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Supporting Information

Cu_3Si@Si core-shell nanoparticles synthesized by a solid-state reaction and their performance as anode materials for lithium ion batteries

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Experimental methods

Preparation of samples. Si particles with diameters below 200 nm are purchased from Shanghai ST-Nano science and technology Co. Ltd. 0.5 g of Si powder and 0.3 g of CuCl were mixed with ball mailing for 2 h under argon condition. After that, the mixture was annealed in tube furnace at 600 ˚C for 10 h with a heating rate of 10 ˚C min^{-1} under argon condition. And then Sample-10 h with core-shell structure was obtained. Sample-20 h, Sample-6 h and Sample-1 h can be obtained when an annealing time of 20 h, 6 h and 1 h was applied with the same other experiment conditions, respectively. The precipitates were collected and dispersed in slightly excess dilute nitric acid solution and stirred for 2 h in a beaker. The final samples were washed with distilled water and ethanol for 3 times and then dried in vacuum oven at 50 ˚C for 10 h, and then Sample-6 h-AT and Sample-10 h-AT were obtained. As examined by XRF, the Cu content in Sample-6 h-AT, Sample-10 h-AT and Sample-20 h-AT is 9.6, 17.3 and 17.1 wt%, respectively. For the contrast experiment, 0.5 g of Si powder and 0.2 g of Cu powder were mixed with ball mailing for 2 h and annealed at 600 ˚C for 10 h under argon condition.

Material characterization. The crystal line phase, morphology and composition of products were characterized by X-ray diffraction (XRD, Philips, X'pert X-ray diffractometer with Cu *K*a, λ=1.54182 Å), transmission electron microscopy (TEM, Hitachi H7650), High resolution transmission electron microscopy (HRTEM, JEM-ARM 200F), energy dispersive x-ray spectroscopy (EDX, JEM-ARM 200F) and X-ray fluorescence (XRF, XRF-1800).

Electrochemical characterization. Because Sample-10 h-AT and Sample-20 h-AT exhibit almost the same morphology and the Cu content for Cu_3Si, we chose Sample-10 h-AT to be measured for the comparison of electrochemical performance with Si and Sample-6 h-AT. Electrochemical properties of the samples were measured by using half cells (2016 R-type). For preparing working electrode, the active materials, acetylene black and carboxymethylcellulose sodium (CMC-Na) with a weight ratio of 70: 20: 10 were homogeneously mixed with water. The slurry was coated on a copper foil and dried at 80 ˚C for 12 h in a vacuum oven. The mass of the

active materials was in the range of 1-2 mg cm^{-2}. To assemble the half cells, lithium foil was used as the counter electrode, a solution of 1.0 M $LiPF_6$ in ethylene carbonate (EC) and diethyl carbonate (DEC) (1 : 1 by volume ratio) was used as the electrolyte, and Celgard 2400 was used as the separator. Cyclic voltammogram (CV) was carried on electrochemical workstation (CHI660D) with a scanning rate of 0.1 mV s^{-1} with a voltage window of 0.01-1.5 V. Galvanostatic charge–discharge was conducted on a battery tester (LANDCT2001A) at different current densities in the voltage between 0.01 V and 1.5 V (vs. Li/Li^+). The electrochemical impedance spectroscopy (EIS) was conducted on a CHI660D electrochemical workstation with an alternating current (AC) voltage of 0.005 V in the frequency range from 100 KHz to 0.1 Hz.

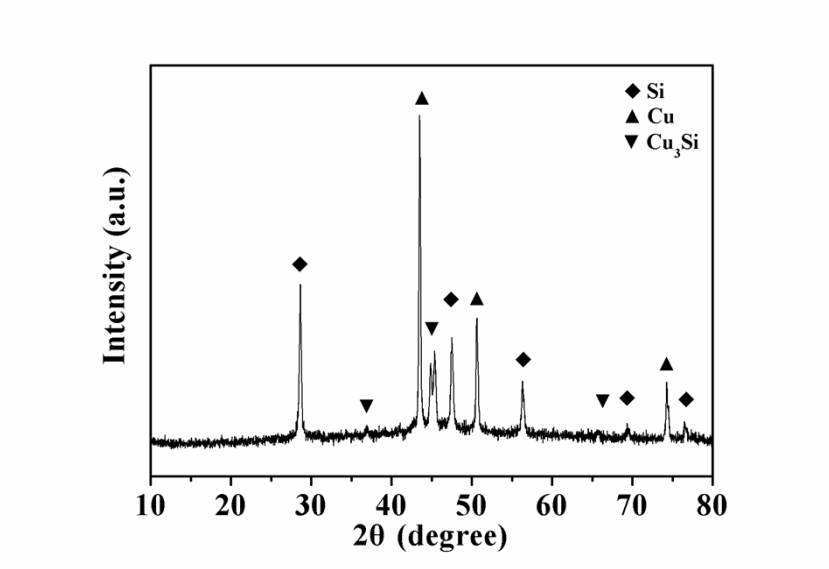

Fig. S1 XRD pattern of Sample-1 h.

