Supporting Information for

Regenerated-Cellulose Directed Hetero-Assembly of Nanoparticles and Carbon Nanotubes for Flexible Battery Anodes

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Experimental

NPs/CNTs Film Electrodes Fabrication

The Fe_3O_4 NPs were synthesized following the method described in the literature.[S1] The weakly oxidized CNTs were obtained by using piranha solutions (4:1, v/v 96% H_2SO_4/30% H_2O_2) treatment.[1] The Fe_3O_4/CNT film was fabricated through a solvation-induced assembly. Firstly, 5 mg of cotton as the cellulose material was dissolved in 3 g of ionic liquid (1-allyl-3-methylimidazolium chloride) in 20 mL container. Then 10 mg of oxidized CNTs were suspended in the above transparent solution, followed by addition of 35 mg of Fe_3O_4 NPs, and keep stirring at 80 ^oC to help a good dispersion of the mixture. The resulted black gel-like paste coated on a nickel foam substrate before entering a deionized-water, which maintained at room temperature for 1 h. The composite on the foam was washed with acetone followed by deionized water, and further dried at 100 ^oC for 12 h. Then the film electrode was peeled off from the nickel substrate with a mass loading of ~1 mg cm^{-2}. The fabricate route for Si/CNTs electrode is similar to that of Fe_3O_4/CNTs. The primary materials are consisted of cellulose (3 mg), CNTs (6 mg), and Si NPs (12 mg).

Materials Characterization

The morphology of Fe_3O_4/CNTs and Si/CNTs composites were investigated by field-emission scanning electron microscopy (SEM; FEI Nova 600), as well as by high-resolution transmission electron microscopy (HRTEM; JEM-2010F). The flexible electrode films were cut into strips for mechanical tests, which were performed on an INSTRON 5564 with a speed of 5.0 mm min^{-1} at

room temperature.

Electrochemical Measurement

The electrode was assembled into 2032-type coin cells, using glass fiber (GF/D, Waterman) as the separator. Metallic lithium discs were applied as the counter electrode, and 1.0 M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) mixture (1:1 by volume) with additional vinyl carbonate (2 % by volume) was used as the electrolyte. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) characterizations were performed on Solartron 1287/1260 electrochemical interface. The galvanostatic charge/discharge measurements were carried out by using LAND CT2000 battery tester at various current densities over a voltage range of 0.005-3 V and 0.01-2 V.

The Fe_3O_4/CNTs film electrode was further assembled into flexible battery, using lithium foil as the counter electrode and polydimethylsiloxane (PDMS) as the packing material. After the injection of electrolyte and sealing with UV-cured glue, the battery was taken out of glove box for test.

References

S1. Y. Cheng, Z. Chen, M. Zhu, Y. Lu, ***Adv. Engery Mater.*** **2015,** *5,* 1401207.

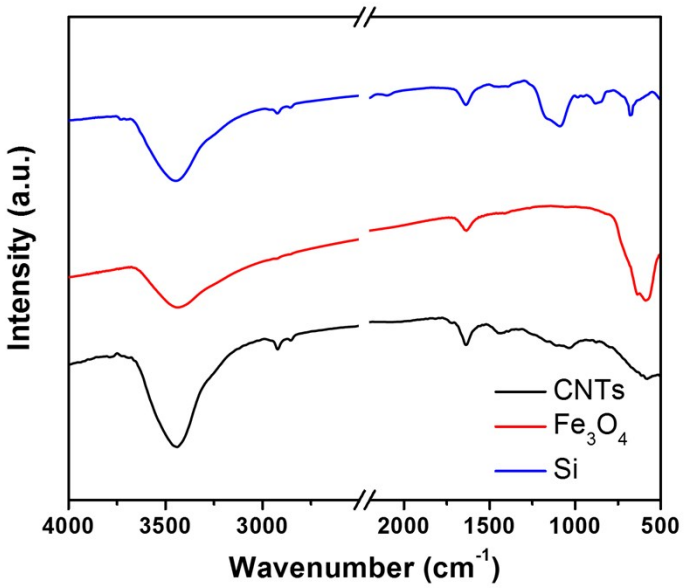

Figure S1. FTIR spectrum of Fe_3O_4 NPs, Si NPs and CNTs. The spectrum band of –OH groups and adsorbed water on the surfaces of NPs and CNTs can be observed in the range of 3000-3600 cm^{-1}.

