

The Nickel Oxide/CNT Composites with High Capacitance for Supercapacitor

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A simple hydrothermal synthesis method is adopted to prepare nickel oxide/carbon nanotube (NiO/CNT) composites. X-ray diffraction, differential scanning calorimetry/thermogravimetric analysis, transmission electron microscopy, scanning electron microscopy, and N₂-adsorption/desorption techniques are employed for morphology and structure characterizations. The different morphologies of NiO are obtained, which change from a two-dimensional flake to a zero-dimensional mesoporous sphere, dispersing on the surface of CNTs by changing the sodium dodecyl sulfate's fraction in the reacting system. The electrochemical performance of NiO/CNT composites is largely affected by the morphology and distribution of the NiO phase. The zero-dimensional mesoporous sphere NiO shows the largest specific capacitance of 1329 F g⁻¹ as well as a good cycle life during 1000 cycles in a 1 M KOH electrolyte at a very high current density of 84 A g⁻¹ by chonopotentiometry measurement. © 2010 The Electrochemical Society. [DOI: 10.1149/1.3425624] All rights reserved.

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Due to the fossil fuel energy depletion and global warming issues, we need to explore and exploit the new energy such as solar radiation, wind, and waves,¹ which are variable in time and diffuse in space. These energy sources require more advanced energy storage and management devices. Supercapacitors offering transient but extremely high powers are probably the most important nextgeneration energy storage device.²

To boost the specific capacitance of supercapacitors, the size and morphology of the electrode materials need to be designed to provide a large amount of superficial electroactive species to participate in faradaic redox reactions. In addition, suitable mesopore sizes of the porous electrode materials are critical to ease the mass transfer of electrolytes via the pores for fast redox reactions and double-layer charging/discharging.³⁻⁶

As to the electrode material, electroactive materials possessing multiple oxidation states that enable rich redox reactions for pseudocapacitance generation are desirable for supercapacitors. Transition-metal oxides are a class of materials that have drawn extensive and intensive research attention in recent years. Among them, RuO₂ is the most prominent one with a specific capacitance as high as 1580 F g^{-1} ,⁷ probably the highest ever reported, but its high cost limits its commercial use. Nickel oxide is considered a potential electrode material for supercapacitors in alkaline electrolytes because of its high specific capacity, low cost, easy preparation, and environmental compatibility. The specific capacitance of nickel oxide electrode materials ranges from 150 to 750 F g^{-1} (from a single electrode) depending on the method of synthesis, which is still far from the theoretical value of 2584 F g⁻¹ within 0.5 V, indicating the low electrochemical utilization of nickel oxide materials. Furthermore, nickel oxide has a serious shortcoming caused by high resistance for practical application to supercapacitors. Therefore, it is crucial to enhance the conductivity and electrochemical utilization of the nickel oxide material to improve the energy density and power density. Nam et al.¹³ reported NiO/carbon nanotube (CNT) films prepared by electrochemical precipitation, and a high specific capacity of 1000 F g^{-1} was obtained, but the prepared method is very complex. Gao et al.¹⁴ used chemical deposit methods followed by thermal annealing to prepare NiO/CNT composites, and a specific capacity of 523 F g⁻¹ was acquired. However, the large rate capability of the NiO/CNT composites is not satisfactory.

Based on the above consideration, CNTs were considered for controlling the nanometer scale and the microstructure of NiO to improve the high resistance and low electrochemical utilization. To the best of our knowledge, NiO/CNT composites, which are prepared hydrothermally, have not been investigated so far. In this paper, a simple hydrothermal synthesis method is adopted to prepare NiO/CNT composites for supercapacitors. We obtain different morphologies of NiO, which change from a two-dimensional flake to a zero-dimensional mesoporous sphere, dispersing on the surface of CNTs by changing the content of the sodium dodecyl sulfate (SDS) in the reaction system.

