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Supporting Information

Critical SiO_x layer on the Si porous structures to construct high-reversible anode materials for lithium-ion batteries

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Experimental Section

Chemicals and Materials. Commercial Mg_2Si (purity >97%), purchased from the corporation of Zhejiang YHL New Energy Material Co., Ltd. of China. HCl and HF were purchased from Aladdin. All the chemicals and materials were used as received.

Preparation of the porous Si/SiOx microparticles. The porous Si/SiOx microparticles were synthesized via an annealing and acid washing processes similar to our previous paper with some modification.[17] The commercial Mg_2Si (purity >97%) was used as the starting material to prepare porous Si/SiO_x microparticles. Briefly, 0.5 g Mg_2Si powder was transferred into a corundum boat and heated to 700 °C at the heating rate of 5 °C min^{-1} under a mix gas (Ar/O_2) atmosphere, for 8 h in a rotary furnace (XY-1700S, XINYOO, Nan Yang Xin YU Electric Components CO., Ltd. of China). Meanwhile, different heat treatment temperature and atmosphere conditions were applied to introduce different thickness of SiOx layer on the surface of porous Si as follows: annealing at 650°C for 8 h in (Ar : O_2=9:1) atmosphere led to the formation of a ~4 nm SiOx coating layer (oxygen content of ~9%), while annealing at 700°C for 10 h in (Ar : O_2=4:1) atmosphere led to the formation of a ~9 nm SiOx coating layer (oxygen content of ~16%), and at 850°C for 12 h in (Ar : O_2=4:1) atmosphere led to the partial oxidation of porous Si (oxygen content of ~35%). After cooling down to room temperature, the powder was washed with HCl (0.2 mol L^{-1}) to remove the MgO. To achieve the SiOx-free sample, some of the final product was treated with HF (1 vol %) to remove the SiOx, that is the sample with oxygen content of 2%. Final product was collected by centrifuged in deionized water and alcohol for three times, and then vacuum dried at room temperature. All the annealed samples were coated with amorphous carbon via thermal decomposition of acetylene gas at 600 °C for 1 h in the tube furnace (SK-GO6123K, TIANJING ZHONGHUAN Experiment Electric Furnace Co., Ltd. of China). For comparison, ball-milled silicon metal powder was annealed in the same procedure to introduce the SiOx coating layer.

Morphological and structural characterizations. The crystal structures of the final products were identified by a high power X-ray diffraction (XRD) using a Rigaku D/max-ga X-ray diffractometer with graphite monochromatized Cu Kα radiation (λ = 1.54 Å). The structure and morphology of the products were observed using scanning electron microscopy (FESEM HITACH S4800) and transmission electron microscopy (TEM, PHILIPS F200). The X-ray photoelectron spectroscopy (XPS) test was performed using a Thermo ESCALAB 250Xi spectrometer with a monochromatic Al Kα line (1486.6 eV). Thermogravimetric analysis (TGA) was used to analysis the carbon content of the samples on SDT Q600 V8.2 Bulid 100: the samples were heated from 20°C to 800 °C at the heating rate of 5 °C min^{-1} under air. The Raman spectra were recorded with a HR800 Raman spectrometer using the 532 nm line of an Ar ion laser operated at 10 mW.

Electrochemical Measurement. The electrochemical properties were tested using a coin-type half cell composed of the porous Si/SiO_x structure as the working electrode and lithium metal as the counter electrode. In a typical synthesis of porous Si/SiO_x structure electrode, the active material was mixed with the binder (Styrene-butadiene rubber, SBR / Carboxymethylcellulose sodium, CMC) and conductive materials (acetylene black, ATB) in a weight ratio of 7: 2: 1 in the de-ionized water. Then, the slurry was spin-coated on the copper foils. The mass loading of the slurry on each copper foils (15mm) is about 1.5-2.5 mg. After dried in a conventional oven at 90 °C for 24 h, the porous Si/SiO_x structure electrodes were assembled in a glovebox (Mbraun, Labstar, Germany). The electrolyte solution consisting of 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1 in volume) was used. Electrochemical impedance spectroscopic (EIS) measurement was obtained by applying an AC voltage of 5 mV in the frequency range of 100 kHz to 0.01 Hz

using CHI660D Shanghai Chenhua, and the test temperature was kept at 25°C. The Galvanostatic discharge-charge was tested using a Land CT2001A system at a current density of 0.4 Ag^{-1} in the potential range of 0.001~1.5 V.

