ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

DLP printing of a flexible micropattern Si/PEDOT:PSS/PEG electrode for lithium-ion batteries

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1. Experimental Section

1.1 Materials

PEDOT:PSS aqueous solution, diacrylated PEG (Mn=600), ethylene glycol, bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (BAPO) were purchased from Aladdin. Silicon nanoparticles (NPs) was purchased from Alfa Aesar. Acetylene black (AB) and carboxymethyl cellulose were obtained from Alfa Aesar. Li foil was purchased from Tianjin Nengli Co., LTD (China). The microporous polypropylene film (2400) was purchased from Celgard. The electrolyte of 1m $LiPF_6$ and 5% fluoroethylene carbonate (FEC) in ethylene carbonate (EC)/diethylene carbonate (DEC) (v/v =1/1, water content <10 ppm) was purchased from Shenzhen Capchem Technology Co.Ltd (China). All chemical solvents were used as received without further purification.

1.2 Fabrication of 3D printing electrode

The 3D printing hydrogel-based electrode was prepared based on the previously reported method.[1] PEDOT:PSS solid was produced from PEDOT:PSS aqueous solution using freeze-drying technique.[2] For incorporation of PEDOT:PSS and Silicon nanoparticles (Si NPs) inside of the PEG hydrogel, 7mL of an aqueous solution including distilled water (DW) and ethylene glycol (8:1) were used to dissolve 70 mg of the totally dried PEDOT:PSS solid. Then, Si NPs (0.3 g) were mixed together with the solution and dispersed by sonication for 20min. Subsequently, Bis(2,4,6-trimethylbenzoyl) phenylphosphineoxide (BAPO), an ultraviolet (UV) photoinitiator, was introduced to the 40% PEG aqueous solution at 0.5 wt% and left to stir overnight for appropriate dissolution before further processing. The weight ratio of PEG/Si/PEDOT:PSS was 60/20/5. The total solid concentration of Si NPs in the solution was controlled at 30 wt%. Before printing, ethanol impregnated clean room tissues were used to remove dust and dirt from the glass slides. The glass slide was then washed with ethanol. Finally, the glass slides were dried for a few seconds and put into the printer.

To fabricate the conductive hydrogel-based Micro-pattern honeycomb 3D printing Si/PEDOT:PSS/PEG electrode, the mixture of the solution was poured inside a plastic petri dish that had been filled to the rim with a dimension of 1mm thickness and allowed to infiltrate for 2 minutes. A slide of glass was put on top of the container and in direct contact with the solution. The Zhiwei® MoonRay-D is a desktop DLP system for designing and fabricating 3D photo-patterned conducting hydrogels. The hydrogel-based

electrode was predesigned in computer-aided design (CAD) software with fiber spacing of 400μm and a line width of 50 mm for the honeycomb micro-pattern architectural models. Printing solutions were put in Z-controlled moveable containers, which were exposed to UV lasers. 3D printing was utilizing the Zhiwei® MoonRay-D platform with UV laser control for X, Y, and Z control of the 3D construction. Printing process parameters were as follows: laser spot diameter was 200μm, UV parameter wavelength was 375 nm, and printing resolution was 75μm. Laser exposure to the bottom of a glass slide enabled the solidified gel to be measured since the gel adhered to the slide's underside during laser exposure. When the laser was activated, a pattern was drawn through the glass slide and into the PEG-based photopolymer solution at varied print parameters.

After that, the photocurable mixture was cross-linked by 3D printing for 20min. The glass slide was removed from the petri dish holding the polymerized gel electrode after polymerization. The thickness (in z) of the hydrogels was then measured with a micrometer. This sample was named "Si/PEDOT:PSS/PEG". The sample was dried in a vacuum oven at 80°C for 8 hours to remove the DI water from the hydrogels, resulting in Si/PEDOT:PSS/PEG electrodes. For the Si/PEDOT:PSS/PEG electrode, the active material loading level was 4.2 mg cm^{-2}.

