Hierarchical porous nickel oxide–carbon nanotubes as advanced pseudocapacitor materials for supercapacitors

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ABSTRACT

Hierarchical porous carbon anode and metal oxide cathode are promising for supercapacitor with both high energy density and high power density. This Letter uses NiO and commercial carbon nanotubes (CNTs) as electrode materials for electrochemical capacitors with high energy storage capacities. Experimental results show that the specific capacitance of the electrode materials for 10%, 30% and 50% CNTs are 279, 242 and 112 F/g, respectively in an aqueous 1 M KOH electrolyte at a charge rate of 0.56 A/g. The maximum specific capacitance is 328 F/g at a charge rate of 0.33 A/g.

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1. Introduction

The world’s focus on global warming and depletion of fossil fuels have driven an increase in demand for renewable energy such as solar, wind and hydro energy. These new technologies however, have certain drawbacks with regards to their operation [1–3]. The use of energy sources such as solar and wind is subject to conditions at the location of harvest. Also, the amount and intensity of sunlight and wind varies throughout the day, as well as through the seasons. The usage of energy is often times not in-sync with the time of energy production. As such, there would be excess and shortage depending on the time and day. To overcome this problem, efficient storage and management of energy is required. Possessing higher power density than batteries, higher energy density than conventional dielectric capacitors, excellent cyclic stability and simple working principle, supercapacitors have recently been considered as the most promising energy storage devices for applications requiring short load cycle and high reliability, such as electric vehicles and forklifts [1–5].

Supercapacitors can be classified into two types based on the energy storage methods: non-Faradaic electric double layer capacitance and Faradaic surface redox reactions (pseudocapacitance) [1–3,5]. Electric double layer capacitors store electrostatic charges on the surface of the electrode materials without a phase transformation while pseudocapacitors rely on pseudocapacitive electron transfer between the electrode and electrolyte. The charge storage in double layer capacitors is achieved by the formation of a double layer on the surface of the material while the charge is stored on the surface and in the bulk of the material via the double layer and Faradaic reaction, respectively. As a result, the charge stored in pseudocapacitors may be higher than that in double layer ones. Carbon-based materials are often used as electrodes for double layer capacitors while conducting polymers, transition metal oxides and hydroxides are used for pseudocapacitors [2,5–7].

Although supercapacitors have many advantages over other energy storage devices, they are still facing challenges for their practical applications, i.e. limited energy density compared to batteries, fuel cells and high production cost [2,3,8]. Therefore, it is essential to explore new cheap electrode materials with high energy density. Transition metal oxides have been considered as promising electrode materials for supercapacitors. Among them, NiO has generated great interest due to its low cost of raw materials, as well as its low toxicity and non-flammable properties making it safe to handle. NiO has also exhibited excellent cycling abilities [9–14]. However, NiO has drawbacks in supercapacitor applications, which are its high resistivity and relatively low surface area. These factors negatively affect its energy density, power density and specific capacitance [15]. As such, there is a need to enhance the electrode conductivity and specific surface area. Carbon nanotubes (CNTs) have been widely known to possess high conductivity and large specific surface area [9–11,13,16]. Also, Carbon Nanotubes have been used in other works as an additive to improve the performance of conducting polymers. Hence, in our work, CNT is mixed with NiO to improve its electrical conductivity and durability. The entanglement of CNTs provide a body of open mesopores,
allowing better access to the NiO material. This composite is expected to increase the performance of NiO for supercapacitor applications in terms of cycling ability [17,18].

2. Experimental

2.1. Materials

Multiwalled CNTs, 10–20 nm in diameter and 5–15 μm in length were purchased from Shenzhen Nanotechnologies Port Co., Ltd. Nickel (II) nitrate hexahydrate, urea, acetylene black and polytetrafluoroethylene (PTFE) were purchased from Sigma–Aldrich. All chemicals were used as received without further purifications.

2.2. Synthesis of Hierarchical NiO–CNT composite materials

Firstly, the CNTs were dispersed in deionized water (DI water) by sonication for 1/2 h. Then, Nickel Nitrate Hexahydrate and urea were dissolved in the suspension and stirred for 5 h at 90 °C under reflux. After refluxing, the precipitant was filtered out, washed with DI water and ethanol, and dried in air at 80 °C for 2 h. Finally, the as-prepared mixture was calcined in argon at 300 °C for 2 h. To investigate the effect of different CNT content to the electrochemical performance, 10, 30 and 50 wt.% of CNT loading in the composite materials were tested and marked as NiO–CNT10%, NiO–CNT30% and NiO–CNT50%.

