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A facile microwave-assisted route to $Co(OH)_2$ and Co_3O_4 nanosheet for Li-ion battery

Gen Chen [a], Engang Fu [b], Meng Zhou [a], Yun Xu [a], Ling Fei [a], Shuguang Deng [a], Vimal Chaitanya [a], Yongqiang Wang [c], Hongmei Luo [a,*]

[a] Department of Chemical Engineering, New Mexico State University, Las Cruces, NM 88003, United States
[b] State Key Laboratory of Nuclear Physics and Technology, School of Physics, Peking University, Beijing 100871, China
[c] Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545, United States

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ABSTRACT

A facile microwave-assisted synthetic route has been successfully developed for preparing hexagonal $Co(OH)_2$ nanosheets with average width of 2 μm and thickness of 100 nm. $Co(OH)_2$ can further convert to porous Co_3O_4 nanosheets *via* thermal decomposition. Their phases, structures and morphologies were investigated by X-ray diffraction (XRD), atomic force microscopy (AFM), and transmission electron microscopy (TEM). Both $Co(OH)_2$ and Co_3O_4 nanosheets can serve as potential candidates for anodes of Li-ion battery. The electrochemical study revealed that $Co(OH)_2$ and Co_3O_4 nanosheets delivered a reversible capacity of 600 and 700 mA h g^{-1} after 40 cycles, respectively. Cyclic voltammetry (CV) curves also confirmed the relative stability of the as-synthesized electrode materials. This effective microwave-assisted route may be a promising approach for preparing other transition metal hydroxide/oxides for energy applications.

1. Introduction

Many important and challenging research areas have the potential to significantly affect our future energy needs. For example, energy efficiency, the integration of energy sources with electricity transmission, and energy storage are of vital significance. Reversible electricity storage using rechargeable batteries has received great attention for potential applications in renewable energy systems [1]. Among the advanced battery systems, lithium-ion batteries (LIBs) have successfully captured the portable electronic market for the last decade [2,3]. However, a great improvement in storage capacity is urgently needed for the conquering of the upcoming markets for large scale energy storage. Cobalt hydroxide ($Co(OH)_2$), as one of the most important functional inorganic materials, can be used in the field of catalysis and electrochemical capacitors [4–6]. It is also reported that $Co(OH)_2$ is a promising alternative conversion-based anode materials for LIBs due to its high capacity [7]. Unfortunately, like other conversion-based anode materials, the implementation in LIBs is greatly hampered by its poor cycling performance. One of the most promising strategies to tackle this obstacle is to make $Co(OH)_2$ into sheet-like structure to improve the structural stability in the electrochemical reactions. Compared with the bulk $Co(OH)_2$, $Co(OH)_2$ nanosheet displays obvious advantages due to large surface area, highly oriented growth direction, tunable interlayer space for the de/insertion of lithium ions.

Various synthetic methods for the preparation of $Co(OH)_2$ nanomaterials with desired properties are under constant investigation, such as sonochemical [8], solvothermal [9,10], hydrothermal process [11–13], and chemical precipitation [14]. Among these strategies, the microwave-assisted route is a fast, simple, and favorable method for the synthesis of transition metal hydroxides due to its clean, cheap, and efficient heating [15–17]. Herein, we demonstrate that single-crystalline $Co(OH)_2$ nanosheets can be successfully synthesized on a large scale *via* a facile microwave-assisted synthetic method under a mild condition. Due to the high heat transfer efficiency of microwave radiation, the reaction time can be significantly reduced compared to hydrothermal method [12,13]. Meanwhile single-crystalline porous spinel cobalt oxide (Co_3O_4) nanosheets can be successfully obtained by a thermal-decomposition of $Co(OH)_2$ nanosheets. Both $Co(OH)_2$ and porous Co_3O_4 nanosheets can be used as anode materials for LIBs. The electrochemical performances show that the stability of $Co(OH)_2$ and Co_3O_4 nanosheets in the electrochemical reactions and high specific capacities enable them to be promising alternative electrode materials for the energy storage application.

