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Preparation of mesoporous NiO with a bimodal pore size distribution and application in electrochemical capacitors

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1. Introduction

Electrochemical capacitors (EC) have been receiving much attention due to their high power capability, excellent reversibility and long cycle life [1]. In these electrochemical capacitors, two basic types can be realized based on different charge-storage mechanisms [2]: one is electric double layer capacitors, mainly focusing on carboneous materials with a high specific surface, whose capacitance arises from the charge separation at the active/solution interface; the other is pesudocapacitors, mainly focusing on conducting polymers and metal oxides, which utilize the capacitance resulting from fast faradaic redox reactions occurred within the active electrode materials. However, electric double layer capacitors are limited in increasing the high energy density because the charge transfer mechanism is not involved in their charge-discharge processes. On the other hand, the pesudocapacitors always exhibit great decrease in capacitance at high scan rate and poor cycle stability due to the repeated redox processes [3].

Recently, interest in mesoporous solids (pore size 2–50 nm) for supercapacitor materials has become intense, for large surface areas enable formation of a larger amount of double layers and a lot of pores cause rapid transfer of the electrolyte [4–6]. It is well known that the pore structure has great effect on the electrochemical performance of the carbon materials. Pores with different size play different roles in the charging/discharging process [7].

ABSTRACT

Mesoporous nickel oxide with a porous structure exhibiting a bimodal pore size distribution (2.6 and 30.3 nm diameter pores) has been synthesized in this paper. Firstly, a mesoporous precursor of coordination complex $Ni_3(bc)_2 \cdot 12H_2O$ (btc = 1,3,5-benzenrtricarboxylic acid) is synthesized based on the metal–organic coordination mechanism by a hydrothermal method. Then mesoporous NiO with a bimodal size distribution is obtained by calcining the precursor in the air, and characterized by transmission electron microscopy and N_2 adsorption measurements. Such unique multiple porous structure indicates a promising application of the obtained biO as electrode materials for supercapacitors. The electrochemical behavior has been investigated by cyclic voltammogram, electrochemical impedance spectra and chronopotentiometry in 3 wt.% KOH aqueous electrolyte. The results reveal that the prepared NiO has high-capacitance retention at high scan rate and exhibits excellent cycle-life stability due to its special mesoporous character with bimodal size distribution.

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Those carboneous materials with larger percentage of bigger pores (>10 nm) are more suitable to high-power supercapacitor application because they can deliver high energy at high rate [8], while increasing the volume of smaller pores (nearly 2 nm) was shown to increase specific capacitance [9,10]. What is more, even the pores with size smaller than 1 nm also contribute to the charge storage[11]. Due to the different effect of the different pore sizes on the capacitive properties, many works [12,13] have focused on preparing carbon materials with multiple pore distribution and studying their electrochemical capacitor behavior. It is assumed that a well balanced micro- or mesoporosity was needed to maximize capacitance and fulfil high rate EC applications. [14,15].

However, only several works ever have focused on preparing and investigating the electrochemical properties of metal oxides with such unique multiple porous structures. Among these metal oxides for supercapacitor application, NiO attracts great attention in view of its low fabrication cost, environmentally friendly character and well-defined redox behavior [16–20]. Zhang and co-authors used a self-assembly method for generating NiO nano/microspherical superstructures [20] and studied its supercapacitive character. Though this method was very facile, the morphology of the prepared NiO was not regular. Bruce and co-authors [21] synthesized ordered mesoporous NiO possessing crystalline walls and an ordered 3D pore structure with the help of silica template, exhibiting a bimodal pore size distribution. However, such approach required a template so as to increase the production cost and complexity.

In this paper, we proposed a novel and controllable method to synthesize mesoporous nickel oxide of bimodal size distributions.

