

Supporting information

Elastic buffer structured silicon/carbon microsphere anodes via polymerization-induced colloid aggregation

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Experimental Section

1. Preparation of the Si@V-V@C microspheres

Preparation of Si@SiO₂: 100 mg Si nanoparticles (~50 nm, Alfa Aesar) were dispersed in a mixture of 80 mL ethanol and 20 mL water by ultrasonication. Then, 1.0 mL concentrated ammonium hydroxide (Sinopharm Chemical Reagent Co. LTD) was added into the mixture. Afterwards, 0.4 mL tetraethoxysilane (TEOS, Sinopharm Chemical Reagent Co. LTD) was added into the dispersion under vigorous magnetic stirring. Finally, keeping the reaction for 24 h at room temperature, the Si@SiO₂ nanoparticles were collected by filtration and washed with excess water.

Preparation of Si@V-V@C: Si@V-V@C were prepared via polymerization-induced colloid aggregation (PICA) method. According to a typical synthesis route, the as-prepared Si@SiO₂ nanoparticles were re-dispersed in 100 mL water, and then 1 g SiO₂ gel (30 wt. % of SiO₂ in glycol, Alfa Aesar) was added into the mixture under mechanical stirring. Afterwards, the pH value of this mixture was adjusted to 1.2~1.8 using concentrated hydrochloric acid (37%, Sinopharm Chemical Reagent Co. LTD), followed by the addition of 1.5 g urea (Sinopharm Chemical Reagent Co. LTD) and 3.2 g formaldehyde solution (Sinopharm Chemical Reagent Co. LTD). Keeping the reaction for 1h with low-speed stirring, the Si@SiO₂/SiO₂/UF composited microspheres were obtained by filtration and washed to neutral pH with distilled water. The obtained microspheres were first calcined at 800 °C for 120 minutes in Ar atmosphere (200 sccm) with heating rate of 2 °C min⁻¹, and then ethylene (50 sccm) was introduced for another 30 minutes. After carbonization and carbon deposition, the

sample was immersed in 5 wt. % HF aqueous solution for 30 minutes to remove the SiO₂. After centrifugation and H₂O washing for three times, the microspheres were obtained after drying in a vacuum oven, denoted as Si@V-V@C, in which the first V represents the “voids”, originated from the removal of the SiO₂ coating layer on the surface of Si nanoparticles, and the second V represents the “void-holes”, originated from the removal of the SiO₂ nanoparticles in the composited microspheres.

For comparison, the Si@V@C microspheres were prepared by the same process except the addition of the SiO₂ gel. There was no void-hole structure in these microspheres.

2. Characterization

Morphologies of the samples were investigated using a FEI Quanta FEG 250 scanning electron microscopy (SEM). Transmission electron microscopy (TEM) and energy dispersion X-ray spectroscopy (EDS) were used to investigate the microstructure and element dispersion in the microspheres with a JEOL JEM-2100 TEM equipped with an EDS attachment. The XRD patterns were recorded on a Bruker D2 Phaser Diffractometer with Cu K α Radiation ($\lambda = 0.154056$ nm). Raman spectra were measured using a Renishaw Raman RE01 scope with a 514 nm excitation argon laser. Weight percentages of Si in the samples were determined by thermal gravity analysis (TGA) from 100 to 800 °C at 5 °C min⁻¹ in air using a Mettler Toledo TGA 1 thermal gravimetric analyzer.

3. Electrochemical measurement

Electrochemical measurements were carried out at room temperature in form of

CR2032 coin cells. The cells were assembled in Argon-filled glove box using the composited microspheres as the working electrode, lithium foil as counter electrode and reference electrode, and 1 M LiPF_6 in ethylene carbonate/dimethyl carbonate (1:1) containing 10% fluoroethylene carbonate as the electrolyte. To prepare the working electrode, the composited microspheres, carbon black (super P) and carboxymethyl cellulose (CMC) were mixed at a weight ratio of 80:10:10 in water to produce a homogeneous slurry, which was then pasted onto a copper foil to form a film and finally dried at 60 °C in a vacuum oven for 24 hrs. The loading of active materials was around 1.0~1.2 mg cm^{-2} . The cyclic voltammetry (CV) and galvanostatic charge-discharge techniques were employed to evaluate the electrochemical performance of the samples. CV curves were measured on an electrochemical station (PGSTAT 302N, Metrohm, Switzerland) in potential range of 0.01~1.5 V at a fixed scan rate. Galvanostatic charge-discharge curves were measured using NEWARE battery testing system in potential range of 0.01~1.5 V versus Li/Li^+ at different current densities. The electrochemical impedance spectroscopy (EIS) measurements were performed using an Autolab workstation by applying a 5 mV amplitude sinusoidal signal in the frequency range from 100 kHz to 0.01 Hz.

