

A Novel Synthesis of Mesoporous Nickel Oxide with Excellent Cycling Stability Used in Supercapacitors

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Mesoporous nickel oxide is synthesized by a novel method by calcining a nickel–organic coordination complex precursor in this work. The prepared NiO has a uniform pore distribution evidenced by TEM and N₂ adsorption–desorption tests. The NiO electrode presents a high specific capacitance of 143 F g^{−1}, excellent rate capability (54.2% capacity retention at 100 mVs^{−1}) and long cycling stability (no decrease in 1000 charge–discharge cycles), indicating a promising electrode material for supercapacitors.

Mesoporous nickel oxide has recently attracted much attention because of its promising application in supercapacitors.^{1–4} The mesoporous NiO with well pore dispersion is expected to exhibit novel or superior electrochemical performance, since existing of the pores will certainly make the electrolyte contact more electroactive sites, resulting in increasing electrical conductivity and electrochemical utilization of the material.^{5–7} Various methods have been developed to prepare mesoporous NiO such as soft or hard template methods,^{8,9} chemical precipitation,^{1,10} and sol–gel technique.¹¹ However, the processes are complicated and lead to aggregated nanostructural NiO with scattered pore size distributions. Therefore, an easy controlled method to prepare ordered mesoporous NiO materials is of great significance in the practical application in supercapacitors. In the present work, we introduce a novel and facile method to prepare ordered mesoporous NiO from the nickel–1,3,5-benzenetricarboxylic acid (Ni–BTC) coordination complex.^{12,13} Generally, this Ni–BTC precursor is a kind of mesoporous material, and the structures of such complex are highly ordered so as to avoid the agglomeration and finally result in well-defined porous materials.¹⁴ Application of this mesoporous NiO as electrode material in supercapacitors was investigated in 3 wt % KOH solution.

Typically, the Ni–BTC precursor was synthesized through a simple hydrothermal method by mixing 0.25 g of Ni(NO₃)₂·6H₂O, 0.30 g of K₂CO₃, 0.15 g of 1,3,5-benzenetricarboxylic acid (H₃BTC, C₆H₃(COOH)₃), and 20 mL of H₂O in a Teflon-lined stainless steel autoclave heated at 120 °C for 24 h. Then according to thermogravimetric and differential scanning calorimetry analysis, the ordered mesoporous NiO was prepared through calcining the precursor in the air at 400 °C for 24 h. The crystalline structure of the product was determined by a XRD-6000 powder diffractometer. The morphology was observed by a S-4800 scanning electron microscope (SEM) and a JEM-2100 high-resolution transmission electron microscope (HRTEM). N₂ adsorption–desorption was determined by BET measurement using a Micromeritics Tristar-3000 surface area and porosity analyzer. Electrochemical tests were carried out in a CHI660b electrochemical workstation.

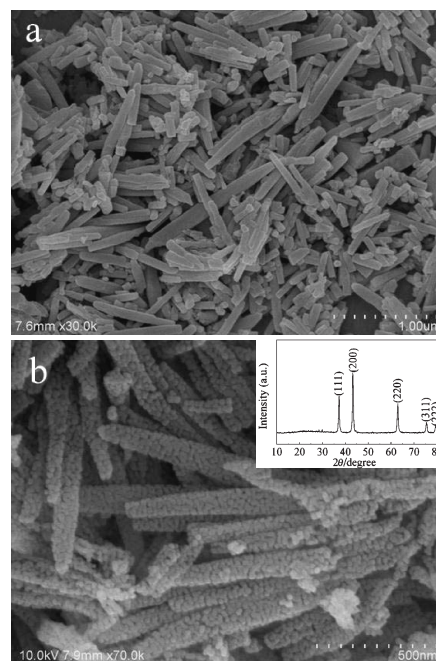


Figure 1. SEM images of (a) the H₃BTA–Ni precursor and (b) the synthesized mesoporous NiO, inset of (b) is the XRD pattern of the prepared NiO.

From the SEM image in Figure 1a, it can be seen that the synthesized precursor mainly shows a rod-like morphology with the diameter range mainly from 65 to 90 nm. As is known that the Ni–BTC coordination complex can form 1-D polymeric Ni–BTC chains.¹⁴ The strong π – π or hydrogen-bonding interactions between the ligands could hold the chains together to form 1-D rods. After calcining, the obtained mesoporous NiO inherits the external morphology from the precursor (Figure 1b) but with two obvious varieties. On one hand, the nanorods are much looser with many small pores on the surface. On the other hand, there is an obvious volume expansion of the nanorods with a diameter range mainly from 85 to 120 nm. These varieties can be ascribed to the release of H₂O and carbon oxide (CO and CO₂) molecules during the calcining process of precursor.¹ The XRD pattern of obtained NiO was shown in inset Figure 1b. The marked peaks are corresponding to (111), (200), (220), (311), and (222) planes respectively (JCPDS: 78-0423), indicating good purity of the obtained NiO.

