Synthesis and Electrochemical Properties of ZnO 3D Nanostructures

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(Received May 20, 2005; CL-050668)

Uniform flower-like ZnO 3D nanostructures were successfully synthesized by a common hydrothermal method using KNO_3 as inorganic mineralizer. The electrochemical properties of as-synthesized ZnO 3D nanostructures were studied by galvanostatic tests, indicating that the ZnO 3D nanostructured products may be good choice for anode materials in the Li ion batteries.

Recently, research on nanostructures is expanding rapidly into the assembly of nanoparticles in two-dimensional (2D) and three-dimensional (3D) ordered superstructures.[1–4] Much effort has been made in the fabrication of patterns of well-arranged nanocrystallites, especially the arrangement of one-dimensional nanotubes and nanorods because of their interesting physical properties and potential applications in many areas.[5–7]

Being a wide band-gap semiconductor with a large excitation binding energy, ZnO has been extensively investigated for its promising applications in short-wavelength light-emitting, transparent conductor, piezoelectric materials, and room temperature ultraviolet (UV) lasing. Many methods have been applied to synthesize 1D ZnO nanostructures, including chemical vapor transport,[8] physical vapor deposition approaches,[9] ligand-assisted synthesis,[10] and anodic alumina membrane template method.[11] But, the synthesis of ZnO 3D nanostructures and the study of their application as anode materials in Li ion batteries is rarely reported.

Herein we report a facile hydrothermal method to synthesize ZnO 3D nanostructures by using KNO_3 as inorganic mineralizer. The electrochemical properties of as-synthesized ZnO 3D nanostructures were studied by galvanostatic tests, which indicated the ZnO 3D nanostructured products may be good choice for the anode materials in the Li ion batteries.

All the reagents used in the experiments were purchased from commercial sources and were used as received without further purification. In a typical reaction, 1 g $ZnSO_4 \cdot 7H_2O$ was dissolved in distilled water and 25 vol % ammonia was dropped in to adjust the pH to the range 8–9. Finally, 10 g of KNO_3 was added into the solution and the solution was transferred into the 50 mL Teflon-lined autoclave. Distilled water was added into the autoclave until 80% of the volume. The mixture was magnetically stirred for around 60 min to get good homogeneity. Afterwards the autoclave was sealed and maintained at 180 °C for 24 h, then cooled to room temperature naturally. Precipitate was collected and washed with distilled water and anhydrous alcohol for several times. The final product was dried in vacuum at 80 °C for 10 h.

The X-ray diffraction was carried out on a Philiphs X'Pert super diffractometer with graphite monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å) in the 2θ range of 10–80°. The morphology of the products was examined by scanning electron microscope (SEM) using an X-650 microanalyzer. The TEM images were performed with a Hitachi 800 transmission electron microscopy with the accelerating voltage of 200 kV. Teflon cells were made to study the electrochemical properties of the product. The positive electrode consisted of the prepared ZnO (80 wt %), carbon black (10 wt %), and polyvinylidene (PVDF, 10 wt %). The cells were assembled in an argon filled glove box in which both the moisture and the oxygen levels were less than 1 ppm. The electrochemical tests were made in the voltage range of 0.01–3.0 V at a current density of 0.5 mA cm^{-2}.

Figure 1 shows the XRD pattern of the hydrothermal synthesis products. All of the diffraction peaks can be indexed as a hexagonal phase of ZnO (JCPDS 80–0075), which implies pure ZnO has been synthesized.

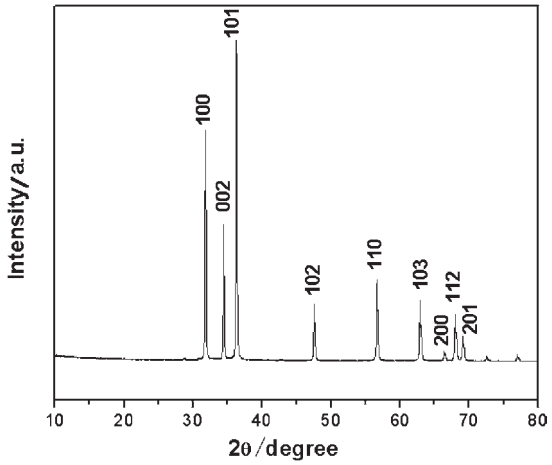

Figure 1. XRD pattern of the as-synthesized ZnO product.

The morphology of the as-synthesized ZnO was observed by scanning electron microscopy (SEM), which were shown in Figures 2a and 2b. It can be observed in the SEM images that 3D nanostructures of ZnO were obtained. The as-synthesized ZnO product shows mainly flower-like morphologies, constituting more than 80% of the total product (Figure 2a). Careful observation (Figure 2b) of the product shows that the flower-like structures consist of uniform nanorods with the diameter of 100–400 nm and length up to several micrometers. Further structural information of the ZnO product is provided by the TEM tests. Figures 2c and 2d show the TEM images of the as-synthesized ZnO product. In Figure 2c, it can be clearly observed that the flower-like nanostructures are constituted by tens of nanorods with diameter of around 200 nm. A single ZnO nanorod is shown in Figure 2d, which has the diameter of 150 nm and length up to about 3 μm. The inset SAED patterns in the TEM images

