Facile approach to prepare loose-packed NiO nano-flakes materials for supercapacitors†

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The nickel oxide nano-flakes materials prepared by a facile approach maintain high power density at high rates of discharge and have excellent cycle life, suggesting their potential application in supercapacitors.

Supercapacitors, also called electrochemical capacitors, are unique energy-storage devices exhibiting 20–200 times greater capacitance than conventional capacitors.[1] Growing demands in electric vehicles, and other devices that require electrical energy at high power levels in relatively short pulses have prompted considerable interest in supercapacitors.[2] Moreover, the energy density of the relatively new pseudocapacitor devices that are based on faradaic processes has been reported many times, because it has been recognized that the energy density based on pseudo-faradaic processes is many times greater than that of the traditional double-layer capacitors.[3]

In particular, supercapacitors based on hydrous ruthenium oxides exhibit much higher specific capacitance than conventional carbon materials and better electrochemical stability than electronically conducting polymer materials. However, the high cost of $RuO_2 \cdot xH_2O$ makes this material unsuitable for commercial applications.[4b,c] Hence, much effort has been made to at search for alternative inexpensive electrode materials with good capacitive characteristics, such as NiO,[4d] CoO_x,[4e] MnO_2,[4f] $Ni(OH)_2$,[4g] $Co(OH)_2$,[4a] *etc*. Among the transitional base metal oxides, nickel oxides have been extensively studied for supercapacitors due to its large surface area and high pseudo-capacitive behavior.[5]

There are several methods used to prepare nickel oxides such as chemical precipitation,[6] electrodeposition[7] and sol-gel technique.[8] Among these synthetic methods, chemical precipitation technique has one advantage over the others: it's a facile method. The sol–gel dip-coating method and cathodic precipitation method will inevitably encounter a serious fall in capacitance during scaling-up,[9] the specific capacitance of devices ranging from 50 to 696 F g^{-1} (for single-electrode system). Therefore, a lot of research work has been done to improve the electrochemical performance of nickel oxides.

In this communication, we report a facile chemical precipitation method to prepare nickel oxides materials. The studies show that the as-prepared NiO material has a low crystallinity and nano-flake structure. We demonstrate that the unique microstructure can accommodate the electroactive species in solid bulk electrode materials. The maximum specific capacitance of 942 F g^{-1} is the highest report of NiO for supercapacitors, which shows better rate capability and great potential as electrode materials for supercapacitors.

The preparation procedure of the NiO materials is described as follows. All of the chemicals were of analytical grade and used without further purification, and the nickel chloride hydrate used was from Strem Chemicals. In the first step, nickel chloride hydrate was dissolved in distilled water (Ni concentration = 1.0 M) in a glass beaker, using a magnetic stir bar. The nickel chloride hydrate solution was slowly adjusted to pH 9 by dropwise addition of 5 wt% aqueous NH_3 for 2 h at a temperature of ~ 10 °C. The resulting suspension was stirred at this temperature for an additional 3 h. Then the solid was filtered off, washed with a copious amount of distilled water, and heated at different temperatures in air for 8 h, *viz.*, 250, 300, 350 °C.

The working electrodes were prepared according to the method reported in the literature.[4f] 80 wt% of NiO powder was mixed with 7.5 wt% of acetylene black (>99.9%) and 7.5 wt% of conducting graphite in an agate mortar until a homogeneous black powder was obtained. To this mixture, 5 wt% of poly(tetrafluoroethylene) was added with a few drops of ethanol. After briefly allowing the solvent to evaporate, the resulting paste was pressed at 10 MPa to a nickel gauze with a nickel wire for an electric connection. The electrode assembly was dried for 16 h at 80 °C in air. Each electrode contained about 8 mg of electroactive material and had a geometric surface area of about 1 cm^2. Electrochemical measurements were carried out in 2 M aqueous KOH in a half-cell setup configuration at room temperature. A platinum gauze electrode (1×1 cm^2) and a saturated calomel electrode served as the counter electrode and the reference electrode, respectively. According to literature,[10] one plausible reaction can occur as a quasi-reversible redox processes during the potential sweep of the NiO electrode:

$$NiO + OH^- \leftrightarrow NiOOH + e^- \qquad (1)$$

The XRD patterns of the $Ni(OH)_2$ precursor and nickel oxide produced by heating the $Ni(OH)_2$ at different temperatures for 6 h in air are shown in Fig. 1. The precursor corresponds to a layered α-$Ni(OH)_2$ structure of low crystallinity. Upon heating at 250 °C for 6 h, almost all of the $Ni(OH)_2$ precursor were converted to NiO of low crystallinity. The wide-angle XRD patterns exhibit the characteristic peaks of rocksalt NiO at $2\theta = 37$, 43 and 63°, which first appeared in the resultant materials at 250 °C, and all these diffraction peak positions

