Electronic Supplementary Information (ESI)

Supplementary Information

Multi-functionalities of natural polysaccharide for enhancing electrochemical performance of macroporous Si anodes

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Experimental Details

1) Synthesis of 3D Porous Silicon: commercially available Si power (2~30 μm, 99.9%) was purchased from High Purity Chemical. For a typical etching process, 10 g Si powder was immersed in a solution of 5 M hydrofluoric acid (HF) and 15 mM copper sulfate ($CuSO_4$) at 50 °C for 24 hrs to synthesize 3D porous Si particles. After chemical etching, Cu nanoparticles were completely removed by concentrated HNO_3 at 50 °C for 2 hrs and rinsed with a copious amount of deionized water, and then dried in a convection oven at 120 °C for 2 hrs. For carbon coating of the chemically etched Si particles, the 3D porous Si powder was immerged in 5 wt% agarose solution and the solution was stirred at 90 °C for 2 hrs. Subsequently, the Si particles wrapped with agarose hydrogel were dried in a convection oven at 70 °C for 24 hrs. After drying, the Si/hydrogel was heated to 250 ^oC to stabilize the structure, and, subsequently, carbonized at 400 ^oC for 1 hr. The carbon contents were measured by an elemental analyzer (Flash EA 1112, Thermo Electron Corp.).

2) Characterization of Si Particles and Electrodes: bare Si, porous Si, and carbon-coated Si were characterized by a scanning electron microscope (SEM, Nano SEM 230, FEI) operating at 10 kV. The crystalline structures of as-synthesized, chemically etched, and carbon-coated porous Si particles were measured by a high power X-ray diffractormeter on a Rigaku D/MAX at 2500 V. Raman spectra were obtained from a JASCO spectrometer (NRS-3000) to investigate the characteristics of the carbon coating layer using a He-Ne laser operating at λ = 632.8 nm. The nitrogen adsorption and desorption isotherms were measured with a VELSORP-mini II (BEL Japan, Inc.) at 77 K in the relative pressure range of P/P_0 from 0.05 to 0.3 to determine the BET surface areas and pore size distribution. Electrodes with different binder were characterized by a SEM. X-ray photoelectron spectroscopy (XPS) analysis is performed on a Thermo Scientific K α

spectrometer (monochromatic AlK α, 1486.6 eV). Total reflectance–Fourier transform infrared (ATR-FTIR) spectra of electrodes were recorded in reflectance measurements using a Varian 670-IR spectrometer with a spectral resolution of 4 cm^{-1} under a nitrogen atmosphere.

3) Electrochemical Test: For the electrochemical tests of Si electrodes, the anodes were composed of porous Si powder, carbon black (super P), binder (6:2:2 weight ratio). The agarose (Aldrich) contents in binder were varied from 0 % to 100 wt%. Poly(acrylic acid) (PAA, weight average molecular weight of 250 kg/mol, Aldrich) contents in binder were varied in the same way. The coin-type half cells (2016R-type) consisted of lithium metal as the counter electrode, a polyethylene separator, and 1.3 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (EC/ DEC, 3/7 v/v) with 5 wt% fluoroethylene carbonate (FEC) as the electrolytes. The first Li insertion and extraction capacities were measured at a rate of C/20. The coin cells were cycled at a rate of C/10 to 5 C between 0.01 and 1.2 V. For impedance measurement, AC complex impedance analysis with an IVIUM frequency response analyzer was used over a frequency range of 10 mHz to 1 MHz.

