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Supporting Information

Hierarchical Si Hydrogel Architecture with Conductive Polyaniline Channels on the Sulfonation-Graphene for High-Performance Li Ion Battery Anodes Having Robust Cycle Life

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Experimental Details

1. Materials

Aniline (ACS reagent, ≥ 99.5%, distilled before use under reduced pressure), ammonium persulfate, phytic acid (50 % w/w in water), hydrazine hydrate solution (80%), potassium permanganate, hypophosphorous acid solution (50 % w/w in water), sodium nitrite, sulfanilic acid, and graphite powder were purchased from Sigma-Aldrich. Silicon nanoparticles (SiNPs, OD ~ 35 nm) were purchased from Beijing DK nano technology Co.LTD (China).

2. Preparation of sulfonated graphene nanosheet (SGN)

Graphene oxide (GO) was prepared and purified by the modified Hummers method.[1] To precooled solution of $KMnO_4$ (15g) in con. sulfuric acid (120mg) under an ice bath, graphite powder (500mg) was portionwise added at < 5℃, after complete oxidation, warmed to 37℃, and kept at this temperature for 2h. Deionized (DI) water (30ml) was added slowly to this reaction mixture, warmed to 95℃, and maintained for 45min. After being diluted with DI water (700ml), 30% H_2O_2 (50ml) was dropwise added for 30min. The solid was then filtered off and washed with 5% HCl and DI water several times, and dried in air for 24h. The resulting GO suspension in DI water (180 ml, 1.0 mg/ml) was reduced with 80% hydrazine hydrate (1.8 ml) at 100 °C for 24 h followed by washing with deionized water several times. The yielded suspension was dialyzed for 48 h to obtain a purified reduced graphene suspension. (*ii*) 4-Benzenediazoniumsulfonate was synthesized by diazotization of sulfanilic acid. To the sulfanilic acid (5.2 g, 0.03 mol) suspension in 1 M HCl (300ml), 10% excess of *aq.* 1 M $NaNO_2$ (33 ml) was added dropwise at 3-5 °C and a clear solution was obtained after all the $NaNO_2$ was added. After stirring for another 1 h at the same temperature, the formed white precipitate was filtered off and washed with DI water. The obtained 4-Benzenediazoniumsulfonate was moved to a three-necked ground flask with DI water (60 ml) and ethanol (60 ml). Reduced graphene (180 mg) was then added at 3–5 °C. Subsequently, 50 wt % H_3PO_2 *aq*. solution (60 ml) was added. After stirring for 30 min, the same amount of H_3PO_2 aqueous solution (60 ml) was added again and stirred for 1 h. The obtained sulfonated graphene nanosheet (SGN) was intensively washed with DI water and then dried under a vacuum overnight.

3. Synthesis of SiNPs/PAni-SGN composites and fabrication of 3D ternary hybrid electrodes.

The SiNPs/PAni-SGN hydrogel composite were prepared *via* the following solution process.[2] First, aniline monomer (30 mg), SGN (20 mg), and phytic acid (PA, 10 mg) were mixed in DI water (0.9 ml) [solution A]. Ammonium persulfate (33 mg) was dissolved in DI water (0.3 ml) [solution B]. Solution A (0.9 ml) and solution B (0.3 ml) were subsequently added to Si nanoparticles (SiNPs) and thoroughly mixed at room temperature and sonicated for 10min to produce homogeneous greenish black viscous gel-like SiNPs/PAni-SGN composites. Finally, a SiNPs/PAni-SGN composite electrode was prepared by doctor-blading the viscous SiNPs/PAni-SGN hydrogel onto a Cu foil current collector and drying at room temperature. The SiNPs/PAni-SGN hydrogel composite film was then mechanically pressed and thoroughly washed in DI water several times to remove excess PA, and the composite electrode film was dried under a vacuum at room temperature for use in half cells as the working electrode. We measured the yield of PAni-SGN in the reaction by obtaining the final weight of a PAni-SGN composite prepared with the same recipe without SiNPs (after washing excessive monomers, acids and dried). The Si content in the SiNPs/PAni-SGN electrode was directly measured by the Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES): 10 mg of the Si/PAin-SGN composite was dissolved in 3ml of co-solvent (HF/HNO_3/Acetic acid) and diluted with dil. water to be 25 ml in the total volume. The ICP plasma spectrometry showed the total mass loading of a cell was ~ 0.65 mg cm^{-2} with the Si mass loading of 0.37 mg cm^{-2}. We also found that the working electrode consisted of ~ 80 % of SiNPs/SGN (~ 57% Si and ~ 23 % SGN) and ~ 20% PAin (0.13mg cm^{-2}), thus giving a theoretical current of 1.61mA cm^{-2} (corresponding to 2480 mA g^{-1}) [3] that was defined as 1C to show the electrochemical performance in the potential range of 0.01 - 1.0 V vs Li/Li^+.

