Three-Dimensional Printed Si/rGO Anode for Flexible Li-ion batteries

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Experimental section

Preparation of the Si/GO ink:

Disperse 50 mg Si nanoparticles (approximately 50 nm) into 10 mL 50 % ethanol solution. Bath sonicate for 1 hour to ensure a uniform suspension of Si. Then, dilute 10.64 g of GO solution (9.4 mg g^{-1}) with 10 mL deionized water. Mix the Si suspension and the diluted GO solution together through bath sonication for another one hour, and the Si/GO suspension is obtained with the concentration of approximately 5 mg mL^{-1}. The Si/GO suspension is then passed through a simple filtration process to achieve a concentration of 70 mg mL^{-1}, whcih exhibits shear-thinning behavior in the rheological tests. The obtained ink is transferred into a 10 mL syringe for the 3D-printing process.

Synthesize of the 3D-printed Si/GO material and the sandwich Si/GO film:

A syringe with the nozzle size of 203.2 μm is filled with Si/GO ink and fixed on an industrial 3D printer (F4200N.1 Compact Benchtop Robot). The air pressure was controlled by a fluid dispenser (DSP501N, Fisnar) and kept within a range of 10 - 100 psi. The printing pattern of the grind structure (length of 2 cm, width of 1 cm, line spacing of 0.8 mm for the printed fibers) is programmed into the printer in three dimensions. The distance between the syringe tip and the substrate is 1 mm when printing the first layer, and the distance is adjusted to 2 mm when printing the second layer. The moving speed of the nozzle are adjusted between 1-10 mm s^{-1} according to the air pressure. The infill density is 50%. Before reducing, the 3D-printed Si/GO are placed in a freeze drying machine (Labconco FreeZone 2.5 Benchtop freeze dry system) for 2 days after quickly dipping in liquid nitrogen. The Si/GO film with the layer-by-layer structure is prepared from the same Si/GO ink but is dried in a dish in air for 2 days after the filtration process.

Preparation of the Si/rGO anodes:

The 3D-printed and freeze-dried Si/GO material and Si/GO films are transferred to a tube furnace and reduced at 800 ℃ for 2 hours in a 5 % H_2/Ar atmosphere. The grid-like structure of the 3D-printed Si/rGO and the porosity obtained from freeze drying are maintained after thermal reduction. Finally, the 3D-printed Si/rGO anodes are thoroughly pressed under 10 MPa for 30 seconds with a final measured thickness of 20 μm. The Si/rGO film anode is ready-for-use after the high-temperature reduction process with the same thickness to the 3D-printed Si/rGO anode.

Analysis of the electrochemical performance:

The 3D-printed Si/rGO anode and Si/rGO film are cut into squares with 1 cm × 1cm dimensions. Lithium metal counter electrodes and NMC532 cathodes (8.2 mg cm^{-2} mass loading) are paired with both anodes in CR 2032-type coin cells and pouch cells, respectively. The electrolyte for the cells is 1.0 mol L^{-1} $LiPF_6$ in ethylene carbonate (EC) and diethylene carbonate (DEC) (1:1 volume ratio) with 10 vol% of fluoroethylene carbonate (FEC) additive. Electrochemical impedance spectroscopy (EIS) is performed on a BioLogic VMP3 potentiostat within the frequency range of 100 mHz to 1 MHz. The galvanostatic charge and discharge curves, the cycle performance, and the rate performance of the half and full cells are measured on an Arbin BT2000 system in the voltage range of 0.05-1.5 V and 3.0-4.3 V, respectively.

Characterization:

The rheological properties of the Si/GO ink were conducted on a rotational rheometer (HAAKE Rheo Stress 6000, Thermo Scientific) at room temperature. The morphologies of the Si/rGO electrodes were observed on a Tescan XEIA FEG SEM at 15 kV. The X-

ray diffusion (XRD) of the electrodes were performed on a D8 Advanced system (Bruker AXS, WI, USA) by a Cu Kα radiation source at 40 kV and 40 mA. The Raman testing was carried out through a Horiba Yvon LabRam ARAMIS confocal Raman microscope with a 532 nm laser. The Si content of the anode materials was determined through thermogravimetric analysis (TGA) measurements conducted in air between room temperature and 650 ℃ with a heating rate of 5 ℃ min^{-1}. N_2 physisorption measurement was performed at 77 K by a ASAP 2460 Version 3.01. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Scientific™ K-Alpha™+ spectrometer equipped with a monochromatic Al Kα X-ray source (1486.6 eV) operating at 100 W.