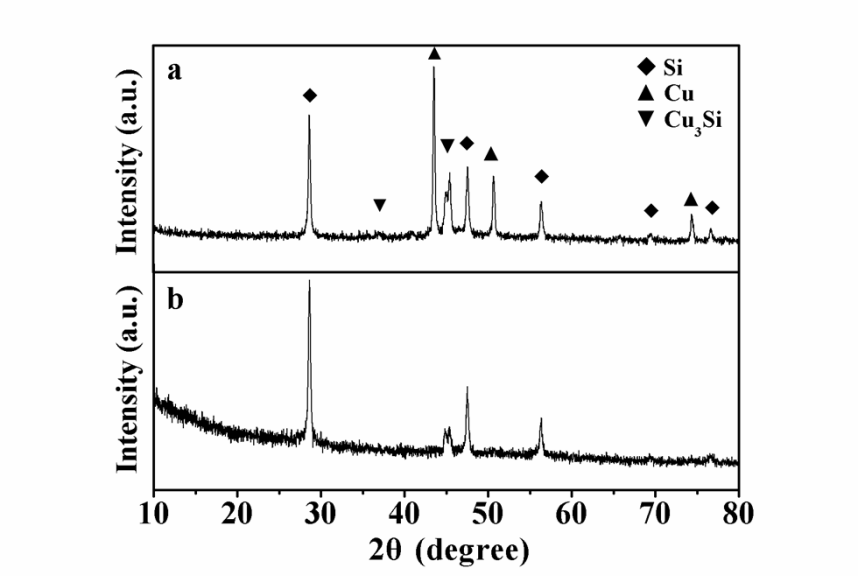

Fig. S2 XRD patterns of Sample-6 h (a) and Sample-6 h-AT (b).

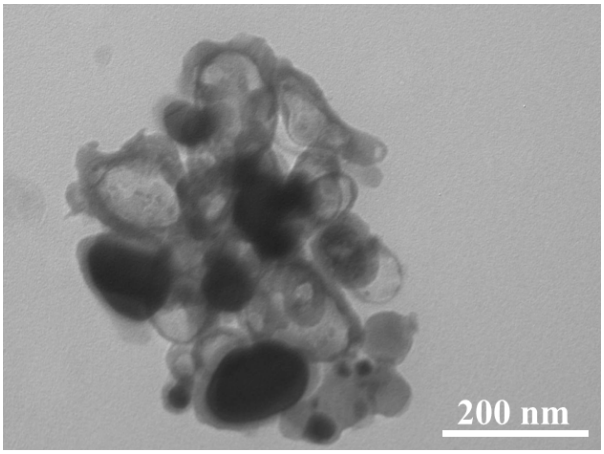

Fig. S3 TEM image of Sample-6 h-AT.

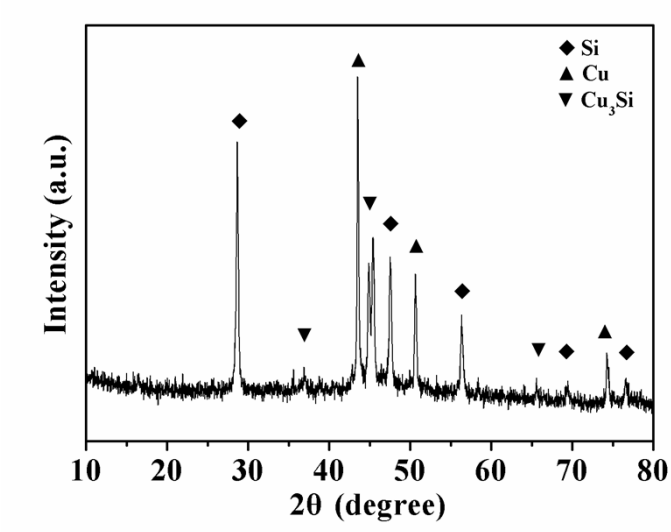

Fig. S4 XRD pattern of Sample-10 h before treated with dilute HNO_3.