Experimental

Synthesis of NiO/CNT composites.— The NiO/CNT composites were prepared by a simple hydrothermal precipitation followed by thermal annealing. The CNTs used were multiwalled CNTs purchased from Shenzhen Nanotechnologies Co. (China). First, 1 g CNTs, 1 g NiCl₂·6H₂O, and 40 g urea were dispersed in 50 mL deionized water by magnetic stirring for 3 h to get a transparent solution. Then, surfactant SDS was added into the solution, and a vigorous stirring was carried on until the solution was homogeneous. The mixture was put into an autoclave and kept stirring at 80°C for 4 h. Finally, the precipitant was filtered, washed, and dried in vacuum at 60°C for 12 h. The resulting NiO/CNT composites were calcined in air at 300°C for 6 h. We used three different SDS contents of 0, 10, and 20 g, and the final products were marked as NiO/CNT-0, NiO/CNT-10, and NiO/CNT-20, respectively.

Measurement of structure and morphology .- A differential scanning calorimetry (DSC)/thermogravimetric analysis (TGA) (SDT-Q600) in air was carried out in the composite first. Then, to investigate the microstructure of the NiO/CNT composites, X-ray diffraction (XRD) (Philips X'Pert Pro Super X-ray diffractometer, Cu K α radiation, an angular range of 10–90° with a step width of 0.0167°), scanning electron microscopy (SEM) (Leo-1530 SEM system), and transmission electron microscopy (TEM) (Tecnai F30, 300kv FEG) were used to characterize the crystal structure, the surface morphology, and the nanostructure of the composites. The composites' Brunauer, Emmett, and Teller (BET) specific surface areas, Barrett-Joyner-Halender (BJH) pore volume, and BJH pore-size distribution were obtained from the N2-adsorption/desorption isotherms recorded at 77 K (Tristar3000, Micromeritics). The BET specific surface areas were calculated using the BET equation. Poresize distributions were calculated by the BJH method using the desorption branch of the isotherm.

Measurement of electrochemical properties.— All electrochemical tests were achieved by a three-electrode system equipped with a working electrode (sample electrode), an active carbon counter elec-

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Figure 1. DSC-TGA curve of synthesized Ni(OH)₂ in air.

trode, and a mercury oxidation electrode (Hg/HgO). Working electrodes were prepared by mixing the active material with 20 wt % carbon (super-p) and 5 wt % poly(tetrafluoroethylene). Then, this mixture was dispersed in a small amount of isopropyl alcohol to obtain a homogeneous mixture, which was pressed on a treated nickel grid (1.2×10^7 Pa). Electrochemical performance was investigated by cyclic voltammetry (CV) using a Perkin-Elmer 273A potentiostat. An Arbin battery tester BT2000 was adopted for the charge and discharge test of the active materials. All measurements were carried out in 1 M KOH electrolyte solution.

Results and Discussion

DSC/TGA.— For the synthesized Ni(OH)₂, as shown in Fig. 1, the apparent weight loss from room temperature to 200°C corresponds to the loss of chemically adsorbed H₂O. The very sharp peak is present between 250 and 350°C on the differential TGA curve corresponding to a weight loss via the conversion of Ni(OH)₂ into NiO and H₂O. When the temperature is above 350°C, the weight decreases slowly because of the removal of a small amount of hydroxyl-group residue during the development of the NiO phase.¹⁵ For the Ni(OH)₂/CNT composites (Fig. 2), an inconspicuous weight loss appears between 250 and 350°C, which also corresponds to a weight loss via the conversion of Ni(OH)₂ into NiO and H₂O. A very sharp peak is present between 500 and 650°C on the DSC curve, which corresponds to an oxidation of CNTs. According to TGA, we chose 300°C as the calcining temperature in this study. The percentage of NiO in NiO/CNT composites can be estimated



Figure 2. DSC-TGA curve of synthesized Ni(OH)₂/CNT composites in air.



