Electrochemical properties of SnO$_2$/rGO nanocomposites

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Abstract
SnO$_2$ nanoparticles were deposited on reduced graphene oxide (rGO) to obtain SnO$_2$/rGO composites with high energy storage capacitance. For this purpose, graphite oxide (GO) was synthesized and hydrothermally treated in presence of Sn precursor. The quantity of GO was varied to tune the heterostructures’ composition and the particles size of the SnO$_2$.

The XRD and SEM analyses revealed that the GO was exfoliated, reduced and decorated with SnO$_2$ nanoparticles during the hydrothermal treatment. With the increase of GO quantity the SnO$_2$ particle size decreased from ~30 nm to ~14 nm. The Cyclic Voltammetry analysis showed that the pure rGO exhibited typical supercapacitor behavior. All the SnO$_2$/rGO composites exhibited significantly increased specific capacitance in comparison to the pure SnO$_2$. The SnO$_2$/rGO composites with the highest GO content showed capacitance ~ 200 F.g$^{-1}$ that was comparable to that of the pure rGO. The result was related to the small particles size of SnO$_2$ and their distribution between the rGO sheets.

Keywords: graphene, SnO$_2$, composites, supercapacitor

1. Introduction
Efficient energy storage in the form of batteries and supercapacitors is believed to solve urgent environmental issues. The n-type semiconductor SnO$_2$ is traditionally used as electrode material for Li$^+$ batteries (Zhao 2019). Also, the decoration of graphene oxide with small amounts of various metal oxides like RuO$_2$, NiO, MnO etc. has been reported to improve its specific capacitance due to the high conductivity, specific surface area and stability against restacking (Liu 2012).

In this study, the SnO$_2$ was coupled with rGO via one-step hydrothermal route aiming at increased capacitance of SnO$_2$ and the rGO.

2. Experimental
GO was prepared by oxidation of natural graphite via Hummers method. Water suspensions (35 mL) with 3, 12 and 120 mg/mL GO were sonicated for 5 min. Then, 3.6 mmol SnCl$_4$.H$_2$O and adequate quantity for 1M NaOH were added under stirring. The suspensions was transferred to an autoclave and treated for 16 h at 200 °C. The collected powders were washed and dried in air. The prepared pure SnO$_2$, rGO and composite materials

nominated as xGS, where x=4, 12 and 120, were characterized using XRD and SEM analyses. TG measurements were carried out in O$_2$ atmosphere. Cyclic Voltammetry (CV) and Impedance measurements were performed in 0.5M KCl employing three-electrode cell with glassy carbon, Pt and Ag/AgCl as working, counting and reference electrodes, respectively.

3. Results and Discussion
The XRD diagrams (Figure 1) revealed the successful synthesis of SnO$_2$ as well as reduction of GO to rGO. The intensity of the SnO$_2$ diffraction peaks decreased with increase of the GO content and for the 120G/S composite SnO$_2$ was not detected.

![Figure 1. XRD patterns of the synthesized materials](image)

The size of its crystallites calculated using Scherrer’s equation decreased from ~35 nm to ~14 nm (Table 1). The mass fraction of SnO$_2$ decreased gradually as well. The presence of small amount of SnO$_2$ in sample 120G/S not detected by XRD, was revealed by the TG analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SnO$_2$</th>
<th>4G/S</th>
<th>12G/S</th>
<th>120G/S</th>
<th>rGO</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS, nm</td>
<td>34.7</td>
<td>16.1</td>
<td>13.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NF, %</td>
<td>100</td>
<td>83.67</td>
<td>66.86</td>
<td>4.94</td>
<td>-</td>
</tr>
<tr>
<td>C$_{CV}$ F.g$^{-1}$</td>
<td>1.5</td>
<td>12.6</td>
<td>162.2</td>
<td>185.9</td>
<td>166.5</td>
</tr>
<tr>
<td>$C_Z$, F.g$^{-1}$</td>
<td>0.31</td>
<td>7.5</td>
<td>170.8</td>
<td>217.9</td>
<td>147.4</td>
</tr>
</tbody>
</table>

Table 1. SnO$_2$ crystallite size (CS) and mass fraction (MF) and the specific capacitance values calculated from CV (C$_{CV}$) and Impedance (C$_Z$) data.
The SEM images of the pure and composite SnO$_2$/rGO materials (Figure 2) revealed typical SnO$_2$ crystals and detached rGO layers. The morphology of the composites decreasing is in accordance with the XRD results with quantity and particle size of the SnO$_2$ component. For the 120G/S composite SnO$_2$ particles were not observed.

![SEM images](image)

**Figure 2.** SEM images of the pure SnO$_2$ and rGO as well as the composites with different SnO$_2$/rGO ratios

The electrochemical analysis showed that the capacitance of SnO$_2$ significantly increased after coupling with rGO. The specific capacitance was calculated on the base of the CV and Impedance (Figure 3) measurements.

![CV curves and Nyquist plots](image)

**Figure 3.** CV curves measured at scan rate 0.1 V.s$^{-1}$ (a) and Nyquist plots in frequency range 0.1 Hz – 100 kHz (b)

Best results were obtained for the composite with the highest rGO content. The $C_{CV}$ and $C_z$ capacitance values of the 120G/SnO$_2$ were comparable and slightly higher than those of the pure rGO.

### 4. Conclusions

SnO$_2$, rGO and their composites were prepared by simultaneous synthesis of SnO$_2$ and GtO reduction via one-step hydrothermal process. The increase of the GtO amount led not only to decrease of the of the SnO$_2$ mass fraction in the composites from ~84 to ~5%, but also to decrease of the crystallite size from ~35 to ~14 nm. The electrochemical analysis revealed that the capacitance of the SnO$_2$ was significantly increased when coupled with reduced graphene oxide. The composite with the highest rGO content exhibited specific capacitance ~ 200 F.g$^{-1}$ comparable with the capacitance of the pure rGO. The outcome was related to the small particle size of the SnO$_2$ and its distribution on the rGO sheets.

### References


### Acknowledgements

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