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Metal-organic complex has been used as a precursor to prepare mesoporous metal oxide [22] in our previous work. Such method can be improved to prepare metal oxides with bimodal size distribution by controlling the synthetic condition. On one hand, the metal-organic complex precursor has a mesoporous structure due to the growth mechanism of the polymer complex precursor [23-25]. On the other hand, when calcining the precursor, new pores generate as the organic ligands decompose, finally resulting in a multiple porous structure. This method needs neither template nor any surfactant. Besides the metal-organic complex precursors have regular morphology due to the metal-organic coordination mechanism. Such unique nanostructure may bring on an exciting performance for utility in supercapacitors. Electrochemical tests have revealed that the prepared mesoporous NiO material is of large specific capacitance, good rate capability and extremely excellent cycling property.

2. Experimental

2.1. Synthesis of the precursor $Ni_3(btc)_2\cdot 12H_2O$ and mesoporous NiO

The Ni₃(btc)₂·12H₂O crystal was synthesized through a simple hydrothermal process. Firstly, a mixture of 0.25 g Ni(CH₃COO)₂·4H₂O, 0.20 g NH₄COOH (Shanghai Chemical Co. Ltd., PR China), 0.15 g 1,3,5-benzenrtricarboxylic acid (H₃BTC, Alfa Aesar) and 20 ml H₂O were placed in a 30 ml Telflon lined stainless steel autoclave and heated at 200 °C for 24 h, followed by cooling to room temperature naturally. Then the precipitate was filtrated, washed with distilled water and dried at 45 °C. Finally, the precursor was heated in the solid state at 400 °C for 24 h with a temperature-increase rate of 3 °C min⁻¹ from room temperature, and the resulted black powder was the synthesized nickel oxide.

2.2. Characterization of the $Ni_3(btc)_2 \cdot 12H_2O$ precursor and prepared NiO

The crystalline structure of the product was determined by a XRD-6000 powder diffractometer (Shimadzu, Japan) using Cu K_{\alpha} radiation between 10° and 80° with a scanning rate of 4° min⁻¹. The morphology of the sample was observed by a scanning electron microscope Model S-4800 (SEM, Hitachi, Japan) and a high-resolution transmission electron microscope Model JEM-2100 (HRTEM, Jeol, Japan). N₂ adsorption/desorption was determined by BET measurement using Micromeritics Tristar-3000 surface area and porosity analyzer.

2.3. Preparation and electrochemical tests of the NiO electrode

The working electrodes of electrochemical capacitors were formed by 80 wt.% of prepared NiO powder with 15 wt.% acetylene black (AB) and 5 wt.% polytetrafluoethylene (PTEF) binder of the total electrode mass. A small amount of isopropanol was then added to the mixture to make them more homogeneous. Then the slurry of the mixture was coated onto nickel foam $(1 \text{ cm} \times 1 \text{ cm})$ and briefly allowed the solvent to evaporate before pressing. The electrodes weighed after being dried in vacuum at 50°C for 4h. The typical mass load was from 3 to 5 mg. All electrochemical measurements were done in a three-electrode experimental setup. Platinum wire electrode and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All the electrochemical measurements were carried out in 3 wt.% KOH aqueous electrolyte by using a CHI660B (Shanghai Chenhua Apparatus, China) and PGSTAT30 (Autolab, EchoChemie, Netherlands) electrochemical workstation.

3. Results and discussion

Fig. 1 shows the XRD patterns of the precursor and the final mesoporous NiO with bimodal size distribution. In Fig. 1a, the narrow and strong diffraction peaks indicate good purity of the obtained NiO, and the peaks correspond to $(1\,1\,1)$, $(2\,0\,0)$, $(2\,2\,0)$, $(3\,1\,1)$ and $(2\,2\,2)$ planes respectively (JCPDS: 78-0423). The precursor can be described as $[Ni_3(btc)_2 \cdot 12H_2O]$ for its XRD pattern in Fig. 1b matches well with the result of the reported literature [26,27].

