Synthesis and Characterization of $Ni(OH)_2$ Single-crystal Nanorods

Jiahe Liang and Yadong Li*
Department of Chemistry and the Key Laboratory of Atomic & Molecular Nanoscience (China Ministry of Education), Tsinghua University, Beijing 100084, P. R. China

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A template-free hydrothermal method to $Ni(OH)_2$ single-crystal nanorods were successfully established based on the 2-D layered structures of $Ni(OH)_2$. The obtained $Ni(OH)_2$ nanorods were 40–90 nm in diameters and 1–3 μm in lengths. It is interesting that $Ni(OH)_2$ nanorods would be converted into NiO nanorings when they were annealed at 500 °C for 6 h.

Nickel hydroxide ($Ni(OH)_2$) is widely used as a positive electrode active material in rechargeable Ni-based alkaline batteries (e.g. Ni/Fe, Ni/Zn, Ni/Cd, Ni/H_2, and Ni/MH) on the basis of its chemical and thermal stability, low self-discharge rate, and low toxicity.[1] Several chemical and electrolytic methods were attempted to synthesize nickel hydroxide, for example, force precipitation of $Ni(NO_3)_2$, direct precipitaion with KOH, electrolytic pricipitation, and sol-gel method and electrochemical method.[2–5] It is well known that, nanoscale 1-D materials have stimulated great interest on the basis of their importance in basic scientific research and potential technology applications.[6,7] However, there are few reports for the synthesis of 1-D nanostructure of nickel hydroxide.[8] In present work, we successfully developed a template-free hydrothermal method to prepare $Ni(OH)_2$ single-crystal nanorods based on the understanding of the mechanism from 2-D layered structure compounds to 1-D nanostructures.[9,10] It is the first time, to our knowledge, to synthesize $Ni(OH)_2$ nanorods by a controlled direct precipitation method. It is expected that the current method may be developed to a general method to 1-D nanorods or nanotubes of hydroxides $M(OH)_2$ (M = Co, Fe, Cd, Mg, Ca) with CdI_2 type.

Nanorods of $Ni(OH)_2$ were synthesized as follows: 1.6 g $NiCl_2 \cdot 6H_2O$ was dissolved in aqueous ammonia ($NH_3 \cdot H_2O$), and the mixtures of solution were stirred for 15 min and then transferred into a 50 mL autoclave up to 80% of the total volume, sealed, and heated at 180 °C for 6 and 12 h, respectively. The system were then allowed to cool to room temperature and the final products were collected by filtration, and washed with deionized water and absolute ethanol, and then dried at 50 °C in air. The XRD pattern of the synthesized $Ni(OH)_2$ nanorod is shown in Figure 1a.

Nanorings of NiO were synthesized when as-obtained $Ni(OH)_2$ nanorods were directly annealed at 500 °C for 6 h in muffle furnace. The XRD pattern of NiO nanoring is shown in Figure 1b.

The size and morphology of the as-synthesized products of $Ni(OH)_2$ were further examined by TEM. Figure 2a displays that the sample is rod-like structure with diameters 40–90 nm and lengths 1–3 μm, and aspect ratios ranging from 20–50. The structure of $Ni(OH)_2$ is further examined by HRTEM (high-resolution transmission electron microscopy) in Figure 2b. It is shown that the lattice fringes in the nanorods are clearly observed, which confirms that the nanorods are structurally uniform. The interplanar spacing is 0.46 nm (4.6 Å), which is good agreement with the *d* spacing of (001) plane of hexagonal $Ni(OH)_2$ and shows that the growth direction is [001]. The inset of Figure 2b is the corresponding SAED pattern, taken on the single $Ni(OH)_2$ nanorod, It is observed that the SAED pattern consists of many spots, which shows that the nanorod of nickel hydroxide is single crystal. All spots are identified as the diffraction from hexagonal $Ni(OH)_2$.

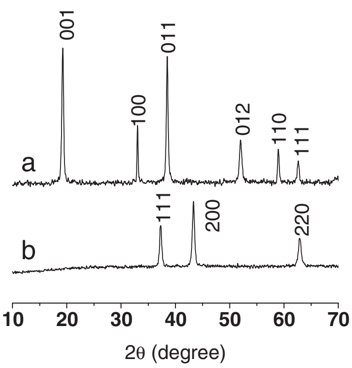

Figure 1. (a) XRD pattern of the samples of $Ni(OH)_2$ nanorods; (b) XRD pattern of the samples of NiO nanorings synthesized when the $Ni(OH)_2$ nanorods were annealed at 500 °C for 6 h.