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† Electronic supplementary information (ESI) available: Calculation method of measured specific capacitance, the schematic formation mechanism of the as-prepared $Ni(OH)_2$ precursor, TG and electrochemical impedance analysis. See DOI: 10.1039/b800264a

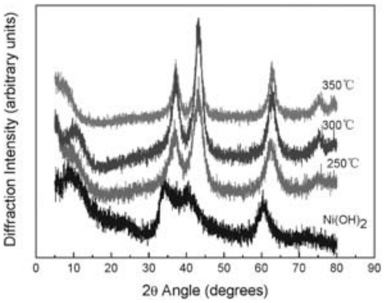

Fig. 1 XRD patterns of the $Ni(OH)_2$ precursor and nickel oxide materials produced from this.

and their relative intensities are in good accordance with the standard spectrum (PDF, card no 44-1159).[5,9]

SEM and TEM measurement were performed on the sample obtained at a temperature of 250 °C. Two morphologies (a: particles and b: nano-flakes) can be seen in Fig. 2(a) and (b). It is noteworthy that the network-like structure (which consists of interconnected nano-flakes) shows anisotropic morphology characteristics and the formation of a loosely packed microstructure in the nanometer scale. The unique structure plays a basic role in the morphology requirement for electrochemical accessibility of electrolyte OH^- to the NiO active material and a fast diffusion rate within the redox phase. It is believed that the unique structure provides an important morphological foundation for the extraordinary high specific capacitances.

To understand the reason why this particular network structure of NiO phase can be formed during the synthesis process, a formation mechanism from aggregation growth to surface growth in the solution can be summarized as follows. The initial precipitations provide numerous $Ni(OH)_2$ nucleation centers. Because of the anisotropy of α-$Ni(OH)_2$ crystals, the growing point of each crystal is located at certain directions, so nano-flakes will be formed. These α-$Ni(OH)_2$ nano-flakes contain a lot of interbedded water, which is distributed at certain directions. When the sizes of these flakes become larger, their tendency to aggregate is increased. As a result, microspheres of nano-flake aggregates will be formed due to the strong hydrogen bonding of H_2O. A the reaction proceeds, new $Ni(OH)_2$ nano-flakes will grow up around the nucleation centers at the surface of the microsphere. The surface growth leads to the continuous increase in size and density of the microsphere to form a network structure.[11] When $Ni(OH)_2$ is transformed to NiO at the subsequent annealing process, however, some of the nano-flakes grow to a stacking structure because H_2O will be lost as the annealing temperature increases. As shown in Fig. 2 both particle and nano-flake phases appeared in the NiO samples.

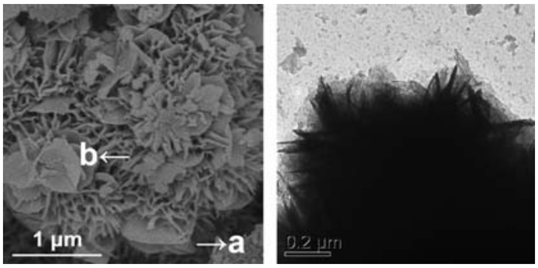

Fig. 2 SEM and TEM image of as-prepared NiO materials.

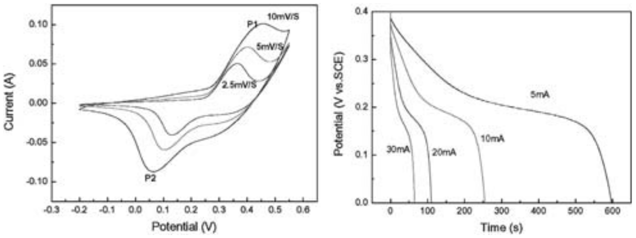

Fig. 3 Electrochemical properties of NiO in 2 M KOH solution: (a) CV curves at different scan rates; (b) discharging curves at different discharging currents

CV and chronopotentiometry measurements have been used to evaluate the electrochemical properties and quantify the specific capacitance of the as-prepared NiO electrodes. Fig. 3(a) shows the CV curves of the NiO obtained at 250 °C. The shapes of the CV reveal that the capacitance characteristic is very distinct from that of electric double-layer capacitance in which the shape is normally close to an ideal rectangular shape. For this electrochemical system, a couple of redox peaks were observed within the potential range −0.2 to 0.55 V, the anodic peak P_1 is due to the oxidation of NiO to NiOOH and the cathodic peak P_2 is for the reverse process.[10] This indicates that the capacity mainly results from the pseudo-capacitance, which is based on a redox mechanism. It should be noted that with the sweep rate increased, the shape of the CV changed, the anodic peak potential and cathodic peak potential shift in more anodic and cathodic directions, respectively, and the capacitance, inevitably, decreased, which is in agreement with the result of chronopotentiometry measurement.