4. Characterization

The prepared graphene oxide (GO) and sulfonated graphene nanosheet (SGN) was characterized by high Resolution Solid State NMR (Bruker Avance 400WB spectrometer) under ambient pressure using a standard Bruker MAS (magic angle-spinning) probe with zirconia rotors that are 4 mm in diameter. In order to acquire ^{13}C data, CP-MAS (Cross-polarization with MAS) was used at 100.64 MHz. To observe the morphologies of various samples, we used a SEM (HITACHI, S-4800) and a Cs-corrected scanning TEM (JEOL, JEM-ARM200F). An energy dispersive spectrometer **(**EDS**)** attached to the TEM apparatus was used to obtain local elemental information.

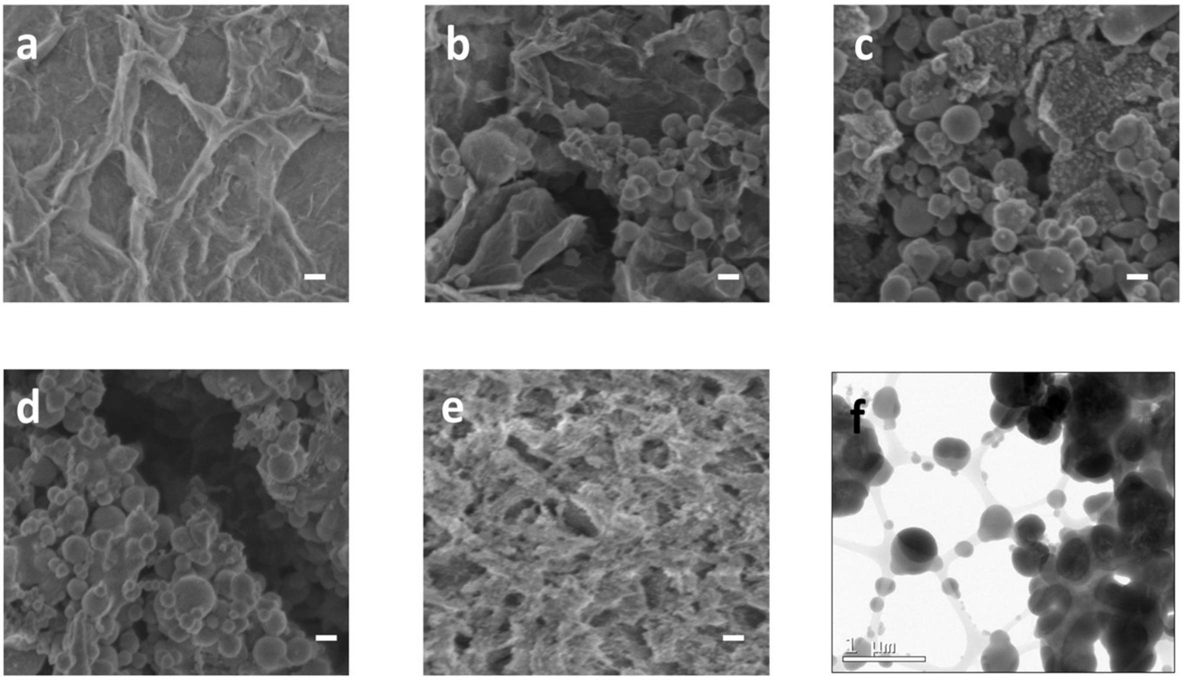

Fig. S1 3D hybrid electrodes were synthesized with SiNPs, aniline, PA, and SGN various mass ratios. (a - e) SEM images of the 3D SiNPs/PAni-SGN hybrid electrodes (scale bar, 100 μm). (a) Ani/SGN (30mg:30mg), (b) SiNPs/PAni-SGN (60mg:30mg:5mg), (c) SiNPs/Ani/PA/SGN (60mg:30mg:20mg:10mg), (d) SiNPs/Ani/PA/SGN (60mg:30mg:20mg:15mg), (e) the optimized SiNPs/Ani/SGN/PA (60mg:30mg:20mg:10mg). SiNPs/Ani/PA/SGN liquid materials were bladed onto a copper foil, dried in air for 3h, and then immersed under DI water for 10h, and (f) TEM image of (e) the nanostructure, which was drop-casted on a copper grid.

