

Synthesis of NiO flower-like microspheres and their Electrochemical Performance

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We have successfully prepared β -Ni(OH)₂ flower-like microspheres by the solvothermal method using 2-butanone and water mixture solvent for the first time. Then NiO flower-like microspheres were obtained by annealing the corresponding precursors at 300 °C. The flower-like microspheres were composed of many nanoplates. The thickness of nanoplates and the diameter of flower-like microspheres were about 20 nm and 6 μ m, respectively. For comparison, the sole β -Ni(OH)₂ and NiO nanoplates were prepared in aqueous solution. Experimental results indicated that the as-synthesized NiO flower-like microspheres kept a relative high capacity retention during charge-discharge process, and their cyclic stability should be improved for potential application in lithium-ion batteries.

Keywords: β -Ni(OH)₂ / NiO / flower-like microspheres / Electrochemical Properties

1. INTRODUCTION

Interstitial-free 3d transition-metal oxides (M_xO_y, M = Fe, Co, Ni, Mn, etc.), are promising high-performance materials for next-generation lithium-ion batteries (LIBs) because of their much higher theoretical capacity and better rate properties than that of commercially used graphite (372 mA h g⁻¹)[1–5]. Among these metal oxides, NiO can be a competitive candidate due to its high theoretical lithium storage capacity (718 mAh g⁻¹)[6]. Up to date, a great number of studies have been dedicated to the synthesis of NiO materials with well defined structures, such as nanoparticles[7–9], nanorings[10], nanosheets[11], and some hierarchical structures[12–16]. It is well established that their sizes, shapes, orientations, and assemblies, which are related to the preparation methodology, have a significant influence on the physical and chemical performances of as-prepared nanomaterials.

In this paper, we have synthesized β -Ni(OH)₂ flower-like microspheres and nanoplates by employing different solvent, and then have obtained NiO flower-like microspheres and nanoplates by annealing the corresponding precursors at high temperature. Finally, we have investigated the electrochemical performances of the NiO flower-like microspheres.

2. EXPERIMENTAL SECTION

2.1 Materials

Nickel acetate tetrahydrate (C₄H₆O₄Ni·4H₂O), Tetrabutylammonium Hydroxide (10% in Water), and 2-butanone (C₄H₈O) were purchased from Shanghai Chemical Reagents Co., Ltd. and were used as-received without further purification.

2.2 Synthesis

In a typical synthesis of the β -Ni(OH)₂ nanoplates, 0.2 g of Ni(CH₃COO)₂·4H₂O was dissolved in 35 mL of deionized H₂O under stirring. Then, 2 ml of Tetrabutylammonium Hydroxide (10% TBAOH aqueous solution) was added to the above solution. The mixture was stirred for about 5 minutes and then was sealed in a Teflon-lined stainless steel autoclave (50 ml capacity). The autoclave was maintained in an oven at 160 °C for 12 h. The raw products were washed with deionized water for three times, and finally dried at 60 °C under reduced pressure. For the β -Ni(OH)₂ flower-like microspheres, the procedures were similar to the synthesis of β -Ni(OH)₂ nanoplates except that the solvent was replaced by the mixture of 37 ml 2-butanone and 3ml H₂O and the reaction temperature was 140 °C, respectively. The NiO nanoplates and flower-like microspheres were obtained by annealing the corresponding β -Ni(OH)₂ precursors in air at 300 °C for 0.5h, respectively.

2.3 Characterization

The as-synthesized products were characterized by X-ray diffraction (XRD) with CuK α radiation (wavelength, λ =1.54056Å). The scanning electron microscopy (SEM) images were taken on a JEOL JSM-6700F field emission scanning electron microscope (FESEM, 20 kV). Transmission electron microscopy (TEM) images were obtained on a JEOL-2010 with an accelerating voltage of 200 kV. The samples used for SEM and TEM characterization were dispersed in absolute ethanol and were slightly ultrasonicated before observation.