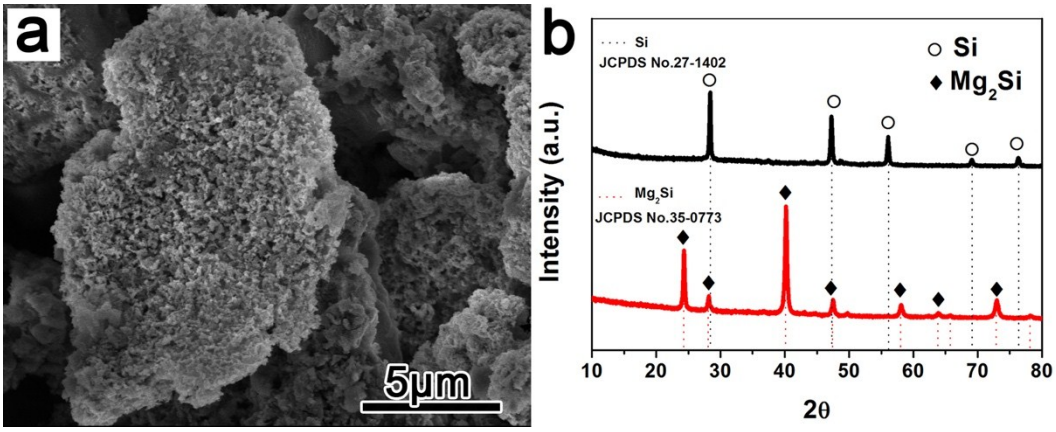

Fig. S1 (a) SEM image of the synthesized porous Si/SiOx microparticles; (b) evolution of the XRD patterns from the raw Mg_2Si materials (◆) to the porous Si (○) as well as the standard diffraction peaks of Si and Mg_2Si.

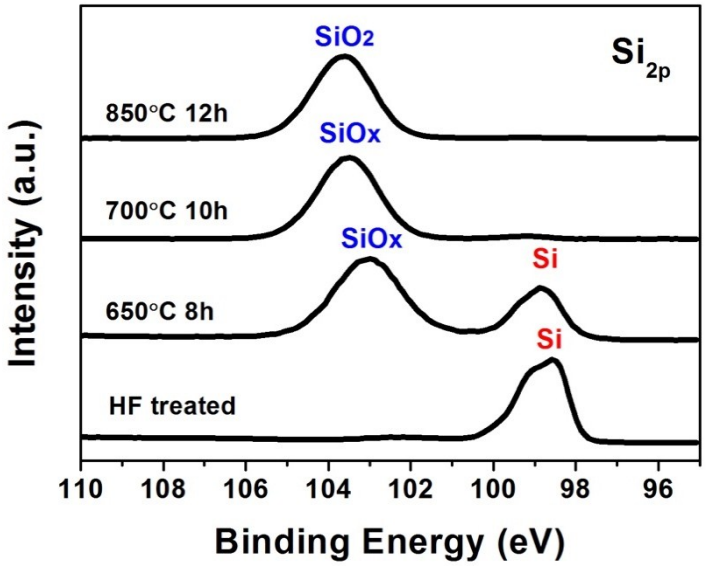

Fig. S2 2p Si XPS spectra of the samples after annealing with different conditions.

