Electronic Supplementary Information (ESI)

Amorphous silicon honeycombs as binder- and carbon-free Li-ion battery anode

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Experimental details

Materials & Instrumentations. The reagents are of analytical grade and used without further purification. Polystyrene spheres (978 ± 32 nm, 10% wt. aqueous suspension) were purchased from MicroParticles GmbH. Silicon sputtering target (undoped, 99.999%) was purchased from Kurt J. Lesker. Lithium hexafluorophosphate ($LiPF_6$, >99.99%, battery grade) were purchased from Sigma-Aldrich. Ethylene carbonate (EC) and dimethyl carbonate (DMC) were purchased from Kishida Chemicals. SEM observation was performed on a Philips XL 30 FEG SEM. Raman spectra were collected from a Renishaw 2000 laser Raman microscope equipped with a 633 nm argon ion laser of 2 μm spot size for excitation. XPS measurement was carried out in an ultrahigh vacuum surface analysis system (VG ESCALAB 220i-XL) using Mg Kα ($h\nu$ = 1253.6 eV) as the exciting source. The galvanostatic charge/discharge and rate performance were conducted on LANHE battery cycler (CT2001A).

Fabrication of PS SAM. Silicon wafer was used as the supporting substrate for PS SAM coating. The silicon wafer was soaked in piranha solution (H_2SO_4:H_2O_2 3:1 v/v) at 80 ºC for 30 min to obtain a clean surface before use. The preparation of PS SAM was conducted in Nunclon dish via a modified self-assembly method. Firstly, proper amount of distilled water was added into Nunclon dish followed by putting a piece of cleaned silicon wafer beneath the water. Then the PS suspension was diluted by mixing with equal volumes of ethanol, and slowly squeezed onto the water surface with a plastic injector until the whole water surface covered by PS SAM, which should show strong and uniform diffraction colours. Afterwards, the Nunclon dish remained still for 12 h to relax the stress and avoid the formation of cracks in the lattice. Finally, the water was pumped out slowly until the PS SAM landed on the Si substrate, followed by PS SAM drying under ambient conditions. The size of the monolayer could reach tens of cm^2, determined by the size of the Nunclon dish and supporting substrate.

Fabrication of a-Si microspheroid arrays and a-Si honeycombs. Before fabrication of a-Si microspheroid arrays, PS SAM was thermally treated at 85 °C for dehydration, which led to average shrinkage of *ca.* 20% in diameter. Then the supporting substrate coated with a PS SAM was loaded in a radio-frequency magnetron sputtering system for a-Si deposition. The chamber pressure was 10^{-3} mTorr and the deposition rate was *ca.* 100 Å min^{-1}. The temperature of the holder was set to room temperature during the whole sputtering process. After sputtering deposition, a-Si microspheroid arrays could be obtained. a-Si honeycombs could also be obtained by soaking the a-Si microspheroid arrays in chloroform. The dissolution of PS SAM would naturally result in peeling off of a-Si microspheroid arrays from the supporting substrate.

Cell assembly and testing. The a-Si honeycombs were firstly detached from the substrate after removal of PS by chloroform. Then the a-Si honeycombs were transferred onto Cu foil and washed repeatedly with chloroform to remove the residual polystyrene. Finally, the a-Si honeycombs/Cu electrode was dried in vacuum at 60 °C before cell assembly. Electrochemical tests of a-Si honeycomb electrodes were carried out in three-electrode H-type cells with two pieces of Li metal foil as the counter and reference electrodes. The size of the working electrode was 0.5 cm × 0.5 cm. The electrolyte was 1M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) with volume ratio 3:7. The potential windows for all electrochemical tests were set to 5 mV – 1 V *vs.* Li^+/Li.

