Supporting Information

for

Carbon Nanofibers Interlayer: A Highly Effective Strategy to Stabilize Silicon Anodes for Lithium-ion Batteries

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Methods

Preparation method of carbon nanofibers (CNFs): 0.85 g polyacrylonitrile (PAN, MW=150 000, Aldrich), were dissolved in 9.15 g *N,N*-dimethylformamide (DMF, Sinopharm Chemical Reagent Co., Ltd.) to prepare the electrospun polymer nanofibers, which was then loaded into one 10 mL syringe with an 18-gauge blunt tip needle (0.86 mm inner diameter and 1.26 mm outer diameter). The solution was consequently electrospun using an electrospinning system (UCALERY Beijing Co., LTD, China). The syringe was pushed by a syringe pump with a flow rate of 19.00

μL·min^{-1}. The collector was a rotating cylinder coated with an aluminum sheet, placed 21 cm in the front of the needle. Two high voltages of +18.50 kV and -1.00 kV were supplied at the spinneret and the cylinder respectively. The collected electrospun nanofibers were stabilized in air at 280 °C for 3h with a heating rate of 2 K·min^{-1}. Subsequently, the above stabilized fibers were heated to 1000 °C under Ar flow of 175 mLmin^{-1}, where the heating rate was kept at 5 K·min^{-1}. Then the CNFs film was cut to disks.

Fabrication of working electrodes: Bare Si electrodes were prepared by mixing 60 wt% of Si nanoparticles (~100 nm), 20 wt% acetylene black and 20 wt% of polyvinylidene fluoride binder in an *N*-methylpyrrolidinone (Sinopharm Chemical Reagent Co., Ltd.) solution. The well-mixed slurry was tape-casted on a Cu foil and allowed to dry in a vacuum oven overnight, following by roll-pressing and cutting into circular electrodes with Si NPs loading of 0.5-0.7 mg/cm^2. Then one CNFs interlayer was roll-pressed onto one Si NPs electrode disk to make the Si NPs with CNFs interlayer electrode.

Characterization: The structure of the obtained materials was characterized by X-ray diffraction (XRD) (TTR-|||, Rigaku, Japan) using Cu Kα radiation. Fourier transform infrared (FTIR) spectra were performed by a Thermo Nicolet 8700 FTIR spectrophotometer. The degree of graphitization in P-CNFs was studied by Raman Spectroscopy. To execute elemental analysis, XPS experiments were performed using the Thermo-VG Scientific instrument. Field-Emission Scanning electron microscopy (FESEM) investigations were performed using a JSM-6700 field-emission scanning electron microscope (JEOL, Tokyo, Japan) operated at 5 keV. A JEOL 4000EX transmission electron microscope (HRTEM) (JEOL, Tokyo, Japan) was used to study the morphology.

Electrochemical Characterization: The Si NPs with CNFs interlayer electrodes were used as the working electrodes to perform batteries with 2032 coin cells with Li

metal as counter and reference electrodes. The electrolyte was 1 M $LiPF_6$ in a mixture of EC and DEC (1:1 = w: w), and Celgard 2400 membrane was used as a separator. The cells were assembled in an argon-filled glovebox. The galvanostatic charge-discharge tests were conducted between 0.001 and 1.2 V. To calculate the specific capacity contribution of Si NPs in the electrodes with the CNFs interlayer, a formula can be carried out as: Specific capacity contribution of Si NPs = (overall capacity of electrode – capacity contribution of CNFs) / the mass of Si NPs.