Figure 3. XRD patterns of $Ni(OH)_2$, CNTs, and $Ni(OH)_2/CNT$ composites, which are prepared with 0, 10, and 20 g SDS, respectively. (A) $Ni(OH)_2$, (B) $Ni(OH)_2/CNT$ -0, (C) $Ni(OH)_2/CNT$ -10, (D) $Ni(OH)_2/CNT$ -20, and (E) CNTs.

according to the weight loss at different temperature ranges. At temperatures of 400 and 800°C, the weight percentages are 88 and 21.2%, which means the mass fractions of the NiO/CNTs and NiO, respectively. Therefore, the loading amount of NiO is 24.09% (21.2%/88%), which is very close to the theory loading amount (calculated based on 1 g NiCl₂·6H₂O), 23.91%.

Structure and morphology.— The power XRD patterns of the samples prepared in our experiment are shown in Fig. 3 and 4. For comparison, the pure CNTs are also listed. As shown in Fig. 3, the characteristic graphitic (002) peak of the CNTs at 26° was clearly observed.¹⁶ The XRD pattern of the Ni(OH)₂ and Ni(OH)₂/CNT composites prepared without SDS corresponded to the well-known layered α -Ni(OH)₂ structure with a characteristic (001) peak at 10.2°. Moreover, the intensity of the (001) reflection decreased with Ni(OH)₂ dispersing on the surface of CNTs. However, the characteristic (001) peak of the Ni(OH)₂/CNT composites synthesized with SDS disappears, and their XRD pattern represents amorphous Ni(OH)₂/CNT composites. In Fig. 4, the characteristic peaks for rocksalt NiO at 2θ = 36.9, 42.8, and 62.4° [corresponding to (111), (200), and (220) reflections, respectively] as well as the CNTs at 26°



Figure 4. XRD patterns of NiO, CNTs, and NiO/CNT composites, which are prepared with 0, 10, and 20 g SDS, respectively. (A) NiO, (B) NiO/CNT-0, (C) NiO/CNT-10, (D) NiO/CNT-20, and (E) CNTs.



Figure 5. SEM images of NiO and NiO/ CNT composites, which are prepared with 0, 10, and 20 g SDS, respectively. (a) NiO, (b) NiO/CNT-0, (c) NiO/CNT-10, and (d) NiO/CNT-20.

were observed in the XRD patterns of the NiO/CNT composites heated at 300°C. This confirmed that nickel oxide with a rocksalt structure had formed on the NiO/CNT composites after heating the Ni(OH)₂/CNT composites to 300°C. The characteristic peaks of rocksalt NiO seriously broaden. It means that we obtain the finer size and amorphous state of electrode materials to provide a large amount of superficial electroactive species to participate in faradaic redox reactions.

To further investigate the different NiO/CNT composites, SEM was adopted. Figure 5a shows the SEM images of pure NiO powder, and Fig. 5b-d displays the SEM images of NiO/CNT powder. Without the addition of CNTs or SDS, a lot of sheets clearly congregate into large secondary particles, and the sizes of NiO are of the micrometer order of magnitude, as shown in Fig. 5a. After the addition of CNTs, the SEM image of NiO/CNT-0 shows uniform sheetshaped NiO dispersing on the surface of CNTs, which demonstrates that CNTs restrain the agglomeration of sheet-shaped NiO, and the sizes of NiO are of the nanometer order of magnitude. Furthermore, with the addition of SDS, the zero-dimensional NiO sphere dispersing on the surface of CNTs and the very fine particles of NiO nanoparticles were obtained (Fig. 5c and d). With the increasing additional mass of SDS, the shape of nano-NiO changes from nanodisk to nanofilament and results in finer zero-dimensional particles. We mainly ascribe the phenomena to attractive interactions between dodecyl sulfate anions and the precursor of bivalent nickel ions with opposite charges. TEM was adopted to observe the nanostructure of the samples Ni(OH)₂/CNT-20 and NiO/CNT-20, which also shows that the nanostructure of the as-prepared $Ni(OH)_2$ is almost the same as that of the NiO after being calcined at 300°C, as shown in Fig. 6. It seems that the calcined temperature is low enough to keep the original nanostructure of the nickel oxide. The $Ni(OH)_2$ and NiOnanoparticles seem to be formed with nanofilaments, which form a loose porous sphere structure adsorbed on the surface of CNTs. Here, the SDS plays a key role in giving a template for the growth of the nano-nickel oxide. In addition, the CNTs give a very good original nanostructure for the nucleation, which strongly affects the nanostructure of the nickel oxide. The zero-dimensional spheres in

the composites are constructed by nanofilaments and have many voids that ensure an easier electrolyte ion transport and more superficial electroactive species.