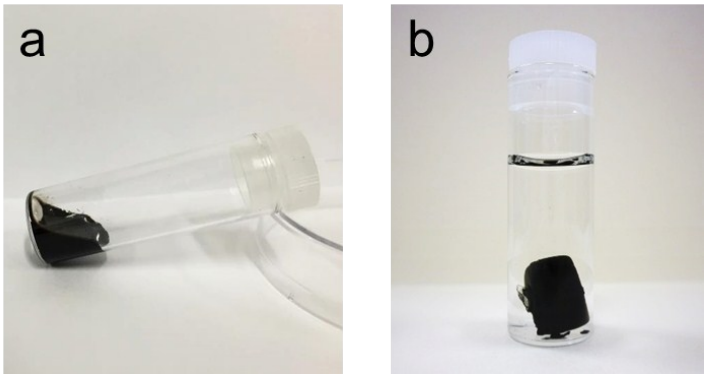

Figure S2. The photographs of (a) IL solution containing of cellulose, CNTs, and NPs and (b) NPs/CNTs composites regenerated from the IL solution by addition of water.

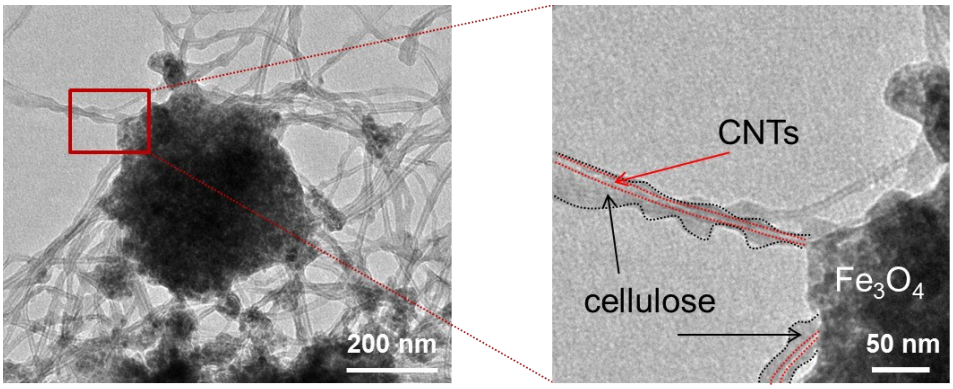

Figure S3. The magnification image (right) of the selected area of TEM image (left, Figure 2c), showing the effective cellulose coating on the surface of Fe_3O_4/CNTs.

