Fabrication of Nickel Nitrate Hydroxide Microsphere with Inheriting Morphology to β-$Ni(OH)_2$ and NiO

Changlin Tang, Guangshe Li, and Liping Li*
State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter,
Graduate School of Chinese Academy of Sciences, Fuzhou 350002, P. R. China

(Received August 11, 2008; CL-080776; E-mail: lipingli@fjirsm.ac.cn)

This work reports on a phase-controlled approach to nickel nitrate hydroxide solid microsphere. This novel weakly ferromagnetic sphere is constructed by nanoparticles as a consequence of the reactions between ethanol and the nitrate species. This sphere is also proved to show distinct morphology-inheriting feature as to the formation of β-$Ni(OH)_2$ or NiO that has potential applications in electrochemical cells and gas sensors.

$Ni(OH)_2$ and NiO are the important materials that have potential applications as positive electrodes in nickel-based rechargeable batteries or gas sensors because of the controllable properties.[1–3] $Ni(OH)_2$ exists in two polymorphic modifications, α-$Ni(OH)_2$ and β-$Ni(OH)_2$. In comparison with β-$Ni(OH)_2$ of a stoichiometric composition, α-$Ni(OH)_2$ is a hydroxy-deficient phase with a hydrotalcite-like structure. Since the exchangeable anions and water molecules can be readily intercalated into the NiO_6 interlayer space, nickel hydroxide, α-$Ni(OH)_2$, exhibits superior electrochemical and magnetic properties[4] over β-$Ni(OH)_2$. However, nickel hydroxide is kinetically unstable and may transform into β-form during the synthesis or on storage in a strong alkaline medium.[5] To obtain high yield nickel hydroxide, sufficient OH^- concentration is required for precipitating Ni^{2+} ions. Obviously, the existence of excess OH^- would promote α-$Ni(OH)_2$ to transform into β-phase. In addition, nickel hydroxide obtained at low temperatures is usually poorly crystallized.[6] Increasing reaction temperature may improve the sample crystallinity, while high temperature favors the formation of β-phase, especially under alkaline reaction medium.[5] As a consequence, phase-controlled fabrication of nickel hydroxide nanostructures remains as a particular challenge.

In the past decades, many methods have been developed to synthesize nickel hydroxide.[6] Coprecipitation in an alkaline condition was commonly used, in which high OH^- concentration, high reaction temperature, and long reaction time usually result in a mixture of α- and β-$Ni(OH)_2$.[5] To decrease the pH value of reaction systems, urea hydrolysis lately is used as an alternative trick.[4] The existence of organic reagents may result in the difficulty in controlling the anions in the interlayer and the interlayer distance. Polyol methods lead to unclear particle surface, poor crystallization, and even uncertain metals in the products;[7] moreover, the yield is sensitively dependent on the ratio of water, polyol, and metal ions.[8] In this work, we initiated a simple solvothermal method to prepare highly crystallized nickel nitrate hydroxide microspheres. The methodological strategy is based on our previous experimental observations that the nitrate species could be reduced by ethanol under hydrothermal condition by releasing OH^- ions,[9] which allows the reactions between OH^- ions and Ni^{2+} for the formation of nickel hydroxides.

In a typical synthesis, given amounts of $Ni(NO_3)_2 \cdot 6H_2O$ were dissolved in ethanol to get a 4 mol/L green transparent solution. The solution was then transferred to a Teflon-lined stainless steel autoclave with a filling degree of 70%, which was allowed to react at 160 °C for 3 h. After cooling to room temperature, the green product was washed with deionized water and dried at 60 °C in air to obtain the final sample. The morphological evolution of the resulting nickel nitrate hydroxide was initiated by immersing the as-prepared samples in a 6 mol/L NaOH solution for 10 days or annealing at 400 °C in air for 2 h.

XRD data (Figure 1a) indicates that the as-prepared sample is a pure phase since the raw XRD data well-matched the standard diffraction data for hexagonal structure of $Ni_3(NO_3)_2(OH)_4$ (PCPDF-No 22-0752). The lattice parameters were determined by a least-squares method to be $a = 0.311$ nm and $c = 0.695$ nm. The interlayer distance along c direction was 0.695 nm, which is much smaller than those reported previously for the insertion of inorganic anions.[10] By analyzing the (001) and (100) diffraction peaks, the crystallite sizes were estimated to be 13.4 and 15.9 nm. However, SEM measurement showed that the as-prepared particles were primarily spherical and of micron scale (Figures 2a and S1[12]). A closer observation of the sphere architecture (Figure 2b) indicates that each sphere was composed of nanoparticles rather than the plate or sheet-like grains often reported by others. The present nickel nitrate hydroxide microspheres are solid and more dense (Figure 2b), which is unlike the flower-like nanostructure obtained in the presence of urea,[4] though hexagonal structure α-$Ni(OH)_2$ prefers the formation of hexagonal plate-like shapes.[5,10]

