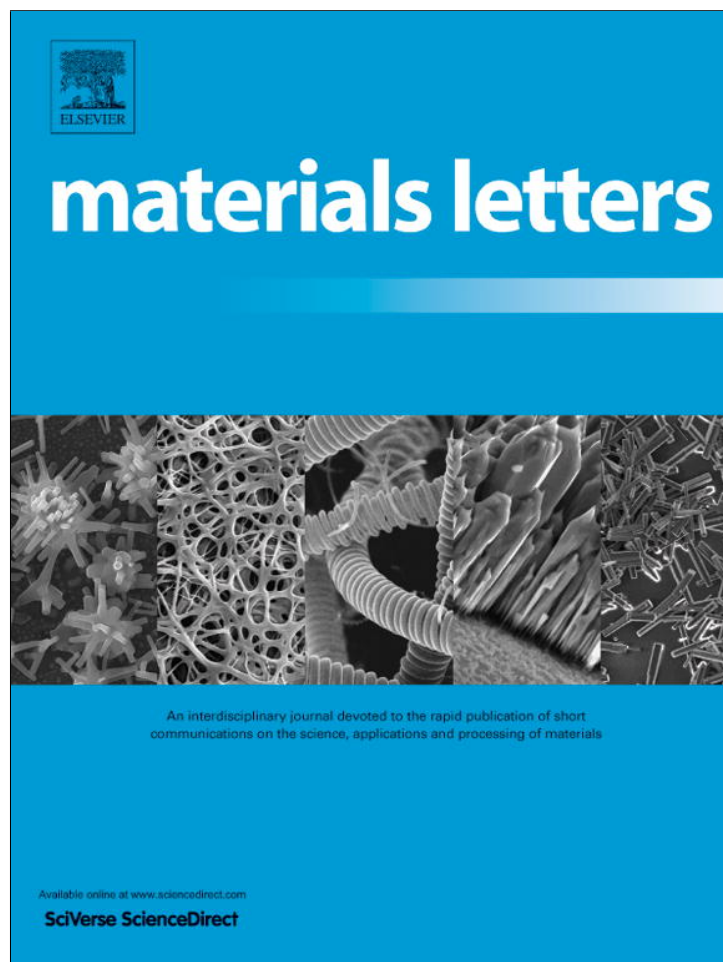


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Size-controlled synthesis of CoCO_3 and Co_3O_4 nanoparticles by free-surfactant hydrothermal method

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ABSTRACT

Uniform cobalt carbonate nanopowders were synthesized through free-surfactant hydrothermal treatment of a mixture of cobalt acetate and ammonium carbonate in an autoclave. The size, phase and purity of CoCO_3 particles were controlled by adjusting reaction time (05–24 h), temperature (80–160 °C), and (1:6–1:0.5) ($\text{Co}^{2+}:\text{CO}_3^{2-}$) molar ratios. Pure cobalt carbonate nanoparticles were obtained in high yield (94%) at 120 °C for 0.5 h, with (1:3) ($\text{Co}^{2+}:\text{CO}_3^{2-}$) molar ratio and crystallite size in ranges 80–90 nm. Moreover, cobalt oxide nanoparticles with an average crystallite size of 25 nm have been obtained by thermal decomposition of cobalt carbonate microspheres at 300 °C for 2 h. Chemical structure of the products was confirmed by powder X-ray diffraction (XRD) and Fourier transform infrared (FT-IR). Morphology of the products was investigated by transmission electron microscope (TEM) and scanning electron microscope (SEM). Optical properties of Co_3O_4 nanoparticles revealed the presence of two band gaps (2.0 and 1.46 eV) whose values confirm the purity and semiconducting properties of the oxide.

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1. Introduction

Nowadays, the nanostructure materials are attracting keen interest of researchers due to their unique electrical, magnetic, optical, and catalytic properties in comparison with those of bulky materials [1–3]. Nanoparticles can be synthesized by several physical and chemical methods [4]. Chemists and material chemists directed most of their effort to investigate morphology of nanostructured materials since nanoparticles with different morphologies show substantial differences in their properties [5]. Spinel Co_3O_4 nanomaterials have been widely considered as promising types of multifunctional materials due to their extensive applications in gas sensing, lithium-ion batteries, data storage, magnetic semiconductors, catalysis and electrochromic devices [6,7]. Different experimental approaches have been used for the synthesis of cobalt oxide nanomaterials [8,9]. It is noteworthy that the hydrothermal method has the priority over various synthetic methods due to its simplicity, low-cost and varying morphologies of products [10]. However, reports on the hydrothermal synthesis of CoCO_3 and its conversion into Co_3O_4 nanostructures are still limited [11–13].