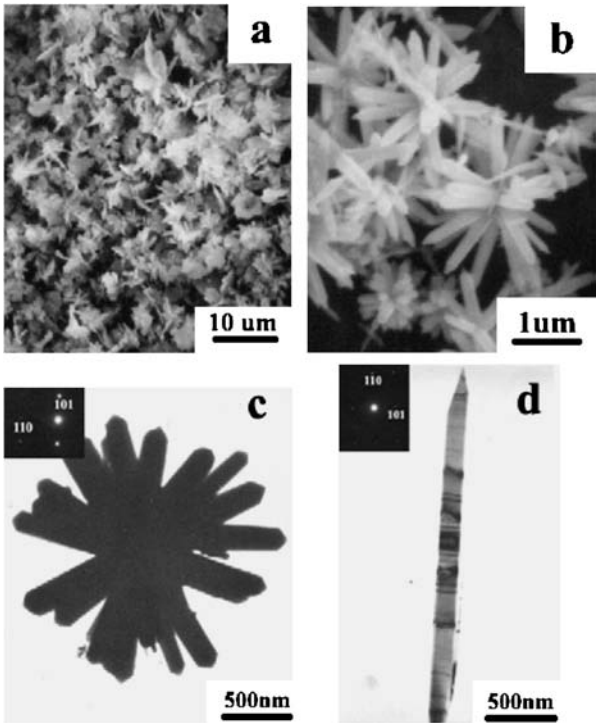

Figure 2. SEM images (a and b) and TEM images (c and d) of as-synthesized ZnO 3D nanostructures (inset of Figure 2c and 2d: SAED patterns of the ZnO product).

indicate that the flower-like nanostructures and nanorods are both well single crystallined.

It is believed that the use of inorganic mineralizer KNO_3 is critical for the successful synthesis of 3D nanostructures of ZnO. Flower-like ZnO nanostructures have been synthesized by several work groups.[12–14] In their synthesis methods, the strong basic environment is decisive for the growth of flower-like structure. In our method, KNO_3 is used to direct the formation of flower-like structure, and the basic environment is not required. A number of experiments were made to study the effect of KNO_3 on the morphology and structure of the final product. It is found that without the addition of KNO_3, only nanoparticles of ZnO product was obtained. The amount of KNO_3 seems not to be the decisive factor in the synthesis of ZnO 3D structures. We varied the amount of KNO_3 used in the reaction in the range of 5–15 g, and found that the morphology of the final product remained nearly unchanged.

The electrochemical property of the as-synthesized ZnO 3D nanostructures is studied by galvanostatic method using ZnO/Li Teflon cells. The voltage versus capacity for the ZnO/Li cell in the voltage range of 0.01–3.0 V at a current density of 0.5 mA cm^{-2} is shown in Figure 3a. The as-synthesized ZnO shows an initial discharge capacity of 2160 mAh g^{-1}. Figure 3b. shows the cycling behavior of the ZnO/Li Teflon cells. The discharge capacity decreases greatly from 2160 mAh g^{-1} to around 1080 mAh g^{-1} during the second charge/discharge cycle, which might be due to the irreversible insertion/deinsertion of lithium into the host structure during the cycle. In the prolonged cycles, the discharge capacity of the as-synthesized ZnO flower-like 3D nanostructures remains relatively stable. After 30 cycles, the discharge capacity still remains 850 mAh g^{-1}. The electrochemical

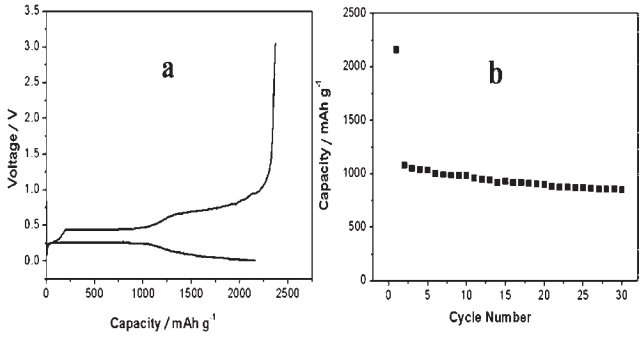

Figure 3. Initial charge/discharge curve (a) and cycling behavior (b) of the as-synthesized the ZnO 3D nanostructures.

property of ZnO nanoparticles products without the use of KNO_3 is also studied. The initial discharge capacity is only 1400 mAh g^{-1}, and after 30 charge/discharge cycles, the discharge capacity rapidly decreased to 400 mAh g^{-1}. The electrochemical study indicates that the as-synthesized ZnO 3D nanostructures might be a good replacement for the carbon-based anode materials currently used in the Li ion batteries.

In summary, uniform ZnO 3D nanostructures were successfully synthesized by a common hydrothermal method using KNO_3 as inorganic mineralizer. The effect of KNO_3 mineralizer on the morphology and structure of the product was studied. This method provides a facile and economic method for the synthesis of ZnO 3D nanostructures. The electrochemical test of the ZnO 3D nanostructures indicated that they might be good replacement for the carbon-based anode materials currently used in the Li ion batteries.

This work is partly supported by the Ministry of Science and Technology of China (No. 2002BA322C). We acknowledge the assistance from the Highstar Chemical Power Source Company Limited.

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Published on the web (Advance View) July 2, 2005; DOI 10.1246/cl.2005.1114