The surface morphology of the nanostructured precursor and NiO has been investigated using SEM. We can find out that the precursor (Fig. 2a) and the prepared NiO (Fig. 2b) display a similar flowerlike regular morphology. After calcining at 400 °C for 24 h, the prepared NiO arrays still inherit the framework from the precursor well, indicating good stability of this multiple mesoporous structure. There is almost no shrinkage though total weight loss is as high as around 65%, indicating large amount of pores left within the particles. HRTEM was used to observe the porosity of the nickel oxide directly. Fig. 2c clearly shows the porous structure of synthesized NiO, and the pores distribute homogeneously through the arrays. In Fig. 2d, we can clearly see the porous character of the prepared NiO, and the shapes of the pores are irregular. The corresponding selected area diffraction pattern is shown as an inset, and the diffraction rings can be indexed to the NiO with a polycrystalline structure.

Nitrogen adsorption-desorption isotherms and the BJH adsorption pore size distribution plots of $Ni_3(btc)_2 \cdot 12H_2O$ and NiO calcined at 400 °C for 24 h are shown in Fig. 3. Their mesoporous







Fig. 2. SEM images of (a) the precursor Ni₃(btc)₂·12H₂O and (b) the synthesized porous NiO calcined at 400 °C for 24 h, (c and d) HRTEM images of the NiO at different magnification, the inset of (d) contains the selected area diffraction pattern.

nature is proved by the irreversible type IV adsorption–desorption isotherms. The prepared NiO has a narrow mesopore size distribution, namely two kinds of pores about 2.6 and 30.3 nm. Compared with the adsorption pore size distribution of the precursor (2.1 nm), we can conclude that the 2.6 nm pores come from the original coordination complex while the pores of 30.3 nm result from the calcination.

In the preparation of $[Ni_3(btc)_2 \cdot 12H_2O]$, the metal ions Ni^{2+} coordinated to both the organic ligand H_3BTC and H_2O . By the intermolecular (Ni–BTC and Ni–OH₂) and intramolecular (COO–H₂O hydrogen-bonding) interactions, it is possible to organize the 1D



Fig. 3. N₂ adsorption–desorption isotherms of (a) the precursor Ni₃(btc)₂.12H₂O and (b) the synthesized NiO calcined at 400 °C for 24 h. The inset shows BJH pore size distributions.

chains, and these chains are held together by the $\pi-\pi$ or hydrogenbonding interactions of the ligands. Then the mesopores (2.1 nm) formed between the chains. After calcination, H₃BTC and H₂O were removed and larger pores (30.3 nm) formed. Because of the removing of the ligands, the interaction between the chains is decreased, enlarging the pore size between the chains from 2.1 to 2.6 nm.

The BET surface area of the synthesized NiO sample is $21.6 \text{ m}^2 \text{ g}^{-1}$, which has been increased from that of the precursor Ni₃(btc)₂.12H₂O, 9.7 m² g⁻¹. We can figure out that such coordination-polymer is an effective precursor for the formation of ordered nano-size metal oxide with a multiple porous structure.

In order to investigate the effect of unique porous structure on the electrochemical properties of the NiO electrode, the performance of the synthesized NiO was tested by cyclic voltammograms (CV). Fig. 4a shows the CV curves of the as-synthesised NiO at different scan rates in 3 wt.% KOH aqueous. The synthesized NiO shows a typical pesudo-capacitive behavior. The obvious redox peaks indicate the pseudo-capacitance arises from the NiO/NiOOH reversible redox progress. The current density is quite high due to abundant surface area of NiO for fast Faradaic reactions. The capacitance can be calculated with Eq. (1):

$$SC = \frac{q}{m\nu} = \frac{1}{0.55m\nu} \int_{0.55}^{0} I(V)dV$$
(1)

Where *m* is the mass of the electroactive materials and *v* is the scan rate. The capacitances under different scan rates are shown in Fig. 4b. It is interesting to note that at a low scan rate 5 mV s^{-1} , the mesoporous NiO has a specific capacitance (C_s) of 94 Fg^{-1} , and the value reduces to 71 Fg^{-1} (74% capacitance of 5 mV s^{-1}) at very high scan rate of 200 mV s⁻¹.