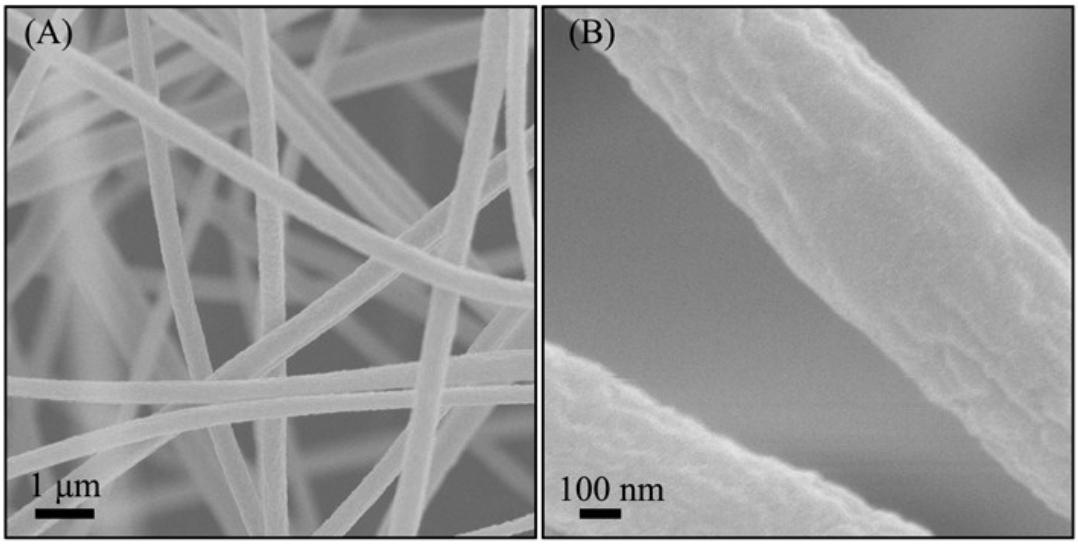

Figure S1 SEM micrographs of as-spun PAN nanofibers

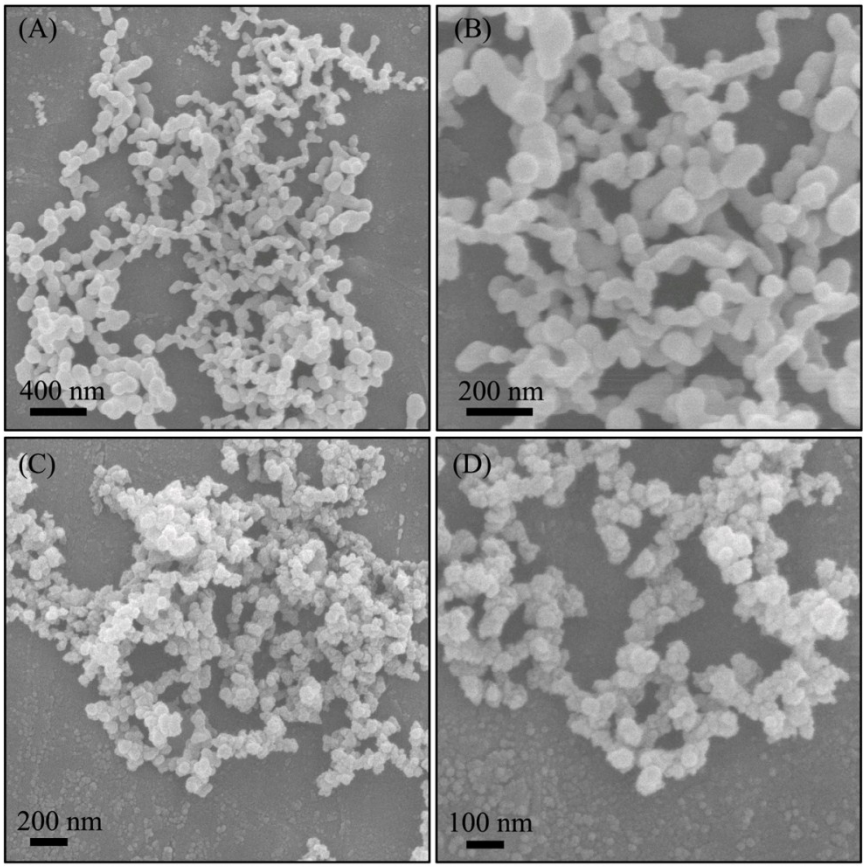

Figure S2 SEM micrographs of Si NPs (A, B) and acetylene black (C, D)

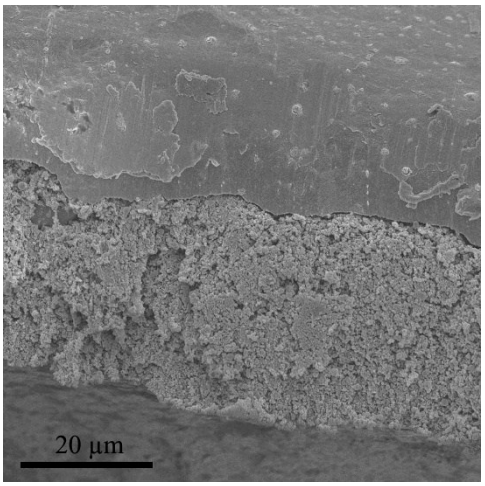

Figure S3 SEM micrograph of the cross-sectional view of Si NPs electrode.

