Short Communication

Constructing Ultrafine Tin Dioxide/Few-Walled Carbon Nanotube Composites for High-performance Supercapacitors

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Received: 1 May 2018 / Accepted: 13 June 2019 / Published: 30 June 2019

A hydrothermal/calcination method was successfully applied to prepare ultrafine tin dioxide (SnO₂)/few-walled carbon nanotube (FWNT) composites (SnO₂@FWNT). The corresponding morphological and structural information were further obtained by the characterization technique of transmission electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. In the SnO₂@FWNT composites, ultrafine SnO₂ nanoparticles with an average size of 2–3 nm were uniformly distributed on the FWNT with a thickness of 2–5 layers. With the synergistic effect of highly conductive FWNT and highly dispersed SnO₂, the SnO₂@FWNT hybrids presented excellent specific capacitance of 220.5 F g⁻¹ at a scan rate of 2 mV s⁻¹ under neutral environment. A power density of 30.63 kW kg⁻¹ and an energy density of 512.79 W kg⁻¹ were obtained, respectively. In addition, a specific capacity retention rate of 89.57% was acquired after 1000 cycles, indicating a superior stability of SnO₂@FWNT hybrids. The results indicate that the SnO₂@FWNT composites can be used as an alternative electrode material for high-performance supercapacitors.

Keywords: electrode material, supercapacitors, ultrafine tin dioxide, few-walled carbon nanotube

Mobile devices and facilities

1. INTRODUCTION

Supercapacitors (SCs) can deliver higher energy density than conventional dielectric capacitors and higher power density than conventional batteries [1]. So, supercapacitors can be potentially applied in electric automobile, sustaining energy supplies, mobile devices and facilities, and DC power systems [2]. The energy in SCs is usually stored by ion adsorption (electrical double-layer capacitors, EDLCs) or reversible redox reactions (pseudocapacitors) [3]. Electrodes are one of the important components in the supercapacitors, affecting the performance of the whole devices. Therefore, the
reactions occurred at the active materials in the electrodes are closely associated with the energy density and power density of the SCs. At present, the active composition in the electrode of EDLCs are usually carbonaceous materials with abundant intrinsic pores, rapid electron transmission and high specific surface areas, which can adsorb ions rapidly. Hence, EDLCs can deliver much higher power density than conventional batteries. However, the stored energy in EDLCs is limited by the intrinsic ion adsorption capacity of carbon-based materials. To improve the energy density of capacitors, transition-metal oxides or electrically conducting polymers with reversible redox activity are employed as the active materials in the so-called pseudocapacitors [4]. But the power density of pseudocapacitors is lower than EDLCs due to the kinetics of redox reactions is quite low. Therefore, carbon and metal oxides hybrid materials are prepared, which can enhance the redox kinetics, synchronously improving the energy density and power density of the SCs[5].

Carbon nanotubes (CNTs) have excellent mechanical and electronic properties, showing a great prospect in transistors [6, 7], photovoltaic devices [8, 9], and supercapacitors [10, 11] etc in combination with their unique nanostructures. The CNTs with sidewalls of 2–6 layers or diameters 3 to 8 nm are commonly regarded as few-walled carbon nanotubes (FWNTs). The lengths of FWNTs are in the range of ten or hundred micrometers. In order to apply the FWNTs in supercapacitors, uniform dispersions of FWNTs are needed to obtain evenly electrodes. However, it is difficult to disperse the FWNTs in various solvents due to their inert surface. To improve the dispersion of the FWNTs, their surface is usually modified by functional group. They can still retain the remarkable mechanical and electronic properties due to the unbroken inner layers [12]. So, transition-metal oxides (such as RuO$_2$, Co$_3$O$_4$, and MnO$_2$) or conducting polymers are incorporated into the FWNTs matrix to further enhance the electrochemical performance of FWNTs [13, 14]. The transition-metal oxides/FWNTs hybrids can serve as suitable electrode materials for supercapacitors, which can deliver excellent rate performance and cyclic stability. Recently, the reported specific capacitance RuO$_2$/carbon composites can reach up to 570 F/g [15]. However, in consideration of the scarcity of RuO$_2$, corresponding alternatives like cheap metal oxides (CMOs) are needed to be developed urgently [16–20]. Among the different CMOs, SnO$_2$ has gained sustained attention due to its excellent chemical stability, low cost, and environmentally friendly features in comparison with RuO$_2$ [3]. The SnO$_2$ nanoparticles can be prepared by various methods like arc plasma, sol–gel synthesis, hydrolysis of tin isopropoxide [20], and chemical reduction of stannous chloride followed by calcination [21]. Furthermore, the electrochemical performance of SnO$_2$ is strongly affected by its corresponding micro-nano structure. So, facile preparation of untrafine SnO$_2$ nanoparticles with high density of electroactive site is very important for the capacitors.

