

Supporting Information

Synchronous synthesis of Si/Cu/C ternary nano-composite as Anode for Li Ion Batteries

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Experimental section

Material fabrication

In a typical experiment, the Si/Cu/C nanocomposite was synthesized through two steps. At first, magnesium silicide (Mg_2Si) is synthesized by reacting Mg with commercial micron-size Si at 700 °C in stainless steel autoclave for 48 h. Then, the obtained Mg_2Si and $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ with a molar ration of 4: 1 were mixed uniformly in an agate mortar, and subsequently loaded into a stainless steel autoclave. The above procedure was conducted in an N_2 -filled glove box. Then, the autoclave was sealed and heated in an electric furnace to 450 °C with a ramping rate of 5 °C min^{-1} 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. After dried in vacuum oven at 50 °C for 5 h, the final product is collected for further characterization.

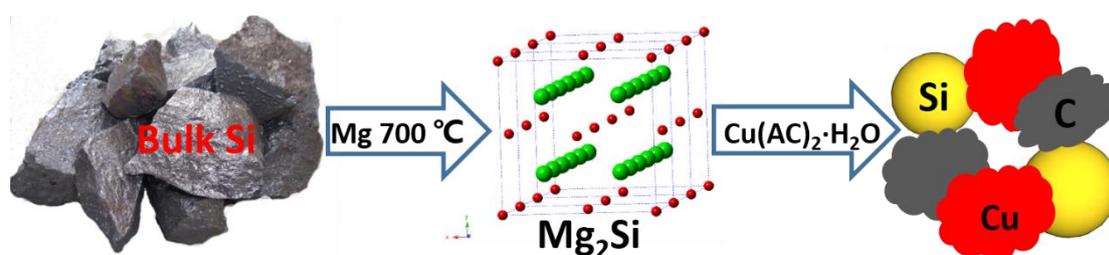
Characterization

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

Electrochemical Measurement

The electrochemical properties of the bulk Si and the as-prepared Si/Cu/Cnanocomposite were evaluated through coin-type half cells (2016 R-type)

which were assembled under an argon-filled glove box (H_2O , $\text{O}_2 < 1$ 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 1.0 mg cm^{-2} . Note that the specific capacity is calculated basing on the total weight of the Si/Cu/C composite. Galvanostatic measurements were conducted using a LAND-CT2001A instrument with a fixed voltage range of 0.005–1.5 V (vs. Li/Li^+) at room temperature. Cyclic voltammetry (CV) was performed on electrochemistry workstation (CHI660D), with a scanning rate of 0.1 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) was also measured with an electrochemical workstation (CHI660D) by applying an alternating current (AC) voltage of 5 mV in the frequency range from 100 kHz to 0.1 Hz.



Scheme S1. The schematic diagram concerning the converting process from bulk Si to nanosized Si/Cu/C ternary composite.