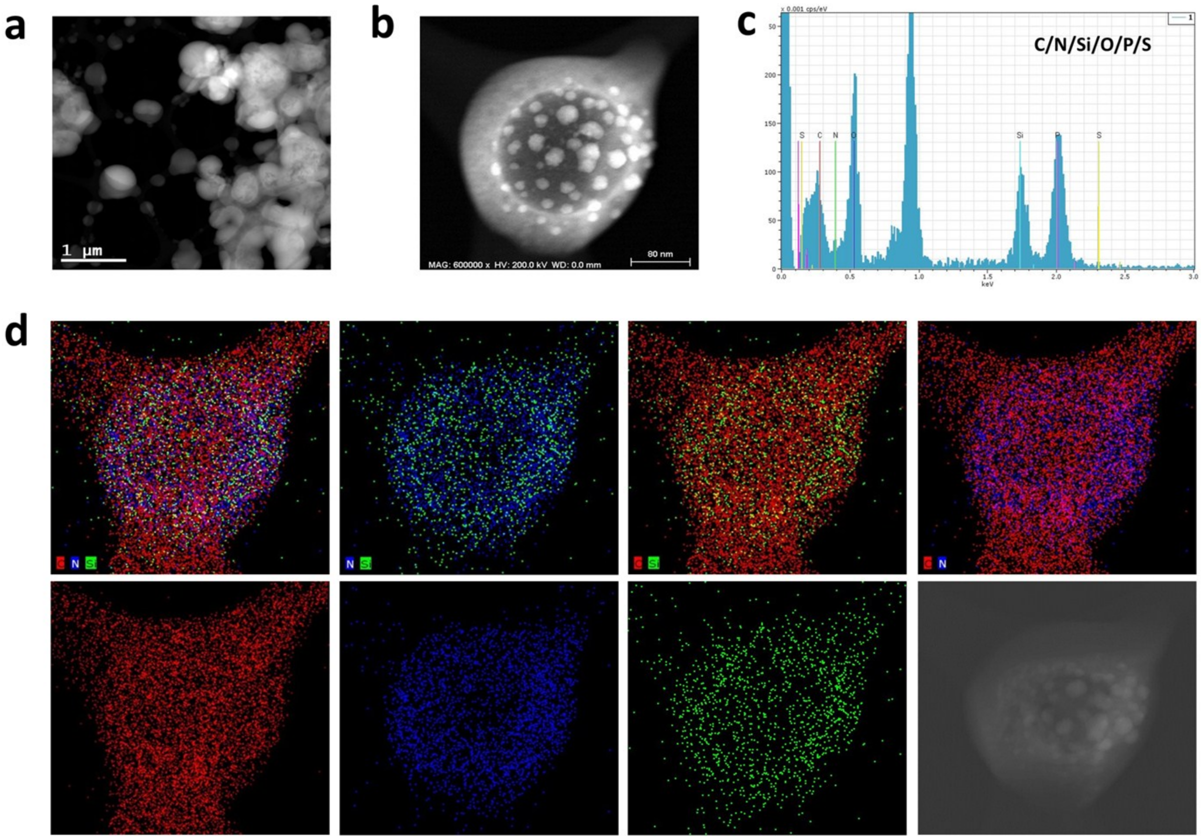

Fig. S2 high-angle annual dark-field images of Scanning-TEM (STEM) and elemental mapping of SiNPs/PAni-SGN nanocomposites. (a) low-magnification STEM image, (b) magnified STEM image, (c) elementary analysis of C, N, Si, O, P, and S elements using elemental mapping, and (d) elemental mapping images where C, N, and Si are in red, blue, and green colors, respectively.

5. Electrochemical measurement

Coin cells (2032 type) were assembled to test the electrochemical performance of the obtained SiNPs/PAni-SGN composite working electrodes, Celgard 2400 separators, and Li metal foil (Honjo Chemical Co.). 1 M lithium hexafluorophosphate ($LiPF_6$), dissolved in co-solvents ethylene carbonate (EC) and diethyl carbonate (DEC)/vinylnene carbonate (EC/DEC/VC = 1:1:0.02, v/v/v) was used as the electrolyte. The entire cell assembly procedure was carried out in an argon-filled glove box. The electrodes were cycled in a potential range of 0.01 V 1 V (vs Li/Li^+) for SiNPs/PAni-SGN based electrodes at room temperature using a battery cycler (Wonatech, WBCS-3000). Cyclic voltammetry characterization was performed at a rate of 0.1 mV s^{-1} in a potential window of 0.01 to 1 V using a potentiostat (Wonatech, WEIS 500). Electrochemical impedance spectra (EIS) measurements were carried out using a multichannel impedance cycler (BIOLOGIC, VSP). The frequency range was from 0.01Hz to 1MHz and the amplitude was 5 mV.

Electrochemical tests of SiNPs/PAni composite and SiNPs/PAni-SGN composite electrodes.

The electrochemical properties were examined by Galvanostatic cycling of coin-type half cells with the SiNPs/PAni composite as the working electrode and lithium foil as the counter/reference electrode. The electrolyte for all tests was 1 M $LiPF_6$ in ethylene carbonate/diethylcarbonate/vinylene carbonate (1:1:0.02 *v/v/v*, Ferro Corporation), and separators (25 μm) from Asahi Kasei Co. were used.

