Synchronously synthesized Si@C composites through solvothermal oxidation of Mg$_2$Si as lithium ion battery anode

Experimental Sections

Prepare Si@C composites:

The method to synthesis Mg$_2$Si has been reported in our previous work.$^1$ 0.50 g Mg$_2$Si powder and 0.76 g acetone was added into a 20 ml stainless autoclave heated at 650 °C for 3 h. Then, the obtained powder was immersed in HCl solution for 1 h to dissolve MgO. Next, the solution was centrifuged at 4000 r/min and washed by water and ethanol three times. After that, dark brown powder was obtained and dried at 60 °C in a vacuum oven overnight. Similarly, 0.50 g Mg$_2$Si powder and 0.60 g ethanol was added into a 20 ml stainless autoclave heated at 650 °C for 3 h.

To compare with the as-synthesized Si@C composites through solvothermal method, Si@C composites were also prepared by ball milling commercial Si with glucose. In the typical method, 0.5 g commercial Si, 0.36 g glucose and 5 mL ethanol were added into an zirconia vial and ball milled at 500 r min$^{-1}$ for 10 h. After the ethanol evaporated, the mixture was heated at 2 °C min$^{-1}$ to 650 °C for 3 h under a flow of Ar in a quartz tube furnace.

Material Characterization:

The X-ray diffraction (XRD) was performed on a Philips X’ Pert Super diffract meter with Cu Kα radiation (λ=1.54178 Å). Scanning electron microscopy (SEM JEOL-JSM-6700F) and Transmission electron microsocopy (TEM, Hitachi H7650 and HRTEM, JEOL 2010) were used to characterize morphologies of the nanoporous Si. The Brunauer- Emmett-Teller (BET) surface area and Barrett-JoynerHalenda (BJH) pore distribution plots were tested on a Micromeritics ASAP 2020 accelerated surface area and porosimetry system. The carbon content was determined using an elemental analyzer (Vario ELIII) in oxygen atmosphere. Raman spectroscopy was carried out with a Renishaw 2000 Raman microscope with a laser wavelength of 633 nm. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Thermo Scientifi c c Kα spectrometer (monochromatic AlKα, 1486.6 eV).

Electrochemical measurements: The electrochemical performances of the nanoporous Si sample were tested with coin-type half cells (2016 Rtype). The cells were assembled in an Ar-filled glove box (H$_2$O and O$_2$ < 1 ppm). The working electrode was prepared by mixing the active material, super P carbon black and sodium alginate (SA) binder in a weight ratio of 60:20:20 in water solvent. The slurry was pasted onto a Cu foil and then dried in a vacuum oven at 80 °C for 12 h. The mass loading level of active materials in electrodes was around 0.7-1.0 mg cm$^{-2}$. Metallic Li sheet was used as counter electrode, and 1 M LiPF$_6$ in a mixture of ethylene carbonate/dimethylcarbonate (EC/DMC; 1:1 by Volume, Zhuhai SmoothwayElectronic Materials Co., Ltd (china) was used as electrolyte.
Galvanostatic measurements were tested using a LAND-CT2001A instrument at room temperature. The electrochemistry impedance spectroscopy (EIS) was tested with an electrochemical workstation (CHI 660E) by applying an alternating current voltage of 5 mV in the frequency from 100 KHz to 0.01 Hz.

Fig. S1. Raman spectrum of Si@C composites obtained from the reaction of acetone.
Fig. S2. SEM image of as-prepared Si@C composites obtained from the reaction of acetone.
Fig. S3. TEM image of the Si@C composites particle.
Fig. S4. EDS spectra of the Si@C composites.

The EDS result was a little higher than elemental analysis. Because the mapping substrate was coating with carbon film, the content of the carbon might be not exact. What’s more, the EDS data could only reflect the partial elements content. It could not reveal the elements content for the whole distribution, especially when the sample was not uniform. In our work, we give the elemental analysis results of the carbon content.
Fig. S5. (a) Nitrogen adsorption curves of the nanoporous Si, (b) the pore size distribution of the porous Si@C particles obtained from the reaction of acetone.
Fig. S6. (a) XRD pattern of the precursor; (b) XRD pattern of the Si@C composites; (c) and (d) Raman spectrum and TEM image of the as-synthesized Si@C composites of the reaction of Mg$_2$Si with ethanol.
The element analysis measurement reveals that the carbon content was about 18 wt. %. The XRD pattern and Raman spectrum reveal that the composites prepared by ball milling contain high crystalline Si and amorphous carbon. The TEM images show that on the surface of Si particles coated some disconnected carbon.
Fig. S8. XPS spectra of as-synthesized Si@C composites obtained from acetone and ethanol.
Figure S9. TEM images of the Si@C composites obtained from the reaction of acetone (a, b, c and d), obtained from the reaction of ethanol (e, f) after 350 cycles.

As indicated by the black arrow in Figure S4 b, the carbon coating can be clearly observed. However, the carbon coating of composites obtained from ethanol was damaged and the shape of the particles has been changed.
Figure S10. (a) TEM image of the composite after 100 cycles, (b) TEM image of the composite after 350 cycles.