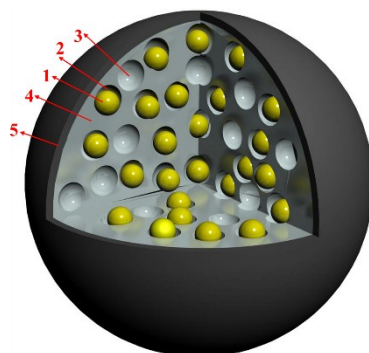


Figure S1. The proposed structure of the Si@V-V@C microsphere: 1) Si nanoparticles; 2) voids, originated from the removal of SiO₂ coating layer on the surface of the Si nanoparticles; 3) void-holes, originated from the removal of the SiO₂ nanoparticles in the carbon framework; 4) carbon framework; 5) C coating layer. The Si@V@C microspheres share the similar structure without void-holes.

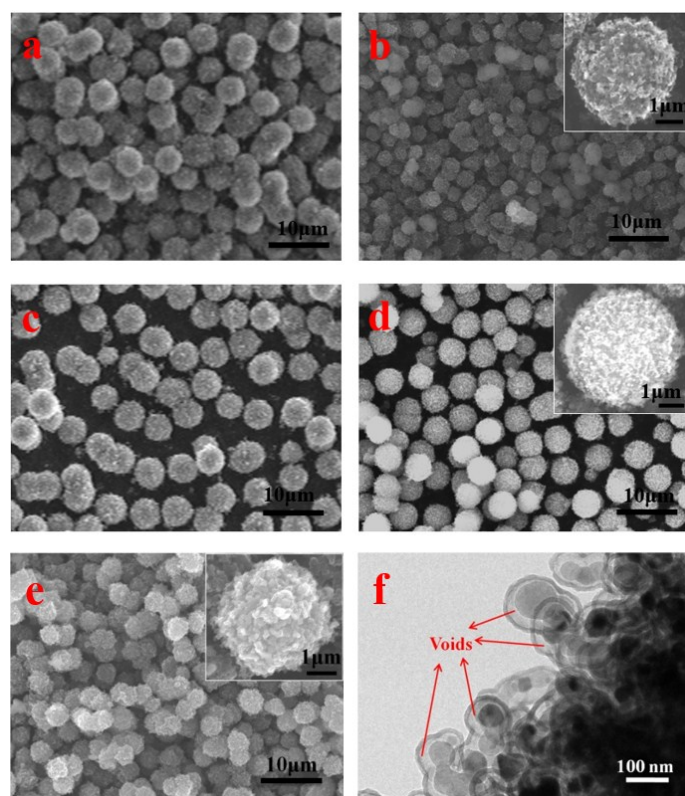


Figure S2. The Si@V@C microspheres (a) Before and (b) After carbonization; The Si@V-V@C microspheres (c) Before and (d) After carbonization; (e) The SEM and (f) TEM image of the Si@V@C microspheres after HF etching.

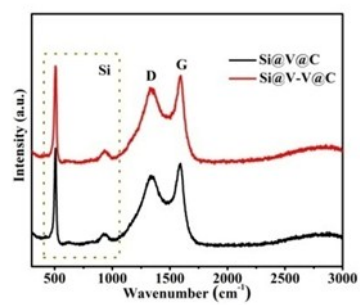


Figure S3. The Raman spectra of Si@V@C and Si@V-V@C.