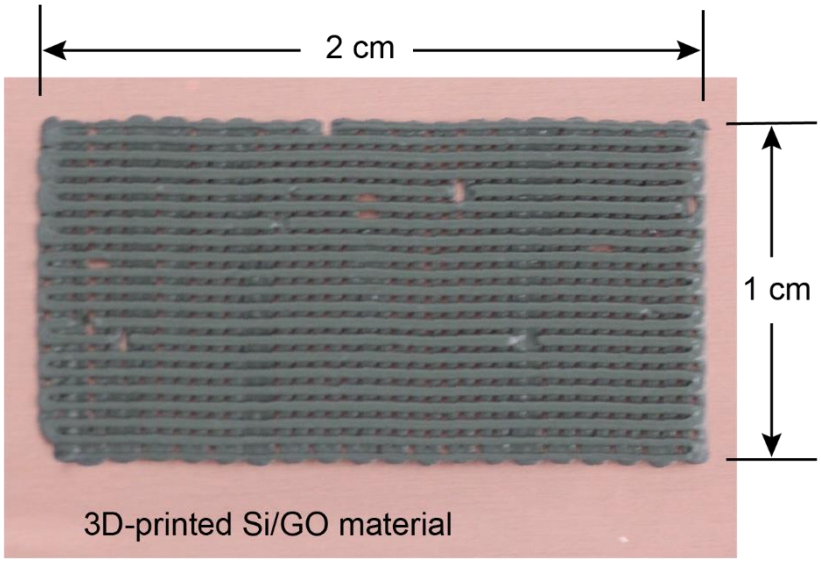

Figure S1. The digital image of the Si/GO material after 3D-printing process. The 3D-printed Si/GO material presents the grid-like structure with 2 cm length and 1 cm width.

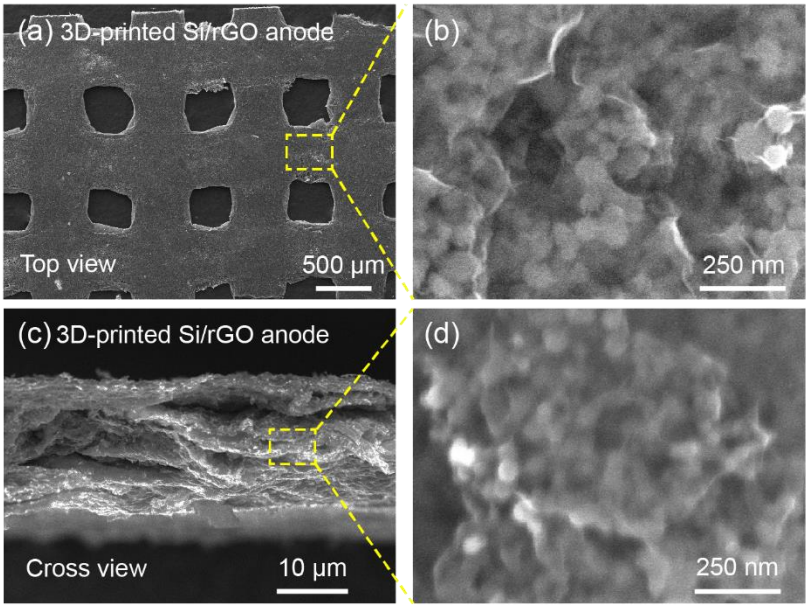

Figure S2. Top view (a-b) and cross view (c-d) of the 3D-printed Si/rGO anode. The top view image shows a typical grid-like structure, and the high magnification images presents well wrapped Si nanoparticles by rGO films. The magnified image of the cross view shows similar Si/rGO structure to the top view image, illustrating that the Si nanoparticles are wrapped by the rGO films uniformly.