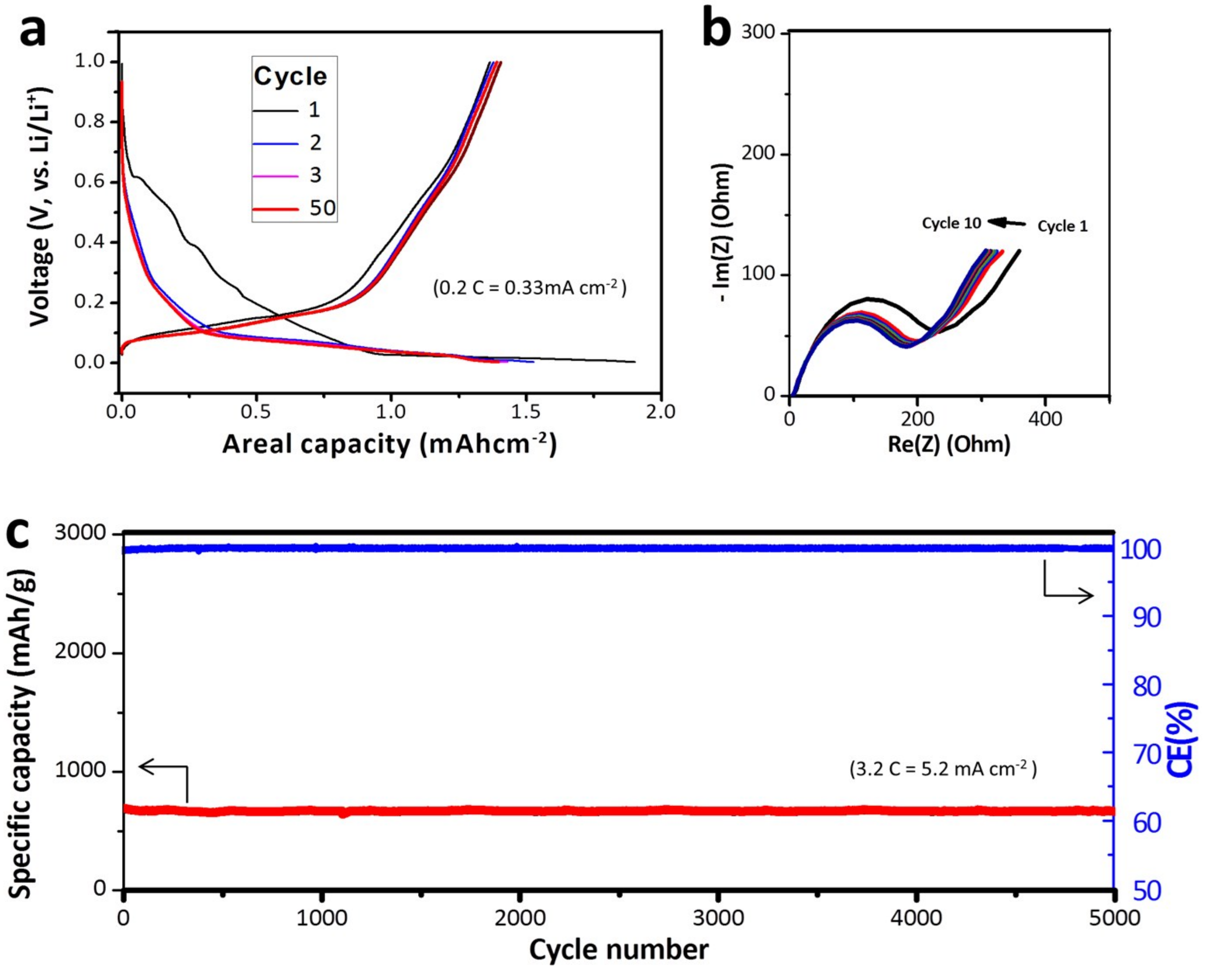

Fig. S3 Electrochemical performance of SiNPs/PAni-SGN nanocomposite electrode. (a) Potential-capacity plot for cycle number 1, 2, 3 and 50. Cycling current density: 0.33 mA cm^{-2}. (b) EIS spectra of the electrode in the frequency range of 0.01 Hz – 1.0 MHz. (c) Lithation/delithiation cycle performance and CE (almost 100 %) of a SiNPs/PAni-SGN composite electrode cycled at a rate of 5.20 mA cm^{-2} (corresponding to 3.2 C) up to 5000 cycles.