2.3. Characterizations

The crystal structure of as-synthesized samples were characterized by powder X-ray diffraction (XRD) using Bruker AXS D8 Advance X-ray diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å) between 20° and 90°. The Raman spectra were collected on WITec CRM200 confocal Raman microscopy system with the excitation line of 488 nm and air-cooled charge coupled device (CCD) as detector. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed on JEOL 3010 instrument to investigate the microstructure of the NiO–CNT composite materials. The morphological features and chemical composition were examined with a field emission scanning electron microscope performed on FE-SEM, JEOL-6701F instrument. The surface area and pore volume were determined from N2 adsorption/desorption isotherm using Micromeretics Tristar 2000, surface area and pore size analyzer. The sample was degassed under N2 at 300 °C for 12 h prior to the measurements.

2.4. Electrochemical measurements

The working electrodes were prepared by mixing 90 wt.% active materials (NiO–CNT), 5 wt.% carbon black and 5 wt.% polytetrafluoroethylene (PTFE) binder in DI water to form a paste. The paste was then spread onto nickel foam (1 cm2) and compressed with 0.5 metric tons of pressure. The mass load of active material on each electrode was 4 mg/cm2. The electrochemical behavior of the electrodes was studied using a three electrode cell with Pt sheet as
counter electrode, and Ag/AgCl as the reference electrode and active material in nickel foam as the working electrode. The electrochemical performance of the electrode was characterized by cyclic voltammetry (CV) and galvanostatic charge–discharge using Autolab PGSTAT302N electrochemical workstation. The galvanostatic charge/discharge was carried out with current densities ranging from 0.2 to 5.0 A/g. The specific capacitance $C$ (F/g) of the electrode materials was calculated from the discharge curve according to the following equation

$$C = \frac{I \Delta t}{V m}$$

where $I$ is the discharge current, $\Delta t$ is the discharge time, $V$ is the voltage change and $m$ is the mass of the electrode materials excluding binder and carbon black. All measurement was carried out in 1 M KOH aqueous solution.

3. Results and discussion

Electron microscopy images of the composite in Figure 1a and b demonstrate that the NiO has an aggregated flake-like morphology with CNTs dispersed in the oxide matrix interconnecting the aggregates. The microscopy images show that the NiO flakes have a distribution of lengths and widths, with a uniform thickness of about 5 nm. The flake-like morphology and the aggregates resulted in an open and porous structure of the NiO–CNT composites. Such an open hierarchical porous structure of NiO could permit easy access for solvated ions to the electrode/electrolyte interface, which is crucial for surface Faradaic reactions [19].

The diffraction rings obtained from SAED analysis in Figure 1d are assigned to diffraction rings of (111), (200), (220), (311) and (222), confirming the rock-like polycrystalline structure of NiO nanoflakes. The XRD pattern of the NiO–CNT composite is shown in Figure 2a. For the NiO–CNT10% sample, the diffraction peaks of NiO at 37.0°, 43.1°, 62.8°, 75.1° and 78.8° corresponding to (111), (200), (220), (311) and (222) reflections respectively were observed. The XRD pattern demonstrates the crystalline nature and phase purity of the as-prepared sample. The most intense peak of NiO in the FCC structure is the (200) reflection at 2\(\theta\) = 43.1°. Additional to NiO peaks, the characteristic graphitic (002) peak of the CNTs at 26° was observed.

The electrochemical surface reactivity of NiO is dependent on its crystallinity, which is related to the calcination temperature. Several reports demonstrated the highest capacitance of NiO electrode materials was achieved by calcination at 300 °C [20–22]. Raman spectrum of hierarchical porous NiO–CNT10% between 200 and 3000 cm\(^{-1}\) is depicted in Figure 2b. It shows the broadened characteristic frequencies at ~1356, ~1588 and ~2711 cm\(^{-1}\), which correspond to the signature D, G and 2D bands of graphitic carbon materials, respectively. The D band is attributed to the presence of defects in the graphite structure; whereas G band corresponds to the graphitic structure [23].