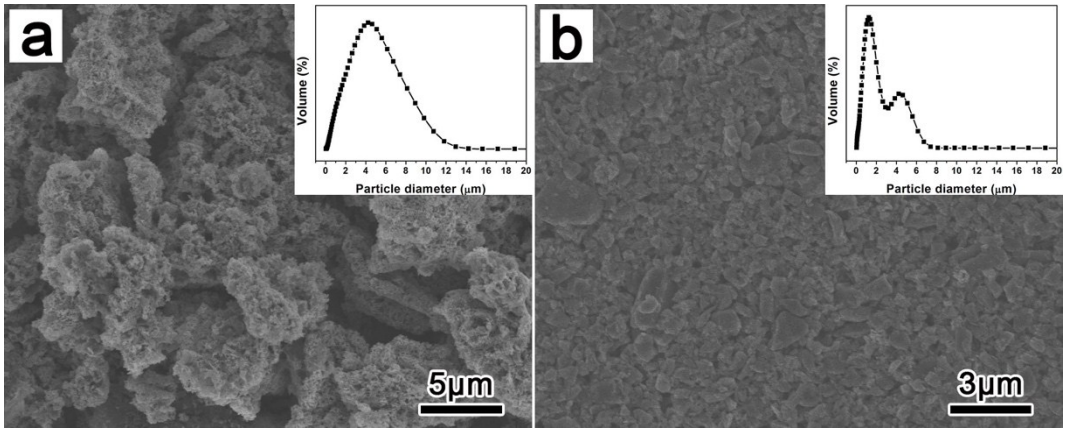

Fig. S3 SEM image and particle size distribution of (a) ball-milled porous Si/SiO_x microparticles with oxygen content of ~16%; (b) the ball-milled silicon metal powder after oxidation (O-SMP).

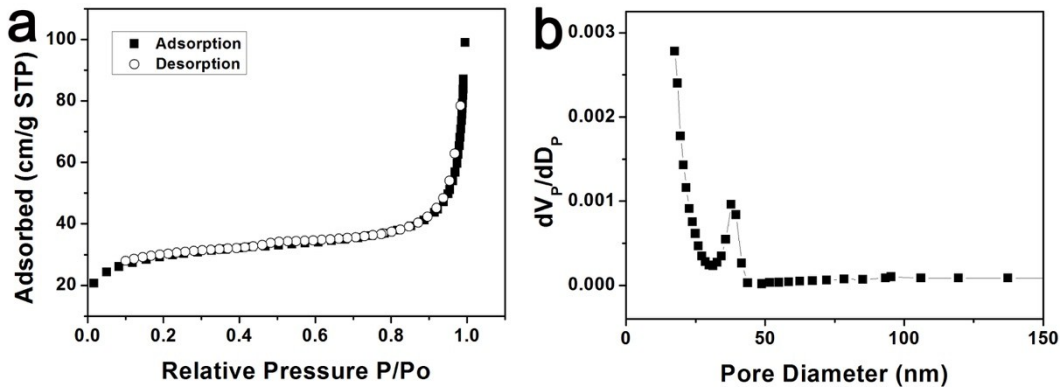

Fig. S4. Nitrogen adsorption and desorption isotherms of the Si/SiOx porous structures s and the pore-size distribution calculated by the BJH method from desorption branch.

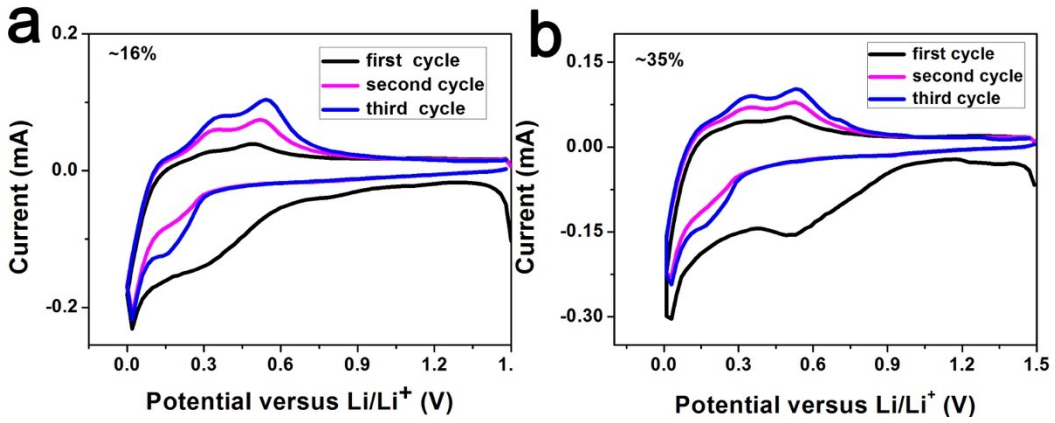

Fig. S5 a. Current-voltage (CV) curves for the Si/SiOx porous structures electrodes with different oxygen content: (a) ~16%; (b) ~35%.