Figure 1b shows the IR spectrum of as-prepared nickel nitrate hydroxide. Three peaks observed at 3640, 656, and 482 cm^{-1} are associated with the ν-OH stretching, σ-OH vibrations and ν-Ni–O vibration, respectively.[10] Two peaks at 3350 and 1640 cm^{-1} are associated with the vibrations of H_2O. The interlayer nitrate anion manifests itself by a set of strong peaks[10] in the range of 1503 to 980 cm^{-1}. No vibrations of organic compounds (C–H vibration around 2900 cm^{-1}) were detected. Elemental analysis indicates that the content of C, H, and N are 1.61%, 1.78%, and 4.74% in mass, respectively. Therefore,

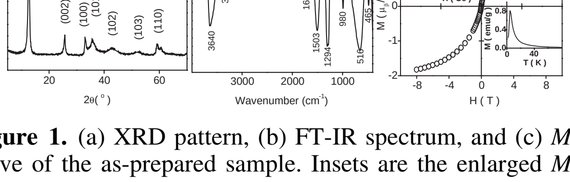

Figure 1. (a) XRD pattern, (b) FT-IR spectrum, and (c) *M–H* curve of the as-prepared sample. Insets are the enlarged *M–H* (top) and the *M–T* curve. H_c is 18 Oe, and the transition temperature is 5.2 K.

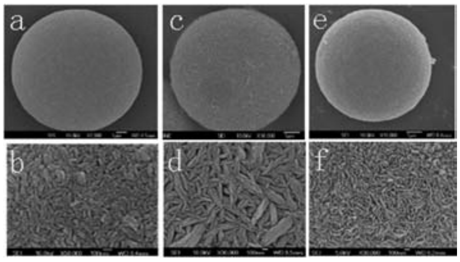

Figure 2. Structural evolution of nickel nitrate hydroxide microsphere (a, b) to β-$Ni(OH)_2$ (c, d) or to NiO microsphere (e, f). (b, d, and f are close views of particle surface of a, c, and e)

the composition of the as-prepared nickel nitrate hydroxide microspheres can be described as $Ni(OH)_{1.23}(NO_3)_{0.43}(CO_3)_{0.17} \cdot 0.5H_2O$. Actually, the content of interlayer components was measured from the TG data (S2). The total weight loss above 300 °C exactly corresponds to the thermal decomposition of interlayer component of 38 wt %.

It is noted that further increasing the reaction temperature to 220 °C or elongating the reaction time to 24 h (S3) did not lead to the α–β-phase transformation. Therefore, this methodology is advantageous in synthesizing the highly crystallized nickel nitrate hydroxide.

To understand the formation mechanism of nickel nitrate hydroxide, it is important to examine the chemical formation processes that involved in the present solvothermal system. Previous study has shown that NO_3^- could be reduced by ethanol to form NH_3 at the elevated temperature as follows:[9]

$$4CH_3CH_2OH + NO_3^- = 4CH_3CHO + NH_3 + OH^- + 2H_2O. \quad (1)$$

OH^- released by eq 1 would further react with Ni^{2+} and NO_3^- ions to form $Ni(OH)_{2-x}(NO_3)_x$ in terms of the process:

$$Ni^{2+} + (2 - x)OH^- + xNO_3^- \rightarrow Ni(OH)_{2-x}(NO_3)_x. \quad (2)$$

The by-product acetaldehyde is not stable and would form a series of new organic species such as $CH_3CH{=}CHCHO$ and $CH_3CH{=}CHCOOC_2H_5$ (S4) by aldol condensation, dehydration, and oxidization.[9] These new organic species as well as ethanol did not enter the lattice of nickel nitrate hydroxide. The d–d transition of Ni^{2+} was not observed for the residual solution, implying that Ni^{2+} ions were fully reacted to give a high yield (>95%) of nickel nitrate hydroxide. Due to the fact that one mole NO_3^- releases one mole OH^- (eq 1), the content of OH^- and NO_3^- is in a nearly chemical stoichiometry to react (eq 2), though there is little CO_3^{2-} in the product. Therefore, the present reaction prefers the formation of nickel nitrate hydroxide, either at high temperature such as 220 °C or for the reaction time as long as 24 h. The condensed sphere morphology may also be associated with the reaction mechanism: Under alkaline condition with excess OH^-, nickel hydroxide has a tendency to form a sheet-like structure.[5] While in the case of urea, NH_3 released may result in the porous flower-like shape.[4] For the present reaction, OH^- is chemically stoichiometric and released only in the reaction process. Therefore, both sheet-like and/or porous structures were completely eliminated.