TEM images were used to directly confirm the porosity of the synthesized NiO in Figure 2. It can be clearly seen that many regular pores are distributed homogeneously within the whole NiO nanorod (Figure 2a). The BET surface area of the

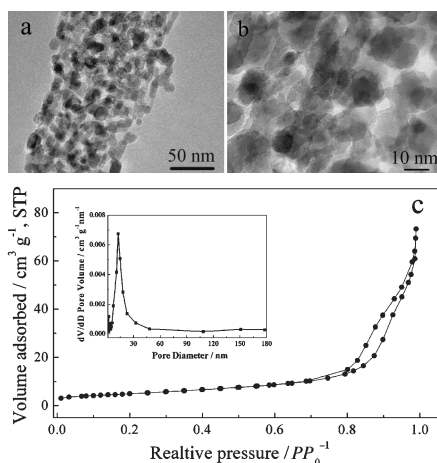


Figure 2. TEM images of (a) the $\text{H}_3\text{BTA-Ni}$ precursor and (b) the prepared NiO, (c) the N_2 adsorption–desorption isotherms of the prepared NiO and BJH pore size distributions of the prepared NiO (inset).

synthesized NiO sample is $17.7 \text{ m}^2 \text{ g}^{-1}$ (Figure 2c). HRTEM image (Figure 2b) shows that the mesoporous NiO has a narrow mesopore size distribution compared to mesoporous NiO prepared by conventional methods,^{15,16} namely, two kinds of pores about 3 and 20 nm evidenced by the pore size distribution (inset of Figure 2c), which would make it great candidate for application in supercapacitors.

Electrochemical performance of the NiO electrode for supercapacitors was studied by cyclic voltammograms and charge–discharge experiments. Figure 3a shows the CV curves of the NiO electrode at various scan rates of 5, 10, and 20 mV s^{-1} in 3 wt % aqueous KOH electrolyte. There is a pair of redox reaction peaks in the potential range from 0.0 to 0.5 V, in which the anodic peak is due to the oxidation of NiO to NiOOH , and the cathodic peak is for the reverse process. This redox process is responsible for the pseudo-capacitive capacitance of the NiO electrodes. Inset of Figure 3a is the specific capacitance at different scan rates. Surprisingly, the synthesized mesoporous NiO still retains 71 F g^{-1} at a scan rate as high as 100 mV s^{-1} . As is known, when the scan rate increases, the diffusion of OH^- is much slower, and the ions can only reach the outer surface of the NiO material, so the effective utilization of the electroactive material has been greatly limited, leading to decrease of the specific capacitance.^{17,18} In the present material, the uniformly distributed mesopores in the NiO can supply enough diffusion channels for the electrolyte ions and reduce the diffusion lengths, ensuring better utilization of the electroactive materials at a high scan rate.²

The cyclability of the NiO electrode is an important quality required for practical applications, and it is demonstrated by continuous charge–discharge measurements over 1000 cycles. Figure 3b gives the typical charge–discharge curves (inset) and the cyclic performance of the NiO electrode. The value of the specific capacitance (C_s) was obtained from the charge–discharge cycling measurements according to the following equation: $C_s = It/(\Delta E m)$, Where, I is the discharge current, t is the discharge time, ΔE is the potential range during discharge, and m is the mass of electroactive materials. The C_s for NiO is 143, 136, and 123 F g^{-1} for different current densities of 0.5, 1.0, and 2.0 A g^{-1} , respectively. No decrease in specific capacitance

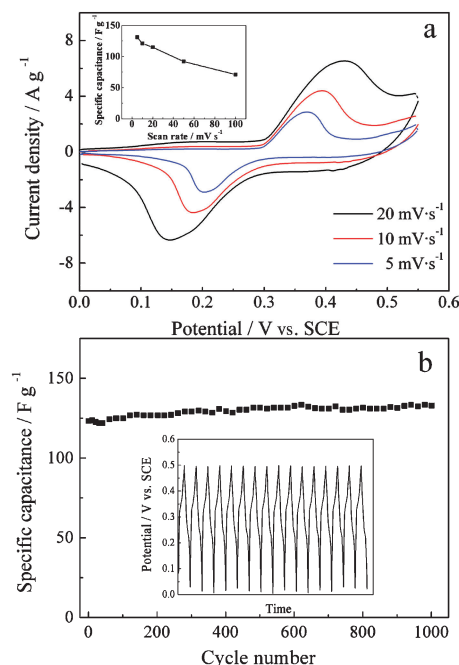


Figure 3. (a) CV curves at different scan rates and the specific capacitance of NiO versus scan rate (inset) and (b) the cycle performance and typical charge–discharge curves (inset).

was observed after 1000 charge–discharge cycles of NiO at a current density of 2.0 A g^{-1} between 0.0 and 0.5 V, suggesting that the mesoporous NiO electrode has high stability for long-term capacitor applications.

In conclusion, we have proposed a novel and easy way for synthesizing ordered mesoporous NiO which shows a uniform mesoporous structure. The mesoporous NiO electrode presents a high specific capacitance, excellent rate capability, and long cycling stability, indicating a promising electrode material for electrochemical capacitors. Our method for synthesizing mesoporous NiO is successful, and it is expected as a versatile method to synthesize other mesoporous metal oxides.

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