

Synthesis and characterization of mesoporous nickel oxide for electrochemical capacitor

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Abstract A mesoporous electrochemical active material NiO with face center cubic structure has been synthesized using supramolecular as template and urea as hydrolysis-controlling agent. The synthesized product was characterized physically by thermogravimetric analysis, X-ray diffraction, transmission electron microscopy, and Brunauer–Emmett–Teller-specific surface area measurement. Electrochemical characterization was performed using cyclic voltammetry and chronopotentiometry in 6 mol/l KOH aqueous solution electrolyte. A specific capacitance of approximately 327 F/g was obtained by annealing the sample at 350 °C. To get a better understanding of the effect of supramolecular template on improving the structure property and electrochemical performance, a compared experiment was also carried out in this work.

Keywords Mesoporous · NiO · Electrochemical capacitors (ECs)

Introduction

Interest in electrochemical capacitors (ECs) for high-power devices in energy storage systems has risen in recent years [1, 2]. Moreover, the energy density of the relatively new pseudocapacitor devices that are based on faradaic processes has been reported many times, which is greater than that of the traditional double-layer capacitors (its capacitance is typically less than 20 $\mu\text{F}/\text{cm}^2$) [3, 4]. Noble metal oxides, such as RuO_2 and IrO_2 , have been identified as possibly the best electrode materials for pseudocapacitors. For example,

hydrated ruthenium oxide exhibits remarkably high specific capacitance values ranging from 720 to 760 F/g (for single-electrode system) as depicted in literature [5]. However, the high cost of this and other noble metal materials has delayed its commercial application [6]. As a result, an intensive search for cheaper candidates with good capacitive characteristics has been underway in recent years.

Transition metal oxides are promising candidates applicable in electrochemical capacitors. For example, porous NiO_x [7], CoO_x [8], and MnO_2 [9, 10] have been considered as possible electrode materials for ECs. Among these candidates, nickel oxide has received a considerable amount of attention over the last few years due to its large surface area and high pseudocapacitive behavior. It is applied in diverse fields [11–13], such as catalyst, battery cathodes, fuel cell electrodes, electrochromic films, magnetic materials, and gas sensors. Up to now, many routes have been developed for the preparation of nickel oxide as electrochemical capacitors' electrode materials. For example, Liu and Anderson [14] developed an ultracapacitor device based on a sol–gel-derived porous metal oxide NiO_x/Ni film. The specific capacitance of this device, ranging from 200 to 256 F/g (for single-electrode system), is considerably higher than that obtained from carbon-based capacitors. Srivasan and Weidner [15] also developed an electrochemical route for making nickel oxide capacitors with relatively large specific capacitances of about 240 F/g (from a single electrode). However, these prepared NiO films were all very thin; when the amount of active material increases, the electrode materials will inevitably encounter a serious fall in capacitance.

The more recent discovery of M41S materials by the supramolecular templating mechanism ushered in a new era in synthesis chemistry [16, 17]. These mesoporous materials exhibit high surface area, narrow pore size

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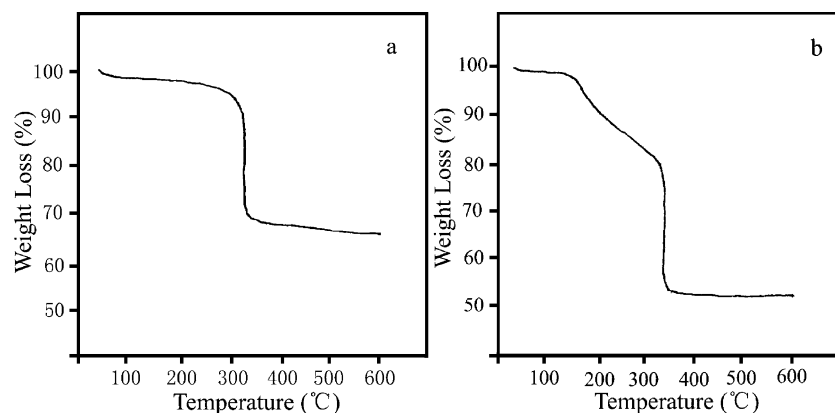


Fig. 1 TG analysis of the samples. **a** Ni(OH)₂ obtained without using supramolecular template, **b** Ni(OH)₂ obtained using supramolecular template

distribution, large pore volume, and high thermal stability, which allow it to be applied as catalysts, molecular sieves, host materials, and battery materials. Therefore, in this work, mesoporous nickel oxide with high surface area was prepared using supramolecular as template and urea as hydrolysis-controlling agent. The unique mesopore system and large surface area of the NiO samples are expected to favor ion transfer in the pore system and increase the NiO–electrolyte interfacial area, respectively. In addition, the unique mesoporous structure of the NiO is expected to help maintain its high specific capacitance when using a large amount of NiO to fabricate an electrode.