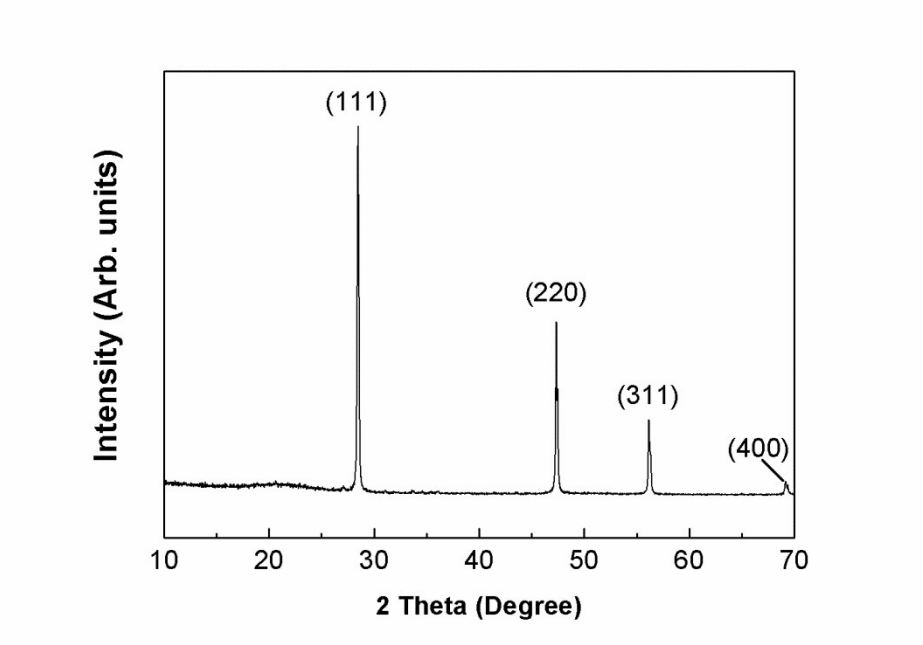

Figure S4 XRD pattern of Si NPs

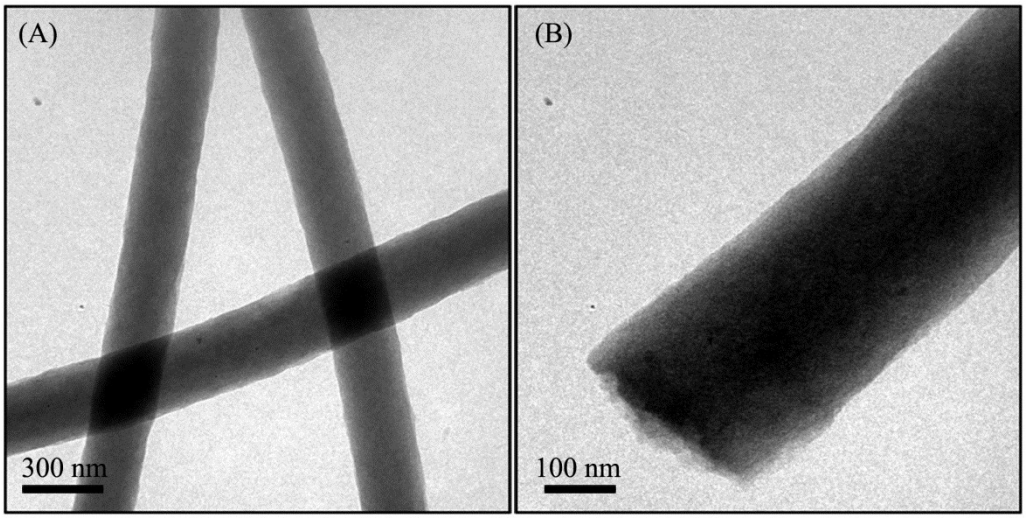

Figure S5 TEM micrographs of CNFs.