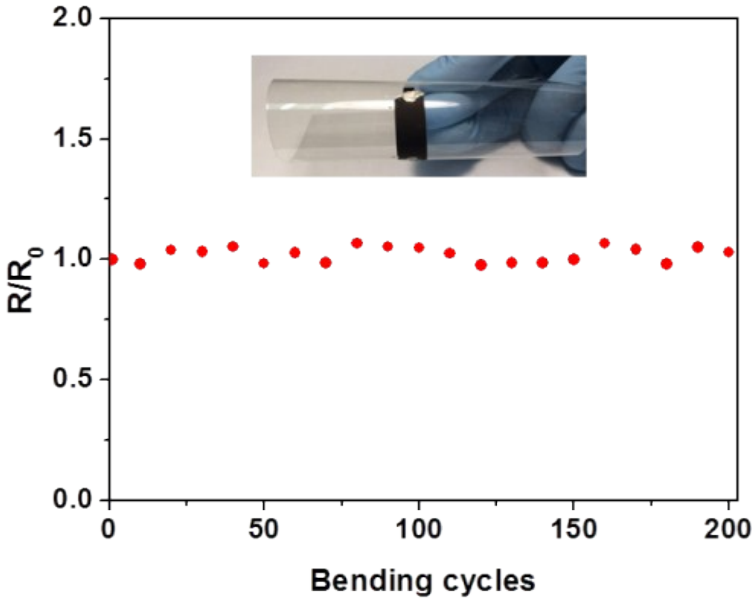

Figure S4. Dependence of film resistance over 200 bending cycles (resistance was normalized).

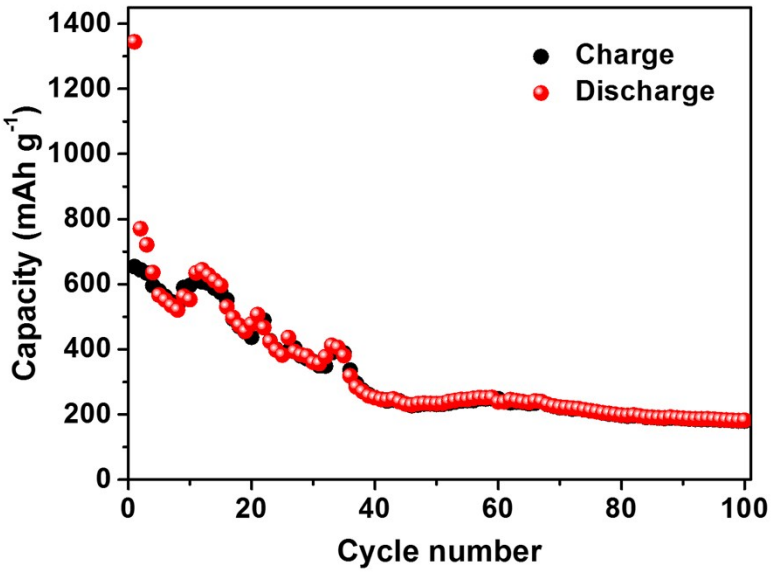

Figure S5. Cycling stability of controlled Fe_3O_4 electrode made in conventional slurry way at current density of 100 mA g^{-1}.