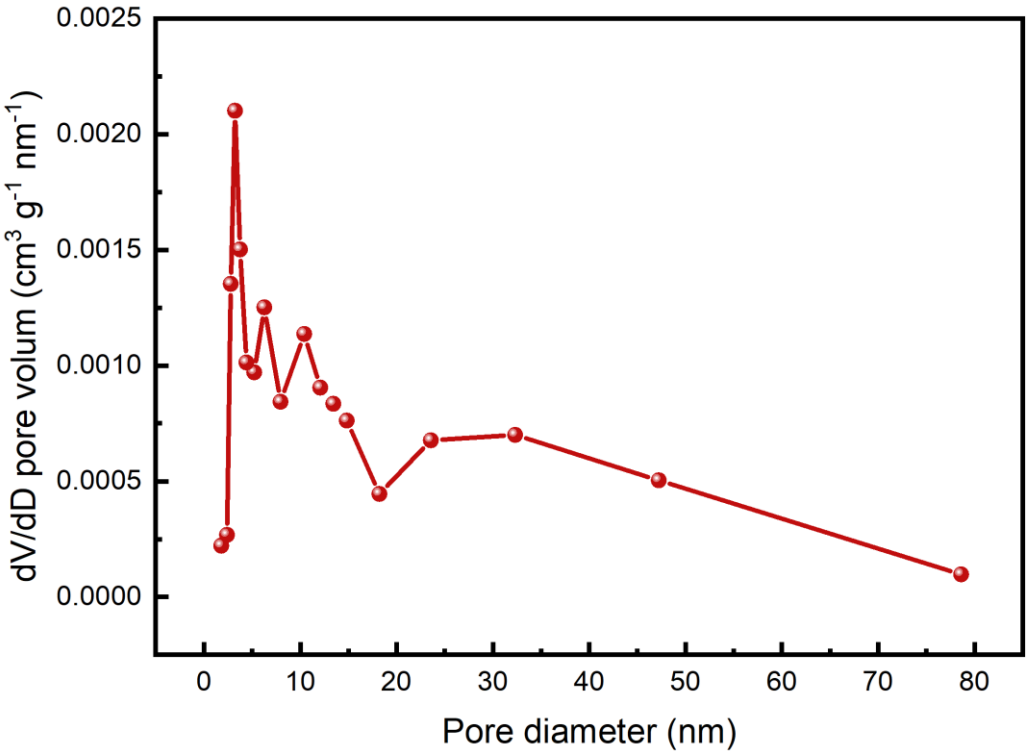

Figure S3. Pore size distribution of the 3D-printed Si/rGO anode

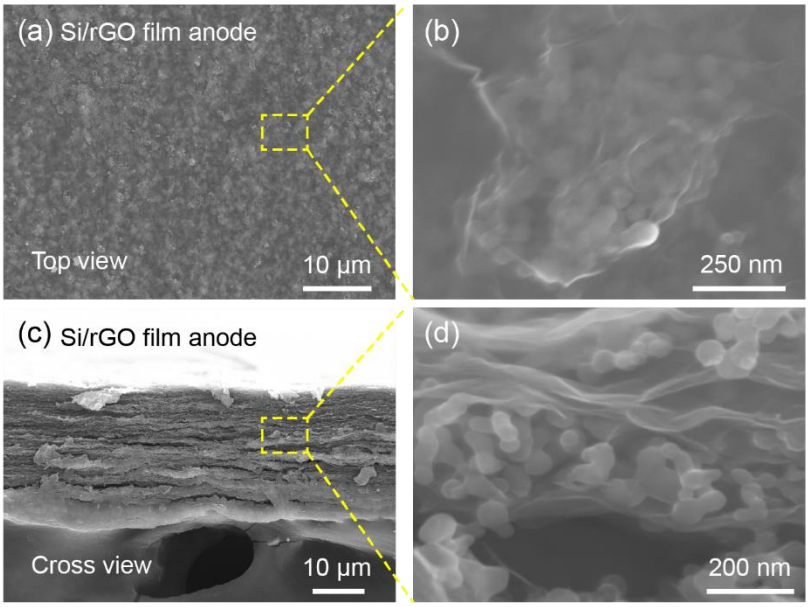

Figure S4. Top view (a-b) and cross view (c-d) of the Si/rGO film anode. The top view image shows the smooth surface and silicon nanoparticles are wrapped by the rGO films. However, the cross view image presents a layer-by-layer structure with the Si nanoparticles sandwiched in the middle of the rGO film layers.

