

Supporting Information

Si/Ge Nanocomposite Prepared by One-step Solid-state Metathesis Reaction and Its Enhanced Electrochemical Performance

Ning Lin^a, Liangbiao Wang^a, Jianbin Zhou^a, Jie Zhou^a, Ying Han^a, Yongchun Zhu^{*a},
Yitai Qian^{*a} and Changhe Cao^b

^a Hefei National Laboratory for Physical Science at Microscale and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, PR China.

^b Ningbo Veken Battery Company Inc., Ningbo, Zhejiang province, 315500, P.R. China.

*Corresponding author: Tel./Fax: (+) 86-551-63601589; ytqian@ustc.edu.cn (Y. T. Qian), ychzhu@ustc.edu.cn (Y. C. Zhu)

1 Experimental section

1.1 Materials synthesis

In a typical procedure, magnesium silicide (Mg_2Si) and germanium dioxide (GeO_2) with a molar ration of 1: 1 were mixed uniformly in an agate mortar, and subsequently loaded into a stainless steel autoclave. The above procedure was conducted in an Ar-filled glove box. Then, the autoclave was sealed and heated in an electric furnace to 500 °C for 10 h. After cooling to room temperature naturally, the solid product was collected and washed with diluted hydrochloric acid, distilled

water and ethanol several times. The residual oxides were removed by dilute ethanol-based HF solution. The molar ratio of Ge and Si is estimated to be about 1:0.78, determined by X-ray photoelectron emission microscopy.

1.2 Characterization

The structure and morphology of the product were characterized by X-ray diffractometer (Philips X' Pert Super diffract meter with Cu K α radiation ($\lambda=1.54178$ Å)), Raman spectrometer (Lab-RAM HR UV/VIS/NIR), X-ray photoelectron spectroscopy (XPS) (ESCA-Lab MKII X-ray photoelectron spectrometer), scanning electron microscopy (SEM, JEOL-JSM-6700F), and transmission electron microscopy (TEM, Hitachi H7650 and HRTEM, JEOL 2010).

1.3 Electrochemical Measurement

The electrochemical properties of as-prepared Si/Ge composite were evaluated through coin-type half cells (2016 R-type) which were assembled under an argon-filled glove box (H_2O , $O_2 < 1$ ppm). Metallic Li sheet was used as counter and reference electrode. 1 M $LiPF_6$ in a mixture of ethylene carbonate/dimethylcarbonate (EC/DMC; 1:1 by volume) was served as the electrolyte (Zhuhai Smoothway Electronic Materials Co., Ltd (china)). For preparing working electrode, the slurry mixed with as-prepared active material, carbon black (super P) and sodium alginate (SA) binder in a weight ratio of 6:2:2 in water solvent was pasted onto a Cu foil and then dried in a vacuum oven at 80 °C for 10 h. The active material density of each electrode was determined to be about 1.5 mg cm^{-2} . Galvanostatic measurements were conducted using a LAND-CT2001A instrument at

room temperature with a fixed voltage range of 0.005–1.5 V (vs. Li/Li⁺). Cyclic voltammetry (CV) was performed on electrochemistry workstation (CHI660D), with a scanning rate of 0.2 mV s⁻¹ at room temperature.

2 TEM image of the prepared Si/Ge nanocomposite.

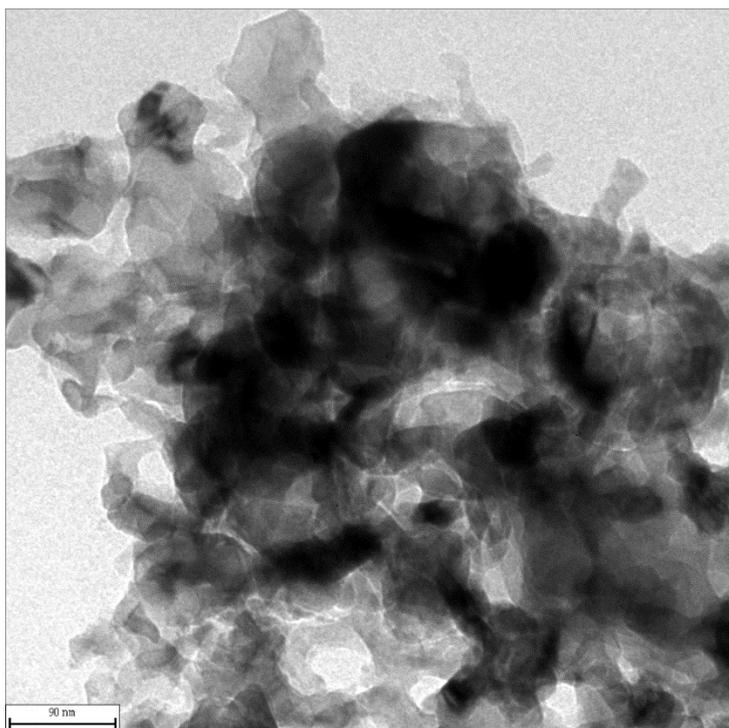


Figure S1. TEM image of Si/Ge nanocomposite.