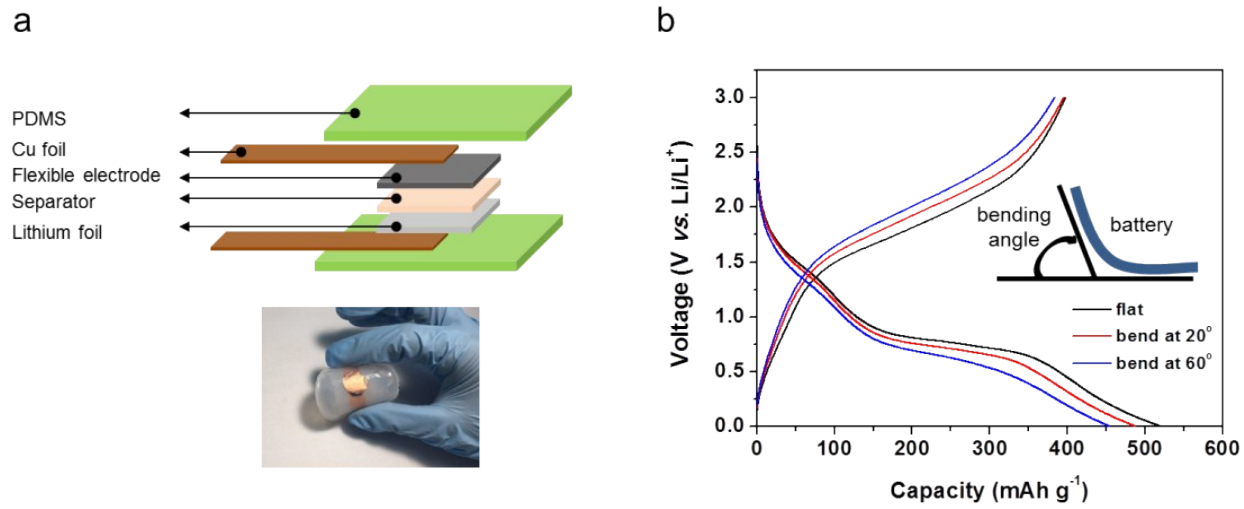

Figure S6. (a) (Top) the schematic structure and (bottom) photograph of flexible battery. (b) The charge and discharge curves of the electrode fixed at different bending states (current density: 500 mA g^{-1}).

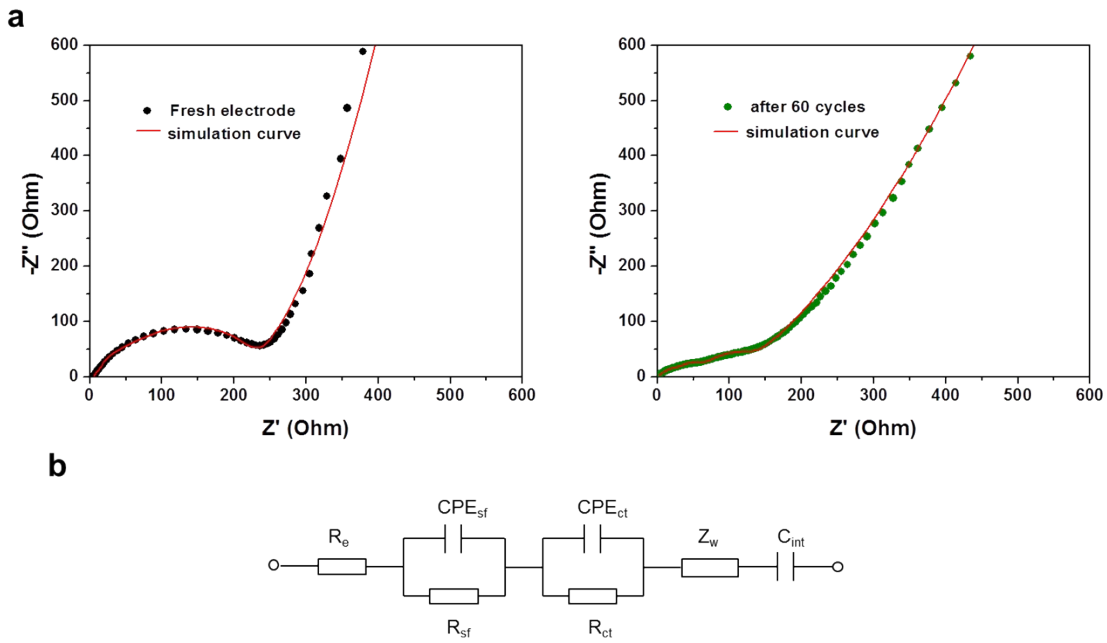

Figure S7. (a) Nyquist plots of the Fe_3O_4/CNTs film electrode at (left) fresh and (right) cycled state. Symbols represent experimental spectra and continuous lines represent fitted data using the equivalent electrical circuit shown in (b).