Experimental

Materials preparation All chemicals were of analytical grade and were used without further purification. Nickel oxide was prepared using supramolecular as template and urea as hydrolysis-controlling agent. The detailed process was as follows: Polyacrylamide (PAM) and polyvinyl alcohol (PVA) were dissolved in distilled water; a certain amount of urea and nickel nitrate were added subsequently with magnetic stirring. The obtained solution was heated and kept at 80 °C for 2 h. The resulting mixture was cooled to room temperature quickly to prevent further hydrolysis of urea. After centrifugation, the solid was washed with ethanol and distilled water several times and were then dried at room temperature in air. The final step was to calcine the prepared precursor at 350 °C for 2 h. In addition, nickel oxide was also prepared following the same procedure without using supramolecular as template for comparison.

Characterization of structure and morphology The structures of the products were characterized by X-ray diffraction (XRD). XRD data were collected using a Rigaku D/MAX 2400 diffractometer with Cu K α radiation

($\lambda = 0.15418$ nm). Transmission electron microscopy (Hitachi 600, Japan) was used to observe the morphology of the product. Nitrogen adsorption and desorption experiments were carried out at 77.3 K by means of a Nova 1200 (Quantachrome) analyzer. The surface area was calculated using the Brunauer–Emmett–Teller (BET) equation. Pore size distributions were calculated by the Barrett–Joyner–Halenda method using the desorption branch of the isotherm.

Electrode preparation and electrochemical characterization The working electrodes of electrochemical capacitors were formed by mixing the prepared powders with 25 wt % acetylene black and 5 wt % polytetrafluorene-ethylene binder. A small amount of ethanol was then added to those mixtures to make them more homogeneous. The mixtures were pressed onto nickel foam current collectors (1.0×1.0 cm²) to fabricate electrodes. All electrochemical measurements were done in a three-electrode experimental setup. Platinum foil with the same area as the working electrode and Hg/HgO electrode were used as the counter and reference electrodes, respectively. All the measurements were carried out in 6 mol/l KOH electrolyte. Cyclic voltammetry and chronopotentiometry were performed using a CHI760 electrochemical workstation (Chenhua, Shanghai, China).

Results and discussion

Thermogravimetric analysis was conducted for as-prepared samples in air atmosphere to examine the conversion process during calcination. Figure 1a displays the thermogravimetric (TG) curve for the Ni(OH)₂ obtained without using supramolecular as template; it shows a distinct weight loss of 29.3 % between 250 and 350 °C corresponding to the removal of chemically bound water in Ni(OH)₂ and the formation of NiO phase. Figure 1b shows the TG curve for the Ni(OH)₂ prepared using supramolecular as template, which indicates obvious weight

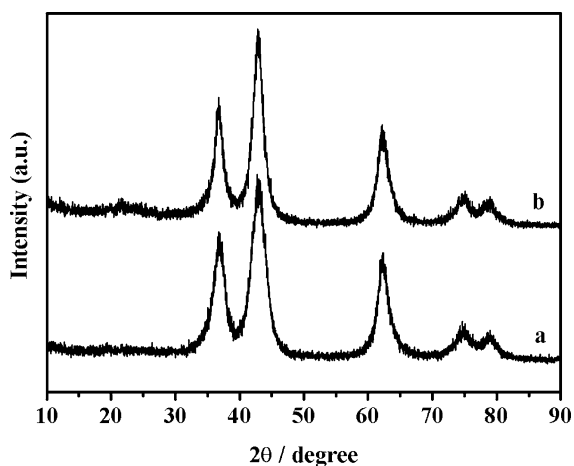


Fig. 2 XRD patterns of the samples calcined at 350 °C for 2 h. **a** NiO obtained without using supramolecular template, **b** NiO obtained using supramolecular template

loss occurs in two temperature regions: (1)150–300 °C and (2) 300–350 °C. The first clear weight loss occurs in the

150–300 °C region which is ascribed to the loss of occluded water in Ni(OH)₂ and the decomposition of partial polymer. In the 300–350 °C region, there is another noticeable weight loss in the TG curve. It is believed that the reaction of Ni(OH)₂→NiO + H₂O occurs in this region. With the increase of temperature, the TG curves become flat, which indicates that no phase transformation occurs, and further heating could only make the structure of the products more crystalline.