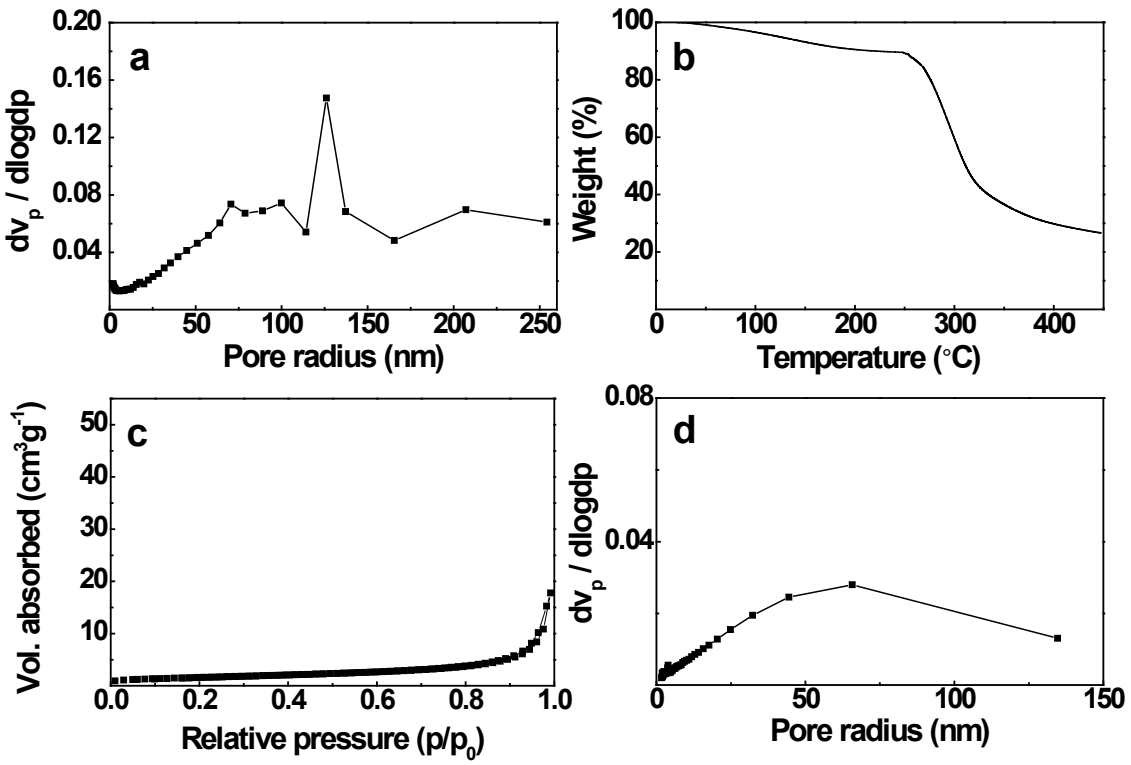

Fig. S1 (a) Pore size distribution of 3D macroporous Si particles. (b) TGA curve of agarose film. (c) BET data and (d) pore size distribution of the carbon-coated porous Si particles.