For comparison, the traditional Si electrode was prepared by coating a slurry of Si particles (active material, 70 wt%), carboxymethyl cellulose (binder, 10 wt%) and acetylene black (conducting agent, 20 wt%) in an aqueous solution onto a copper foil. The obtained electrode was then dried at 80 °C overnight under a vacuum and then pressed to obtain the traditional Si electrode sheets with coating thickness of 20μm. The loading mass of the active material was 2.2 mg cm^{-2} for the traditional Si electrode.

1.3 Characterization

The morphologies of the samples were characterized by a HITACH SU8010 field emission scanning electron microscope (SEM). The thermal properties of Si NPs and Si/PEDOT:PSS/PEG electrode was determined by a TA Q500 thermogravimetric analyzer (TGA) and DSC (Netzsch STA 449F5) under an air atmosphere with a flow rate of 30 ml/min from room temperature to 800℃ with a heating rate of 10℃ min^{-1}.

1.4 Viscosity properties

The viscosity properties of the Si/PEDOT:PSS/PEG was studied using a rotational rheometer (MCR702MutiDxive, Anton Paar） with a 25 mm parallel plate and 0.55 mm measurement gap. Shear viscosity test in a range of shear rate 0.01-1000 l/s at room temperature.

1.5 Electrochemical measurement

The coin-type half cells (CR2025) were assembled to test the electrochemical performance of Si electrodes. The half cells were assembled in an Ar filled glove-box (water content <1 ppm), using 1 M $LiPF_6$ EC/DEC (v/v＝1/1) with 5% FEC as the electrolyte, celgard 2400 as the separator and Li foil as the counter electrode. The cells were then galvanostatically charged and discharged at 25℃ on a LANHE battery cycler (china) between cut-off voltages of 0.01 and 1.5 V (vs. Li/Li^+). The specific capacity was calculated based on the Si active mass in the electrode. Electrochemical impedance spectroscopic (EIS) measurements were carried out on the PGSTAT302N electrochemical workstation (Metrohm, Switzerland) at 25℃ by applying an oscillating voltage of 5 mV over the frequency ranging from 10^{-2} to 10^{-6} Hz.

2. Viscosity characterization

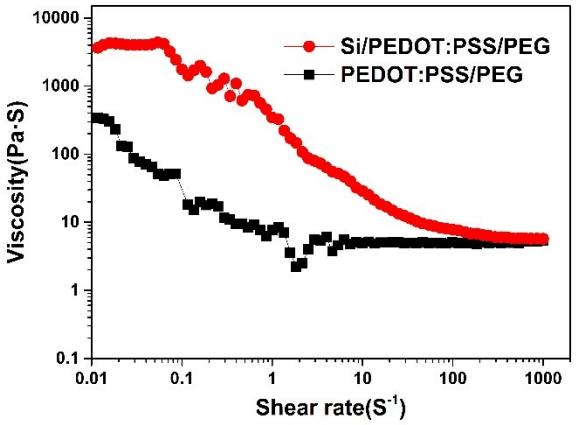

Figure S1. Viscosity of Si/PEDOT:PSS/PEG and PEDOT:PSS/PEG plotted with respect to shear rate.

3. SEM analysis

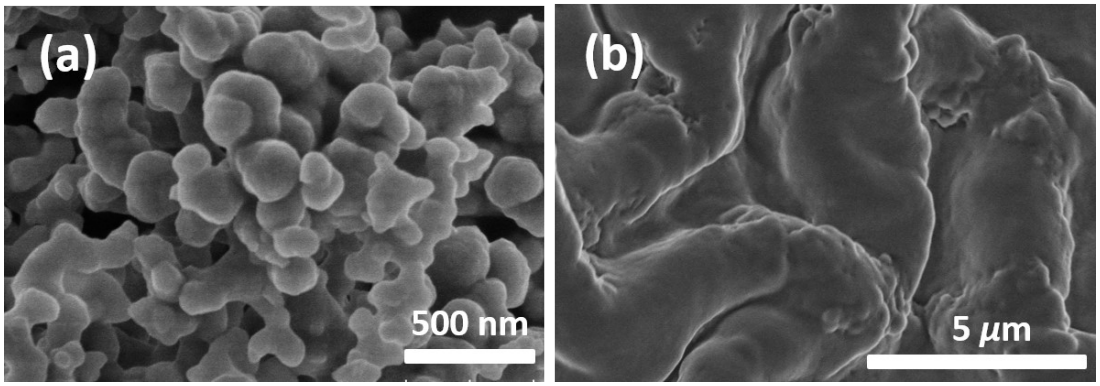

Figure S2. SEM images of the Si NPs (a) and 3D-printed Si/PEDOT:PSS/PEG electrode (b).