The TG curve of the Ni(OH) obtained using supramolecular as template is different from that of the Ni(OH) without using supramolecular as template. As can be seen from Fig. 1, the weight loss of the Ni(OH) formed using supramolecular as template is bigger than that of the Ni(OH) obtained without using supramolecular as template. This indicates that the precursor of sample prepared using supramolecular as template has certain amounts of supramolecular, which is very effective for forming mesoporous structure of materials.

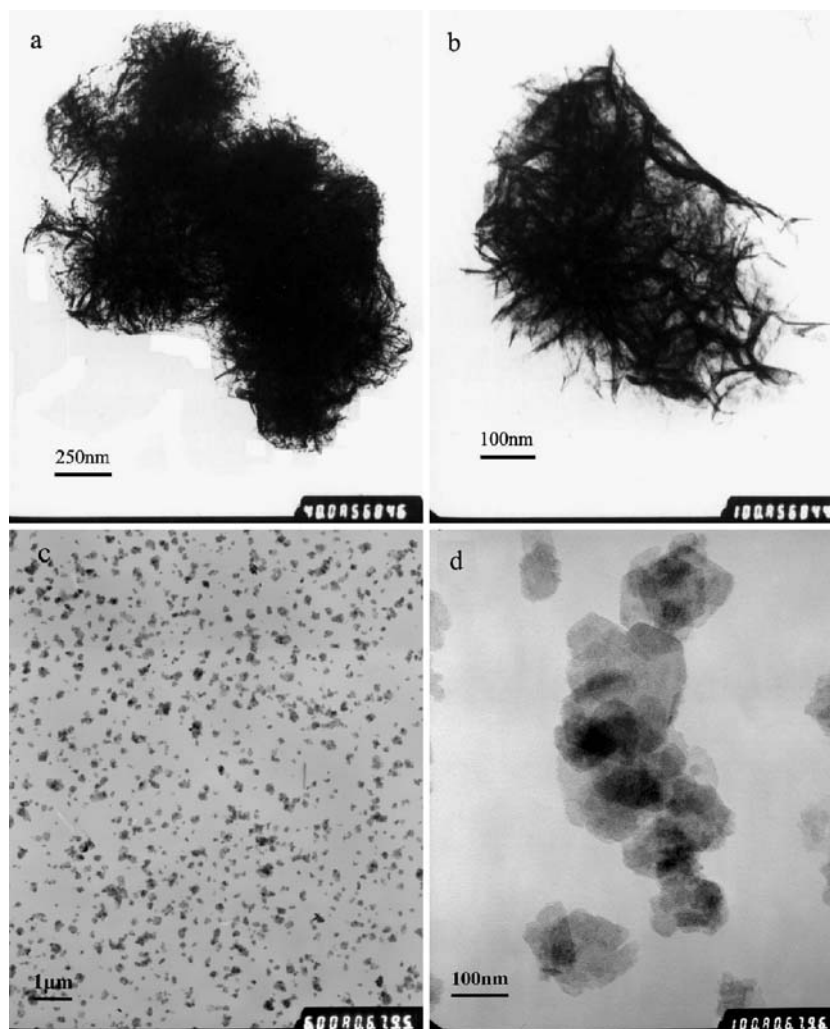


Fig. 3 TEM of NiO obtained by different preparation conditions. **a, b** NiO obtained without using supramolecular template; **c, d** NiO obtained using supramolecular template