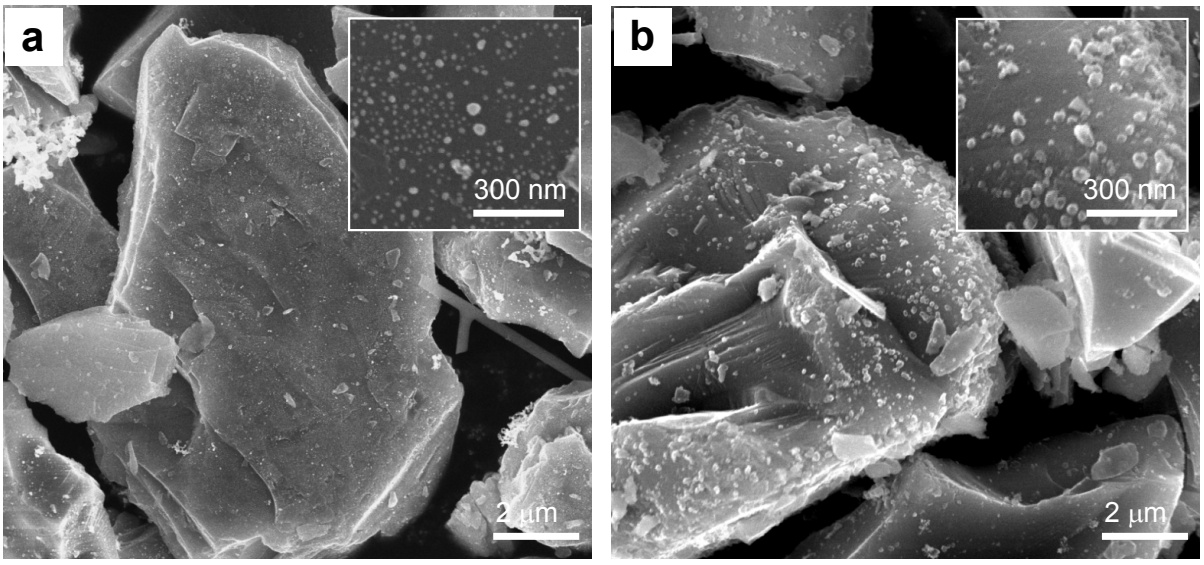

Fig. S2 SEM image showing (a) Ag and (b) Cu deposited bulk Si particles at the same deposition condition. Cu nanoparticles on the Si surface are much bigger than Ag particles.

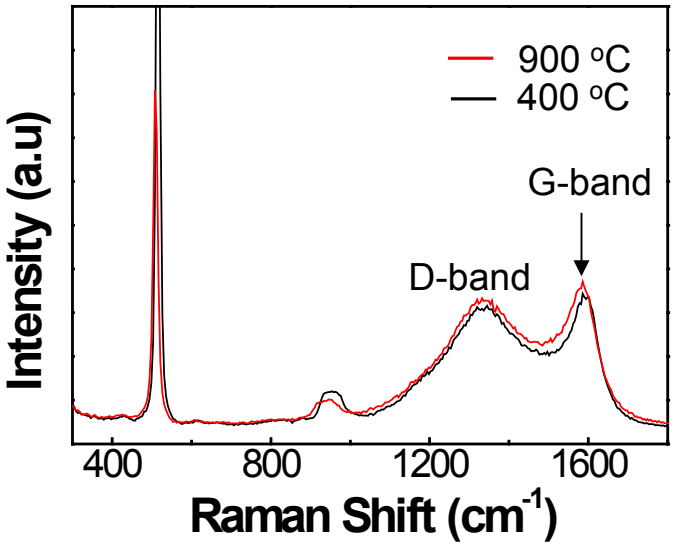

Fig. S3 Raman spectra of agarose carbonized at 400 °C (black line) and 900 °C (red line).