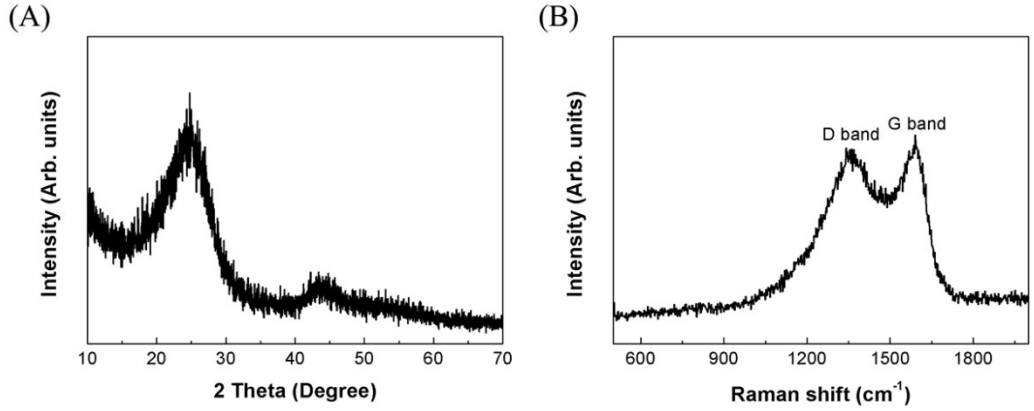

Figure S6 XRD pattern (A) and Raman spectrum (B) of CNFs. In the Raman spectrum, the D-band at ~1348 cm^{-1} reveals defects and disorder portions, while the G-band at ~1589 cm^{-1} is related to the graphitic layers. The R_I ($R_I = I_D/I_G$) value corresponds the disorder degree of carbon (0.94 for CNFs).

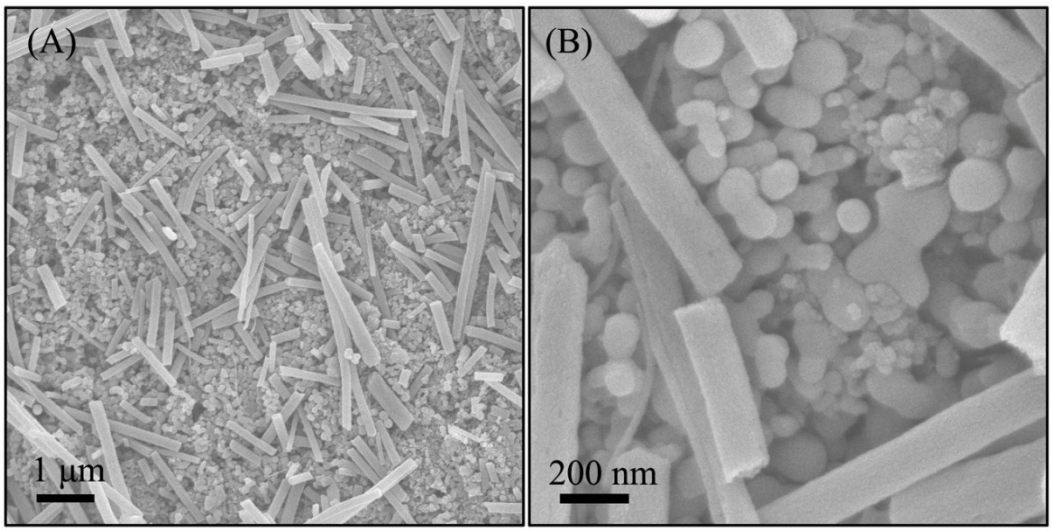

Figure S7 SEM micrographs of the Si NPs with CNFs interlayer after removing partial CNFs on the surface by a scalpel.