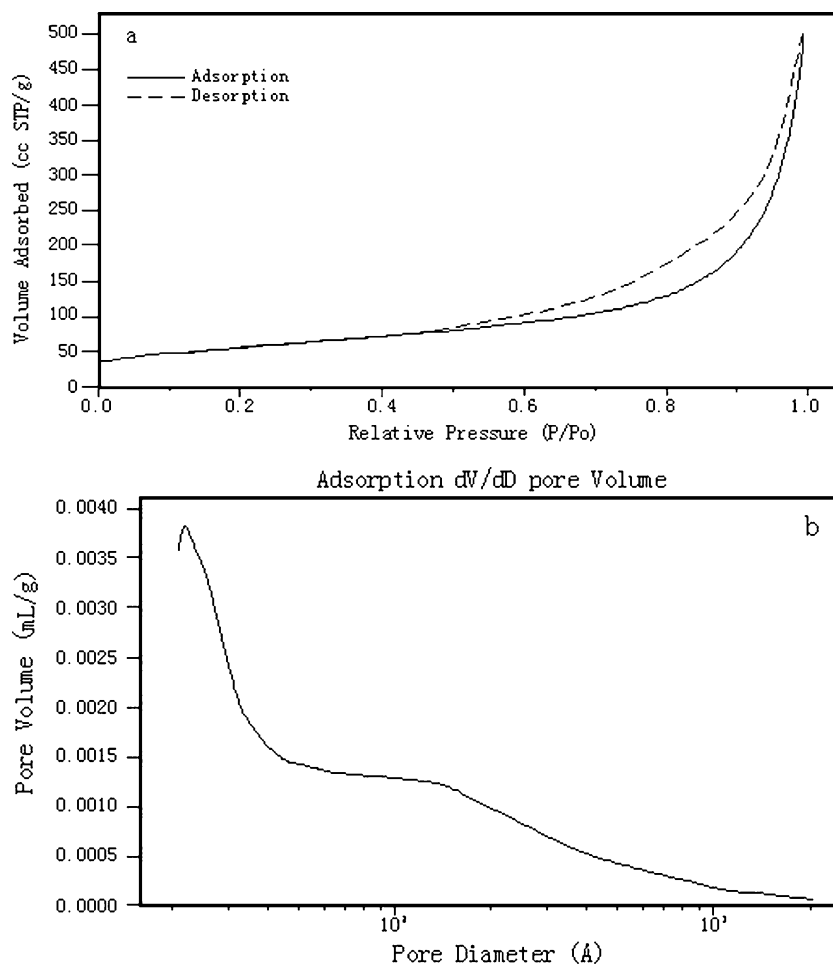


Fig. 4 N₂ gas adsorption–desorption isotherm (a) and pore size distribution (b) of NiO obtained using supramolecular template. Dashed line, desorption; straight line, adsorption

The result of TG analysis indicates that these samples have converted to NiO phase completely after being calcined at 350 °C for 2 h. As reported in literature [11, 18], with the further increase of annealing temperature, the specific surface area and specific capacitance of the samples will decline. With these considerations, further studies were focused on the NiO obtained by heating at 350 °C in this work.

Figure 2 illustrates the XRD patterns of the samples obtained under different preparation conditions. After heating at 350 °C for 2 h, all the prepared Ni(OH)₂ samples were converted to NiO with a crystalline structure, and all these diffraction peak positions and their relative intensities are in good accordance with the standard spectrum (JCPDS, card no 04-0835), indicating that the NiO are crystalline with face center cubic structure. This result is in agreement with that of the TG analysis.

The morphology of the samples prepared under different conditions was observed by transmission electron microscope. Figure 3a presents the morphology of the NiO powders obtained without using supramolecular as tem-

plate; it shows urchin-like morphology. Figure 3b represents the TEM image of the sample in high magnification to reveal the actual feature of the urchin-like morphology, indicating that the urchin-like microstructure of the sample was consist of NiO thin ribands. Figure 3c,d display the morphology of NiO obtained using supramolecular as template. As can be seen from Fig. 3c, the NiO powders disperse very well. Figure 3d, a higher magnification image of this sample, suggests that these particles are actually made up of small lamellar nanoparticles that agglomerate with each other to form the clusters.

Comparing the morphology of NiO obtained under different conditions, great distinctions could be clearly seen, which indicates that the supramolecular template (polyacrylamide and polyvinyl alcohol) have played an important role in controlling the morphology of samples.

BET surface areas, calculated from adsorption isotherms, show that the surface area of the NiO obtained using supramolecular template is 203 m²/g, which increases significantly compared with that of the NiO prepared without using supramolecular template (98 m²/g).