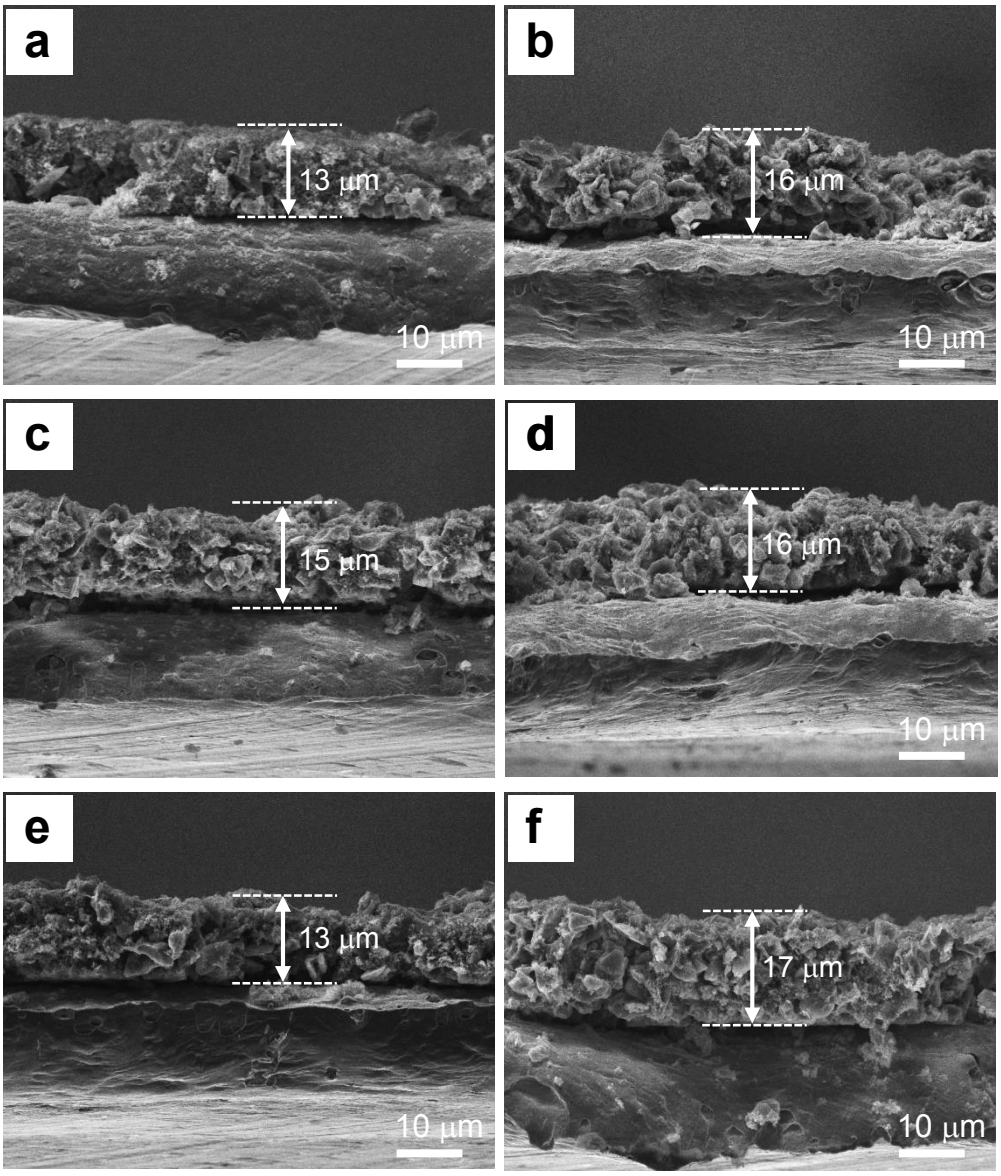

Fig. S4 Thickness change of electrodes with different binders before and after swelling test in the electrolyte. The pristine electrodes with (a) PAA binder (A0), (c) agarose PAA binder (A40), and (e) agarose binder (A100). The electrode with (b) PAA binder (A0), (d) agarose PAA binder (A40), (f) agarose binder (A100) after swelling test in the electrolyte at 60 °C for 18 hr.

Table S1. Binder composition of electrodes

Electrodes	Agarose (wt%)	PAA (wt%)
A0	0	100
A20	20	80
A40	40	60
A60	60	40
A80	80	20
A100	100	0

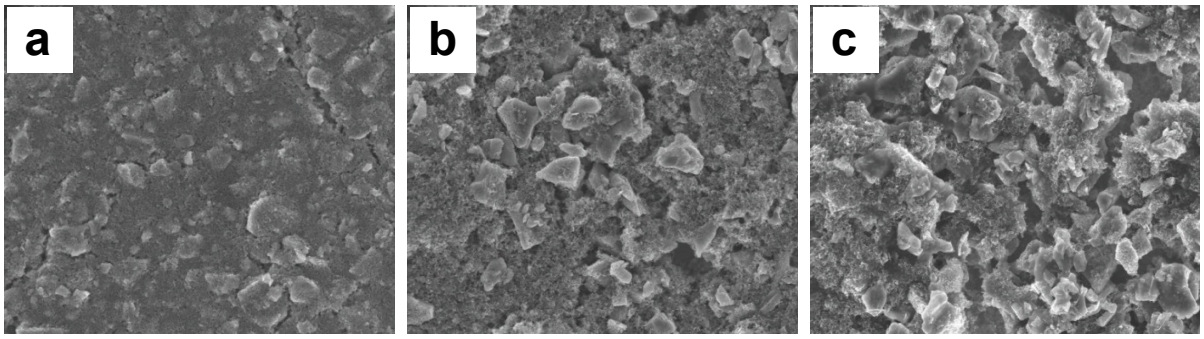

Fig. S5 SEM image of electrode with (a) PAA binder (A0), (b) Agarose PAA binder (c) Agarose binder.

Table S2 BET surface area, mass loading and electrode thickness of electrodes with different binders.