The nickel nitrate hydroxide exhibited a weak ferromagnetism with a critical temperature of 5.2 K (inset of Figure 1c), which is, however, much lower than that of 16 K previously reported.[10] Moreover, the coercive force and saturated magnetic moment at 5 K are only 18 Oe and $1.6\mu_B$ at 5 T. Taibi et al.,[10] studied the magnetic properties of nickel nitrate hydroxide obtained using an anion exchange method and obtained $H_c = 1430$ Oe and $M_s = 1.95$ μB. It is well known that magnetic properties of nanomaterials are controlled by particle size.[11] Present nickel nitrate hydroxide microspheres are composed of small nanoparticles with crystallite size of about 15 nm as estimated by XRD analysis. Obviously, the smaller constituent particles contributed to the weak ferromagnetism of nickel nitrate hydroxide, though there might exist some contributions from the reduction of interlayer distance. For our nickel nitrate hydroxide, the interlayer distance is 0.695 nm, which is much smaller than that of 0.75 nm reported in the literature.[10] The decreased interlayer distance would result in the competition of short range superexchange and dipolar interactions. The superexchange interaction leads to antiferromagnetism, while the dipolar interaction gives rise to ferromagnetism. As the interlayer distance decreases, superexchange interaction would become dominant to weaken the ferromagnetism.

Since for almost all solids, material properties are always a function of morphology, here we initiated the structural evolution of nickel nitrate hydroxide microspheres to either β-$Ni(OH)_2$ or NiO. We found that by soaking nickel nitrate hydroxide in a 6 mol/L NaOH solution at room temperature for 10 days, nickel nitrate hydroxide microspheres completely transform into β-$Ni(OH)_2$ (S5), retaining the solid sphere morphology (Figures 2c and S1[12]) with the notable sheet-like structure of the small particles (Figure 2d). It is very interesting when nickel nitrate hydroxide microspheres were annealed at 400 °C for 2 h, the resulting NiO also exhibited the sphere-like morphology (Figures 2e, 2f, and S1[12]) but with a novel strip-like structure for the sphere surface.

In a word, a simple self-precipitate method was employed to fabricate the high yield nickel nitrate hydroxide microspheres, which are weakly ferromagnetic and transform into β-$Ni(OH)_2$ or NiO, maintaining the spherical morphology.

This work was financially supported by NSFC under the Contract (Nos. 20773132, 20771101, and 20831004) and the National Basic Research Program of China (No. 2009CB9939801).

References and Notes

1 W. Hu, D. Noréus, *Chem. Mater.* **2003**, *15*, 974.
2 K. Watanabe, T. Kikuoka, N. Kumagai, *J. Appl. Electrochem.* **1995**, *25*, 219.
3 F.-S. Cai, G.-Y. Zhang, J. Chen, X.-L. Gou, H.-K. Liu, S.-X. Dou, *Angew. Chem.* **2004**, *116*, 4308.
4 L. Xu, Y. Ding, C. Chen, L. Zhao, C. Rimkus, R. Joesten, S. Suib, *Chem. Mater.* **2008**, *20*, 308; Y. Luo, G. Li, G. Duan, L. Zhang, *Nanotechnology* **2006**, *17*, 4278.
5 L. Dong, Y. Chu, W. Sun, *Chem.—Eur. J.* **2008**, *14*, 5064.
6 G. G. C. Arizaga, K. G. Satyanarayana, F. Wypych, *Solid State Ionics* **2007**, *178*, 1143.
7 L. Poul, S. Ammar, N. Jouini, F. Fiévet, F. Villain, *J. Sol–Gel Sci. Technol.* **2003**, *26*, 261.
8 V. Prevot, C. Forano, J. P. Besse. *Chem. Mater.* **2005**, *17*, 6695.
9 X. Sun, X. Qiu, L. Li, G. Li, *Inorg. Chem.* **2008**, *47*, 4146.
10 M. Taibi, S. Ammar, N. Jouini, F. Fiévet, P. Molinié, M. Drillon, *J. Mater. Chem.*, **2002**, *12*, 3238; B.-H. Liu, S.-H. Yu, S.-F. Chen, C.-Y. Wu, *J. Phys. Chem. B* **2006**, *110*, 4039.
11 C. A. F. Vaz, J. A. C. Bland, G. Lauhoff, *Rep. Prog. Phys.* **2008**, *71*, 056501.
12 Supporting information is also avaliable electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) October 11, 2008; doi:10.1246/cl.2008.1138