However, herein, as a continuation to our research, the synthesis of cobalt carbonate microspheres in high yields by using a free-surfactant hydrothermal reaction of cobalt acetate and ammonium carbonate as a cheap carbonate source is reported. The as-prepared

cobalt carbonate microspheres were then thermally converted into pure phase cobalt oxide nanoparticles in high yield.

2. Experimental procedures

2.1. Synthesis of cobalt carbonate and Co_3O_4 oxide nanoparticles

In a typical hydrothermal synthesis, an aqueous solution of ammonium carbonate (1.86 g, 19.32 mmol) (60 mL) was added dropwise to a stirring cobalt acetate aqueous solution ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4 \text{H}_2\text{O}$; 0.80 g, 3.22 mmol) (20 mL). The reaction blend was transferred into an autoclave with a capacity of 100 mL which was then hydrothermally treated at 160 °C for 24 h. After getting the room temperature (ca. 25 °C) naturally, the obtained pink-colored products of cobalt carbonate (CoCO_3) were collected, washed and dried in an oven at 60 °C for 24 h to give pink colored cobalt carbonate in high yield (94%). The effects of ($\text{Co}^{2+}:\text{CO}_3^{2-}$) molar ratios, reaction time, and reaction temperature were investigated using similar experiments. Finally, the prepared CoCO_3 microspheres under the optimum conditions were thermally decomposed at 300 °C for two hours in air to produce nano-sized cobalt oxide.

2.2. Characterization

XRD patterns of the as-prepared samples were recorded using a Bruker X-ray powder diffractometer (model D8 Advance)

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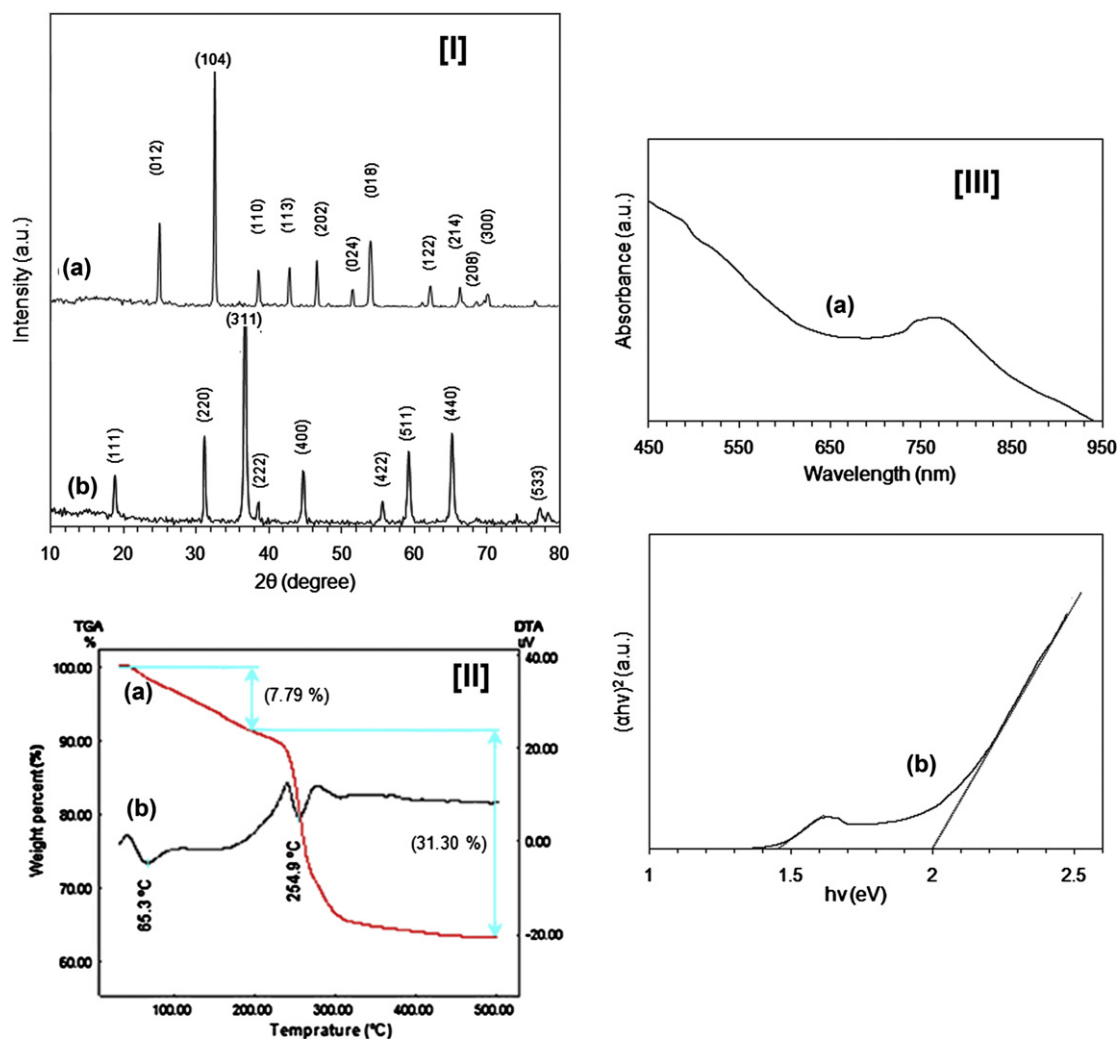