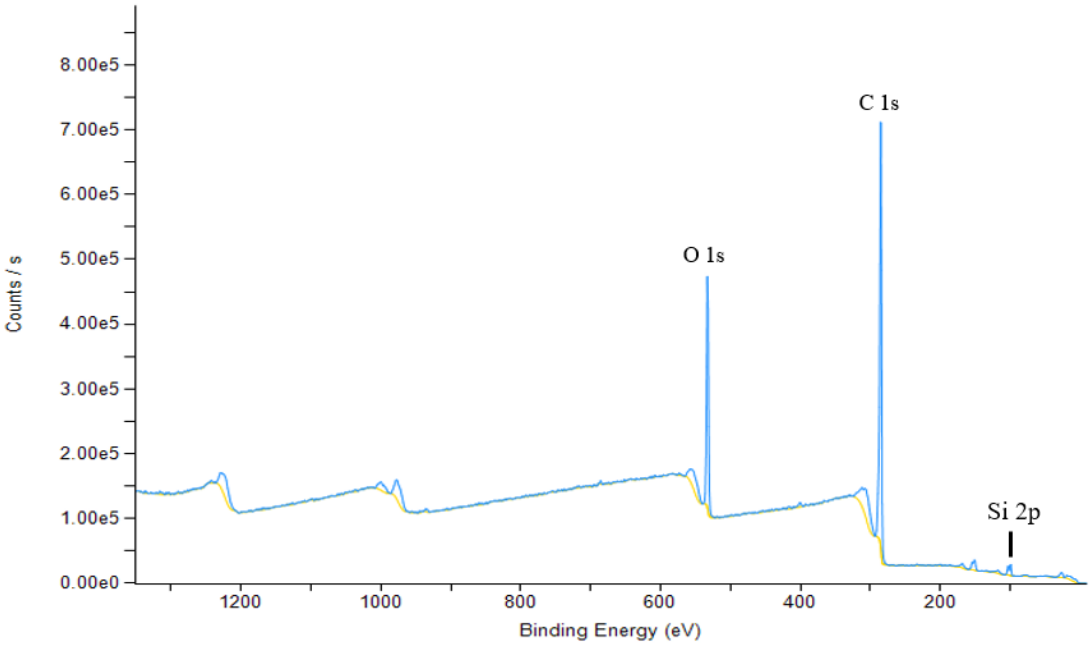

Figure S5. XPS spectroscopy of the 3D-printed Si/rGO anode before cycling.

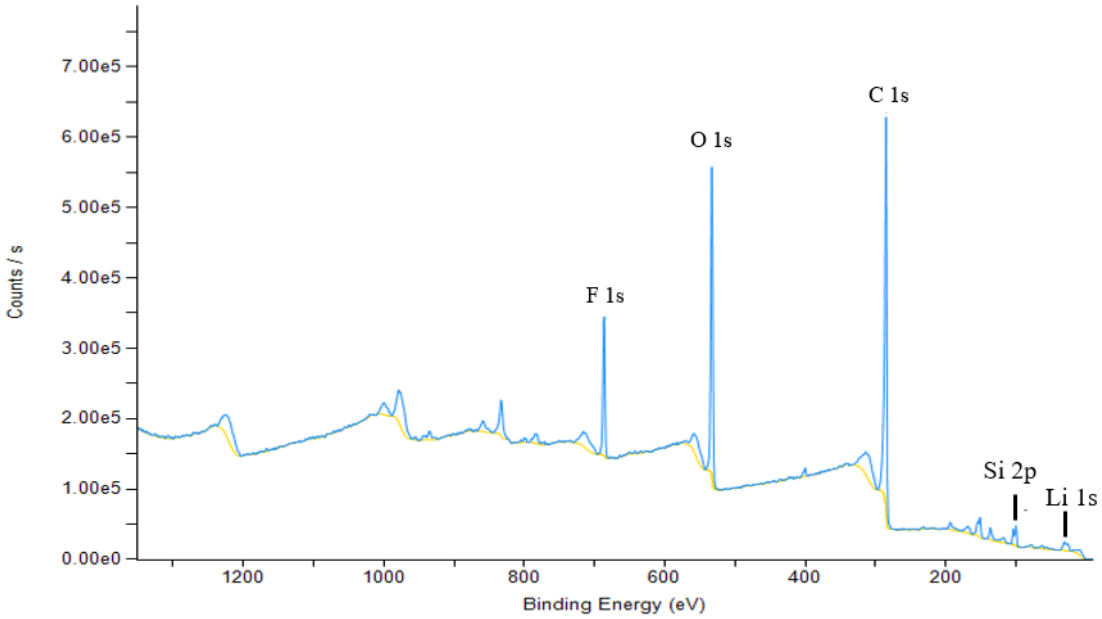

Figure S6. XPS spectroscopy of the 3D-printed Si/rGO anode after cycling.

