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Short communication

Hydrothermal synthesis of ultrathin hexagonal nickel hydroxide nanosheets

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ABSTRACT

Nickel hydroxide, $Ni(OH)_2$ is widely used in electrodes of nickel-based alkaline secondary batteries. Ultrathin hexagonal $Ni(OH)_2$ nanosheets of space group P-3*m*1 were hydrothermally prepared at 200 °C for 10 h. Their diameter and thickness were 200–300 and 3–5 nm, respectively. Their formation was attributed to the oriented assembly of growing particles, which was assisted by surfactant molecules. The specific surface area of the $Ni(OH)_2$ nanosheets was 8.66 m^2/g. Their magnetization curve exhibited linear paramagnetic behavior across the entire measurement region.

Introduction

Assembling nanoscale building blocks into architectures of desired shapes and sizes is an exciting area of materials chemistry, because of their interesting properties and potential applications (Mahajan & Joy, 2013; Tian et al., 2012; Yao et al., 2011). The growth and design of assemblies is usually related to the size and shape of initial nuclei, the type and concentration of surfactants, and the reaction parameters (Shi, Song, & Zhang, 2013; Zhuang, Peng, & Li, 2011). Nanoscale nickel hydroxide, $Ni(OH)_2$, has widespread applications, especially in positive electrodes of alkaline rechargeable batteries (Liu, Pan, Yan, & Gao, 2010). $Ni(OH)_2$ provides high power, high energy and is of low toxicity. $Ni(OH)_2$ can exist in the α-$Ni(OH)_2$ and β-$Ni(OH)_2$ polymorphs. The former is more disordered with a larger interlayer spacing (47.5 Å), while the latter contains well-oriented $Ni(OH)_2$ layers with a smaller interlamellar distance (4.60 Å) (Coudun & Hochepied, 2005; Wang, Luo, Parkhutik, Millan, & Matveeva, 2003). Because of its multi-electron reaction, α-$Ni(OH)_2$ has a larger potential electrochemical capacity than β-$Ni(OH)_2$ (Gao & Yang, 2010). The performance of Ni-based alkaline rechargeable batteries depends on the size, phase, crystallinity, and morphology of the Ni component. Much effort has been given to synthesizing morphology-controlled $Ni(OH)_2$ architectures, such as tubes, wires, rods, cubes, and dendrites (Park, Ju, Park, & Roh, 2014; Tong et al., 2012; Wang et al., 2010; Wu & Huang, 2011).

Zhang, Liu, Pan, Li, and Gao (2014) synthesized three-dimensional hierarchical porous α-$Ni(OH)_2$/graphite nanosheets using a homogeneous precipitation method, which exhibited a large specific capacitance, good rate capability, and long cycle stability. Mondal et al. (2014) synthesized $Ni(OH)_2$ nanosheets using a microwave-assisted method, which exhibited a maximum specific capacitance of 2570 F/g at a current density of 5 A/g. Jiang, Zhao, Li, and Ma (2011) synthesized uniform $Ni(OH)_2$ hierarchical nanostructures using a solution method, which consisted of ~7.4-nm-thick ultrathin nanoflakes. The composite exhibited high rate capability and good cycle stability. Straightforward economical methods for the controlled synthesis of ultrathin $Ni(OH)_2$ architectures are important for promoting the application of nanoscale $Ni(OH)_2$ architectures.

Herein, ultrathin $Ni(OH)_2$ nanosheets were hydrothermally synthesized in a controlled manner, based on the growth and design of functional inorganic nanocrystals (Gao et al., 2013). This process is shown in Fig. 1. The resulting hexagonal $Ni(OH)_2$ nanosheets were ~3.5 nm thick, which is significantly thinner than previously reported values (~7.4 nm). The $Ni(OH)_2$ nanosheets were prepared in a 100-mL reactor, which is larger than that of typical studies (50 mL). The synthesis employed a mixed surfactant, which could

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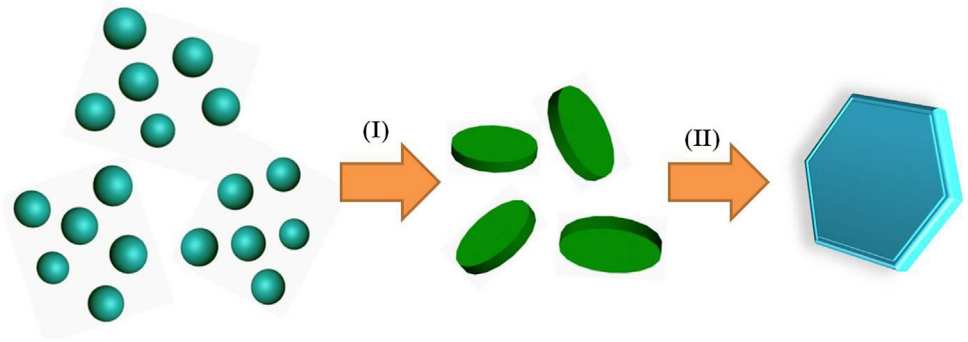

Fig. 1. Schematic of the hydrothermal synthesis of hexagonal $Ni(OH)_2$ nanosheets.

be adapted for synthesizing other inorganic nanocrystals of desired shapes and sizes.