Pore distributions.— Then, the mesoporous characteristics of the product were investigated with the N₂-adsorption/desorption isotherms. Important structural parameters were derived from the isotherms and tabulated in Table I. From Table I, we found that the BET specific surface areas are gradually decreased, but the BJH pore sizes are gradually increased after the addition of CNTs and SDS. It must be considered that the content of NiO in samples NiO/CNT-0, NiO/CNT-10, and NiO/CNT-20 is only 24 wt % and the BET surface of the CNTs is only about 20–50 m² g⁻¹. So, the addition of CNTs and SDS actually increases the BET surface area, which means that a better nanostructure is obtained. The typical pore-size distribution of the samples is shown in Fig. 7, which exhibits the major BJH pore diameter centered at 4.4 nm.

In summary, the SEM results exhibit the morphology of Ni(OH)₂, changing from a two-dimensional disk to a zerodimensional sphere with an increasing additional amount of SDS, and these results are also demonstrated by the characteristic (001) peak of the layered α -Ni(OH)₂ structure that disappears. N₂-adsorption/desorption results also demonstrate that the addition of CNTs brings a nanostructure of NiO with a larger size pore diameter.

Electrochemical performance.— The electrochemical properties of the products were compared by performing CV in a 1 M KOH solution. Figure 8 shows the cyclic voltammograms of CNTs, NiO, and NiO/CNT-20 composite electrodes at a scan rate of 10 mV s⁻¹ in a 1 M KOH electrolyte. The cyclic voltammograms of NiO show a roughly rectangular mirror image with respect to the zero-current line, a representation of a capacitive behavior.^{17,18} The cyclic voltammograms of NiO/CNT-20 shows the diagnostic peaks of anodic/cathodic redox reactions at 0.54 and 0.34 V (vs the Hg/HgO electrode), which are responsible for the Ni(OH)₂/NiOOH redox reaction.^{8,13,19,20}



Figure 6. The TEM images of Ni(OH)₂/CNT-20 and NiO/CNT-20 composites prepared with 20 g SDS. d1: Ni(OH)₂/CNT-20; d2: NiO/CNT-20.

It is believed that NiO, in contact with an alkaline solution, tends to change into nickel hydroxide at the surface, forming a surface layer onto NiO probably within several angstroms of the nickel oxide. ^{8,13,19,20} To rationalize the above results, possibly the morphology and size effect of NiO may affect the generation of nickel hydroxide. With the increasing additional mass of SDS, the shape of nano-NiO changes from a two-dimensional disk to a zerodimensional sphere. Compared with the two-dimensional flake, the

| Table I. Structural parameters of the samples. | | | |
|--|---|--|------------------------------|
| Sample | BET specific surface area (m ² g ⁻¹) | BJH pore volume (cm ³ g ⁻¹) | BJH pore diameter (nm) |
| NiO | 176.3506 | 0.1193 | 4.3661 |
| NiO/CNT-0 | 128.9194 | 0.1833 | 7.3492 |
| NiO/CNT-10 | 111.9441 | 0.1765 | 7.3776 |
| NiO/CNT-20 | 111.3016 | 0.1246 | 7.7310 |



Figure 7. Pore-size distribution plots of sample NiO/CNT-20.

zero-dimensional porous sphere has a looser pore structure and a larger specific surface area, which means that the access of electrolyte ions to reaction sites is easier and that there are more formation sites of nickel hydroxide. So, compared with NiO, NiO/CNT-0, NiO/CNT-10, and NiO/CNT-20, sample NiO/CNT-20 shows the largest pore size in a series of composites, indicating the highest capacitance. Such enhanced capacity proves our deduction from the above section. Adding SDS to NiO/CNT composites can improve the dispersion of Ni(OH)₂ nucleation on the surface of CNTs and can change the crystalline structure, size, and morphology of Ni(OH)₂ so as to change the conductivity and electrochemical utilization of NiO.