Herein, we develop a convenient strategy to produce ultrafine SnO$_2$ nanoparticles, which are supported on FWNTs, forming SnO$_2$@FWNT composites. A series supercapacitors were fabricated with SnO$_2$@FWNT composites or FWNTs as the electrode, and each electrochemical performance was evaluated. In result, the hybrid SnO$_2$@FWNT exhibited good electrochemical performance, which showed great potential in energy devices like supercapacitors.
2. EXPERIMENTAL

2.1. Chemicals and Reagents

FWNTs were purchased from Nanjing XF Nano Technology (China). After an activated approach according to the literature [20], the FWNTs can be used to grow SnO$_2$ nanoparticles. Other reagents (analytical grade) were bought from Aladdin reagent (China) and were used directly without further purification. The aqueous solutions were prepared with pure water (>18 MΩ).

2.2. Preparation of SnO$_2$/FWNT composites

Firstly, to activate FWNTs, they were uniformly dispersed in a nitric acid solution with the assistance of ultrasonic. The resulting dispersion was then heated to 110 °C and refluxed for 8 h under a vigorous stirring. After that, the activated FWNTs were subjected to repeated centrifugation and washing with deionized water until the supernatant liquid became neutral. Next, the activated FWNTs were dried at 60 °C before use. To prepare the SnO$_2$/FWNT composites, the 100 mg as-purified FWNTs were dispersed into 100 mL ethylene glycol solution with a round-bottom flask. The mixture was under an ultrasonic treatment till forming a uniform suspension. Then, 1 M NaOH solution was added dropwise into the suspensions until the pH of the dispersions changed to 12. After that, 1 M SnCl$_4$·H$_2$O solution was added into the dispersions under stirring. The resulting homogeneous dispersions were heated to 198 °C and refluxed for 8 h in an oil bath. The products were collected by centrifuging, washing with water several times, and drying under vacuum at 80 °C overnight. Finally, the obtained products were annealed at 500 °C for 2 h, getting the SnO$_2$@FWNT composites. The preparation process the SnO$_2$@FWNTs composites is illustrated in Scheme 1.

![Scheme 1. Illustration of the preparation process of SnO$_2$@FWNT composites.](image-url)
2.3. Material Characterization

The morphology of the SnO$_2$@FWNT composites was characterized by a transmission electron microscope (TEM, Hitachi, JEM-2100) operated at 200 kV. The corresponding structural information was obtained by a powder X-ray diffractometer (XRD, Shimadzu, X-6000, Cu Kα radiation, λ= 0.154 nm) and an X-ray photoelectron spectrometer (XPS, Thermo Fisher, equipped with Al radiation as the probe).

2.4 Preparation of electrode with the SnO$_2$@FWNT composites

The electrochemical measurements were performed with a CHI 660E electrochemical workstation with a three-electrode system in 1 M Na$_2$SO$_4$ solution. The working electrodes were prepared as follows: active materials (SnO$_2$@FWNT composites), binder (polytetrafluoroethylene) and conductive agent (acetylene black) with a mass ratio of 90:5:5 were dispersed in ethanol, forming a homogeneous slurry under strong stirring. Then, the slurry was coated onto a nickel foam (1 cm × 1 cm) using a doctor blade. After that, the electrode was dried at 80 °C for 12~18 h. A Platinum wire and Ag/AgCl (KCl-saturated) electrode were used as the counter electrode and reference electrode, respectively.

3. RESULTS AND DISCUSSION

![TEM images of (A) FWNTs and (B) SnO$_2$@FWNT nanocomposites, respectively.](image)

Figure 1. TEM images of (A) FWNTs and (B) SnO$_2$@FWNT nanocomposites, respectively.