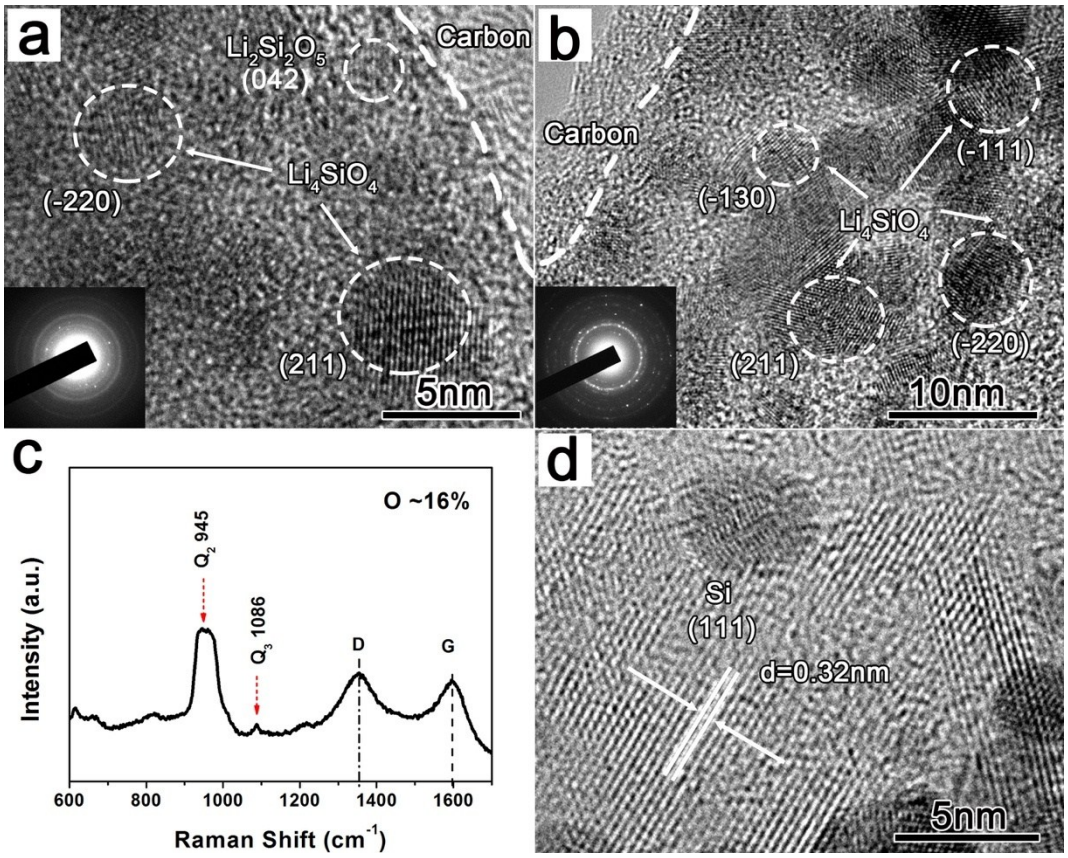

Fig. S6 (a) ex situ HRTEM and selected area electron diffraction(SAED) images of the Si/SiOx porous structures with oxygen contents of (a) ~16% and (b) ~35% after lithiation to 0.01V; (c) Raman spectra of the Si/SiOx porous structures with oxygen content of ~16%; (d) ex situ HRTEM images of the Si/SiOx porous structure with oxygen content of ~35%.