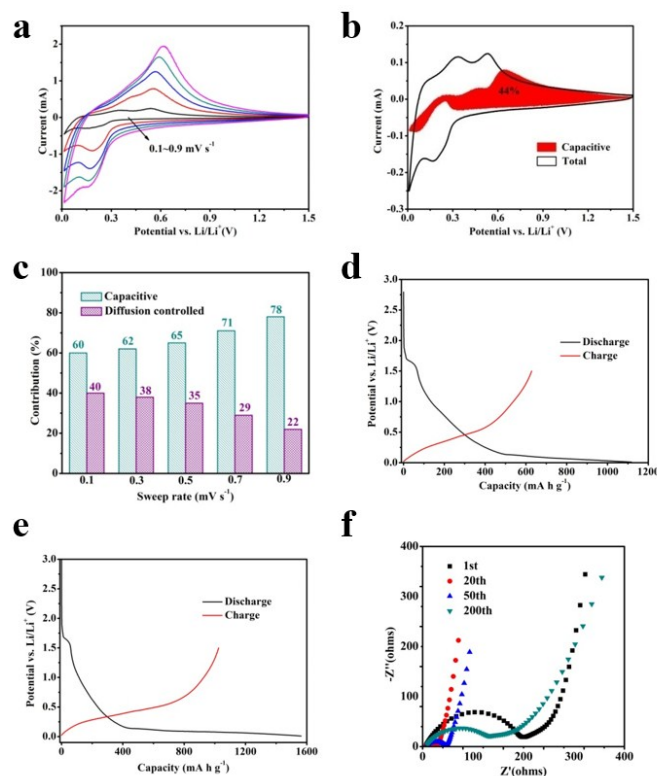


Figure S4. (a) Cyclic voltammetry curves of Si@V@C at different sweep rates; (b) Capacitive contribution of the Si@V@C electrode at the sweep rate of 0.1 mV s⁻¹; (c) Capacitive contribution of the Si@V@C electrode at different sweep rates; (d) The initial discharge/charge profiles of the Si@V@C electrode at 0.05 A g⁻¹; (e) The initial discharge/charge profiles of the Si@V@C electrode at 0.05 A g⁻¹; (f) EIS spectra of the Si@V@C electrode (charge state) .

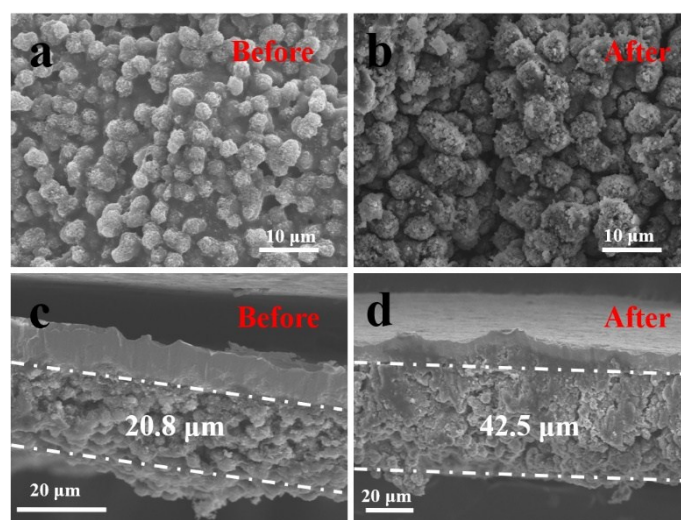


Figure S5. SEM images of the Si@V@C electrode (a) Before and (b) After 200 cycles.

Cross-sectional SEM images of the Si@V@C electrode (c) Before and (d) After 200 cycles.

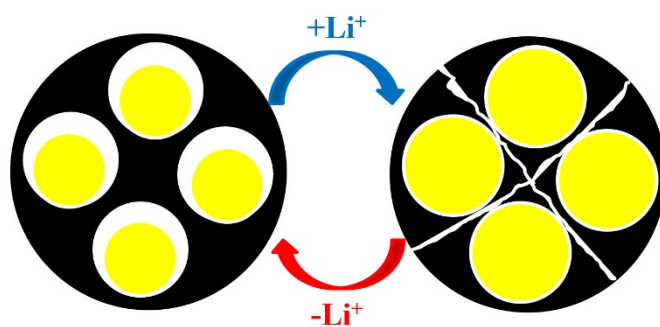


Figure S6. Schematic illustration of the (de)lithiation process in the Si@V@C electrode.