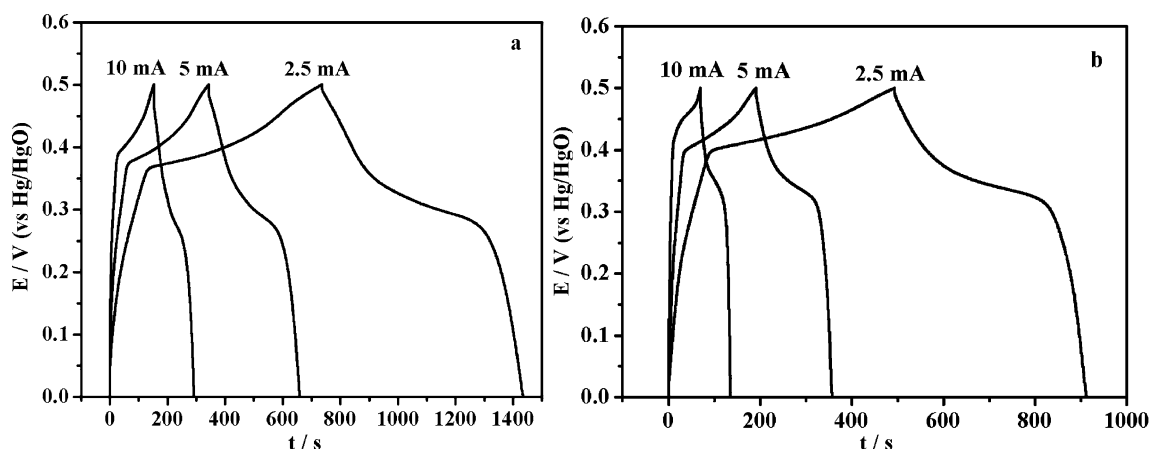


Fig. 5 Charge/discharge curves of NiO formed at different preparation conditions at different current rates. **a** NiO obtained using supramolecular template. **b** NiO obtained without using supramolecular template

Figure 4a is the adsorption/desorption isotherm of the samples obtained using supramolecular template. It shows a strong hysteresis loop, which is an adsorption–desorption characteristic of the porous materials. Figure 4b displays pore size distribution of the sample. This means that polyacrylamide and polyvinyl alcohol are very helpful to control and maintain the mesopore structure. In the process of Ni(OH)₂ precipitation, the supramolecular provides a fixed template, and the hydrolysis rate of nickel nitrate is well controlled by urea hydrolysis at 80 °C, which contributes to the stable skeleton of the mesoporous nickel hydroxide. After calcination at 350 °C for 2 h, some supramolecular template residues and hydroxyl groups are removed from the pore system, but the pore skeleton of the sample is well sustained.

To investigate the effect caused by different preparation conditions on the capacitance of the samples, the performance of the active materials was examined by chronopotentiometry. Figure 5 shows the charging and discharging behavior of the NiO powders synthesized under different

conditions at various current rates (2.5, 5, and 10 mA). The specific capacitance can be obtained from Eq. 1

$$C = \frac{I \Delta t}{m \Delta V} \quad (1)$$

In this equation, I is the discharge current, m is the mass of the composite, ΔV is the potential drop during discharge, Δt is the total discharge time, and C is the specific capacitance. In this way, the specific capacity of the NiO obtained using supramolecular template at 2.5, 5, and 10 mA were 358, 327, and 292 F/g, whereas that of the specimen without using supramolecular template were 208, 169, and 124 F/g, respectively. So, the NiO obtained using supramolecular template exhibited higher specific capacitance than that of the NiO obtained without using supramolecular template.

Figure 5 also shows that the NiO powders formed using supramolecular template exhibit better rate capability. Its discharge capacity at 5 mA is 91.3 % of that discharged at 2.5 mA, whereas the discharge capacity of the specimen without using supramolecular template was only 81.3 %. This is mainly due to the mesopore structure and large surface area of the NiO sample obtained using supramolecular template which is useful to transfer ion in the pore system and to increase the NiO–electrolyte interfacial area. Because a high rate discharge capability is one of the most important electrochemical performances in the application of electrode and battery [19], the excellent rate capability of the sample makes it attractive particularly for a practical application.