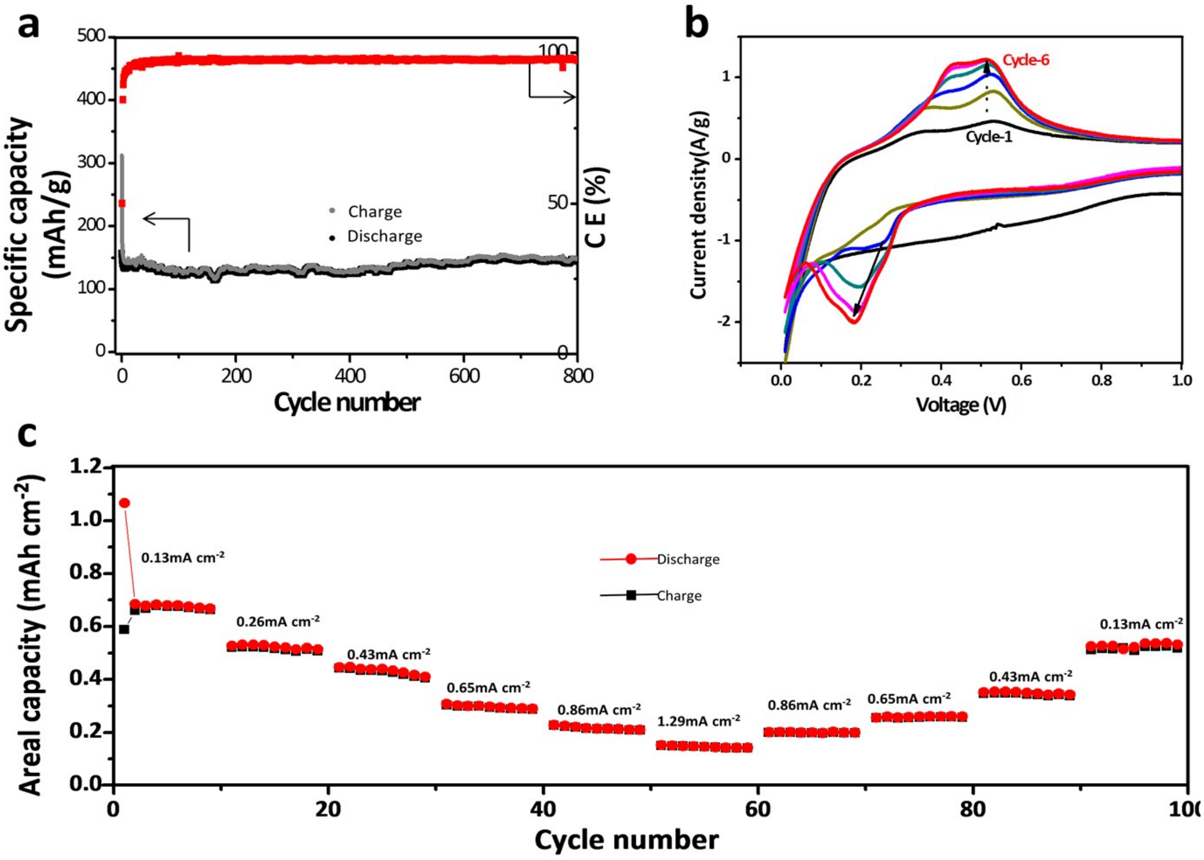

Fig. S4 Electrochemical performance of SGN/PAni and SiNPs/PAni composite electrode. (a) Lithiation/delithiation cycle performance and CE of a SGN/PAni composite electrode. (b) Cyclic voltammogram of the SiNPs/PAni electrode at a scanning rate of 0.1 mV/s between 0.01 and 1.0 V (versus L/Li$^+$) to 6 cycles. (c) The rate capacity of the SiNPs/PAni composite binary electrode.

Entry	Current Density (mA cm^{-2})	Capacity by mass (mAh g^{-1})	Capacity by square centimeter (mAh cm^{-2})	Capacity by volume, C_v (mAh cm^{-3})
1	0.30(0.2 C)	2,250	1.46	1,829
2	0.65(0.4 C)	1,500	0.98	1,219
3	5.20(3.2 C)	662	0.43	550

Table S1 The summery of the specific capacity by mass, square centimeter, and volume.