S1. Thermal treatment of PS SAM

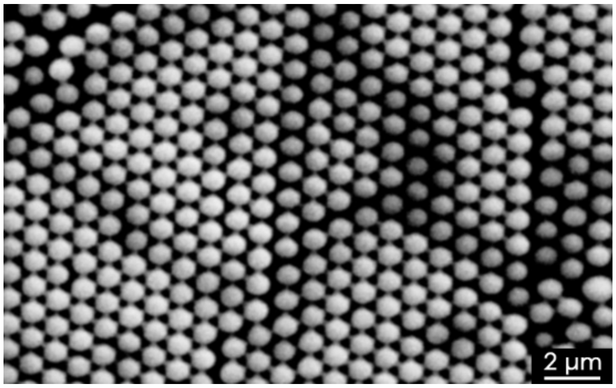

Fig.S1 SEM image of thermal treated PS SAM. The PS in situ dehydrated to yield deducted diameter of ~ 780 nm. The hexagonal close packing is well reserved.

S2. a-Si microspheroid arrays

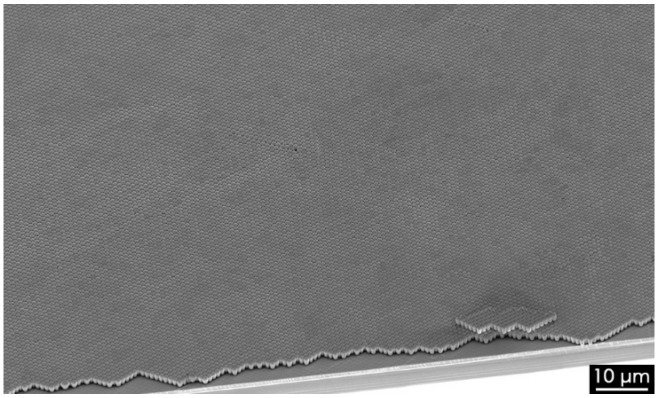

Fig.S2 Panoramic SEM image showing the large-scale hexagonal arrangement of a-Si microspheroid arrays on silicon wafer.

S3. Aspect control of a-Si microspheroids

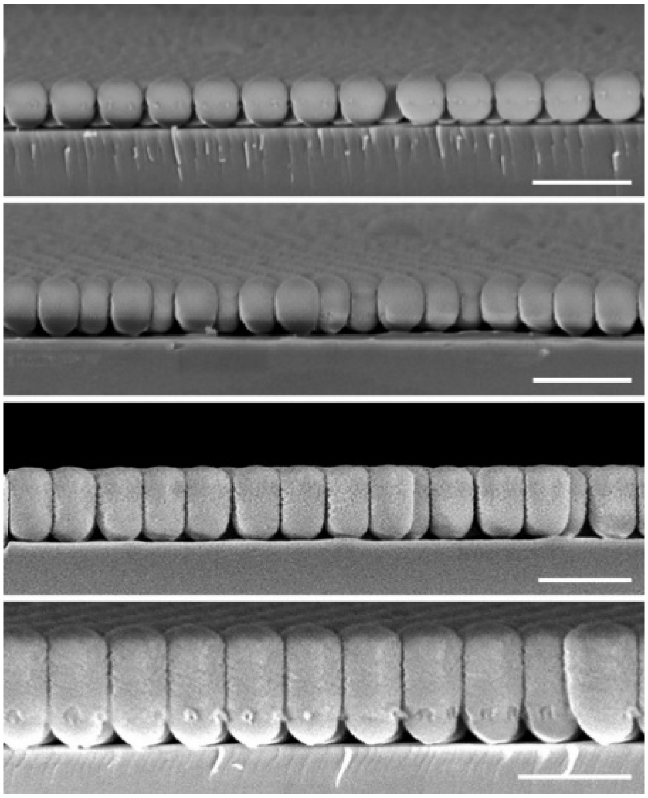

Fig.S3 Cross-sectional SEM images of a-Si microspheroid arrays obtained with deposition time of 1, 2, 3 and 4h, respectively (top to down). The aspect ratio of the microspheroids gradually increased from *ca.* 1.2:1 to ca. 2:1. Scale bars: 2 μm.