The \(N_2\) adsorption–desorption isotherms of hierarchical porous NiO–CNT composite materials are shown in Figure 3a. The NiO–CNT composite materials exhibit type IV isotherms with a well-defined characteristic condensation step at $P/P_0 \approx 0.3–0.6$. It clearly indicates that these materials possess mesoporous structure [24]. The typical pore-size distribution of the samples calculated from the BJH method in Figure 3 shows abundance of mesopores centered at 3.7 nm. The corresponding texture properties of the NiO–CNT composite materials with 10, 30 and 50 wt.% CNT loading are summarized in Table 1. BET study revealed that the NiO nanoflake prepared without the CNTs has a surface area of 186 m\(^2\)/g with total pore volume of 0.47 cm\(^3\)/g. It is found that the BET specific surface area are gradually decreased and total pore volume and BJH pore size are gradually increased with the increasing CNT contents from 10 to 50 wt.%.

![Figure 2](image-url)  
**Figure 2.** (a) XRD pattern and (b) Raman spectrum of the as-prepared NiO–CNT10% composite.

![Figure 3](image-url)  
**Figure 3.** \(N_2\) adsorption–desorption isotherm and BJH pore size distribution of NiO–CNT10%.

<table>
<thead>
<tr>
<th>Materials</th>
<th>S.A. (m(^2)/g)</th>
<th>Total pore vol. (cm(^3)/g)</th>
<th>Avg pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>186</td>
<td>0.473</td>
<td>9.3</td>
</tr>
<tr>
<td>NiO–CNT10%</td>
<td>179</td>
<td>0.469</td>
<td>13.2</td>
</tr>
<tr>
<td>NiO–CNT30%</td>
<td>174</td>
<td>0.602</td>
<td>14.3</td>
</tr>
<tr>
<td>NiO–CNT50%</td>
<td>169</td>
<td>0.704</td>
<td>16.1</td>
</tr>
<tr>
<td>CNT</td>
<td>161</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The NiO nanoflake structure facilitates ion transport paths throughout the mesoporous wall, which is an essential site for electric double layer charge storage. The high specific surface area is one of the prerequisites for the electrode
materials, because electric energy is stored in aggregated charges at the surface of electrode materials.

The capacitive behavior of the NiO–CNT electrodes was investigated by CV, galvanostatic charge–discharge in a three-electrode system with 1 M KOH as the aqueous electrolyte. Figure 4 represents the discharge profiles of the samples at different current density. The discharge profiles in Figure 4 demonstrate varying plateaus corresponding to the cathodic peaks seen in Figure 6. These peaks can be observed in the 0.2 and 0.3 V region of the NiO–CNT10% composite, and signify the occurrence of redox reactions. The presence of 2 redox reaction peaks suggest that there is trace amounts of impurities that contribute in a small portion to the results. The specific capacitance calculated from galvanostatic discharge curve at constant current are summarized in Figure 5. The NiO–CNT10% sample electrode exhibits a specific capacitance of 297 F/g at current density of 0.5 A/g. The specific capacitance of the composites shows a gradual decrease with increasing CNT content. 50 wt.% of CNT content reduces the reduced the capacity to 113 F/g. The decrease in the specific capacitance may be contributed by the low specific capacitance of the non-functionalized CNTs used in this Letter [25].

The high specific capacitance of the porous NiO–CNT in comparison with CNTs is mainly from Faradic redox between NiO particles and KOH electrolyte according to the following electrochemical reaction:

\[
\text{NiO} + \text{OH}^- \rightarrow \text{NiOOH} + e^-
\]

In contrast, the contribution of double-layer capacitance through surface adsorption of OH\(^{-}\) by CNTs is negligible for all NiO–CNT samples. Comparison of Figure 5 suggests there seem to be an optimum value where the CNTs stabilize the specific capacitance at higher discharge current. This is observed for NiO–CNT30% sample. Further evidence can be seen in Table 2, which further shows that the specific capacitance derived from the NiO–CNT30% sample exhibiting better capacitance relative to weight of NiO present. The synergetic interaction between NiO and CNTs may have originated from improved electronic conductivity and ionic accessibility in the sample with the optimum loading and thus good dispersion of CNTs in the NiO matrix.

![Figure 4](image-url)

*Figure 4.* Galvanostatic discharge profiles of the NiO–CNT10% (a), NiO–CNT30% (b) and NiO–CNT50% composites at different current densities.