In this work, we developed a facile in-situ preparation of FWNTs decorated with ultrafine SnO$_2$ nanoparticles. The typical procedure is illustrated in Scheme 1. The morphology of as-purified FWNTs is shown in Figure 1A, revealing that the FWNTs like spaghetti, having transparent and one-dimensional (1D) tubular structure. The FWNTs have about 2–5 layers, and the surface of FWNT is clean, indicating that the HNO$_3$ treatment is very effective for clean-up of the impurities. The TEM image shows that SnO$_2$ nanoparticles with an average size of 2–3 nm are distributed on the surface of FWNTs as shown in Figure 1B. The SnO$_2$ particles are ultrafine and SnO$_2$@FWNT composites still maintain 1D tubular structure, indicating the FWNTs can stabilize the structure of composites. The
formation mechanism of ultrafine SnO$_2$ particles may be described by the following chemical reactions

\[
\text{Sn}^{4+} + 4\text{OH}^- \xrightarrow{\text{reflux}} \text{Sn(OH)}_4 \xrightarrow{\text{annealing} \ 500^\circ\text{C}} \text{SnO}_2
\]

The FWNTs and SnO$_2$@FWNT composites are characterized by powder X-ray diffraction (PXRD), respectively. As shown in Figure 2, the FWNTs show a broad diffraction peak at \(\sim 25^\circ\), which can be indexed to the characteristic (002) plane of carbon. The broad peaks in SnO$_2$@FWNTs composites appear at diffraction angles of 27.5°, 34.6°, 52.5°, and 63.5°, corresponding to the (110), (101), (211), and (301) planes of SnO$_2$, respectively. It indicates that SnO$_2$ nanoparticles were successfully loaded onto the surface of FWNT and have ultrafine sizes.

![Figure 2. XRD pattern of pure FWNTs and SnO$_2$@FWNT composites.](image)

The XPS spectra can be used to confirm the existence of Sn and corresponding chemical states in the composites. The characteristic peaks of C1s, O1s, Sn4d, Sn3d, and Sn3p can be clearly

![Figure 3. XPS spectra of SnO$_2$/FWNT composites (A) and (B) high-resolution Sn 3d, respectively.](image)
identified from the XPS survey spectra as shown in Figure 3A. The high-resolution Sn3d spectra (Figure 3B) shows the peaks of Sn 3d$_{3/2}$ (495.8 eV) and Sn 3d$_{5/2}$ (487.5 eV). The calculated spin–orbit separation is 8.3 eV, consistent with the reported data of Sn 3d$_{3/2}$ and Sn 3d$_{5/2}$ in SnO$_2$ [22]. This indicates that SnO$_2$/FWNT composites are successfully prepared.

Cyclic voltammetry (CV) is a facile and effective measurement to analyze the capacitive behavior of the nanomaterials. CV measurement of FWNTs or SnO$_2$/FWNT composites is performed in a 1 M Na$_2$SO$_4$ solution at a scan rate of 100 mV/s. The CV of pure FWNT has a rectangular shape, meeting the characteristics of an ideal double-layer capacitor as shown in Figure 4. In addition, the CV curve of SnO$_2$/FWNT composites has a near-rectangular shape without obvious redox peaks, which indicates that Faraday redox reaction is an electrochemical reversible process [23]. In addition, the SnO$_2$/FWNT composite shows a higher integrated area than the FWNT electrode, indicating a better capacitance at more negative potential.

![Figure 4](image_url)

**Figure 4.** CV curves of FWNTs and SnO$_2$@FWNT composites at a scan rate of 100 mV/s

Generally, the specific capacitance (Cs) of a material is proportional to the integral area of CV curve. Figure 4 shows that the Cs of SnO$_2$/FWNT is much larger than FWNT. The electrochemical properties of the capacitor have been significantly improved, which can be attributed to the following structural characteristics. For one thing, the ultrafine SnO$_2$ nanoparticles can absorb Na$^+$ on the electrode surface from mild Na$_2$SO$_4$ aqueous electrolyte, which are depicted as equation [24]:

$$\text{(O=Sn=O) surface + Na}^+ + e \rightarrow \text{(O=Sn=O Na$^+$) surface}$$

It is beneficial to provide more sites of the charge storage. For another, SO$_4^{2-}$ is easy to pass through the well-distributed MWCNT network in Na$_2$SO$_4$ aqueous solution. As a result, both Na$^+$ and SO$_3^{2-}$ are fully utilized on the composite electrode.
The CV curves of SnO$_2$/FWNT composites at different scan rates from 2 mV/s to 200 mV/s as shown in Figure 5A. The current gradually improve with the increase of the scan rates. To be noted, all the CV curves present irregular rectangular shapes, especially at high scan rates, indicating pseudocapacitive behaviors in the SnO$_2$/FWNT composites. It can be ascribed to the intercalation of Na$^+$ from the electrolyte into the composites and its de-intercalation from the composites to the electrolyte during continuous charging−discharging process. The CV curves of SnO$_2$/FWNT composites are symmetric, implying a stable structure. It can be attributed to uniform sizes of SnO$_2$ nanoparticles and the strong anchoring effect of the FWNTs.