Figure 6 shows the C – V curves of the NiO obtained using supramolecular template. The typical result was measured from 0 to 0.6 V at various voltage scan rates in 6 mol/l KOH. As can be seen from Fig. 6, the characteristic of the capacitance is very different from that of the electric double-layer capacitance, in which the C – V curve is close to the ideal rectangular shape. The present results imply that

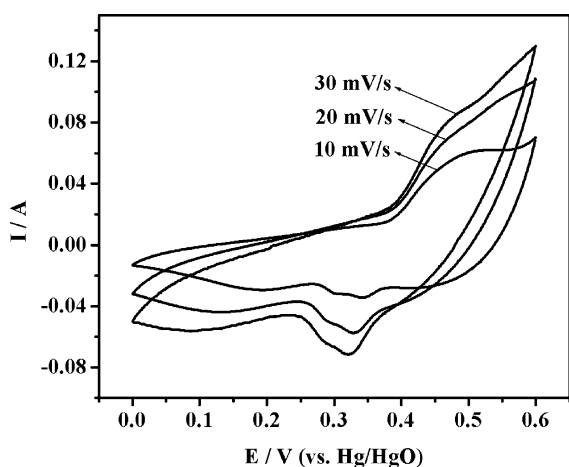


Fig. 6 C – V curves of NiO obtained using supramolecular template

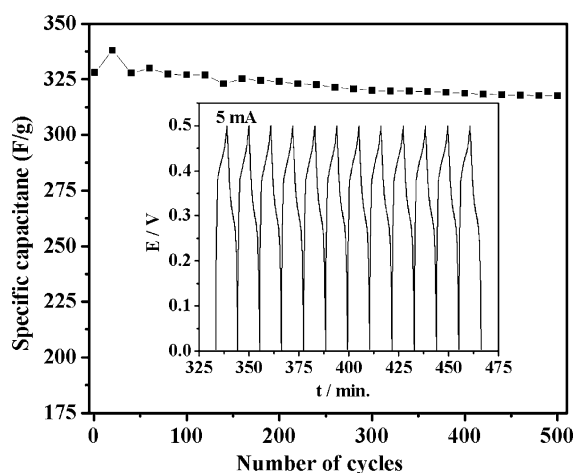
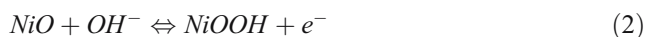


Fig. 7 Cycle life of the NiO electrode at 5 mA in 6 mol/l KOH electrolyte. The inset is charge/discharge curves of the NiO electrode (the NiO obtained using supramolecular template)

the measured capacitance is mainly associated with the redox mechanism. It should be noted that with the sweep rate increased, the shape of the $C-V$ changed, and the capacitance, inevitably, decreased, which is in agreement with the result of chronopotentiometry measurement.

For NiO electrode material, it is well accepted that the surface faradaic reactions will proceed according to the following reaction [7, 12]:

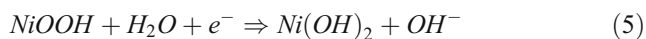
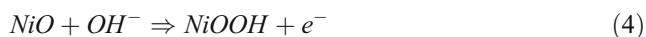


But the redox of the electrode in Fig. 6 is similar to Ni(OH)₂/NiOOH redox couple; this might be explained as depicted in literature [20].

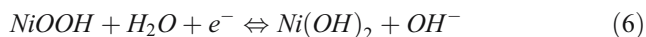
When the Ni(OH)₂ sample is only calcined 2 h at 350 °C, it can convert to NiO, but its crystal degree is not well. For this kind of NiO electrode material, the surface faradaic reactions might be expressed as the following reaction:



or



The reversible pseudocapacitance redox reaction might be expressed as:



In this kind of electrode materials, a part of NiO might store charge according to reaction 1, but another part of the

NiO would transform to Ni(OH)₂ as reaction 2 or 3. The Ni(OH)₂ might also store charge on the oxide surface.

As long cycle life is very important to the electrochemical capacitor, the cycle charge/discharge test was employed to examine the service life of the NiO electrode (the NiO was obtained using supramolecular template). Figure 7 shows approximately 3.2 % loss of capacitance after 500 cycles, implying that the very stable mesoporous NiO is an excellent electrode material for electrochemical capacitor.

In conclusion, an excellent mesoporous NiO with high specific surface area has been synthesized successfully. The mesoporous NiO obtained using supramolecular template exhibited a maximum specific capacitance of 327 F/g and showed better rate capacity and longer cycle life, so it is suitable to be used as electrode material for electrochemical capacitors.

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