Experimental

Synthesis of ultrathin $Ni(OH)_2$ nanosheets

All the chemical reagents were analytical grade, purchased from China National Medicine Group Shanghai Chemical Reagent Company and used without further purification. 10 mL of 0.1 M cetyltrimethylammonium bromide (CTAB) was mixed with 50 mL of 0.2 M $NiCl_2{\cdot}6H_2O$. 5 mL of polyethylene glycol (PEG)-200 was added, and the reaction mixture was stirred for 10 min. 50 mL of 0.2 M NaOH was gradually added. After the reaction was complete, the mixture was transferred to a 100-mL Teflon-lined autoclave, which was then heated to 200 °C for 10 h. CTAB was used to control the initial dispersion of the growing particles. CTAB dissociated into $R(CH_3)_3N^+$ and Br^- in solution. $R(CH_3)_3N^+$ was adsorbed to the surface of the initial growing particles, such that its hydrophobic alkyl chain protruded outwards and reduced the attractive van der Waals or hard-sphere interactions between growing particles. PEG-200 was used to control the oriented assembly of the building blocks. PEG-200 is a long chain polymer, and has been previously used to hydrothermally synthesize one-dimensional (1D) nanowires (Muraliganth, Murugan, & Manthiram, 2009). The high hydrothermal temperature promoted the fusion of building block edges, which led to formation of the hexagonal $Ni(OH)_2$ nanosheets. The autoclave was cooled to room temperature, and the samples were separated by centrifugation, washed three times with deionized water, and freeze-dried under vacuum.

Characterization

Samples were characterized by X-ray diffraction (XRD, Bruker-Axs, D8 Advance, Germany), thermogravimetric analysis (TGA, Pyris 1, PerkinElmer, USA), scanning electron microscopy (SEM, FEI-Sirion 200, Netherlands), transmission electron microscopy (TEM, JEM-2010, JEOL, Japan), and atomic force microscopy (AFM, Multimode Nanoscope, DI, Bruker, Germany). Magnetic measurements were performed using a physical property measurement system (PPMS-9T EC-II, Quantum Design, USA) at room temperature.

Results and discussion

Fig. 2 shows the XRD pattern of the synthesized $Ni(OH)_2$ sample. All diffraction peaks could be indexed to the (0 0 1), (1 0 0), (0 1 1), (0 1 2), (1 1 0), and (1 1 1) crystal planes of the space group P-3*m*1 (JCPDS card 73-1520). The pattern could therefore be assigned to

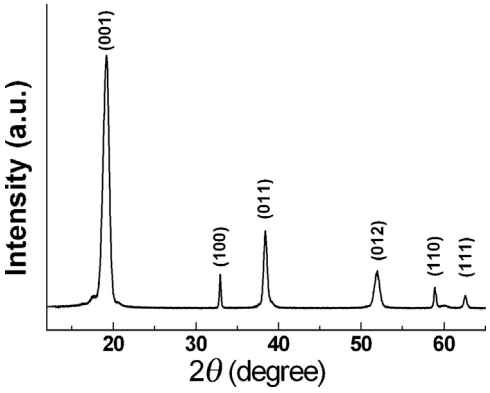

Fig. 2. XRD pattern of the synthesized $Ni(OH)_2$ nanosheets.

that of hexagonal $Ni(OH)_2$. The high intensity of diffraction peaks indicated a high crystallinity of the $Ni(OH)_2$. No diffraction peaks of impurities (e.g. NiO) were observed, indicating that the $Ni(OH)_2$ was of high purity. The N_2 adsorption-desorption analysis indicated the specific surface area of the $Ni(OH)_2$ was 8.66 m^2/g.

Fig. 3(a) shows a SEM image of the as-prepared hexagonal $Ni(OH)_2$ nanosheets, which existed as many nanosheets of relatively uniform shape and size. The nanosheets all exhibited hexagonal structures. Their diameters were typically 200–300 nm, and they were very thin. Fig. 3(b) shows a TEM image of the $Ni(OH)_2$ nanosheets, confirming their hexagonal structure. Fig. 3(c) shows a high-resolution TEM (HRTEM) image of the $Ni(OH)_2$ nanosheets, indicating that each nanosheet consisted of numerous thinner sheets. The HRTEM image in Fig. 3(d) shows that the diameter of the thinner sheets was ~5 nm, and clear lattice fringes indicated their high crystallinity. The selected area electron diffraction (SAED) pattern in Fig. 3(e) shows that the edges of the hexagonal $Ni(OH)_2$ nanosheets were single-crystalline. The shapes of initial growing particles and the relative growth rates of their crystalline faces dictated the resulting nanomaterial's morphology. CTAB was present in the $NiCl_2{\cdot}6H_2O$ precursor solution, and may have directed the initial shape of the growing particles. We previously demonstrated that PEG-200 facilitates the oriented assembly of growing particles (Gao et al., 2011). Upon addition of NaOH, dispersed particles formed from the assistance of CTAB and PEG-200 (Stage I, Fig. 1). Increasing the reaction temperature caused the oriented assembly of growing particles assisted by CTAB and PEG-200, which formed the hexagonal $Ni(OH)_2$ structure (Stage II, Fig. 1). The HRTEM images in Fig. 3(c and d) were consistent with this two-stage assembly process. Fig. 3(f) shows an AFM image of the $Ni(OH)_2$ nanosheets, which indicated their well-defined hexagonal structure. The AFM image height analysis indicated the hexagonal

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