Fig. 1. (I) XRD patterns of the as-prepared CoCO₃ and Co₃O₄ products; (II) thermal analysis of the as-prepared CoCO₃; and (III) UV-vis spectrum (a) and $(\alpha h\nu)^2 \sim h\nu$ curve (b) of Co₃O₄ nanoparticles. The CoCO₃ samples here are prepared at the optimum conditions: (1:3) (Co²⁺:CO₃²⁻) molar ratio, 120 °C, and for 0.5 h.

(Cu K α , $\lambda=1.54178$ Å). Morphology of the as-prepared cobalt carbonate samples was examined using scanning electron microscope (JEOL; model JSM-5410). The TEM images were taken using a transmission electron microscope (JEOL; model 1200 EX). FT-IR spectra were collected using FT-IR spectrometer (Bomem; model MB157S). The thermal analysis measurements were recorded on a thermal analyzer instrument (Shimadzu; model TA-60WS) with a heating rate of 15 °C/min in a nitrogen atmosphere. The UV-vis spectra were recorded on a UV-vis spectrophotometer (Jasco; model 530).

3. Results and discussion

Fig. 1(Ia) shows the XRD pattern of the CoCO₃ nanoparticles prepared by the hydrothermal treatment of a mixture of aqueous solutions of cobalt acetate and ammonium carbonate at the optimum conditions: 1:3 (Co²⁺:CO₃²⁻) molar ratio, 120 °C temperature, and 0.5 h reaction time. The diffraction peaks can be indexed as a pure hexagonal phase of CoCO₃ with cell constants: $a=4.661$ Å, and $c=14.96$ Å, which match well with the standard patterns of cobalt carbonate (space group R3c, JCPDS card 78-0209) [14]. No peaks for impurities were detected. The required optimum conditions for this reaction were reached by studying different experimental parameters such as Co²⁺:CO₃²⁻ molar ratios, reaction time, and temperature. Fig. 1SI (in the

Supporting Information) shows XRD patterns of the products obtained by the hydrothermal reaction for 24 h, at 160 °C, and with different Co²⁺:CO₃²⁻ molar ratios (1:6, 1:3, 1:1.5, 1:1, and 1:0.5). It can be seen that molar ratio $\geq 1:3$ gives pure cobalt carbonate but at lower carbonate ion concentrations, a mixture of cobalt carbonate and cobalt oxide is produced. Hence the following four equations can be used to explain the proposed mechanism for this reaction. At molar ratio $\geq 1:3$ (i.e. excess of CO₃²⁻), the hydrothermal reaction gives only pure phase of cobalt carbonate and the reaction is forced to proceed only according to Eq. 1. However, at lower molar ratios (i.e. low CO₃²⁻ concentration), there is a competition between reactions 1 and 2. Reaction 1 does not go to its completion to give pure CoCO₃ but some unreacted cobalt acetate can undergo hydrolysis to form OH⁻ ions (Eq. 2) which provides an alkaline medium for the formation of cobalt hydroxide (Eq. 3) that is consequently converted into cobalt oxide (Eq. 4) under the applied hydrothermal conditions.

