Electronic Supplementary Information

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

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Experimental

Preparation

The sawteeth-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.^{1, 2} For preparation of the C-Ni-SiC composite, 1 g of SiC was dispersed into 60 mL of 0.05 mol L⁻¹ Ni(NO₃)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⁻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 K α 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 $^{\circ}$ C min⁻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 my s⁻¹ from -0.4 to 0.6 V (Ni+2OH⁻ \rightarrow Ni(OH)₂

 $+2e^{-}$).^{3,4} The specific capacitance (SC) is calculated by the follow equation:

$$C = It /(m\Delta V)$$

where *I* denotes the discharge current (A), *t* is the discharge time (s), and ΔV 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 SiO₂ in SiC surface.



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



Figure S2. TG result of the C-Ni-SiC composite.

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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.

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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.

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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 Ω and 1.03 Ω , respectively), indicating a good ion diffusion ability and charge-transfer ability of the C-Ni-SiC electrode. Electronic Supplementary Material (ESI) for Chemical Communications This journal is © The Royal Society of Chemistry 2013

Table S1. The cycle performances of the reported electrode materials and our sample.

Electrode materials	Current density	Original capacitance	Cycles	Stability	References
graphene/MnO ₂ /CNT	1 mA cm^{-2}	380 F g ⁻¹	3000	96%	5
graphene/Ni ²⁺ /Al ³⁺	10 mA cm^{-2}	781 F g ⁻¹	200	86%	6
NiCo ₂ O ₄	25 mA cm^{-2}	1065 F g^{-1}	3000	83%	7
NiO quasi-nanotubes	2 A g ⁻¹	345 F g ⁻¹	1500	91%	8
NiO/graphene	10 Ag^{-1}	460 F g ⁻¹	3000	82%	9
Ni(OH) ₂ nanowall	30 mA cm^{-2}	1160 F g ⁻¹	500	96%	10
C-Ni/SiC	$60 \text{ mA cm}^{-2} / 52 \text{A g}^{-1}$	540 F g ⁻¹	2500	96%	This work

Reference

- X. N. Guo, R. J. Shang, D. H. Wang, G. Q. Jin, X. Y. Guo and K. N. Tu, *Nanoscale Research Letters*, 2009, 5, 332.
- D. H. Wang, D. Xu, Q. Wang, Y. J. Hao, G. Q. Jin, X. Y. Guo and K. N. Tu, *Nanotechnology*, 2008, 19, 215602.
- 3. J. L. Weininger and M. W. Breiter, *Journal of The Electrochemical Society*, 1963, **110**, 484.
- 4. A. Seghiouer, J. Chevalet, A. Barhoun and F. Lantelme, *J Electroanal Chem*, 1998, **442**, 113.
- G. Yu, L. Hu, N. Liu, H. Wang, M. Vosgueritchian, Y. Yang, Y. Cui and Z. Bao, *Nano Letters*, 2011, 11, 4438.
- Z. Gao, J. Wang, Z. Li, W. Yang, B. Wang, M. Hou, Y. He, Q. Liu, T. Mann, P. Yang, M. Zhang and L. Liu, *Chemistry of Materials*, 2011, 23, 3509.
- 7. G. Zhang and X. W. D. Lou, *Advanced Materials*, 2013, **25**, 976.
- 8. S. Xiong, C. Yuan, X. Zhang and Y. Qian, *CrystEngComm*, 2011, **13**, 626.
- 9. M. S. Wu, Y. P. Lin, C. H. Lin and J. T. Lee, *Journal of Materials Chemistry*, 2012, 22, 2442.
- 10. Z. Lu, Z. Chang, W. Zhu and X. Sun, *Chemical Communications*, 2011, 47, 9651.