In practice, the ability to discharge at high rate is crucial in capacitors. The relationship between specific capacitance and current density was therefore investigated and Fig. 3(b) shows the results obtained for the NiO (calcined at 250 °C) electrode in the potential range of 0–0.4 V in 2 M KOH at various current rates (5, 10, 20 and 30 mA). The corresponding specific capacitance was calculated using the formula provided in ESI.† In this way, the specific capacitance of the NiO materials at 5, 10, 20 and 30 mA were 942, 804, 696 and 613 F g^{-1}. This result indicates that the nano-flake structure increases the specific capacitance of NiO greatly. The shape of the discharge curves does not show the characteristics of a pure double-layer capacitor, but mainly pseudo-capacitance, which is in agreement with the result of the CV curves.[12] Fig. 3(b) also shows that the NiO sample obtained at 250 °C exhibits the best rate capability. As the discharge current increases, a large voltage drop is produced, and finally the capacitance decreases. This phenomenon may be explained by referring to the OH^- ion diffusion processes during the charging/discharging for the electrode. At high sweep rates with high current density significant OH^- ions are required to intercalate swiftly at the interface of electrode/electrolyte, however, the relatively low concentration of OH^- ions can not meet this demand and the processes would be controlled by the ion diffusion.[13] Despite this, the discharge capacitance at 10 mA is 85.4% of that discharged at 5 mA, so the excellent rate capability of the sample makes it attractive particularly for a practical application.

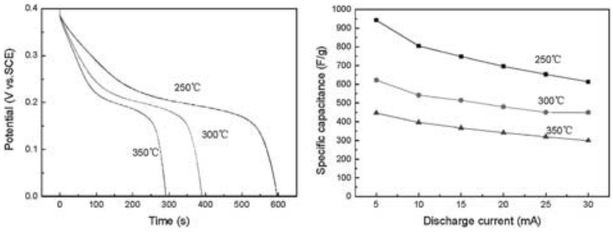

Fig. 4 Electrochemical properties of NiO samples heated at different temperatures in 2 M KOH solution: (a) discharging curves at the discharging current of 5 mA and (b) specific capacitance as a function of discharge currents.

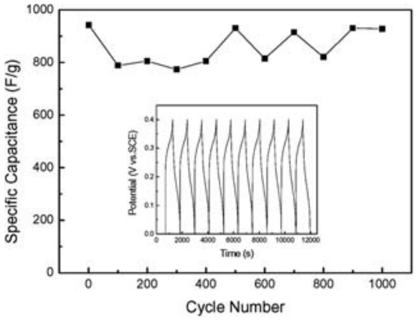

Fig. 5 Cycle life of as-prepared NiO electrode at a discharge current of 5 mA in 2 M KOH electrolyte. The inset is the charge/discharge curves of the NiO electrode.

To evaluate the electrochemical capacitance of the NiO samples as a function of the heating temperatures, chronopotentiometry measurements were conducted on NiO samples with different annealing temperature. As shown in Fig. 4(a) and (b), with increasing annealing temperature, the decline of the specific capacitance is similar to that found for increasing discharge currents. Once the oxide phase is formed, further heat-treatment at higher temperature may cause the increase in crystal size, and accordingly a decrease in specific surface area, and also possibly its reactivity for surface chemical processes, thereby leading to a decreased capacitance.[4d] Just as in the case of RuO_2, the NiO amorphous phase exhibited far greater specific capacitance than the crystalline counterpart.[14]

As long cycle life is very important in supercapacitors, cycle charge/discharge testing was employed to examine the service life of the NiO electrode (the NiO was obtained at an annealing temperature of 250 °C) employing a discharging current of 5 mA in 2 M KOH electrolyte. Fig. 5 shows approximately 1.5% loss of capacitance after 1000 cycles, and the lowest capacitance between the 1000 cycles also remains 82% of the maximum capacitance. This demonstrates that, within the voltage window 0.0–0.4 V, the charge and discharge processes do not seem to induce significant structural or micro-structural changes of the nano-flakes NiO electrode materials as expected for pseudo-capacitance reactions. The long-term stability implies that the flake-like NiO is an excellent electrode material for supercapacitors.