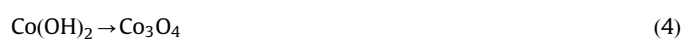


Fig. 1SII (in the Supporting Information) presents the effect of reaction time (24, 18, 12, 6, 3, 1, and 0.5 h) on the hydrothermal reaction at 160 °C with a molar ratio of 1:3. All X-ray diffraction patterns showed the high purity of the as-prepared CoCO_3 with an average crystallite size (D) (calculated by using the Debye–Scherrer formula, Eq. 5 [15]) from 80 to 90 nm on increasing the reaction time from 0.5 to 24 h, respectively. Finally, the effect of reaction temperature (160, 140, 120, 100, and 80 °C) on the hydrothermal reaction for 0.5 h and at a molar ratio of 1:3 was studied and presented in Fig. 1SIII (in the Supporting Information). At temperatures ≤ 100 °C, the reaction gives impure CoCO_3 with poor crystallinity. However, at temperatures ≥ 120 °C, pure cobalt carbonate with good crystallinity is produced and there is no noticeable effect on the degree of crystallinity of the produced CoCO_3 on increasing the temperature over 120 °C.

$$D = 0.9\lambda / \beta \cos\theta_B \quad (5)$$

where λ , β , θ_B are the X-ray wavelength, the full width at half maximum (FWHM) of the diffraction peak and the Bragg diffraction angle, respectively.

Fig. 2(Ia) shows the SEM images of the as-prepared CoCO_3 nanostructures under the optimum conditions. A low-magnification view (Fig. 2I_a) shows the high yield and uniformity of the synthesized CoCO_3 . However, the magnified SEM image (Fig. 2(Ib)) shows that the morphology of CoCO_3 product is well-defined and well-dispersed sphere-like hierarchical structure. The average diameters of the spheres are ca. 3 μm , and the surface of CoCO_3 microspheres is almost smooth which means that there is no preferential direction for the growth of the CoCO_3 particles.

The IR spectrum of the as-prepared CoCO_3 sample (Fig. 2(IIa)) exhibited absorptions at 3305, 1388, 1056, 856, and 736 cm^{-1} which represent the characteristic absorbance of high purity CoCO_3 product. The band at 3305 cm^{-1} can be attributed to the

stretching vibration of the O–H group of surface molecular water interacting with carbonate anions of the CoCO_3 . The evidence for the presence of CO_3^{2-} in the CoCO_3 samples is confirmed by its fingerprint peaks of D_{3h} symmetry at 1388, 1056, 856, and 736 cm^{-1} [16]. The band shown at 2476 cm^{-1} is also ascribed to vibrational mode of the carbonate anions [17]. Additionally, the weak band that appeared at 1778 cm^{-1} can be attributed to an overtone or combination of some vibrational modes of divalent metal ions and the carbonate groups bond [17].

The thermal behavior of the as-prepared CoCO_3 sample (Fig. 1(IIa)) revealed two weight loss steps with a total weight loss of 39.09%. The first weight loss of about 7.79% can be attributed to the elimination of adsorbed/trapped water molecules in the sample. The second weight loss of about 31.30% (theoretical value (32.5%)), which occurred when the temperature increased above 240 °C, could be attributed to the decomposition of CoCO_3 into Co_3O_4 , CO, and CO_2 in nitrogen atmosphere. Moreover, the thermal behavior of the as-prepared CoCO_3 samples has been also confirmed by the DTA analysis (Fig. 1(IIb)) which exhibited mainly two endothermic peaks at 65.3 °C and 254.9 °C. The first one is due to elimination of adsorbed water and the second endothermic peak at 254.9 °C can be attributed to the thermal decomposition of CoCO_3 .

3.1. Preparation of Co_3O_4 nanoparticles

CoCO_3 microspheres were heated at 300 °C for 2 h to give pure spinel cobalt oxide nanoparticles as shown by the XRD pattern in Fig. 1(Ib), and all the diffraction peaks can be perfectly indexed to a pure cubic Co_3O_4 phase (space group $Fd\bar{3}m$, lattice constant $a=8.084$ Å, JCPDS card 74–1657). By using the Debye–Scherrer formula (Eq. 5) [15], the average crystallite size of the produced Co_3O_4 was estimated to be ca. 25 nm. Morphologies of Co_3O_4