2.4 Electrochemical measurements.

The electrochemical performance was tested by using coin-type cells (CR2016) at room temperature. The working electrodes were made by mixing the products, acetylene black and polyvinylidene fluoride (PVDF) in N-methylpyrrolidone (NMP) at a weight ratio of 8:1:1. The

resulting paste was uniformly coated onto a Cu foil and dried in the vacuum chamber at 100 °C for 10 h, before being cut into disks with a diameter of 8 mm. The coin-type cells were assembled in an glove box under argon atmosphere with the prepared disks as working electrodes, lithium metal as the counter electrodes, microporous membrane (Celgard 2300) as separators and 1M LiPF₆ mixed in a solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1) in volume as electrolyte. The charge–discharge measurements were conducted on a Land CT 2001A automatic battery tester (Wuhan, China).

3. RESULTS AND DISCUSSION

The phase purities of the as-synthesized β -Ni(OH)₂ products were examined by X-ray diffraction, which are shown in Figure 1. All the diffraction peaks can be assigned to hexagonal β -Ni(OH)₂, agreeing well with the calculated diffraction pattern (JCPDS card no.14-0117). No other diffraction peaks are detected in the spectrum within the instrumental resolution, which indicates that the products are β -Ni(OH)₂ with high purity. However, the product obtained in TBAOH aqueous solution only displays one strong peak of (001) planes except for the other very weak signals ascribed to (101), (002) and (102), signifying the high crystal orientation. By contrast, the samples obtained in 2-butanone doesn't exhibit this phenomenon.

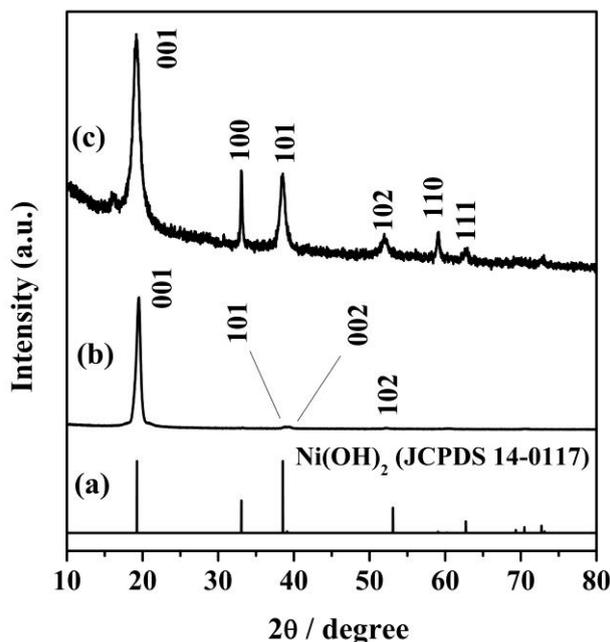


Figure 1. XRD patterns of the as-synthesized β -Ni(OH)₂ products: (a) the reference pattern from standard hexagonal β -Ni(OH)₂ (JCPDS 14-0117), (b) the sample obtained in TBAOH aqueous solution, (c) the sample obtained in 2-butanone.

For further investigate the effect of solvent on the morphologies and microstructures, the typical products have been characterized by scanning electron microscopy (SEM). Figure 2 shows the SEM images. It is clear that the two morphologies are very different. The product obtained in TBAOH aqueous solution exhibits well dispersed 2-dimensional nanoplates with a mean thickness of ~ 20 nm and a diameter of ~ 200 nm. These nanoplates naturally lie on the copper plate (Figure 2a-c), which results in high crystal orientation, consistent with the XRD results. However, in 2-butanone solvent, the synthesized product is composed of nearly dispersed flower-like microspheres in the size of 4-8 μm in diameter (Figure 2d-e). The local magnified image of an individual microsphere indicates that those flower-like microspheres are built from nanoplates with a thickness of about 20 nm, which connect with each other to form the hierarchical 3-dimensional (3D) flower-like microspheres (Figure 2f).

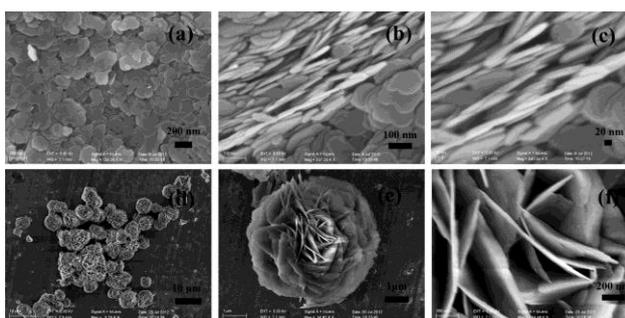


Figure 2. SEM images of $\beta\text{-Ni(OH)}_2$: (a-c) the sample obtained in TBAOH aqueous solution, (d-f) the sample obtained in 2-butanone.