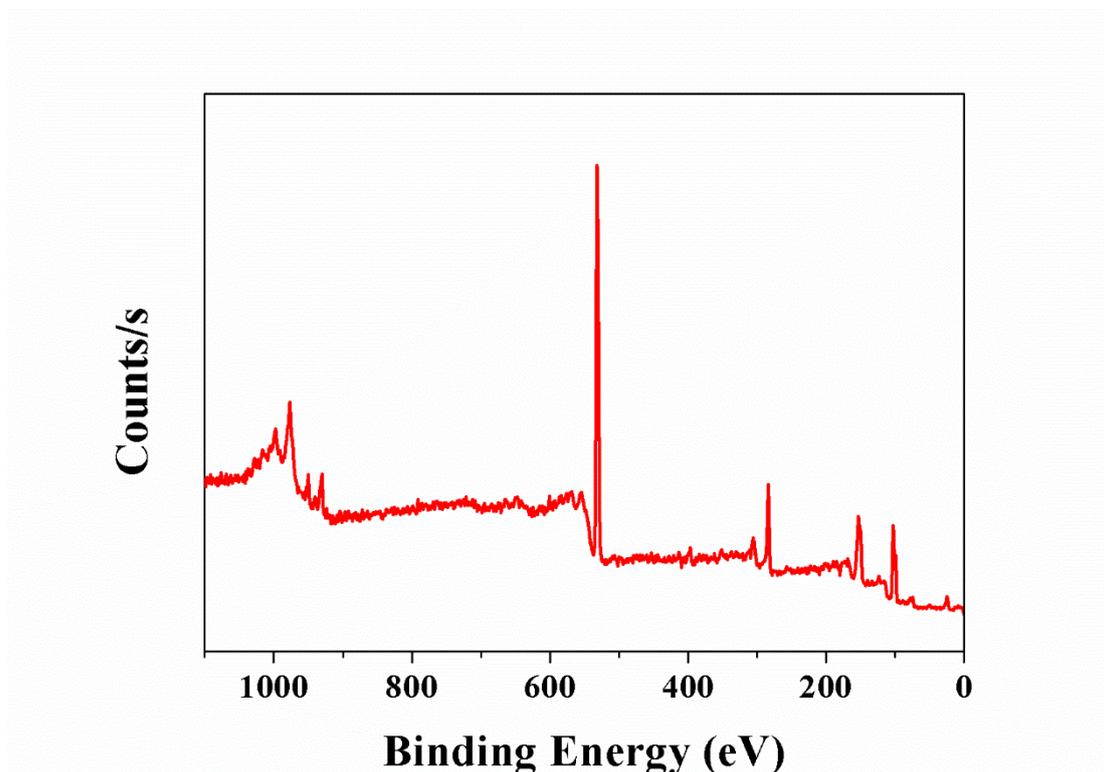


Figure S1. The XPS plots of the as-prepared Si/Cu/C nano-composite.

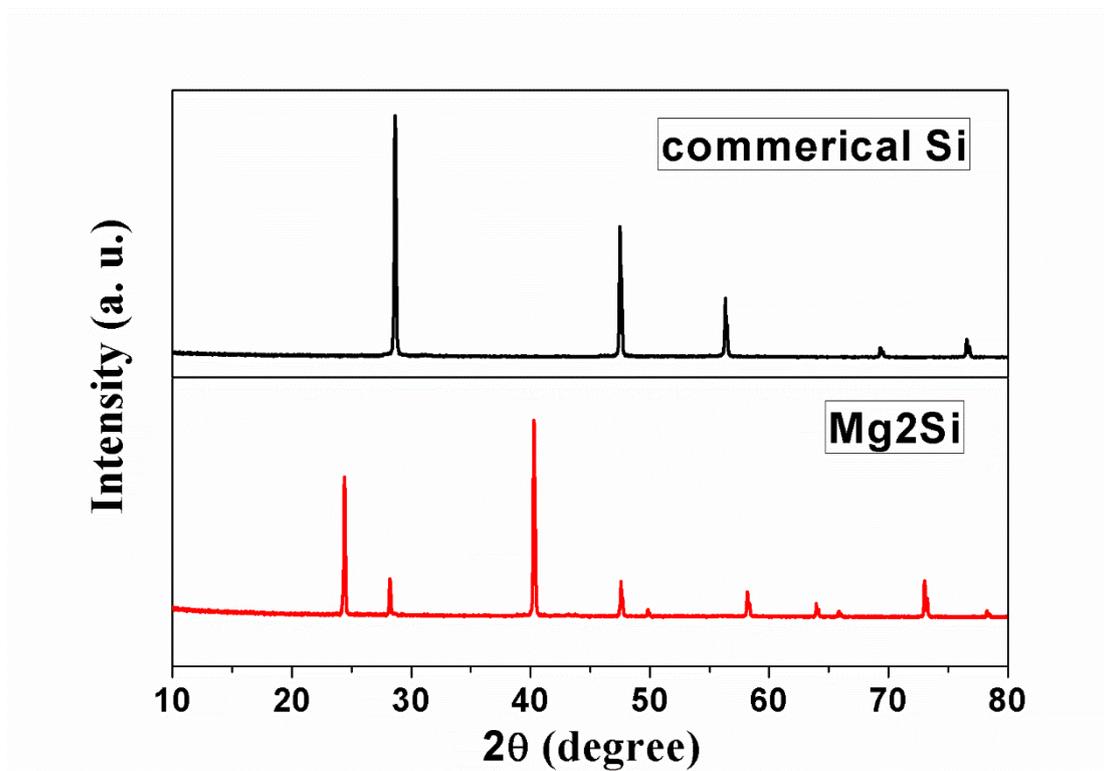


Figure S2. XRD patterns of the commercial micro-sized bulk Si and the pre-synthesized Mg₂Si.

EIS data analysis

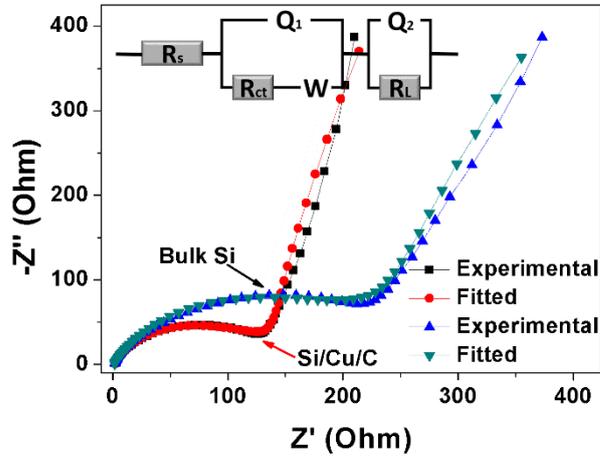


Figure 5. The experimental and fitted Nyquist plots of the bulk Si and the Si/Cu/C composite. The equivalent Randles circuit is shown in the inset.