S4. a-Si honeycomb electrode after cycling

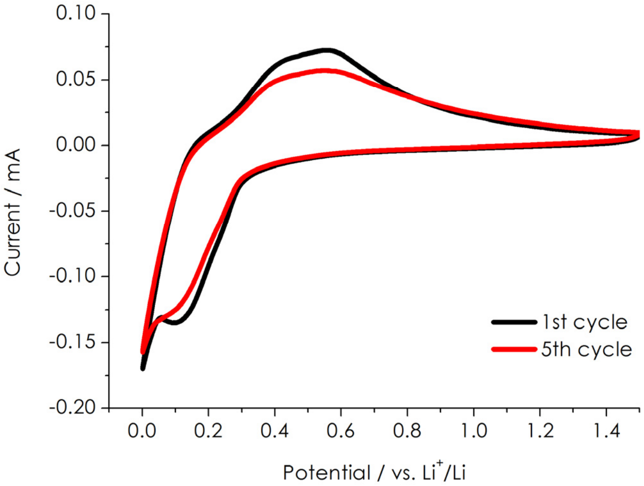

Fig.S4 The first and fifth cyclic voltammetry profiles of the a-Si honeycombs at a sweeping rate of 0.5 mV s^{-1} in the potential range of 0 – 1.5 V vs. Li$^+$/Li. The cathodic and anodic peaks located at 0.4 and 0.2 V vs. Li$^+$/Li, respectively, are characteristic of amorphous silicon.

S5. a-Si honeycomb electrode after cycling

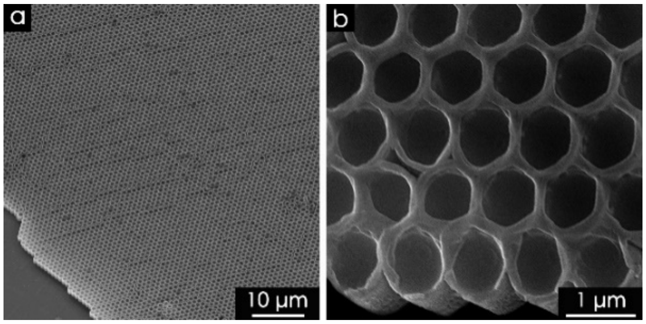

Fig.S5 Galvanostatically cycled a-Si honeycomb electrode. (a) Low-magnification SEM image showing a good adhesively between a-Si honeycombs and Cu foil. (b) High-magnification SEM image showing the structural integrity of a-Si honeycombs.

S6. Planar a-Si film after cycling

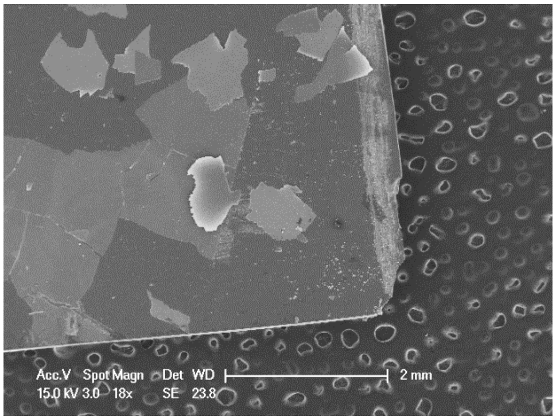

Fig.S6 SEM image of galvanostatically cycled planar a-Si film, in which large amount of cracks formed upon cycling. The planar a-Si film is also easily detached from the Cu foil.

S7. Centimetre-scale patterning of a-Si

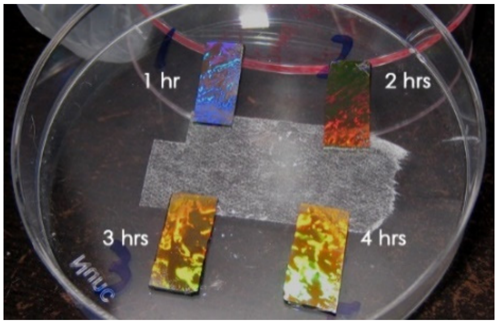

Fig.S7 Digital image showing the as-prepared a-Si microspheroid arrays with different deposition time on Si substrate. The Si substrates are approximately 1 cm × 2 cm in size.