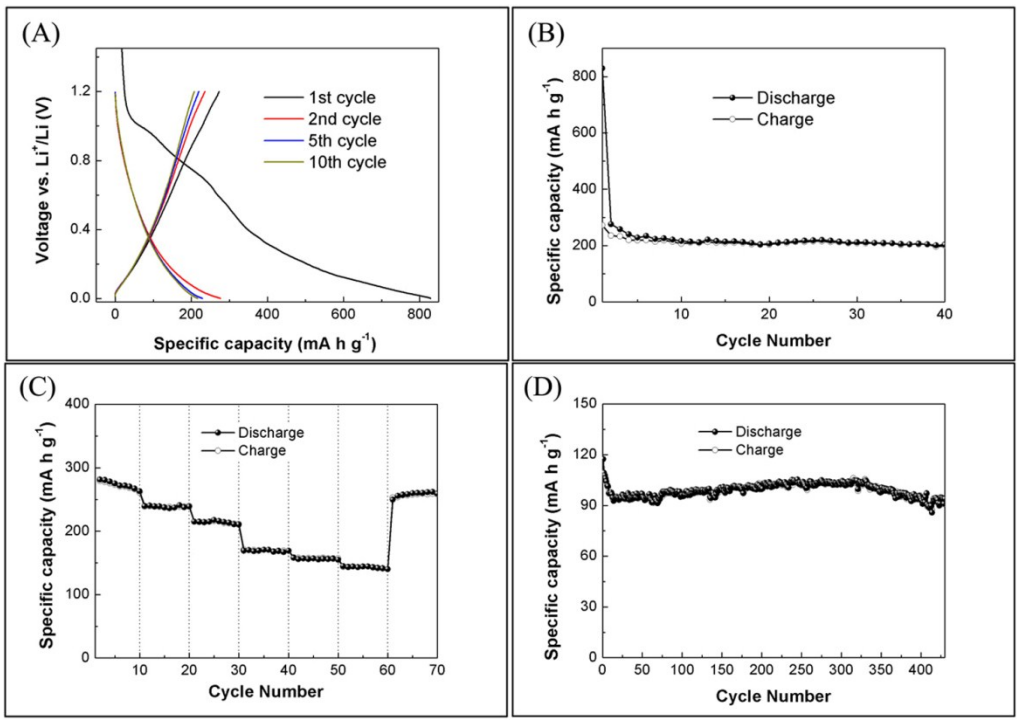

Figure S8 (A) Voltage profiles of CNFs interlayer cycled between 0.001V and 1.2 V vs. Li^+/Li at 1/20 C. (B-D) Electrochemical performance of CNFs interlayer. (B) Capacity retention of the electrodes a cycling rate of 1/20 C; (C) Rate performance of the electrodes cycled at various current densities same to the Si NPs with CNFs

interlayer; (D) A Long-term cycling performance at a high current density same with the Si NPs with CNFs interlayer (1.5 Ag^{-1}) for 430 cycles with activation firstly a low current density for five cycles.

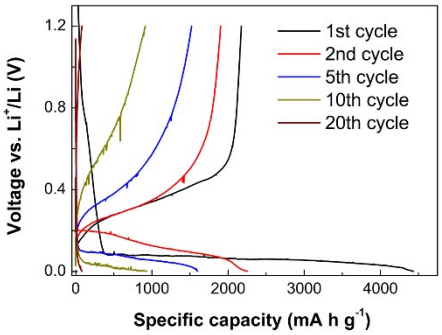

Figure S9 Voltage profiles of Si NPs electrodes without CNFs interlayer cycled between 0.001V and 1.2 V vs. Li^+/Li at a cycling rate of 200 mAg^{-1}.

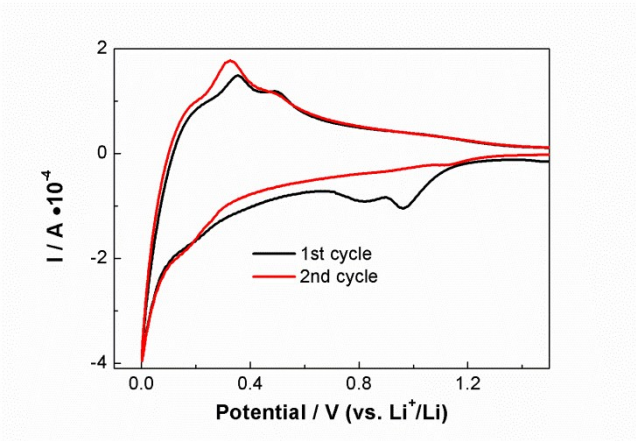

Figure S10 Cyclic voltammograms of Si NPs with CNFs interlayer at a scan rate of 0.1 mV/s (voltage range: 1mV–1.5 V).