A large decrease in the C_s value was reported [28] for some other low-cost metal oxides when the scan rate increased to 100 mV s⁻¹. However, in this study, only 26% decrease in C_s was observed



Fig. 4. (a) CV curves of NiO synthesized through calcining the metal–organic coordination precursors in 3 wt.% KOH aqueous electrolyte under different scan rate 5, 10, 20, 50, 100, 200 mV s⁻¹ and (b) the capacitances under different scan rates.

from 5 to 200 mV s^{-1} . Compared with previous literatures, this decrease is very small. Prasad and co-authors [29] have reported an electrochemical capacitor using nanowhiskers NiO prepared through electrochemical deposition method; nearly 30% decrease in $C_{\rm s}$ was observed between the scan rate 100 and 200 mV s^{-1} . NiO nanoplatelets prepared by calcining Ni(OH)₂ at $300 \,^{\circ}\text{C}$ was reported by Wu [16], and the capacitance retention from 10 to 200 mV s^{-1} is 74%. The results reveal that such mesoporous NiO has a large electroactive area on the surface layer, and it shortens diffusion paths for high rate charge/discharge [29,16]. The small decrease in specific capacitance with increasing scan rate indicates good ion transportation, which can be mainly attributed to the larger pores (about 30 nm).

To further investigate the influence of such multiple porous structure on electrolyte diffusion, electrochemical impedance spectra (EIS) was conducted on the prepared NiO. Fig. 5a shows the Nyquist plots of the prepared NiO at the potential of 0.38 V with a frequency range from 10⁵ to 0.01 Hz in 3 wt.% KOH aqueous. In EIS test, the supercapacitor behaves as a series combination of a resistance and capacitance and both of them depend on the frequency. At high frequency, a small capacitance is observed because only a limited part of electrode surface is utilized as a capacitor while in low frequency extreme, the capacitive behavior is more obvious for most of the pore surface is utilized as a capacitor and results in a maximum capacitance [30]. A pure capacitor should exhibit a vertical line at low frequency. The deviation from the vertical line is ascribed to the inner mesopore diffusion, which is strongly dependent on the measured potentials [31]. In the low frequency region, the capacitance (C) can be defined as the combination of imaginary (C') and real part (C) of the capacitance, and they can be expressed as follows according to the references [32–34]:

$$C(\omega) = C'(\omega) + jC''(\omega)$$
⁽²⁾

$$C'(\omega) = \frac{-Z''(\omega)}{\omega |Z(\omega)|^2}$$
(3)

$$C''(\omega) = \frac{Z'(\omega)}{\omega |Z(\omega)|^2} \tag{4}$$

where *C* corresponds to the capacitance measured under low frequency alternating current conditions and *C'* is directly proportional to resistance and corresponds to losses in the form of energy dispersion. Fig. 5b presents the variation of the real (*C'*) and imaginary (*C'*) part of the capacitance over frequency. The real capacitance (*C*) decreases as the frequency increases, and at high frequency, the capacitance value is nearly to zero. The relaxation time constant τ_0 is a quantitative measure of how fast the device can be discharge. It can be deduced according to $\tau_0 = 1/2\pi f_0$, where f_0 corresponds to the peak frequency in the imaginary capacitance plot [34]. At the potential of 0.38 V, *C'* has a maximum value at 0.2 Hz, and thus the relaxation time is 795 ms. This time is very short, showing a fast ions transport in the pores during the charge–discharge process.