The Cs of SnO$_2$/FWNT composite is calculated from the CV curves with the following equation:

$$C = \frac{1}{m v (V_c - V_a)} \int_{V_c}^{V_a} I(V) dV$$

where $I$ (A) is the response current, $v$ (V/s) is the potential scan rate, $V_c$−$V_a$ (V) is the potential window, and m (g) is the mass of active electrode material. The specific capacitances at the scan rate of 2, 5, 10, 20, 30, 50, 100, and 200 mV/s are 220.5, 203.8, 196.2, 195.5, 185.6, 184.7, 169.3, and 166.5 F/g are, respectively (Figure 5B). The corresponding retention rate at each scan rate is 100%, 92.5%, 90%, 86.6%, 84.2%, 83.8%, 76.8%, and 75.5%, respectively, showing an excellent specific capacitances and power capability. Moreover, the energy density and power density of SnO$_2$/FWNT composites are 30.63 Wh/kg and 512.79 W/kg, respectively. The results indicate that SnO$_2$/FWNT composites can be used as an ideal material for the electrode of supercapacitors.
Figure 6. Cycling stability of SnO$_2$@FWNT composites measured at 2 mV/s

Table 1. Partial list of reported SnO$_2$-based composites electrode for Cs

<table>
<thead>
<tr>
<th>SnO$_2$-based composites</th>
<th>Electrolyte</th>
<th>Cs (F/g)</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>SnO$_2$/MWCNTs</td>
<td>1 M Na$_2$SO$_4$</td>
<td>133</td>
<td>[25]</td>
</tr>
<tr>
<td>SnO$_2$/Vulcan carbon</td>
<td>1 M Na$_2$SO$_4$</td>
<td>112.14</td>
<td>[25]</td>
</tr>
<tr>
<td>SnO$_2$/CNT</td>
<td>2 M KCl</td>
<td>118.42</td>
<td>[26]</td>
</tr>
<tr>
<td>SnO$_2$/Graphene</td>
<td>1 M H$_2$SO$_4$</td>
<td>99.7</td>
<td>[27]</td>
</tr>
<tr>
<td>SnO$_2$/Carbon</td>
<td>1 M KOH</td>
<td>25.8</td>
<td>[28]</td>
</tr>
<tr>
<td>SnO$_2$/Polyaniline</td>
<td>1 M H$_2$SO$_4$</td>
<td>305.3</td>
<td>[29]</td>
</tr>
<tr>
<td>SnO$_2$/FWNT</td>
<td>1 M Na$_2$SO$_4$</td>
<td>220.5</td>
<td>this work</td>
</tr>
</tbody>
</table>

To evaluate the cycling stability of SnO$_2$/FWNT composites, a CV test is performed at 2 mV/s for 1000 cycles. As shown in Figure 6, the Cs of SnO$_2$/FWNT composites decreased from 220.5 F/g to 197.6 F/g after 1000 cycles. The specific capacitance retention rate is 89.57%, demonstrating a excellent long-term cycling stability. The slight loss of the Cs can be attributed to the dissolution of SnO$_2$ in the electrolyte during a continuous charge–discharge process.

To demonstrate the superiority of the SnO$_2$/FWNT composites, a series SnO$_2$-based composites and corresponding Cs is listed in the Table 1. The SnO$_2$/FWNT composites in this work have a much higher Cs than the reported references [23-27]. Among these SnO$_2$-based electrode materials, the good capacitance obtained in this work can be attributed to two aspects: (1) well-dispersed FWNTs not only can provide extra double-layer capacitance, but also can serve as mechanical supporter and conductive network. (2) The in-situ growth of SnO$_2$ can not only prevent the aggregation of FWNTs, but also leads to the formation of uniform and highly-dispersed SnO$_2$ particles on FWNTs. The excellent electrochemical performances are attributed to synergic effect between ultrafine SnO$_2$ nanoparticles and highly conductive FWNTs.
4. CONCLUSIONS

We fabricated SnO$_2$@FWNT composites via a facile hydrothermal and calcination process using FWNT and SnCl$_4$•H$_2$O as the raw materials. The capacitive performance of the SnO$_2$@FWNT composites was investigated in detail. The composites showed a specific capacitance of 220.5 F/g at a scan rate of 2 mV/s in Na$_2$SO$_4$ electrolyte and ~89.57% capacitance retention after 1000 cycles. The power density and energy density were 30.63 kW/kg and 512.79 W/kg, respectively. The results indicate that the SnO$_2$@FWNT composites have a good potential of in supercapacitors or the other energy devices.

ACKNOWLEDGEMENT
This work is funded by NSF of Jiangxi Province (20171BAB206016), Foundation of Jiangxi Educational Committee (GJJ160536).

References

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