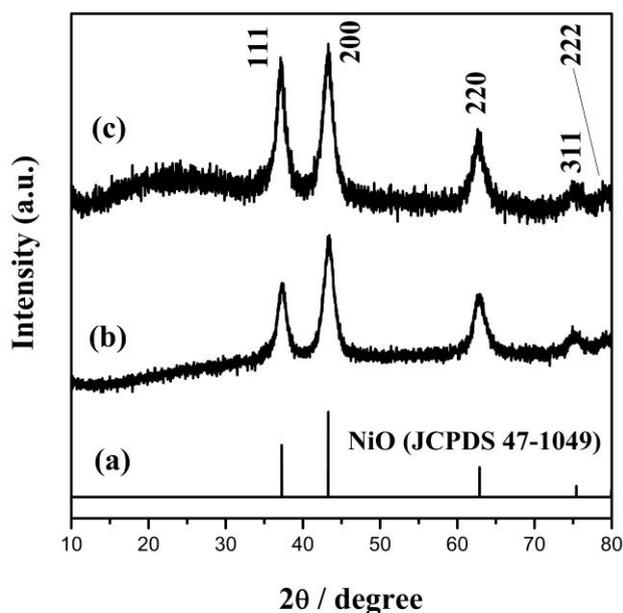


Figure 3. XRD patterns of the corresponding NiO nanomaterials: (a) the reference pattern from standard face-centered cubic NiO (JCPDS 47-1049), (b) the sample derived from $\beta\text{-Ni(OH)}_2$ nanoplates, (c) the sample derived from $\beta\text{-Ni(OH)}_2$ flower-like microspheres.

Fig. 3 exhibits the corresponding XRD patterns of the thermally decomposed products from the β -Ni(OH)₂ precursors. All the diffraction peaks can be indexed to a single phase of face-centered cubic NiO, matching well with JCPDS card no. 47-1049. No peaks from the β -Ni(OH)₂ precursor can be observed in the XRD pattern, which signifying the complete transformation of β -Ni(OH)₂ to NiO after 0.5h at 300 °C.

The morphology and microstructure of the NiO samples were researched by SEM as well, which are shown in Fig 4. It is very clear that the NiO samples still reserves their precursors' microstructures and sizes, that is, the products are still nanoplates or flower-like microspheres. TEM images can also exhibit the same resules (Figure 5).

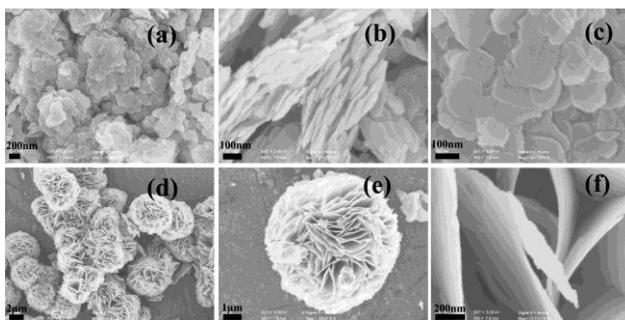


Figure 4. SEM images of NiO: (a-c) the sample derived from β -Ni(OH)₂ nanoplates, (d-f) the sample derived from β -Ni(OH)₂ flower-like microspheres.

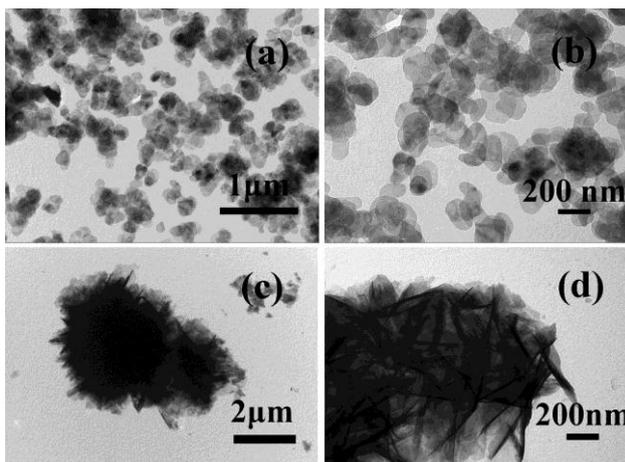


Figure 5. TEM images of NiO: (a-b) the sample derived from β -Ni(OH)₂ nanoplates, (c-d) the sample derived from β -Ni(OH)₂ flower-like microspheres.