To further understand the different reaction kinetics between Bulk Si and Si/Cu/C, the electrochemical impedance spectrum (EIS) is measured. Figure 5 shows the experimental and equivalent Nyquist plots of the Bulk Si and Si/Cu/C electrodes, the insert is the equivalent circuit used for fitting of the EIS plots. R_s (also known as the solution resistance) is the equivalent series resistance (ESR), which generally describes the resistance of the electrolyte combined with the internal resistance of the electrode. The R_{CT} corresponds to the charge transfer resistance in the electrode/electrolyte interface. Q_1 is the constant phase element (CPE) representing double layer capacitance, which occurs at interfaces between solids and ionic solutions due to separation of ionic and/or electronic charges. R_L is the leakage resistance which is placed in parallel with Q_2 . This is usually very high and can be ignored in the circuit. W is the Warburg element, which indicates the diffusion of ions into the electrode. The exact ion diffusion coefficient can be calculated by

$$D = \frac{1}{2} \left[\left(\frac{V_m}{AF\delta} \right) \left(\frac{dE}{dx} \right) \right]^2$$

where δ is the slope of the Warburg straight line (Ωs^{-1}), A (cm^2) is the effective contact area between the electrolyte and sample. V_m is the molar volume of active materials, F is the Faraday constant ($96486 C mol^{-1}$). As shown in Figure 5, the Warburg straight line of Si/Cu/C electrode displays higher slope than that of bulk Si. And the other parameters are supposed to be same. Therefore, Based on the above equation and fitted EIS data, it is reasonable to speculate that the Si/Cu/C electrode exhibits higher ion diffusion coefficient compared with bulk Si electrode.

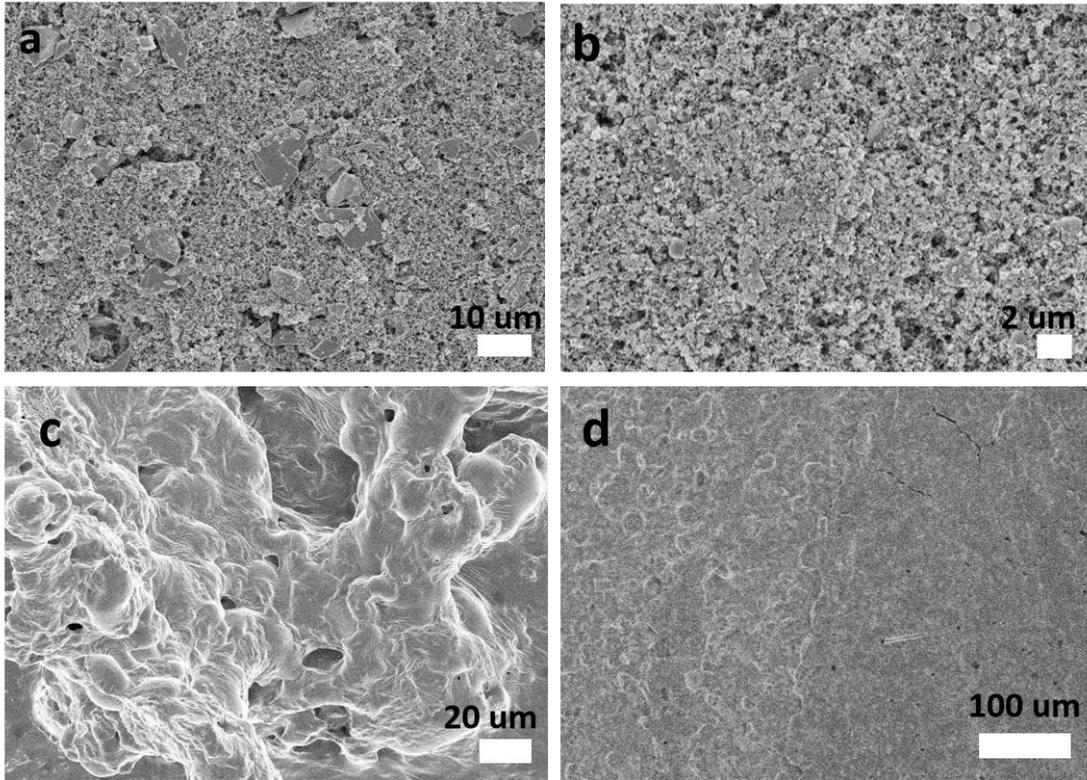


Figure S3. The morphology of the un-cycled (a) bulk Si and (b) Si/Cu/C composite, and after 10 cycles (c) bulk Si, (d) Si/Cu/C composite.