To further evaluate the electrochemical capacity of the synthesized NiO/CNT composites, we used these composites to fabricate electrodes for supercapacitors and characterized them with chronopotentiometric measurements.

Our research on CNTs shows that its capacity is about 7.9 F g⁻¹ in 1 M KOH; hence, we can deduce that the capacitive behaviors of these composites are mainly attributed to the pseudocapacity of NiO. So, the specific capacity of the NiO/CNT composites (*C*) and NiO in the composites (C_{NiO}) is calculated as Eq. 1



Figure 8. Cyclic voltammograms of CNTs, NiO, and NiO/CNT-20 composite electrodes at a scan rate of 10 mV/s in 1 M KOH electrolyte.



Figure 9. Cyclic life of the different conditions of composites at a constant current density of 84 A g^{-1} . The pure NiO powder measured at 20 A g^{-1} .

$$C_{\rm NiO} = \frac{C}{m \times \theta} = \frac{I \times \Delta t}{\Delta V \times m \times \theta}$$
[1]

where I is the discharge current, m is the mass of the composite, ΔV is the potential drop during discharging, Δt is the total discharge time, and C is the specific capacity. θ is the weight percent of NiO in NiO/CNTs.

The cycle life of all samples is monitored by a chronopotentiometry measurement at 84 A g^{-1} in 1 M KOH, as shown in Fig. 9. Meanwhile, based on Eq. 1, the highest measured capacity of each electrode is listed in Table II. The SEM micrographs of the initial and cycled samples of NiO/CNT-20 composite electrodes are shown in Fig. 10a and b. Evidently, no readily distinguishable difference in morphology can be observed before and after cycling. The results indicate that the composites have excellent stability in terms of morphology structural integrity (devoid of any pulverization) even after 1000 cycles. Compared with pure NiO and NiO/CNT electrodes, the two-dimensional sheet NiO dispersing on the surface of CNTs shows a significant improvement in specific capacity. We think that the size of sheet-shaped NiO becomes smaller and has more formation sites of nickel hydroxide than pure NiO. The zero-dimensional porous sphere NiO dispersing on the surface of CNTs showed the highest specific (1329 F g^{-1}) capacity at 84 A g^{-1} , which may be because the zero-dimensional mesoporous sphere has large specific surface areas and easier electrolyte ion transport. All the electrodes reveal a stable specific capacity during consecutive cycle tests.

Conclusion

A simple hydrothermal synthesis method is adopted to prepare nickel oxide/CNT (NiO/CNT) composites. We obtain different morphologies of NiO, which change from a two-dimensional disk to a zero-dimensional mesoporous sphere, dispersing on the surface of CNTs by altering reaction experimental conditions. The electro-

| Table II. The specific capacity of NiO in the composite was cal- culated from charge/discharge curves according to Eq. 1. | | | |
|--|---|--|--|
| Weight percent of NiO in | | | |
| NiO/CNT composite | Capacity of the NiO | | |
| (wt %) | in composite at 84 A/g (F g- | | |
| 100.00 | 260.89 (20 A g ⁻¹) | | |
| 23.91 | 707.37 | | |
| 23.91 | 1145.40 | | |
| 23.91 | 1329.02 | | |
| | specific capacity of N charge/discharge curv Weight percent of NiO in NiO/CNT composite (wt %) 100.00 23.91 23.91 23.91 23.91 | | |





Figure 10. The SEM images of NiO/CNT-20 composite electrodes. (a) Before and (b) after cycling for 1000 cycles.

chemical performance of NiO/CNT composites is largely affected by the morphology, size, and crystalline structure of NiO. The NiO/ CNT composite electrode shows a maximum specific capacitance of 1329 F g^{-1} as well as a good cycle life during 1000 cycle in a 1 M KOH electrolyte at a very high current density, 84 A g^{-1} .

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