Figure 6 shows voltage versus discharge capacity curves at the 1st, 2nd and 13th cycles for the NiO flower-like microsphere cell during 0.01-3V at a current density of 50 mA g⁻¹. Obviously, a stable discharge plateau appears at about 1.2 V, which can be ascribed to the reversible reaction of NiO \rightleftharpoons Ni/Li₂O[17].

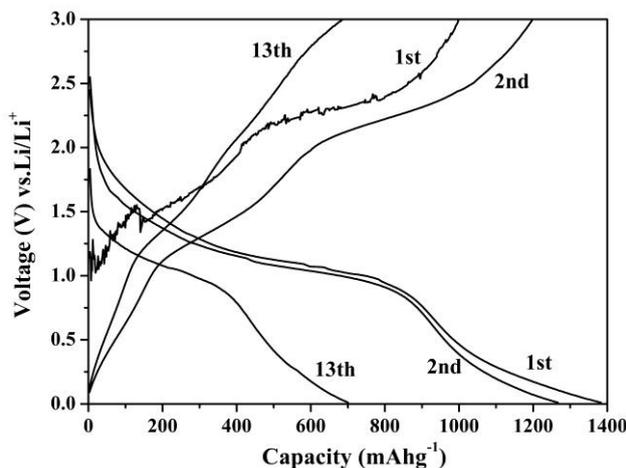


Figure 6. The charge-discharge voltage profiles of the NiO flower-like microspheres

Figure 7 demonstrates the curves of specific capacity vs cycle number for the electrodes made from NiO flower-like microspheres. Generally, the reversible capacity decreased with cycling. In this work, the capacity decreases rapidly all the time. However, the capacity after 15th cycle still reaches to 530 mAh g^{-1} , higher than the reported NiO nanoplates[18]. As mentioned in some reported researches, a large amount of pores exist in the NiO flower-like microspheres, which leads to a relative high capacity retention[18]. For the NiO electrodes, the severe capacity degradation should be due to the large volume expansion–constriction resulting in the pulverization and degradation of the electrode, similar to noncarbon anode materials[16,19-20]. Therefore, the cyclic performance of this kind of nanostructured anode material must be improved in the next researches for their practical use.

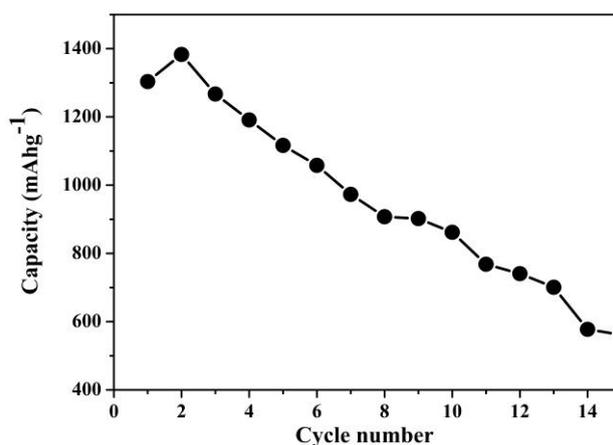


Figure 7. The cycling performance of the NiO flower-like microspheres.

4. CONCLUSIONS

In conclusion, we have successfully prepared NiO flower-like microspheres by the solvothermal method using 2-butanone and water mixture solvent. The NiO microspheres consisted of

a lot of nanoplates. The thickness of nanoplates was about 15nm and the diameter of the microspheres was 6 μm . NiO flower-like microspheres were prepared by calcinating $\beta\text{-Ni(OH)}_2$ precursors at 300 $^\circ\text{C}$. Experimental tests indicated that the as-synthesized NiO microspheres kept a relative high capacity retention during charge-discharge process, and their cyclic stability should be improved for potential application in lithium-ion batteries.

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