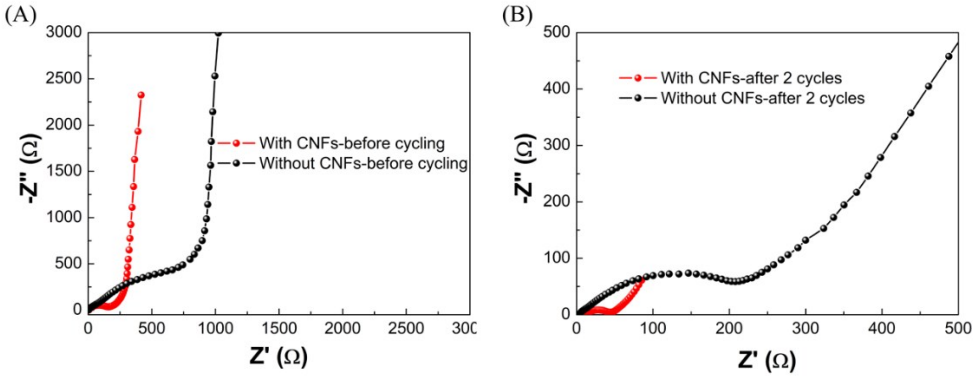

Figure S11 Nyquist plots of the Si NPs electrodes with and without the CNFs interlayer before cycling and after 2 cycles at a current of 200 mAg^{-1}. The open-circuit-voltage of electrode was controlled similarly (~ 1.2 V).

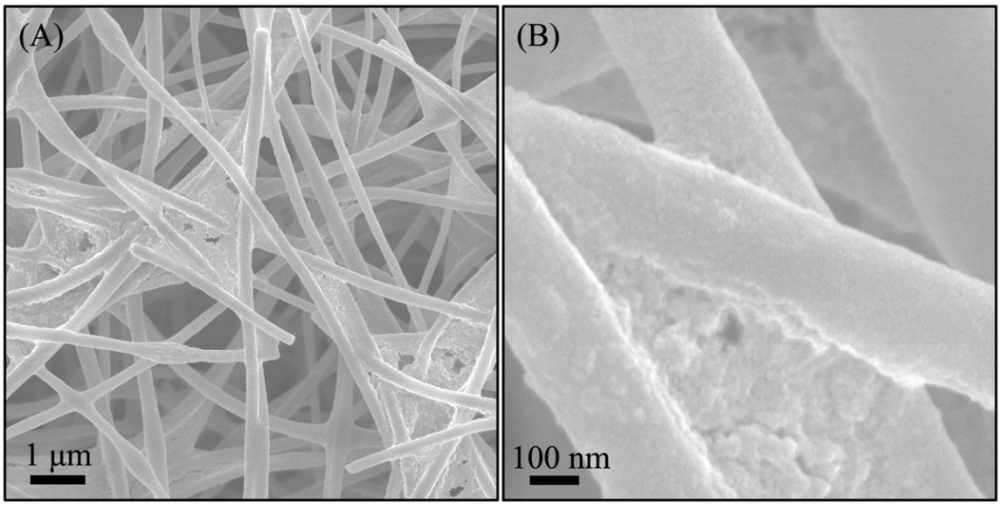

Figure S12 SEM images of bare CNFs after 40 cycles at 1/20 C.

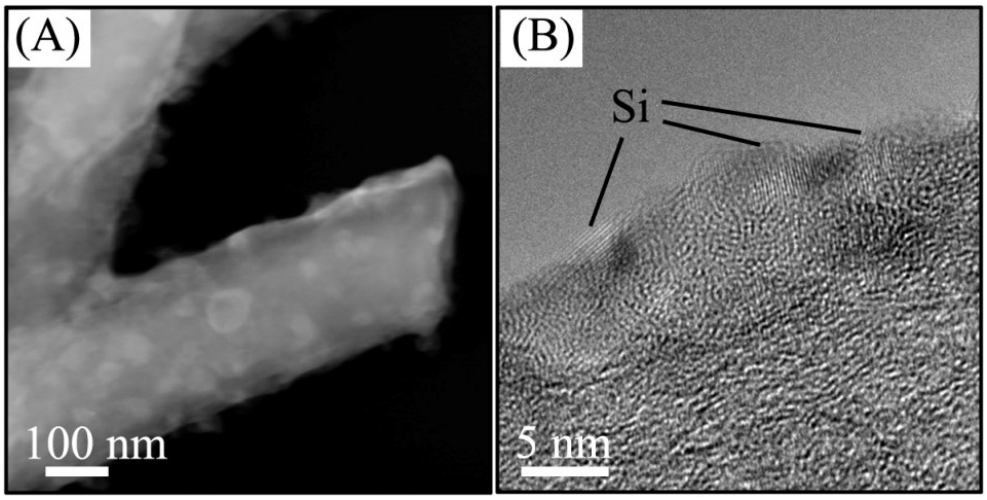

Figure S13 (A) Scanning Transmission Electron Microscope (STEM) and (B) High Resolution Transmission Electron Microscope (HRTEM) images of the CNFs interlayer after 40 cycles at 200 mAg^{-1}.