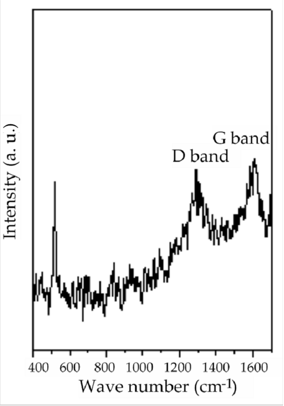
Experimental Details

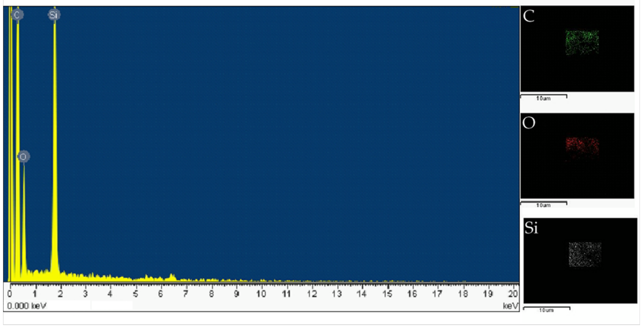
Preparation of Si@SiO$_2$@C nanocomposite: Li metal, Si powder (about 50 nm, Kaier, China) and glucose were used as starting materials in the following steps. Firstly, Si–Li composite was directly prepared by milling 0.5 g Li , 3.5 g Si powder and 10 mL acetone as a lubricant in a 100 mL stainless steel vial at 400 rpm for 4 h. The milling process was continued under Ar atmosphere in a planetary–type ball–mill with the ball–to–powder mass ratio of 20:1. The product was sintered at 400 °C for 2 h in a Muffle furnace. Then, the obtained material (0.5 g) was transferred to a clear and dense solution of pure glucose (5.6 g) dissolved in 20 mL of deionized water. The mixture was placed in a 30 mL Teflon–sealed autoclave and maintained at 180 °C in an oven for 3 h, since glucose is carbonized at 180 °C under hydrothermal conditions. The as–prepared product was centrifuged and washed with deionized water for at least five times and dried at 100 °C over night, and finally the powder was further annealed at 750 and 900 °C for 4 h in flowing argon. For comparison, Si@C composite was prepared via the same process except that pure Si powder was used in the hydrothermal treatment.

Sample Characterization: The as–prepared samples were characterized by XRD (Rigaku D/Max III diffractometer with Cu K$_\alpha$ radiation), scanning electron microscope (SEM, Hitachi S–3500N), EDS (JSM–6700), TEM (FEI Tecnai 20), TG–DTA (ZRY–2P), and Roman spectroscopy (RFS100–S) with 1064 nm laser excitation.

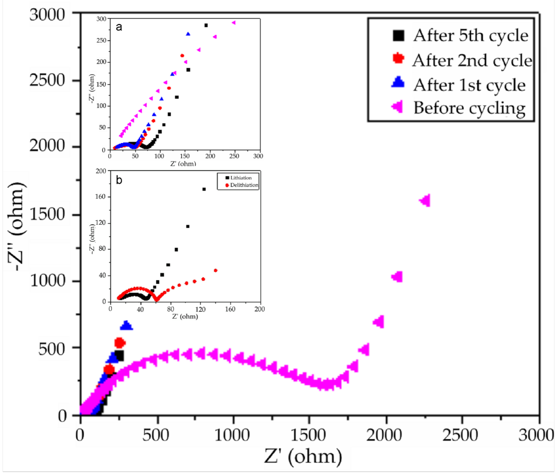
Electrochemical tests: The working electrodes were comprised of active material, acetylene black and polytetrafluoroethylene (PVDF) at the weight ratio of 15:3:2. Lithium metal was used as the counter and reference electrode. The electrolyte was 1M LiPF$_6$ dissolved in a 1:1:1 mixture of ethylene carbonate (EC), ethylene methyl carbonate (EMC), and dimethyl carbonate (DMC). The cells were assembled in a glove box filled with high–purity argon. Discharge/charge measurements of the cells were carried out at the current density of 50 and 200 mA g^{-1} between the potential range of 0.001–1.5 V (vs Li$^+$/Li) using a LAND–CT2001A instrument. EIS was taken using an IM6e electrochemical workstation at 25 °C with the frequency ranging from 10 kHz to 10 mHz and an AC signal of 5 mV in amplitude as the perturbation. The specific capacity was calculated according to the corresponding active material in each electrode, i.e., Si@SiO$_2$ for Si@SiO$_2$@C and Si for Si@C.



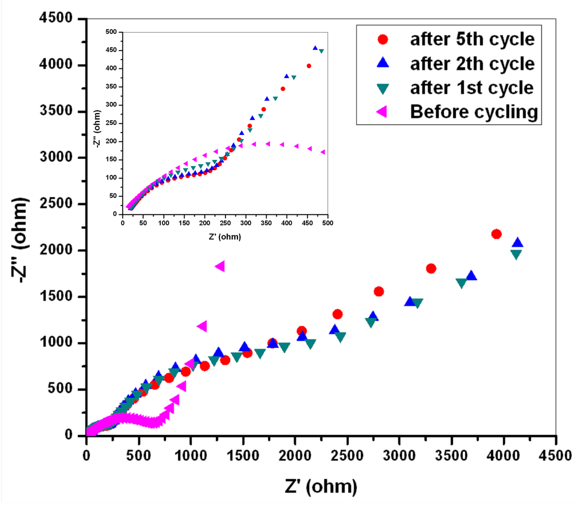
SI 1. Raman spectrum of Si@SiO$_2$@C composite.



SI 2. EDS phases showing homogenous distribution of C, O, and Si elements in the surface of Si@SiO$_2$@C nanoparticles.



SI 3. EIS of Si@SiO$_2$@C (a) before cycling and after the 1st, 2nd, and 5th cycle, (b) after the initial lithiation and delithiation process.



SI 4. EIS of the pure Si electrode showing great differences from Si@SiO$_2$@C, due to the coexistence of SiO$_2$ and carbon layer.