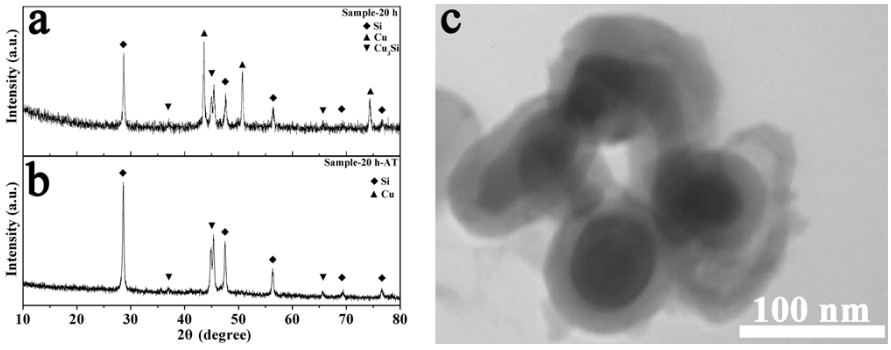

Fig. S5 XRD patterns of Sample-20 h (a) and Sample-20 h-AT (b), and TEM image of Sample-20 h-AT (c).(a), (b) and (c) showed no much difference from these of Sample-10 h and Sample-10 h-AT.

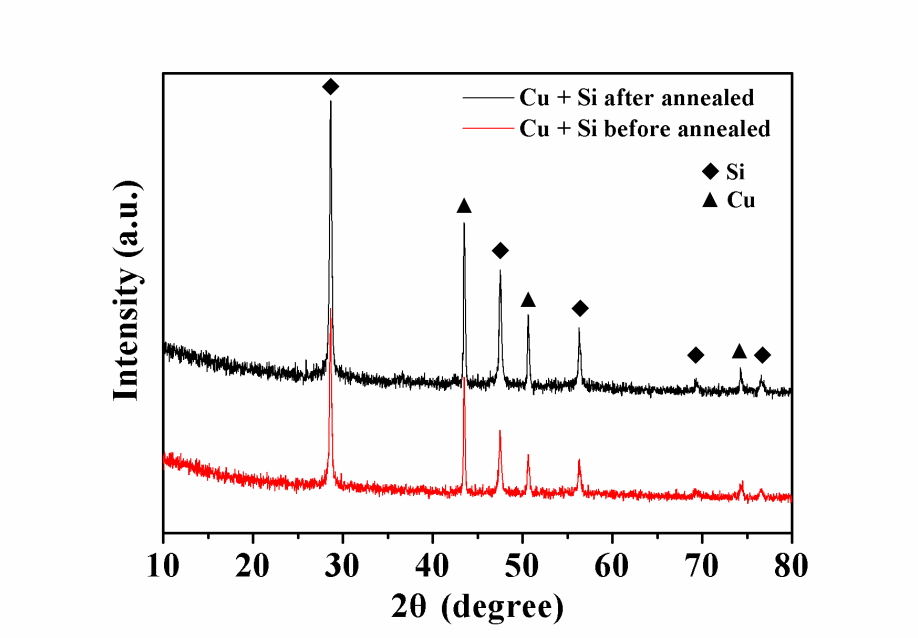

Fig. S6 XRD pattern of sample from contrast experiment. 0.5g of Si powder and 0.2 of Cu powder were mixed with ball-melling and annealed at 600 ^{o}C for 10 h and no Cu_3Si can be detected by XRD.

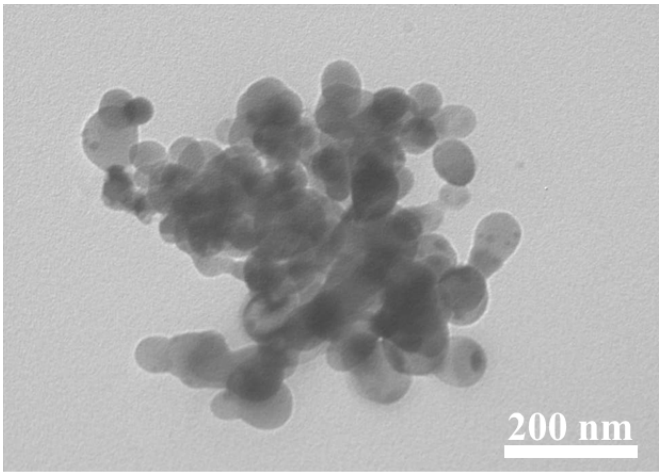

Fig. S7 TEM image of samples from the contrast experiment. No core-shell structure can be observed.