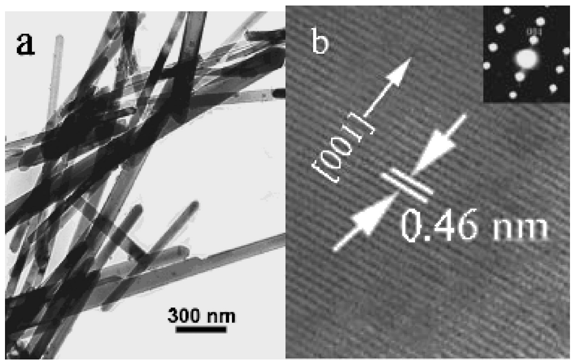

Figure 2. (a) A TEM image showing the morphology of $Ni(OH)_2$ nanorods. (b) A HRTEM photo, taken on an individual nanorod, of $Ni(OH)_2$ nanorods, the inset is a SAED pattern of $Ni(OH)_2$ nanorods.

The factors on the formation of $Ni(OH)_2$ nanorods have been investigated. We find that moderately higher temperature and relatively longer time and higher ammonia concentration will facilitate the rod-like structure formation. On the basis of previous work, many 1-D nanostructures (nanotubes or nanorods) have been successfully synthesized from layered structures, the so-called 2-D structures.[9–13] It is well known that $Ni(OH)_2$ is a layered compound of CdI_2 type, therefore, we may justly suppose that the formation of $Ni(OH)_2$ nanorods might be related to the nature of its lamellar 2-D structures. The further research is on the way.

It is interesting that $Ni(OH)_2$ nanorods would be converted into NiO nanorings when $Ni(OH)_2$ nanorods were annealed at 500 °C for 6 h. Quantum ring-like structures, with the capability of trapping magnetic flux in their interiors, are regarded as the ideal candidates for observing Aharonov–Bohm (AB) effects, such as energy oscillation and persistent currents,[14] which has triggered a strong interest in recent years.[15]

Figures 3a and 3b shows the overviews of TEM images of NiO nanorings with different magnifications. It is shown that the NiO nanorings are uniform and the range is 42–87 nm in diameter. The size and morphology of NiO nanorings are further examined on a HRTEM and the images of single NiO nanorings are shown in Figure 3c. The magnification of Figure 3c is 400000, and the shape of single NiO nanoring is clearly observed. It is shown that the ring is a quasi-circle structure and more like an irregular pentagon structure, of which the longer outer diameter is about 68.5 nm and the shorter outer diameter is about 57.5 nm, and of which the longer inner diameter is about 22.5 nm and the shorter inner diameter is about 12.5 nm. The inset of Figure 3d is the corresponding SAED pattern of NiO nanorings, and it is shown that the SAED pattern consists of many spots, which shows that the NiO nanoring is single crystal. All spots were identified as the diffraction from cubic NiO. The lattice fringes in the nanorings are shown in Figure 3d, which confirms that structurally uniform and the high crystallizability of the NiO nanorings. The inset of bottom of Figure 3d corresponds to the area covered by the block plan. It can be calculated that the interplanar spacing is 0.24 nm (2.4 Å), which is in good agreement with the *d* spacing of (111) plane of cubic NiO.

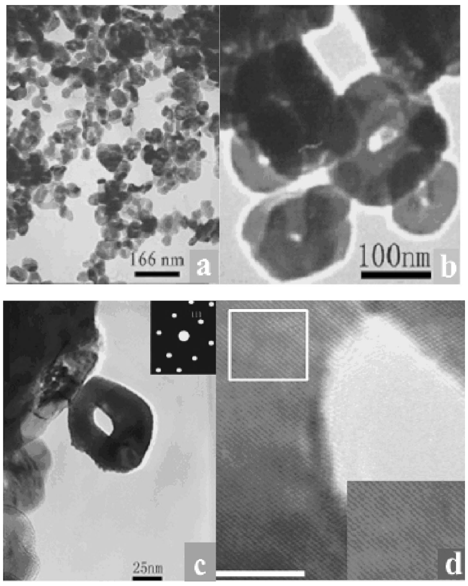

Figure 3. The typical TEM (HRTEM) images of the NiO nanorings (a), (b) the overview of TEM images of NiO nanorings with different magnifications; (c) the amplified TEM images of single NiO nanoring, the inset is the SAED pattern of single NiO nanoring; (d) the HRTEM image corresponding to single NiO nanoring of (c), the inset in the bottom is the HRTEM image of lattice fringes corresponding to the area the block plan indicated, and the interplanar spacing is 0.24 nm (2.4 Å), (the bar in (d) is equal to 50 nm).

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