* Corresponding author. Tel.: +1 575 646 4204; fax: +1 575 646 7706.
E-mail address: hluo@nmsu.edu (H. Luo).

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2. Experiment

2.1. Synthesis

$Co(NO_3)_2{\cdot}nH_2O$ from Sigma–Aldrich Co. LLC. is of analytical grade and used as starting materials without further purification. In a typical synthesis procedure, 1 mmol of $Co(NO_3)_2{\cdot}nH_2O$ was dissolved in 25 mL of deionized water, and then 1 mL of NH_4OH (28.0–30.0% NH_3 basis) was added dropwise under continuous stirring. The cluster formed and the mixture was transferred into a 45 mL vessel and sealed in a Parr 4848 autoclave. The autoclave was heated by a microwave oven (Panasonic, NN-SN778S, 2.45 GHz, maximum power 1250 W) with 40% of the maximum power of 1250 W for 3 min. After the reaction, the autoclave was cooled down to room temperature naturally. The resulting precipitate was collected and washed with absolute ethanol and distilled water in sequence for several times. The product $Co(OH)_2$ was dried in a vacuum oven at 60 °C overnight. For the synthesis of Co_3O_4, $Co(OH)_2$ product was annealed in air at 600 °C for 2 h. The color of the sample was changed from grey to black in the thermal-decomposition process.

2.2. Characterization

The phase and structure of the obtained products were determined on a Rigaku MiniFlex II X-ray powder diffractometer (XRD) with Cu Kα radiation (λ = 1.5418 Å). The operation voltage and current were kept at 40 kV and 30 mA, respectively. The size and morphology were determined by Hitachi H-7650 transmission electron microscope (TEM), JEOL-2010 high resolution transmission electron microscope (HRTEM), and Bruker Dimension FastScan atomic force microscope (AFM). Thermal behavior of $Co(OH)_2$ nanosheets was characterized by PerkinElmer Pyris 1 thermogravimetric analysis (TGA) in the temperature range of 25–800 °C at a heating rate of 10 °C/min in air.

2.3. Electrochemical test

The electrochemical experiments were performed using 2032-type coin cells, which were assembled in an argon-filled dry glovebox (Vigor Gas Purification Technologies, Inc.). The $Co(OH)_2$ and Co_3O_4 working electrodes were prepared by casting the slurry (70 wt% of active material, 20 wt% of Super P carbon black, and 10 wt% of polyvinylidene fluoride binder) on nickel foam. The electrode loading amount is around 2.0 mg/cm^2. The Li metal was the counter electrode. 1 M $LiPF_6$ in a mixture of ethylene carbonate and dimethyl carbonate (1:1 by volume) was used as the electrolyte. The electrochemical performance was evaluated by galvanostatic charge/discharge cycling on an LAND CT2001A multi-channel battery testing system at room temperature in the voltage range between 0.01 and 3 V vs. Li^+/Li. Specific capacity is calculated based on the mass of active material. Cyclic voltammetry (CV) curves of as-prepared samples were obtained on a VersaSTAT 4 with a scan rate of 5 mV s^{-1} in the form of coin-cells.

3. Results and discussion

X-ray diffraction (XRD) was firstly carried out to determine the structure and crystallinity of the as-prepared products. Fig. 1A shows typical XRD pattern of as-obtained $Co(OH)_2$. All diffraction peaks in the XRD pattern can be indexed as the hexagonal $Co(OH)_2$ (JCPDS 45-0031) with lattice constants a = 3.191 Å and c = 4.664 Å (space group: *P3_m1* (No. 164)). No other peaks were observed, indicating the high purity of $Co(OH)_2$. The size and morphology of the as-prepared $Co(OH)_2$ were examined by TEM and AFM. The TEM image (Fig. 1B) indicates that a large quantity of hexagonal $Co(OH)_2$ nanosheets with good uniformity were achieved by using this approach. These nanosheets had an average width of about 2 μm. Fig. 1C shows a typical close shot of a single hexagonal $Co(OH)_2$ nanosheet. Here, the angle between adjacent edges of the nanosheet is determined as 120° and the edge length is about 1 μm. AFM image shown in Fig. 1D also confirms the uniform hexagonal $Co(OH)_2$ nanosheets. The average thickness of these hexagonal nanosheets is about 100 nm according to the cross-section height profile as displayed in the inset of Fig. 1D.