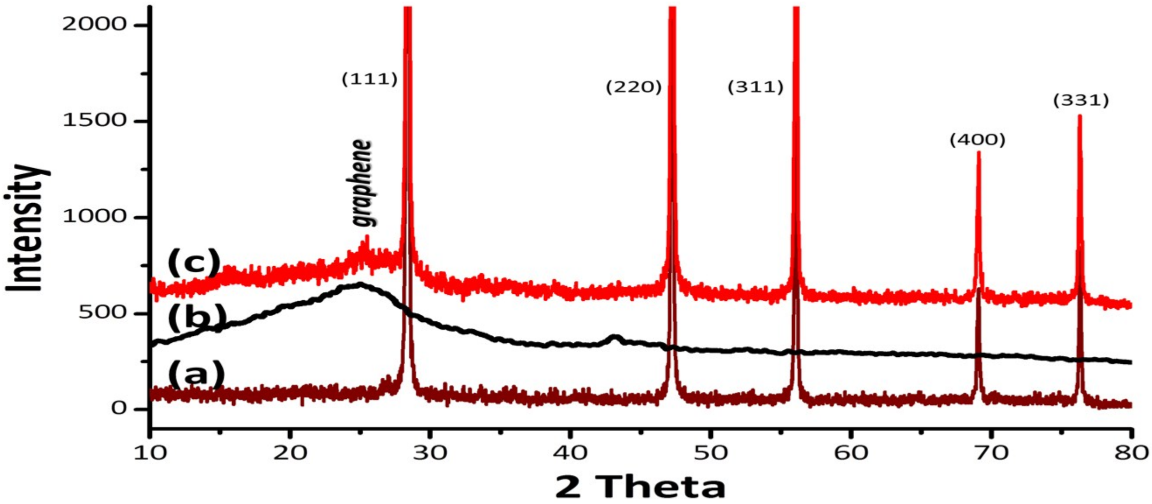

Fig. S5 XRD patterns of (a) pure silicon nanoparticles (SiNPs), (b) pure sulfonated graphene nanosheets (SGNs), and (c) SiNPs/PAni-SGN nanocomposite. The sulfonated graphene exhibited two broad and weak diffraction peaks at 2θ = 24° and 43°, corresponding to those for the graphitic crystalline planes (002) and (100), respectively.[4]

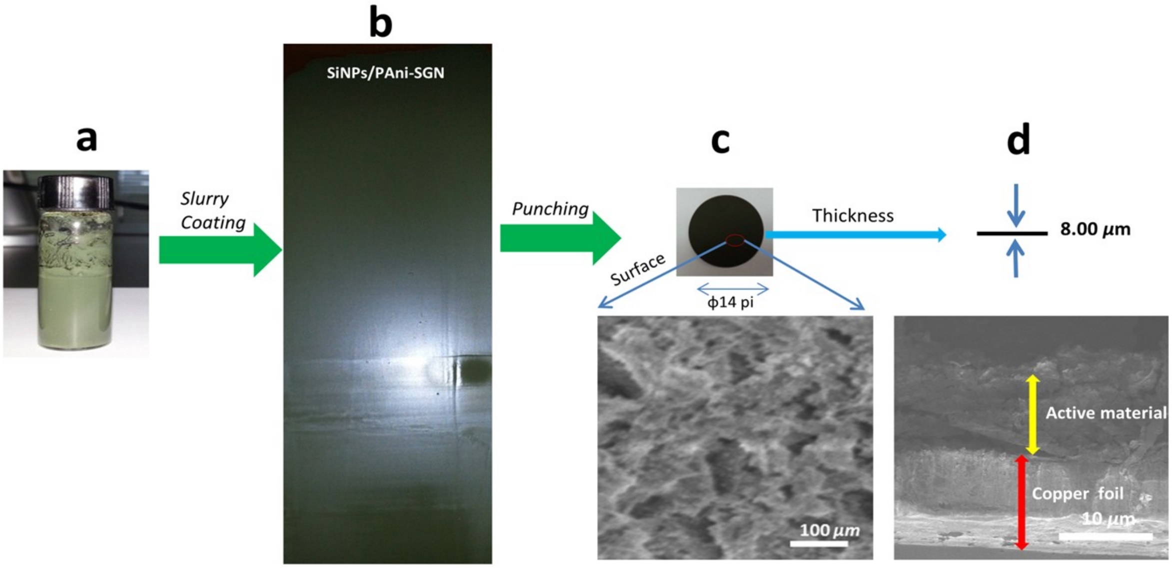

Fig. S6 3D electrode fabrication and characterization: (a) the SiNPs/PAni-SGN composite, where the aniline monomer was cross-linked and forming a viscous gel. (b) The viscous gel was then bladed onto a 5 × 25 cm^2 copper foil current collector, washed and dried. (c) The cell fabricated by a punching machine to obtain the 3D ϕ14 pi type and its SEM image. (d) The thickness of the active composite layer measured by the SEM.

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