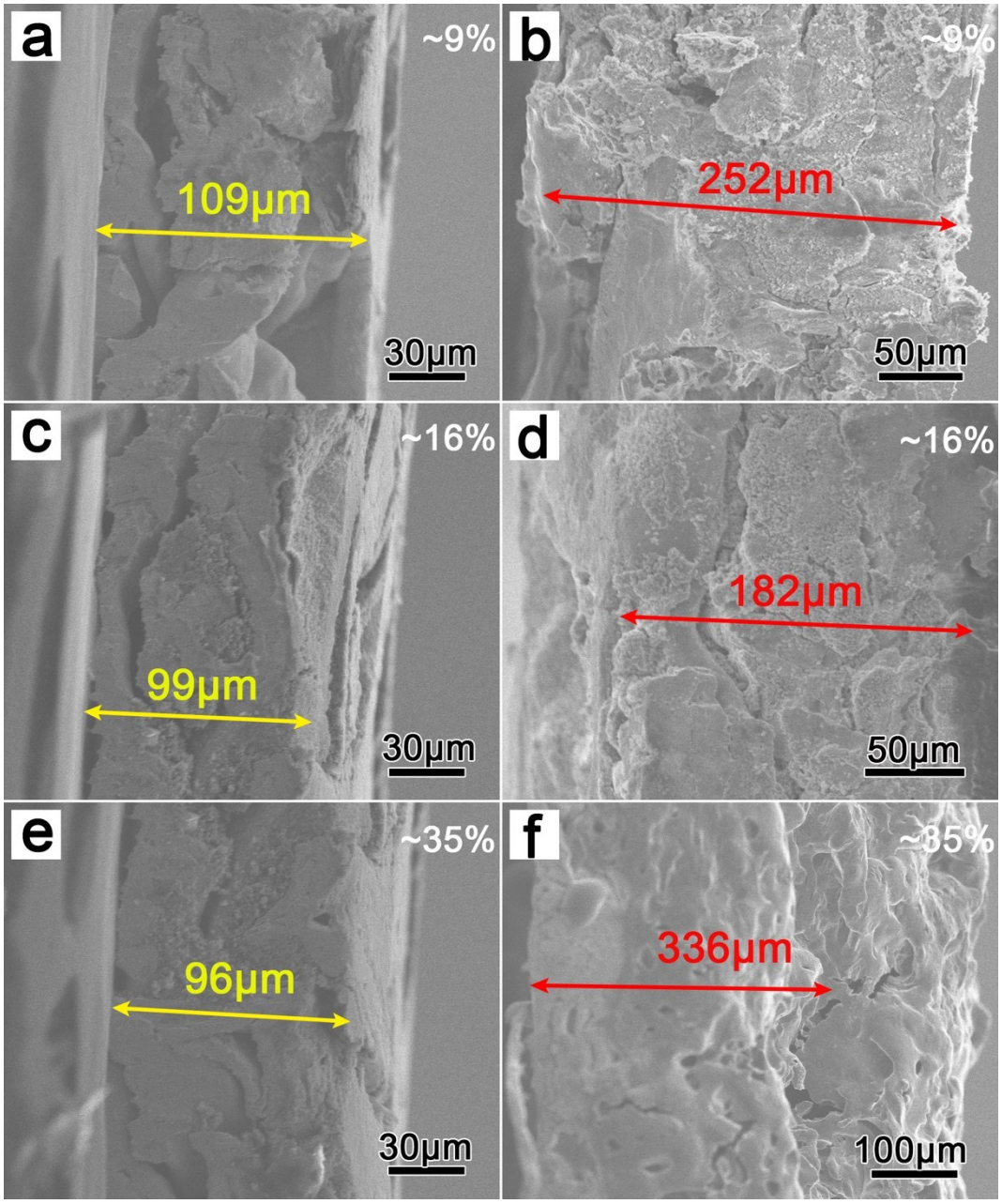

Fig. S7 SEM images of cross-sectioned electrodes for the Si/SiOx porous structures (a), (c) and (e) with oxygen content of ~9%, ~16% and ~35%, respectively; and (b), (d) and (f) after 50 cycles, respectively.