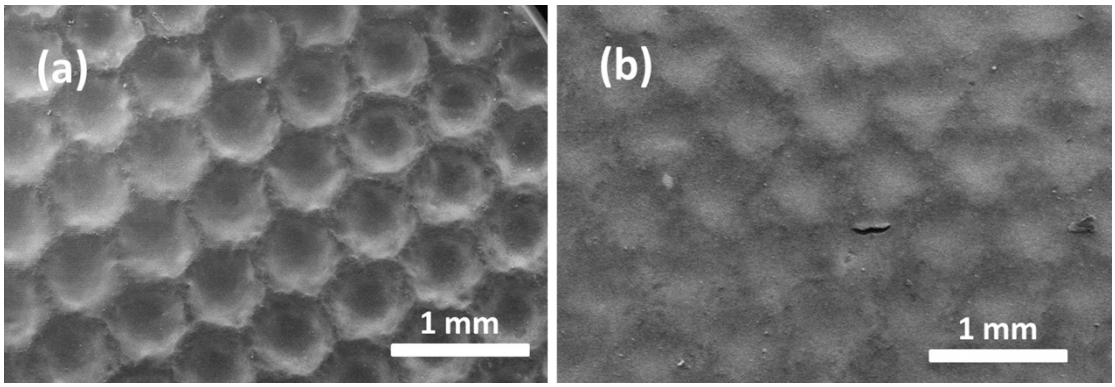

Figure S3. SEM images of the 3D-printed Si/PEDOT:PSS/PEG electrode structure (a) before and (b) after cycles.

4. DSC-TGA measurement

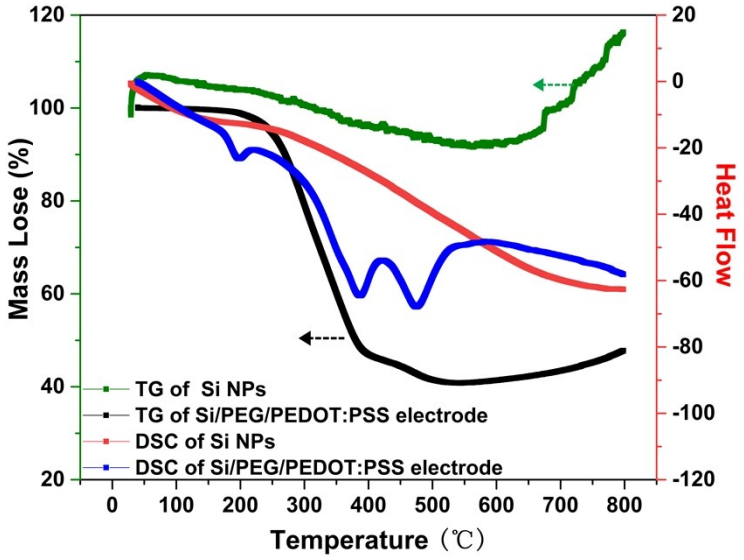

Figure S4. TGA curves of traditional Si NPs and Si/PEDOT:PSS/PEG electrode under an air atmosphere.

1 D.Y. Heo, N. Acquah, J.H. Kim, S.J. Lee, N.J. Castro and G.L. Zhang, *Tissue engineering, Part A,* 2018, **24**(7-8), 537-545.

2 Y.Y. Lee, H.Y. Kang, S.H. Gwon, G.M. Choi, S.M. Lim, J.Y. Sun, Y.C Joo, *Adv. Mater,* 2016, **28**(8), 1636-1643.