In summary, we have synthesized loose-packed flake-like NiO materials using a facile chemical precipitation method, and applied its microstructure for supercapacitors. XRD, SEM and TEM studies show that the as-prepared NiO material has a low crystallinity and a nano-flake structure. The unique microstructure can accommodate the electroactive species in the solid bulk electrode materials. The specific capacitances of the NiO material at 5, 10, 20 and 30 mA were 942, 804, 696 and 613 F g^{-1}, which shows better rate capability and great potential for electrode materials for supercapacitors. The maximum specific capacitance is the highest reported of NiO for supercapacitors. Even though we do not fully understand the fundamental structure of the NiO materials, the strategy reported here should be viable to extend to other transition metal oxides systems.

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Notes and references

1 (*a*) B. E. Conway, *Electrochemical Supercapacitors*, Kluwer Academic/Plenum Press, New York, 1999; (*b*) M. Winter and R. J. Brodd, *Chem. Rev.*, 2004, **104**, 4245; (*c*) K. H. An, W. S. Kim, Y. S. Park, Y. C. Choi, S. M. Lee, D. C. Chung, D. J. Bae, S. C. Lim and Y. H. Lee, *Adv. Mater.*, 2001, **13**, 497.
2 (*a*) L. Z. Fan, Y. S. Hu, J. Maier, P. Adelhelm, B. Smarsly and M. Antonietti, *Adv. Funct. Mater.*, 2007, **17**, 3083; (*b*) C. M. Yang, Y. J. Kim, M. Endo, H. Kanoh, M. Yudasaka, S. Iijima and K. Kaneko, *J. Am. Chem. Soc.*, 2007, **129**, 20.
3 (*a*) S. C. Pang, M. A. Anderson and T. W. Chapman, *J. Electrochem. Soc.*, 2000, **147**, 444; (*b*) K. R. Prasad, K. Koga and N. Miura, *Chem. Mater.*, 2004, **16**, 1845; (*c*) B. V. Tilak and C. P. Chen, *J. Electrochem. Soc.*, 1996, **143**, 3791; (*d*) C. Lin, J. A. Ritter and B. N. Popov, *J. Electrochem. Soc.*, 1998, **145**, 4097; (*e*) K. H. An, W. S. Kim, Y. S. Park, J. M. Moon, D. J. Bae, S. C. Lim, Y. S. Lee and Y. H. Lee, *Adv. Funct. Mater.*, 2001, **11**, 387.
4 (*a*) L. Cao, F. Xu, Y. Y. Liang and H. L. Li, *Adv. Mater.*, 2004, **16**, 1853; (*b*) Y. F. Ke, D. S. Tsai and Y. S. Huang, *J. Mater. Chem.*, 2005, **15**, 2122; (*c*) T. Cottineau, M. Toupin, T. Delahaye, T. Brousse and D. Belanger, *Appl. Phys. A: Mater. Sci. Process.*, 2006, **82**, 599; (*d*) V. Srinivasan and J. W. Weidner, *J. Electrochem. Soc.*, 1997, **144**, L210; (*e*) L. Cao, M. Lu and H. L. Li, *J. Electrochem. Soc.*, 2005, **152**, A871; (*f*) M. Toupin, T. Brousse and D. Bélanger, *Chem. Mater.*, 2004, **16**, 3184; (*g*) L. Cao, L. B. Kong, Y. Y. Liang and H. L. Li, *Chem. Commun.*, 2004, 1646.
5 D. B. Wang, C. X. Song, Z. S. Hu and X. Fu, *J. Phys. Chem. B*, 2005, **109**, 1125.
6 Q. S. Song, Y. Y. Li and S. L. I. Chen, *J. Appl. Electrochem.*, 2005, **35**, 157.
7 V. Srinivasan and J. W. Weidner, *J. Electrochem. Soc.*, 1997, **144**, L210.
8 (*a*) K. C. Liu and M. A. Anderson, *J. Electrochem. Soc.*, 1996, **143**, 124; (*b*) J. Cheng, G. P. Cao and Y. S. Yang, *J. Power Sources*, 2006, **159**, 734.
9 W. Xing, F. Li, Z. F. Yan and G. Q. Lu, *J. Power Sources*, 2004, **134**, 324.
10 Y. G. Wang and Y. Y. Xia, *Electrochim. Acta*, 2006, **51**, 3223.
11 R. N. Wang, Q. Y. Li, Z. H. Wang, Q. Wei and Z. R. Nie, *Chem. J. Chin. Univ.*, 2008, **29**, 18.
12 D. D. Zhao, S. J. Bao, W. J. Zhou and H. L. Li, *Electrochem. Commun.*, 2007, **9**, 869.
13 R. Kötz and M. Carlen, *Electrochim. Acta*, 2000, **45**, 2483.
14 J. P. Zheng, P. J. Cygan and T. R. Jow, *J. Electrochem. Soc.*, 1995, **142**, 2699.