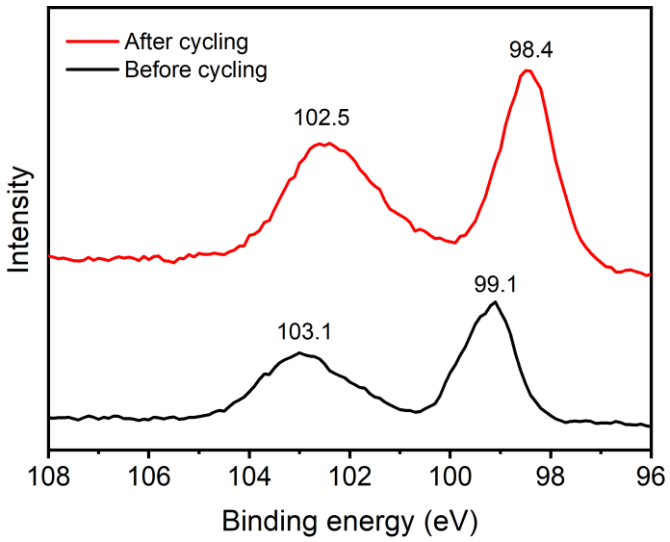

Figure S7. Si 2p XPS of the 3D-printed Si/rGO anode before and after cycling.

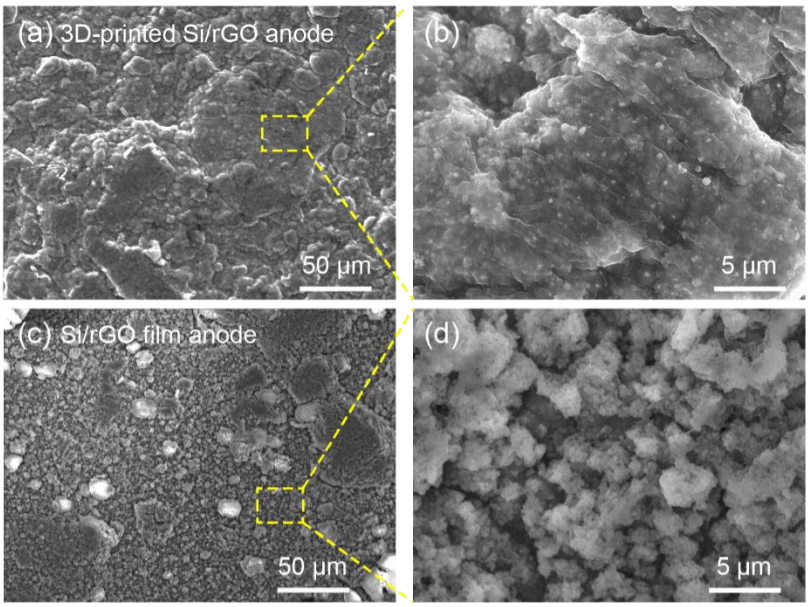

Figure S8. SEM images of the 3D-printed Si/rGO anode (a-b) and Si/rGO film anode (c-d) after 350 cycles in half cells. The 3D-printed Si/rGO anode could keep intact after the long cycle process because of the alleviation effect from the grid structures, while the Si/rGO film anode are pulverized into small particles due to the repeated volume expansion and shrinks. The damage on the Si/rGO film anode will result in fast capacity decay in the batteries.

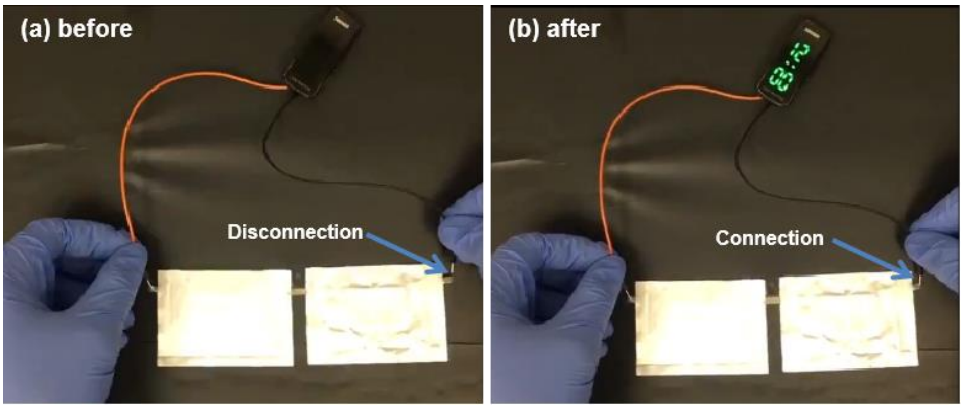

Figure S9. Digital images of the flexible pouch cell demonstration, which powers an electronic watch.