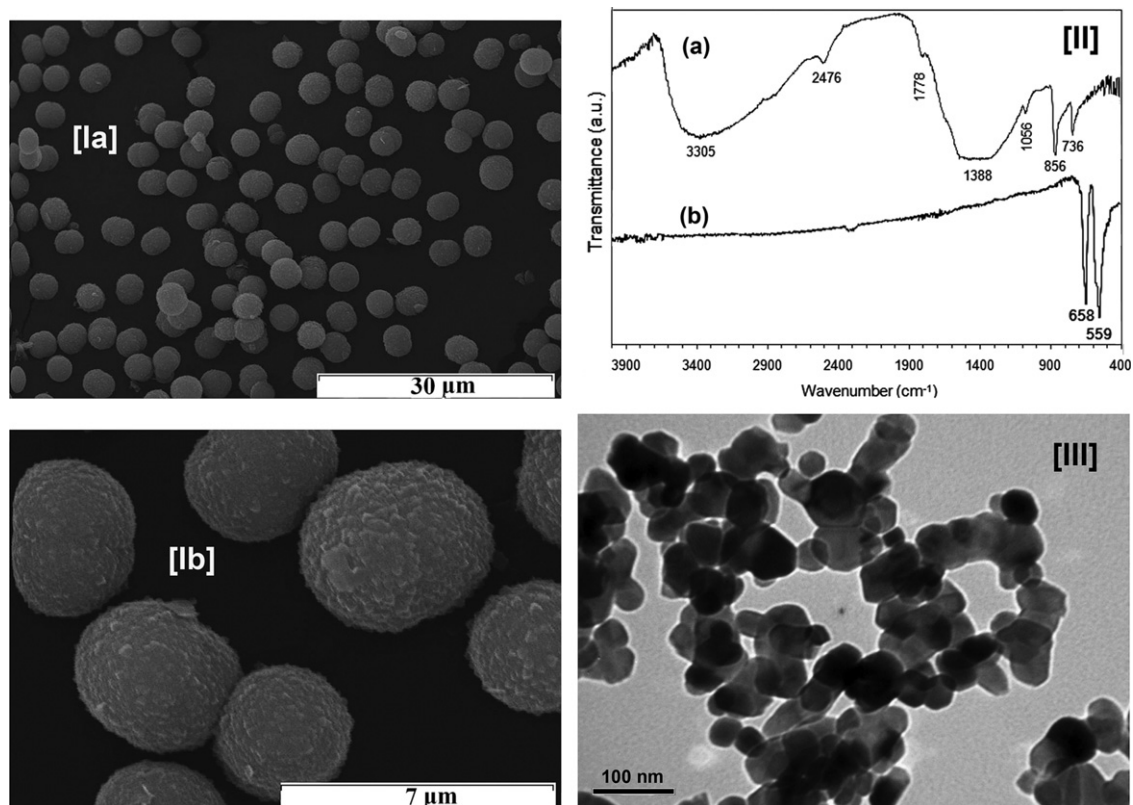


Fig. 2. (I) SEM images (low (a) and high (b) magnification) of the as-prepared CoCO_3 ; (II) IR spectra of the as-prepared CoCO_3 (a) and Co_3O_4 (b) products; and (III) TEM image of Co_3O_4 nanoparticles. The CoCO_3 samples here are prepared at the optimum conditions: (1:3) (Co^{2+} : CO_3^{2-}) molar ratio, 120 °C, and for 0.5 h.

particles were investigated by TEM as shown in Fig. 2(III). From the micrograph, it is observed that Co_3O_4 particles have almost hexagonal and square shapes with an average diameter of ca. 28 nm which is close to the value obtained from the XRD analysis. The FT-IR spectrum (Fig. 2(IIb)) revealed two strong absorption bands at 658 and 559 cm^{-1} which confirm the spinel structure of Co_3O_4 . The band that appeared at 658 cm^{-1} can be attributed to the stretching vibration mode of M–O in which M is Co^{2+} , and is tetrahedrally coordinated, while the band at 559 cm^{-1} can be assigned to the M–O in which M is Co^{3+} and is octahedrally coordinated [18,19].