Porous Co_3O_4 nanosheets can be obtained *via* the calcination of corresponding $Co(OH)_2$ nanosheets in air at 600 °C for 2 h. As shown in Fig. 2A, X-ray diffraction peaks can be indexed as pure face-centered-cubic spinel Co_3O_4 (space group: *Fd3m* (No. 227)) with lattice constant a = 8.084 Å (JCPDS 43-1003). No impurity

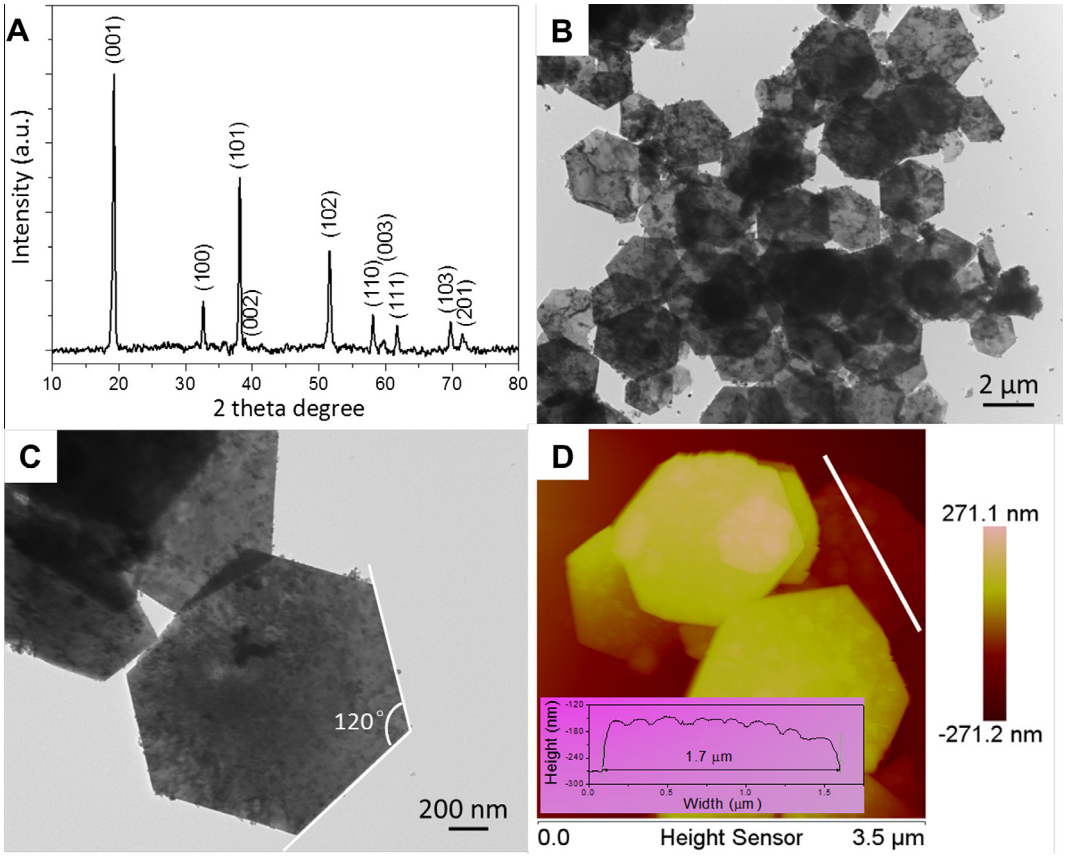

Fig. 1. (A) XRD pattern of $Co(OH)_2$ nanosheets; (B) low-, (C) high-magnification TEM images of $Co(OH)_2$ hexagonal nanosheets; (D) AFM image and cross-section height profile (inset) of as-prepared $Co(OH)_2$.