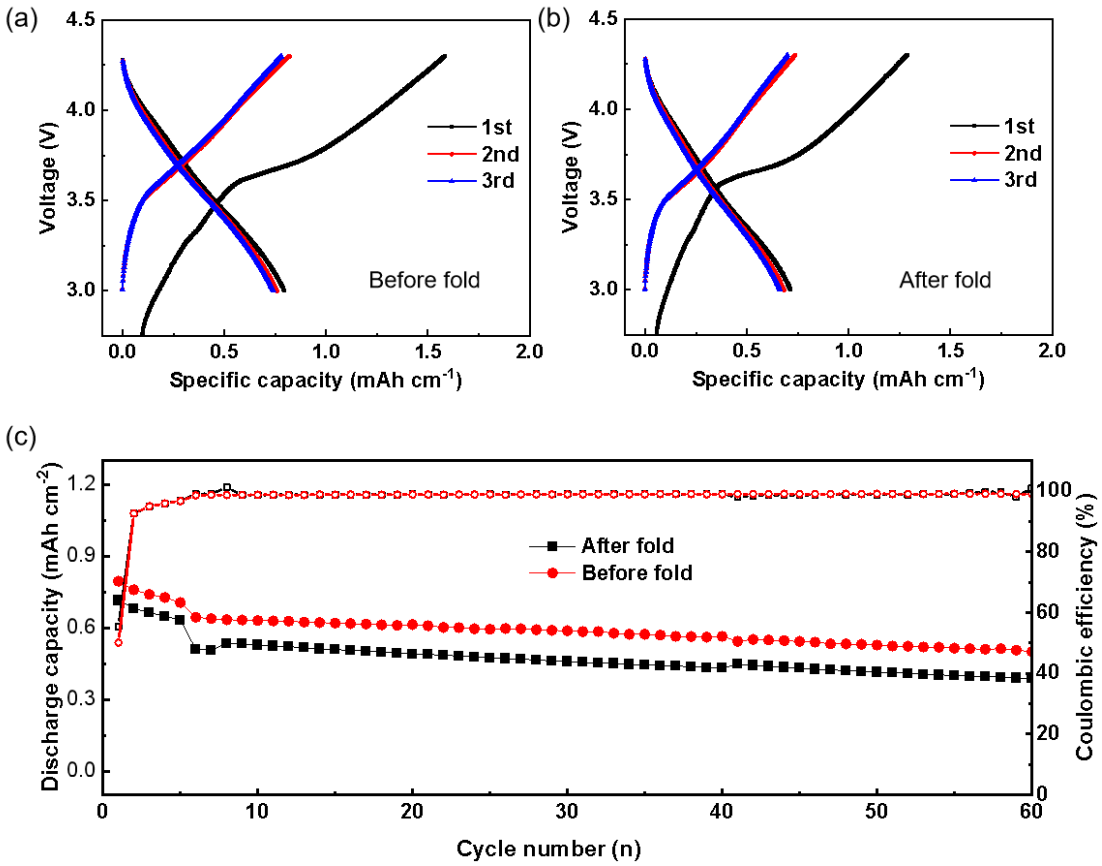

Figure S10. The electrochemical performance of the 3D-printed Si/rGO full cell before and after folded. (a, b) The galvanostatic charge and discharge curves of the 3D-printed Si/rGO full cell before (a) and after (b) folded at C/25. (c) The cycling performance of the 3D-printed Si/rGO full cells before and after folded at C/5.

Table S1. Surface composition of the 3D-printed Si/rGO anode before and after cycling.

Element	Atomic content before cycling (%)	Atomic content after cycling (%)
C	78.61	47.56
Si	2.87	3.48
O	18.52	15.99
F	-	27.71
Li	-	5.26