The charge–discharge behavior of NiO was measured by Chronopotentiometry between 0.0 and 0.5 V (*vs.* SCE) at different current densities of 0.5, 1.0 and 2.0 Ag^{-1} , which is displayed in Fig. 6a. The value of specific capacitance (C_s) of the electrode can be calculated according to the equation: $C_s = It/(\Delta Em)$, where *I* is dis-



Fig. 5. (a) Nyquist plots for NiO electrode at potential of 0.38 V (the inset shows the expanded high-frequency region of the plot) and (b) the variation of the real and imaginary part of the capacitance with the frequency at 0.38 V.



Fig. 6. Charge–discharge (a) curves at different current density of 0.5, 1.0, 2.0 A g⁻¹ and (b) cycle number of the mesoporous NiO with bimodal size distribution prepared from nickel–organic complex.

charge current, ΔE represents for the potential difference during the time t. Here we take the potential range (0.0-0.5 V) to calculate the C_s and *m* is the mass of electrochemical active material. The specific capacitances of the nickel oxide are 130, 125, 112 Fg^{-1} for different current densities of 0.5, 1.0 and 2.0 A g⁻¹, respectively. The specific capacitance of the prepared NiO is not only related to the mesoporous structure, but also greatly affected by the annealing temperature. It appears that sintering and crystalling under high temperature affects negatively on the active area of the materials, leading to a great decrease in the specific capacitance of the NiO samples [16,18]. In Zhao's work [18], when annealing temperature increases from 250 to 350 °C, the specific capacitance decreases from 590 to 47 F g⁻¹. In this paper, after calcining at 400 °C for 24 h, the prepared NiO still has a specific capacitance of $130 \,\mathrm{Fg}^{-1}$. Such relatively high capacitance can be mainly attributed to the smaller mesopores (2.6 nm), for large percentage of smaller mesopores can increase the utilization of the active material. It is anticipated that such novel porous metal oxide material may have potential applications in electrode materials.

The cycle stability is another important quality required for practical applications and demonstrated by continuous charge-discharge measurements over 1000 cycles. Fig. 6b shows the variation of specific capacitance over 1000 cycles of the mesoporous NiO with bimodal size distribution at a current density of 2.0 Ag⁻¹ between 0.0 and 0.5 V (vs. SCE). No decrease in specific capacitance after the initial 1000 cycles is observed. In Xu's work [35], 3.2% decrease in capacitance was observed after only 500 cycles and in Prasad's report [29], a decrease of 8% of the $C_{\rm s}$ was obtained after 1000 cycles. Compared with them, our mesoporous nickel oxide with superior cyclability can behave reversibly as an excellent capacitor material for a large number of charge-discharge cycles. During the charging/discharging process, the oxidized (NiOOH) and reduced (NiO) forms do not have the same volumetric density. This change in the active masses volume (active mass breathing) may cause a defect in electronic percolation and loss of active mass [36]. Excellent cyclability of the prepared NiO with bimodal size distribution is probably related to the stable mesoporous structure, for the pores can act as buffer for the volume change in the whole process.

4. Conclusions

In conclusion, we introduced a coordination-polymer synthesis method using $Ni_3(btc)_2 \cdot 12H_2O$ as a precursor to fabricate nanoporous NiO with bimodal size distribution(2.6 and 30.3 nm). The easily prepared $Ni_3(btc)_2 \cdot 12H_2O$ crystal was synthesized

through a simple hydrothermal process and well-crystallized NiO with a multiple mesoporous structure was obtained after calcining the precursor at 400 °C for 24 h. Through the pore distribution analysis, we can conclude that the smaller pores generate due to the growth mechanism of metal–organic complex and the bigger ones are realized through decomposition of organic ligands and H₂O. Electrochemical tests demonstrate that the prepared NiO with bimodal size distribution has an excellent rate capability and offers no degradation of capacitance after 1000 cycles. Furthermore, the method for preparing multiple porous NiO described here was both facile and effective, and it can be used for synthesizing other multiple porous metal oxide electrode materials.

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