![Figure 5](image-url)

*Figure 5.* Specific capacitance of NiO–CNT10% (a), NiO–CNT30% (b), NiO–CNT50% (c) composites at different current density.
From Figure 5 a general behavior of the electrodes showing gradually decreased capacitance with the increase of the current density. In contrast to CNTs electrode that stores charges through EDLC, the hierarchical porous NiO–CNTs electrode shows an evident decrease of specific capacitance as the current density increase from 0.2 to 0.5 A/g, Moreover, the NiO–CNT composite electrode still give appreciable specific capacitance of 91 F/g at a current density of 5.0 A/g. The excellent capacitive performance of the hierarchical porous NiO–CNT electrode was also verified from the CV curves at various scan rates depicted in Figure 6. It is observed that the current response show corresponding increases with the increase of the scan rate, revealing a good capacitive behavior of the porous NiO–CNT composite electrode. Also, the reduced peak separation observed as CNT content increases shows that the conductivity of the material increases with an increase in CNT%. The porous NiO–CNTs electrode still exhibit a relatively consistent cathodic peak at scan rate as high as 30 mV/s in the NiO–CNT30% and NiO–CNT50% composites. This superior rate performance is suggested to be closely related to the synergy between the CNT’s conductivity and the composite’s unique hierarchical architecture with mesoporous texture.

The long-term cycling performance of hierarchical porous NiO–CNTs electrode in a potential window of 0–0.495 V (vs Ag/AgCl) was measured by the consecutive galvanostatic charge–discharge at current density of 1 A/g as shown in Figure 7. The specific capacitance of hierarchical porous NiO–CNTs electrode was found to gradually decrease from 100% to 64.3% retention after 300 continuous cycles (Figure 7). In the literature the poor cycle performance of NiO-based electrode is generally affected by two factors: NiO dissolution and O2 evolution. In our experiment, the applied potential of 0–0.495 V (vs Ag/AgCl) is considered to be a stable electrochemical window, where the O2 evolution reaction is effectively suppressed. Thus, the poor cyclability of the hierarchical porous NiO–CNTs electrode may be related to the loss of pseudocapacitive NiO, resulting in a capacitance decay of 35.7% after 300 cycles. We believe such severe NiO dissolution may be related to the reaction of OH/CO3 into and out of NiO nanostructure during the charge–discharge process. The pseudocapacitive charge storage mechanism together with the continuous volume expansion/contraction of electrode, leads to a physical detachment of NiO nanoflakes with the CNTs or the current collector. Nevertheless, the Coulombic efficiency calculated from the ratio between discharge time and charged time remains a quite high value of 64.3% during the whole cycling.

4. Conclusion

A hierarchical porous architecture consisting of NiO nanoflakes and multiwalled CNT composite has been synthesized by refluxing and post-annealing. The CNTs was dispersed on NiO nanoflakes aggregates with uniform mesoporous structure. To investigate the capacitance of NiO–CNT composite in 1 M KOH solution, we measured the specific capacitance of NiO–CNT10%, NiO–CNT30%, and NiO–CNT50% composites at different current densities.

Table 2

<table>
<thead>
<tr>
<th>Charge/discharge Current (A/g)</th>
<th>NiO–CNT10% specific capacitance</th>
<th>NiO–CNT30% specific capacitance</th>
<th>NiO–CNT50% specific capacitance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(F/(\text{g}_{\text{composite}}))</td>
<td>(F/(\text{g}_{\text{oxide}}))</td>
<td>(F/(\text{g}_{\text{composite}}))</td>
</tr>
<tr>
<td>0.56</td>
<td>279</td>
<td>310</td>
<td>242</td>
</tr>
<tr>
<td>1.11</td>
<td>245</td>
<td>273</td>
<td>216</td>
</tr>
<tr>
<td>2.22</td>
<td>203</td>
<td>226</td>
<td>219</td>
</tr>
<tr>
<td>3.33</td>
<td>89</td>
<td>99</td>
<td>220</td>
</tr>
</tbody>
</table>

Figure 7. Cycle performance of NiO–CNT10% composite.

Figure 6. Cyclic voltammetry of NiO–CNT10% (a), NiO–CNT30% (b), and NiO–CNT50% (c) at varying scan rate with aqueous 1 M KOH electrolyte.
the effect of CNTs content, the hierarchical porous NiO–CNT composite with 10, 30 and 50 wt.% of CNT loading were prepared. The specific capacitance of hierarchical porous NiO–CNT composite depends on the contents of CNT, and a maximum specific capacitance of 297 F/g was achieved for NiO–CNTs10% electrode at current density of 0.56 A/g. Moreover, the NiO–CNTs10% electrode also shows an excellent rate performance and a superior Coulombic efficiency (64.3%) after 300 cycles of consecutive galvanostatic charge–discharge in 1 M KOH aqueous electrolyte. Such excellent performances make the hierarchical porous NiO–CNTs composite to be the promising electrode for electrochemical energy storage.

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