3 Mapping image of the as-prepared Si/Ge nanocomposite.

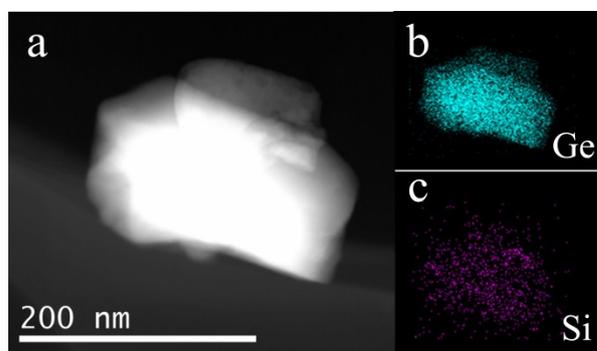


Figure S2. TEM image of Si/Ge nanocomposite and the corresponding distribution of Si and Ge elements.

4 The comparison of cycling stability between our work and most of previous report is exhibited in the below table.

Materials	Reversible capacity	Current density	Ref.
Si/Ge Double-Layered Nanotube Array	1314.6 mAh g ⁻¹ after 50 cycles	0.2 C	[8] ACS Nano 6 (2012) 303-309
Si/Ge core –shell nanoarrays	395 mAh cm ⁻² after 55 cycles	20 mA cm ⁻²	[9] J. Mater. Chem. A 1 (2013) 14344-14349
SiGe-based three-dimensional nanoporous electrodes	1311 mAh g ⁻¹ after 45 cycles	4 Ah g ⁻¹	[20] J. Power Sources 229 (2013) 185-189
NixSiy–SiGe core–shell nanowire arrays	around 1000 mAh g ⁻¹	2 A g ⁻¹	[22] RSC Adv., 2013, 3, 7713–7717
Si-Ge core-shell nanowires	974.5 mAh g ⁻¹ after 50 cycles	0.2 C	[12] Adv. Funct. Mater. 2014, 24, 1458–1464
Si–Ge core-shell Nanorod Arrays	~ 75 μ Ah cm ⁻² after 60 cycles	20 μA cm ⁻²	[25] ACS Appl. Mater. Interfaces 6 (2014) 5884-5890.
Si/Ge nanocomposite	2404.7 mAh g ⁻¹ after 60 cycles and 1260 mAh g ⁻¹ after 500 cycles	0.5 A g ⁻¹ and 5 A g ⁻¹	Our work

Table S1. Cycling stability of our work and most of previous reports.

5 Comparison of rate performance between our Si/Ge composite and previous reports is exhibited in the below table.

Materials	Reversible capacity	Current density	Ref.
Si/Ge Double-Layered Nanotube Array	2376, 2112, 1848, and 1610 mAh g ⁻¹	0.5C, 1C, 2C, and 3C	[8]ACS Nano 6 (2012) 303-309
Si/Ge core –shell nanoarrays	95, 80, 75, 60 μ Ah cm ⁻²	50, 100, 150, and 200 μ A cm ⁻²	[9]J. Mater. Chem. A 1 (2013) 14344-14349
SiGe-based three-dimensional nanoporous electrodes	1378, 1228, 1047, 769, 513 mAh g ⁻¹	4, 8, 16, 32, and 64 Ah g ⁻¹	[20]J. Power Sources 229 (2013) 185-189
NixSiy–SiGe core–shell nanowire arrays	1000, 880, 680, 480 mAh g ⁻¹	2, 4, 8, 16 A g ⁻¹	[22]RSC Adv., 2013, 3, 7713–7717
Si-Ge core-shell nanowires	1373, 1292.6, 1278, and 1211 mAh g ⁻¹	0.5, 1.0, 2.0, and 3.0 C	[12]Adv. Funct. Mater. 2014, 24, 1458–1464
Si–Ge core-shell Nanorod Arrays	~ 130, 108, 85, 70, 63 μ Ah cm ⁻²	20, 50, 100, 150, and 200 μ A cm ⁻²	[25]ACS Appl. Mater. Interfaces 6 (2014) 5884-5890.
Si/Ge nanocomposite	2422, 2186, 2143, 1986, 1803, 1365, 1099, 661, and 414 mAh g ⁻¹	0.5, 1.0, 1.5, 2, 3, 6, 9, 15, and 20 A g ⁻¹	Our work

Table S2. Rate performance of our Si/Ge composite and previous reports.

6 The AC electrochemical impedance spectroscopy data of the as-prepared Si/Ge composite and the commercial Si electrode.

Nyquist plots of the as-prepared Si/Ge composite and the commercial Si are measured and exhibited in below picture, also in the revised Supporting Information. The charge transfer impedance in the electrode/electrolyte interface can be estimated by the diameter of the semicircle in the high-frequency range. Remarkably, the bare Si electrode shows higher layer resistance than that of the as-prepared Si/Ge electrode. It is believed that the Ge component is helpful for improving the electron/ion transfer rate.

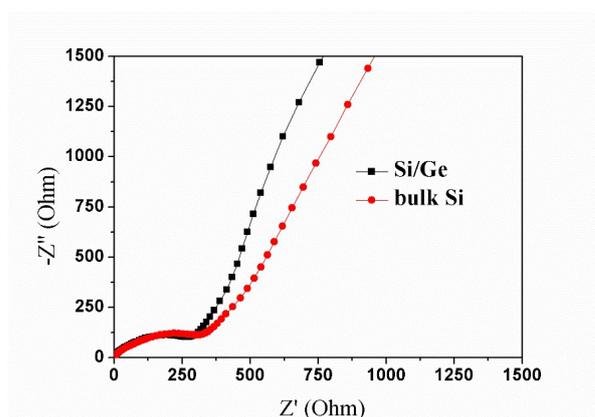


Figure S3. Nyquist plots of the as-prepared Si/Ge composite and the commercial micro-Si.