3.2. Optical properties of Co_3O_4 nanoparticles

The optical absorbance properties of the obtained cobalt oxide were investigated by recording its UV–vis absorption spectrum (Fig. 1(IIIa)) at room temperature. The optical band gap (E_g) of the spinel Co_3O_4 can be calculated using the following equation [20]:

$$\alpha = A(h\nu - E_g)^n / h\nu$$

where α is the linear absorption coefficient, $h\nu$ is the photon energy, A is a constant involving properties of the bands, and n is $1/2$, $3/2$, 2 , and 3 for directly allowed, directly forbidden, indirectly allowed, and indirectly forbidden transitions, respectively. Plotting $(\alpha h\nu)^2$ values versus $h\nu$ values (Fig. 1(IIIb)) and then extrapolating of the graph to $(\alpha h\nu)^2 = 0$ gave two optical band gaps (E_g): 2.0 eV (which can be attributed to $\text{O}^{2-} \rightarrow \text{Co}^{2+}$ charge transfer process) and 1.46 eV (which can be assigned to $\text{O}^{2-} \rightarrow \text{Co}^{3+}$ charge transfer) for the spinel Co_3O_4 . Additionally, the presence of two band gaps with the specific assigned values proves the purity and the semiconducting properties of the prepared Co_3O_4 , and these data are in good agreement with the reported literatures [12].

4. Conclusions

Pure phase spinel Co_3O_4 nanoparticles with 25 nm average size can be synthesized by employing a thermal decomposition ($300\text{ }^\circ\text{C}$) of the as-prepared cobalt carbonate microspheres prepared in high yield (94%) with high purity using a simple hydrothermal treatment of cobalt acetate and ammonium carbonate aqueous solutions at $120\text{ }^\circ\text{C}$ for 0.5 h with (1:3) ($\text{Co}^{2+}:\text{CO}_3^{2-}$) molar ratio. Optical properties of the as-prepared cobalt oxide nanoparticles revealed the presence of two band gaps whose

values (2.0 and 1.46 eV) confirm the semiconducting properties of the produced spinel cobalt oxide. It is believed that this novel methodology can be generalized to prepare other metal carbonates and their metal oxides.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.matlet.2012.12.039>.

References

- [1] Wu BH, Guo CY, Zheng NF, Xie ZX, Stucky GDJ. Am Chem Soc 2008;130:17563.
- [2] Oxtermann R, Li D, Yin YD, McCann JT, Xia YN. Nano Lett 2006;6:1297.
- [3] Han XG, Kuang Q, Jin MS, Xie ZX, Zheng LSJ. Am Chem Soc 2009;131:3152.
- [4] Luisetto I, Pepe F, Bemporad EJ. Nanopart Res 2008;10:59.
- [5] Burda C, Chen X, Narayanan R, El-Sayed MA. Chem Rev 2005;105:1025.
- [6] Xie XW, Li Y, Liu ZQ, Haruta M, Shen WJ. Nature 2009;458:746.
- [7] Gu HW, Xu KM, Xu CJ, Xu B. Chem Commun 2006;9:941.
- [8] Ding Y, Xu L, Chen C, Shen X, Suib SL. J Phys Chem C 2008;112:8177.
- [9] Man L, Niu B, Xu H, Cao B, Wang J. Mater Res Bull 2011;46:1097.
- [10] Tenga YH, Yamamoto S, Kusanoc Y, Azumaa M, Shimakawa Y. Mater Lett 2010;64:239.
- [11] Li CC, Yin XM, Wang TH, Zeng HC. Chem Mater 2009;21:4984.
- [12] Nassar MY, Ahmed IS. Polyhedron 2011;30:2431.
- [13] Bhattacharjee CR, Purkayastha DD, Das N. Mater Lett 2013;90:111.
- [14] Cong HP, Hu SH. Cryst Growth Des 2009;9:210.
- [15] Jenkins R, Snyder RL. Chemical Analysis: Introduction to X-ray Powder Diffractometry. New York: John Wiley and Sons, Inc.; 1996.
- [16] Nakamoto K. Infrared and raman spectra of inorganic and coordination compounds; Pt. B: Applications in coordination, organometallic, and bioinorganic chemistry. 5th Ed USA: Wiley-Interscience; 1997.
- [17] Ehlsissen KT, Delahaya-Vidal A, Genin P, Figlarz M, Willmann PJ. Mater Chem 1993;3:883.
- [18] Salavati-Niasari M, Davar F, Mazaheri M, Shaterian M. J Magn Magn Mater 2008;320:575.
- [19] Herrero M, Benito P, Labajos FM, Rives V. Catal Today 2007;128:129.
- [20] Dare-Edwards MP, Goodenough AH, Hammett A, Trevellick PR. J Chem Soc, Faraday Trans 1983;9:2027.