Electrodes	Specific surface area (m^2 g^{-1})	Mass loading ($mgcm^{-2}$)	Electrode thickness
A0	11.42	~1	15
A40	14.15	~1	19
A100	18.46	~1	24

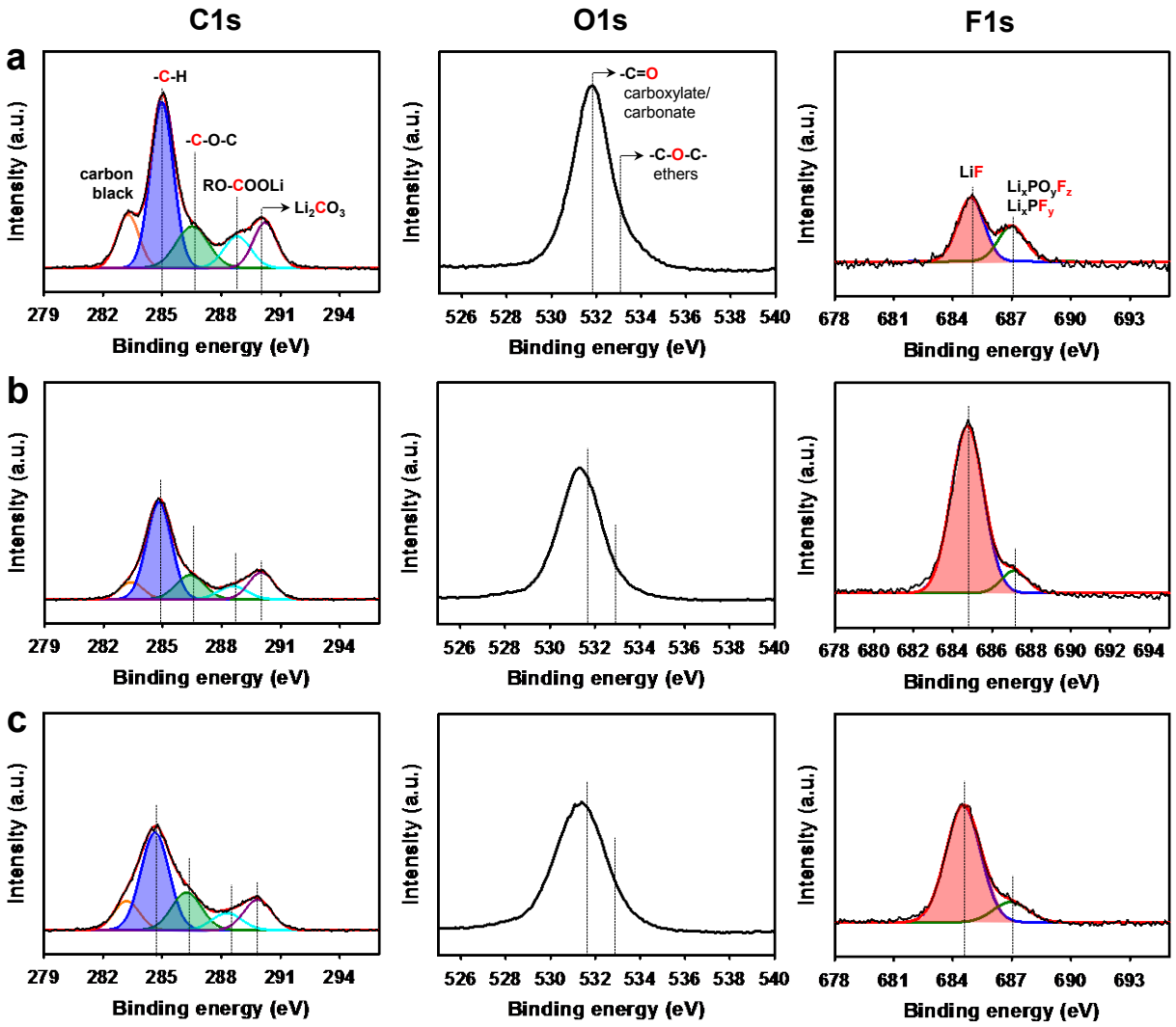

Fig. S6 C1s, O1s, and F1s XPS spectra of (a) A100, (b) A40, (c) A0 electrodes after first cycle.