Electronic Supplementary Information

In-situ graft carbon on sawteeth-like SiC supported Ni for high-performance supercapacitor electrodes

Song Xie, Xiao-Ning Guo, Guo-Qiang Jin, Xi-Li Tong, Ying-Yong Wang and Xiang-Yun Guo

a State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Taiyuan 030001, PR China

b University of Chinese Academy of Sciences, Beijing 100039, PR China

* Corresponding author. Tel.: +86 351 4065282; fax: +86 351 4050320.

Email address: xyguo@sxicc.ac.cn (X-Y. Guo).
Experimental

Preparation

The sawtooth-like SiC (Figure S1) used in this work was purchased from Taiyuan Siconano Co. Ltd., which was prepared by a modified sol-gel and carbothermal reduction method.\textsuperscript{1, 2} For preparation of the C-Ni-SiC composite, 1 g of SiC was dispersed into 60 mL of 0.05 mol L\textsuperscript{-1} Ni(NO\textsubscript{3})\textsubscript{2} solution under stirring, then 0.73 g of cetyltrimethyl ammonium bromide and 0.6 g of urea were added into the suspension. After stirring for 1 hour, the suspension was transferred to a Teflon-lined stainless steel autoclave of 80 ml capacity and then heated at a temperature of 150 °C for 12 h. After natural cooling the autoclave to room temperature, a solid sample was collected by centrifugation. The sample was dried in a drying oven at 100 °C for 10 h, and then calcined in a muffle furnace at 450 °C for 4 h to obtain NiO/SiC composite. In order to graft the carbon, the NiO/SiC composite was placed in a quartz tube and heated to 700 °C at a rate of 5 °C min\textsuperscript{-1}, under a methane flow of 60 sccm. The reaction time was 3 h.

Characterization

The crystalline phases of the composites were analyzed by X-Ray diffraction (XRD) with Cu Kα radiation (Model D/max-RB, Rigaku, Japan). Their morphologies were observed by field emission scanning electron microscope (FE-SEM, Model JSM-7001F, Japan) operating at an accelerating voltage of 10 kV, and by a high-resolution transmission electron microscope (HRTEM, Model JEM-2100, Japan) operating at an accelerating voltage of 200 kV. The Ni content of the samples was measured by inductively coupled plasma optical emission spectrometer (ICP-OES, Thermo iCAP 6300, America). Thermogravimetric (TG) results were obtained by a thermal analysis system (Model STA 409 PC, Netzsch, Germany) using ca. 5.0 mg of samples and a heating rate of 10 °C min\textsuperscript{-1} in air. Electrochemical experiments were performed on a CHI 832 electrochemical workstation (Chenhua, China) at room temperature. The working electrode was prepared by pressing 10 mg of C-Ni-SiC sample (5% PVDF as binder) on 1 cm×1 cm Ni foam. Before each experiment, the electrodes were activated via CV at a scan rate of 50 mv s\textsuperscript{-1} from -0.4 to 0.6 V (Ni+2OH\textsuperscript{-} → Ni(OH)\textsubscript{2} \textsuperscript{3+})
The specific capacitance (SC) is calculated by the following equation:

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

where $I$ denotes the discharge current (A), $t$ is the discharge time (s), and $\Delta V$ is the discharging potential range (V), $m$ is the mass of active material (g). According to the ICP analysis, the nickel content in NiO/SiC is 11.71%. The ratio of Ni:C:SiC in C-Ni-SiC is 7.3: 39.5: 53.2, i.e. there is 0.73 mg nickel in 10 mg C-Ni-SiC, the equivalent of 1.15 mg of Ni(OH)$_2$. From the TG result (Figure S2), the carbon content in C-Ni-SiC composite is about 33.7%. This result is smaller than the ICP analysis due to the oxidation of Ni to NiO and the generation of SiO$_2$ in SiC surface.

Figure S1. The TEM images of sawtooth-like SiC.

Figure S2. TG result of the C-Ni-SiC composite.
Figure S3. The TEM (A, B, C) and SEM (D) images of the C-Ni-SiC composite.

Figure S4. Cyclic voltammogram of NiO/SiC sample at a scan rate of 5 mV s⁻¹.
Figure S5. The TEM image of C-Ni-SiC after 2500 charge/discharge cycles.

Figure S6. Charge/discharge curves of NiO/SiC, SiC and nickel foam samples at 10 mA cm$^{-2}$.

Excluding the SC arising from nickel foam, the SC of NiO/SiC is about 10.9 F g$^{-1}$ (calculated by the mass of NiO, about 1.49 mg in 10 mg NiO/SiC), the SC of SiC is 0.5 F g$^{-1}$. The low capacitance NiO/SiC can be attributed to the low conductivity of the sample. It is noteworthy that we did not add any extra conductive agent (carbon or acetylene black) in our samples.
Figure S7. Nyquist plot of C-Ni-SiC electrode. Inset: equivalent circuit diagram.

Electrochemical impedance spectroscopy (EIS) was carried out at open circuit potential with an ac perturbation of 5 mV in the frequency range of 100 kHz–0.01 Hz. The EIS data can be fitted by an equivalent circuit consisting of a bulk solution resistance $R_s$, a charge-transfer resistance $R_{ct}$, a Warburg impedance $W$, a double layer capacitor $C_{dl}$ and a Faradaic pseudocapacitor $C_F$. The bulk solution resistance $R_s$ and charge-transfer resistance $R_{ct}$ can be obtained from the Nyquist plot, where the high frequency semicircle intercepts the real axis at $R_s$ and $(R_s + R_{ct})$, respectively.\(^5,6\) As shown in Figure S7, both the $R_s$ and $R_{ct}$ are relatively small (0.58 $\Omega$ and 1.03 $\Omega$, respectively), indicating a good ion diffusion ability and charge-transfer ability of the C-Ni-SiC electrode.
Table S1. The cycle performances of the reported electrode materials and our sample.

<table>
<thead>
<tr>
<th>Electrode materials</th>
<th>Current density</th>
<th>Original capacitance</th>
<th>Cycles</th>
<th>Stability</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphene/MnO₂/CNT</td>
<td>1 mA cm⁻²</td>
<td>380 F g⁻¹</td>
<td>3000</td>
<td>96%</td>
<td>5</td>
</tr>
<tr>
<td>graphene/Ni²⁺/Al³⁺</td>
<td>10 mA cm⁻²</td>
<td>781 F g⁻¹</td>
<td>200</td>
<td>86%</td>
<td>6</td>
</tr>
<tr>
<td>NiCo₂O₄</td>
<td>25 mA cm⁻²</td>
<td>1065 F g⁻¹</td>
<td>3000</td>
<td>83%</td>
<td>7</td>
</tr>
<tr>
<td>NiO quasi-nanotubes</td>
<td>2 A g⁻¹</td>
<td>345 F g⁻¹</td>
<td>1500</td>
<td>91%</td>
<td>8</td>
</tr>
<tr>
<td>NiO/graphene</td>
<td>10 A g⁻¹</td>
<td>460 F g⁻¹</td>
<td>3000</td>
<td>82%</td>
<td>9</td>
</tr>
<tr>
<td>Ni(OH)₂ nanowall</td>
<td>30 mA cm⁻²</td>
<td>1160 F g⁻¹</td>
<td>500</td>
<td>96%</td>
<td>10</td>
</tr>
<tr>
<td>C-Ni/SiC</td>
<td>60 mA cm⁻² / 52 A g⁻¹</td>
<td>540 F g⁻¹</td>
<td>2500</td>
<td>96%</td>
<td>This work</td>
</tr>
</tbody>
</table>

Reference