Table S1. Impedance Parameters Extracted by Fitting the Spectra to the Circuit Elements

Condition	$\mathbf{R_{sf} + R_{ct}}$ **(Ω)**	$\mathbf{CPE_{sf} + CPE_{dl}}$ **(μF)**
Fresh	193	10.2
After cycling	97	130

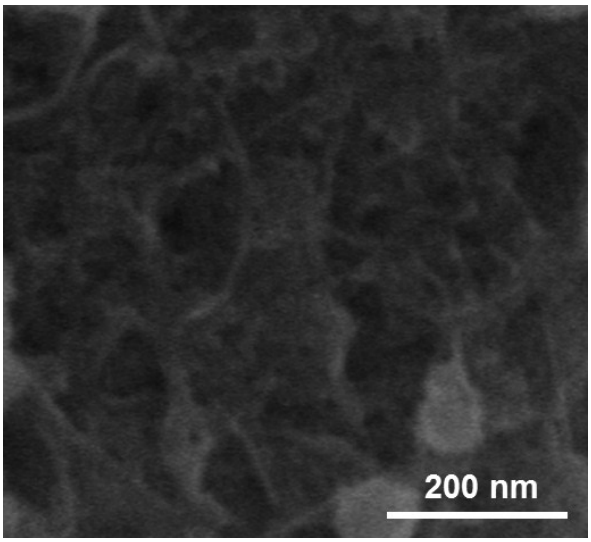

Figure S8. Morphology of the Fe_3O_4/CNTs electrode with retained architecture after cycling.

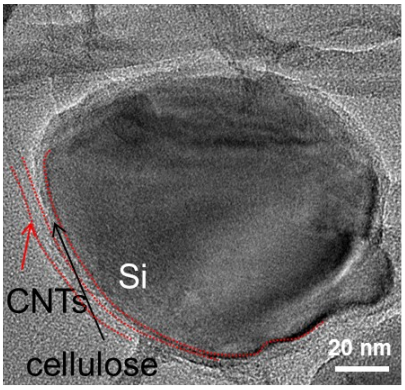

Figure S9. The TEM image of Si/CNTs shows good intimate interfacial contacts between Si NP and CNTs with the assistance of cellulose.

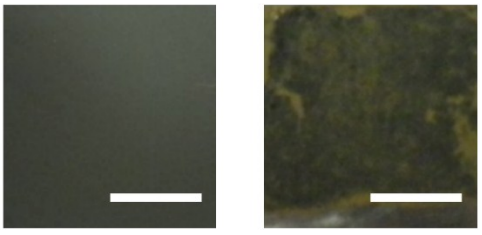

Figure S10. The photographs of the flexible Si/CNTs film electrode (left) fabricated by cellulose directed assembly way, and controlled Si electrode (right) made by conventional slurry way, respectively. The scale bar is 5 mm.

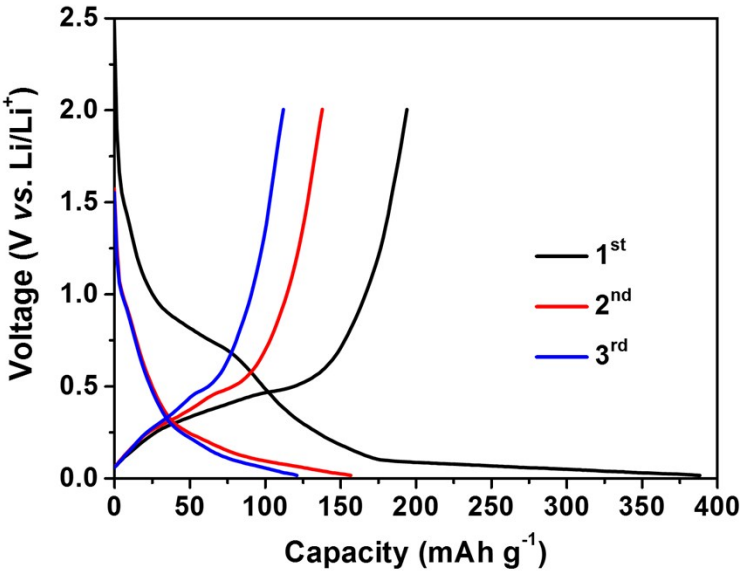

Figure S11. Charge-discharge voltage profiles at 200 mA g^{-1} of controlled Si electrode in the voltage window of 0.01-2 V (V *vs*. Li^+/Li).