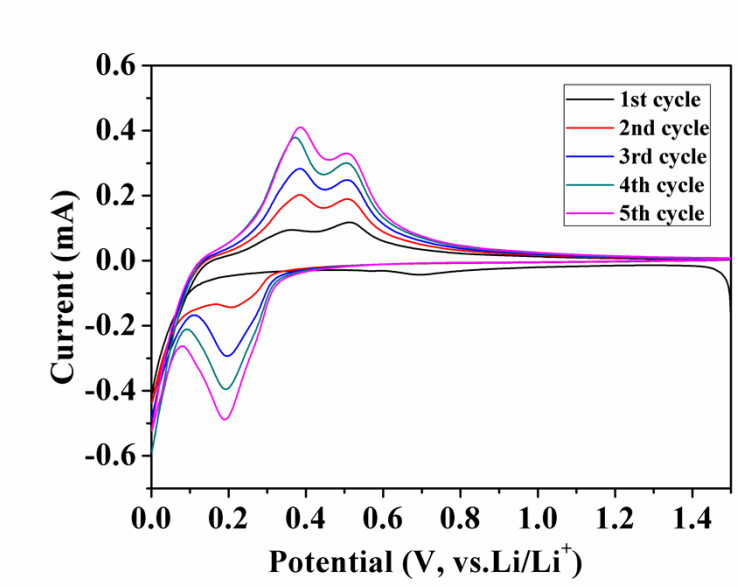

Fig. S8 Cyclic voltammetry curves of the Si electrode of 1st-5th cycles.

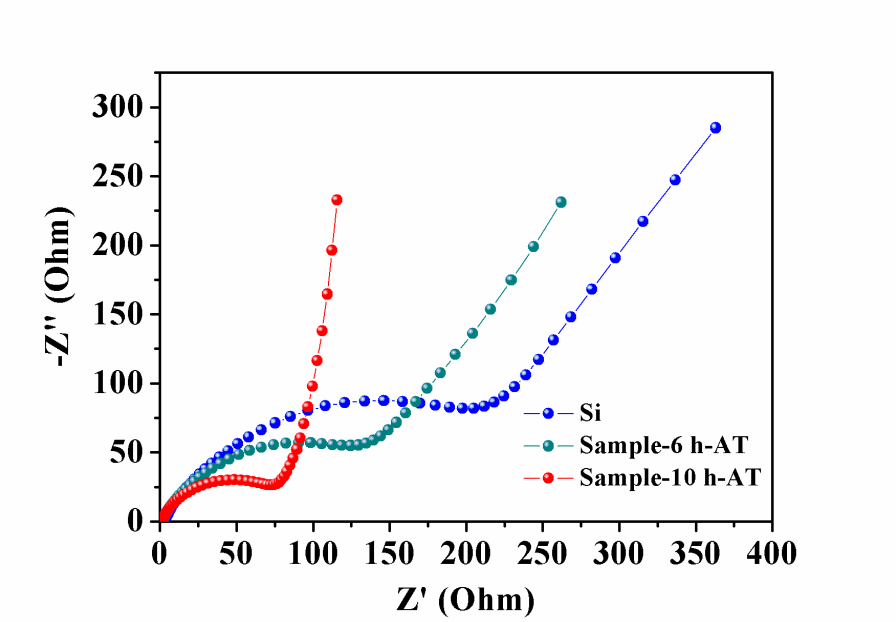

Fig. S9 Electrochemical impedance spectra of electrodes made of Si, Sample-6 h-AT and Sample-10 h-AT.

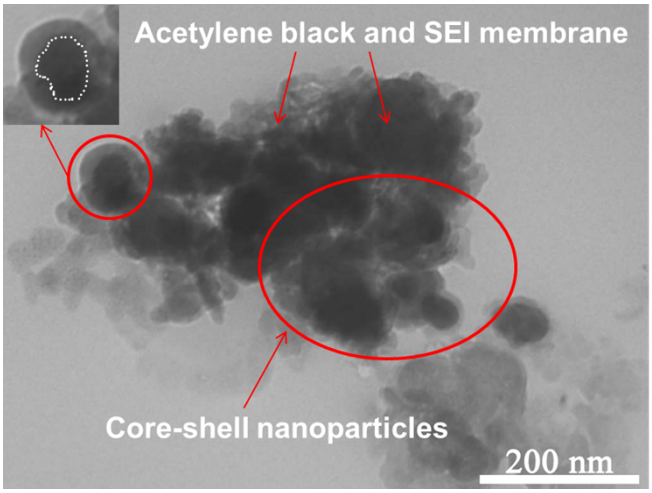

Fig. S10 SEM image of Sample-10 h-AT after 400 cycles at the current density of 2 A g^{-1}.