Supporting Information

Vine-like MoS_2 anode materials self-assembled from 1-D nanofibers for high capacity sodium rechargeable batteries

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Experimental Procedure

Synthesis of MoS_2 nanofibers: Ammonium molybdate tetrahydrate (ATTM), poly(styrene-acrylonitrile) (SAN, M_w = 130,000), sulfur and N,Ndimethylformamide (99.8%) as starting chemicals were purchased from Sigma-Aldrich Co., Ltd. MoS_2 nanofibers (NFs) were synthesized by a one-step electrospinning technique using a single nozzle. The precursor solution was prepared by dissolving the ATTM (1.2g) and the SAN (1.3g) into DMF (8g) and stirring for 8 h at room temperature. The precursor solution was loaded into a syringe with a metal needle, and the electrospinning process was carried out with the following parameters: applied voltage, 15 kV; feeding rate, 10 μl/min; needle size, 25 G; distance between the metal needle and collector, 15 cm; and rotor speed, 200 rpm. MoS_2 NFs were obtained by annealing the as-spun mat at 900 °C for 6 h with a heating rate of 5°C/min under a reducing atmosphere (H_2/N_2, 5%/95%). Excess sulfur was placed just beside the electrospun nanofibers to supply a sulfur source at the annealing atmosphere. The ATTM was converted into the MoS_2 phase and the SAN was burnt away during the annealing treatment.

Atomic layer deposition of TiO_2 onto the MoS_2 NF electrodes To improve the cycleability of the MoS_2 NFs, a uniform TiO_2 layer was coated onto the MoS_2 NF electrodes by means of atomic layer deposition (ALD). The electrode was fabricated on copper foil by casting a slurry consisting of 80 wt% active material, 10 wt% carbon (Super-P), and 10 wt% polyvinylidenedifluoride (PVDF) binder in N-methyl-2-pyrrolidone (NMP). After drying in air at 75 °C, the electrode was roll-pressed and then dried again under vacuum at 75 °C. The average loading density of the active materials was 0.5 mg/cm^2. The TiO_2 layer on the MoS_2 NF electrode was coated by ALD at 150 °C using tetrakis-dimethyl-amino-titanium (TDMAT, 99.999% purity, DNF Co. Ltd.) and thermal H_2O as a precursor and a second reactant, respectively. The ALD cycle consisted of initially 3 s of TDMAT precursor pulse time, 5 s for an evacuative Ar purge, and then 4 s exposure to the second reactant H_2O.

Structural characterization: The surface morphologies of the MoS_2 NFs were observed by field emission scanning electron microscopy (FE-SEM, Nova230, FEI). A transmission electron microscope (TEM, Tecnai F30 S-Twin, FEI) equipped with an energy dispersive spectrometer (EDS) was used to obtain information on the atomic distributions and internal microstructure of the MoS_2 NFs. The crystal structure of the MoS_2 NFs was examined by means of X-ray diffraction (XRD, D/MAX-RC, Rigaku). A surface analysis to verify the TiO_2 coating layer after ALD was carried out with X-ray photoelectron spectroscopy (XPS, Thermo, MultiLab 2000). The specific surface area and pore distribution of the samples were analyzed with a Brunauer–Emmett–Teller (BET) surface area analyzer (Micromeritics ASAP 2020 M+C).

Electrochemical characterization: The electrochemical performances of the MoS_2 NFs were evaluated in coin-type cells (2032, Hohsen). A Na-metal foil was used as the counter electrode. 1 M $NaClO_4$ in PC and a glass microfiber filter (Whatman Co. Ltd.) were used as the electrolyte and the separator, respectively. All cells were assembled in a dry box which had an Ar atmosphere and all of the potentials refer to Na/Na^+. All electrochemical experiments were performed at room temperature.

[Figure S1]

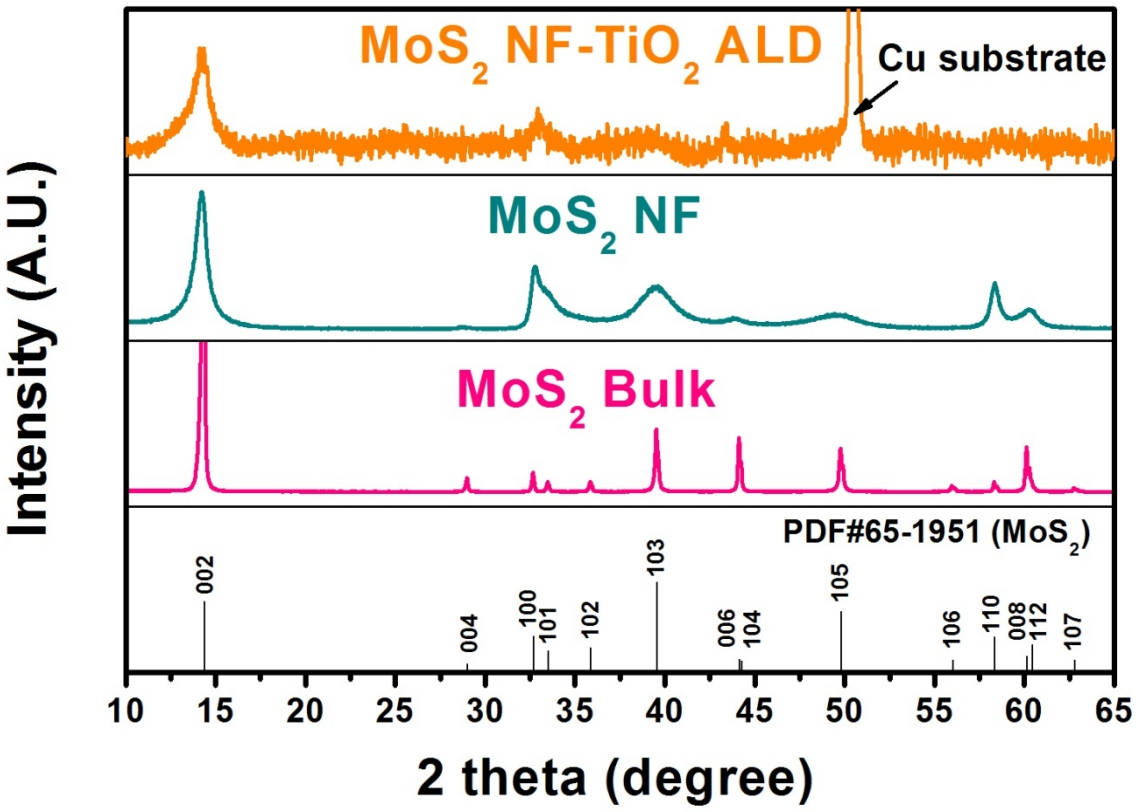

Figure S1. X-ray diffraction patterns of the bulk MoS_2 electrode, the MoS_2 NF electrode, and the TiO_2-coated MoS_2 NF electrode with reference peaks of MoS_2 (PDF#65-1951)

[Figure S2]

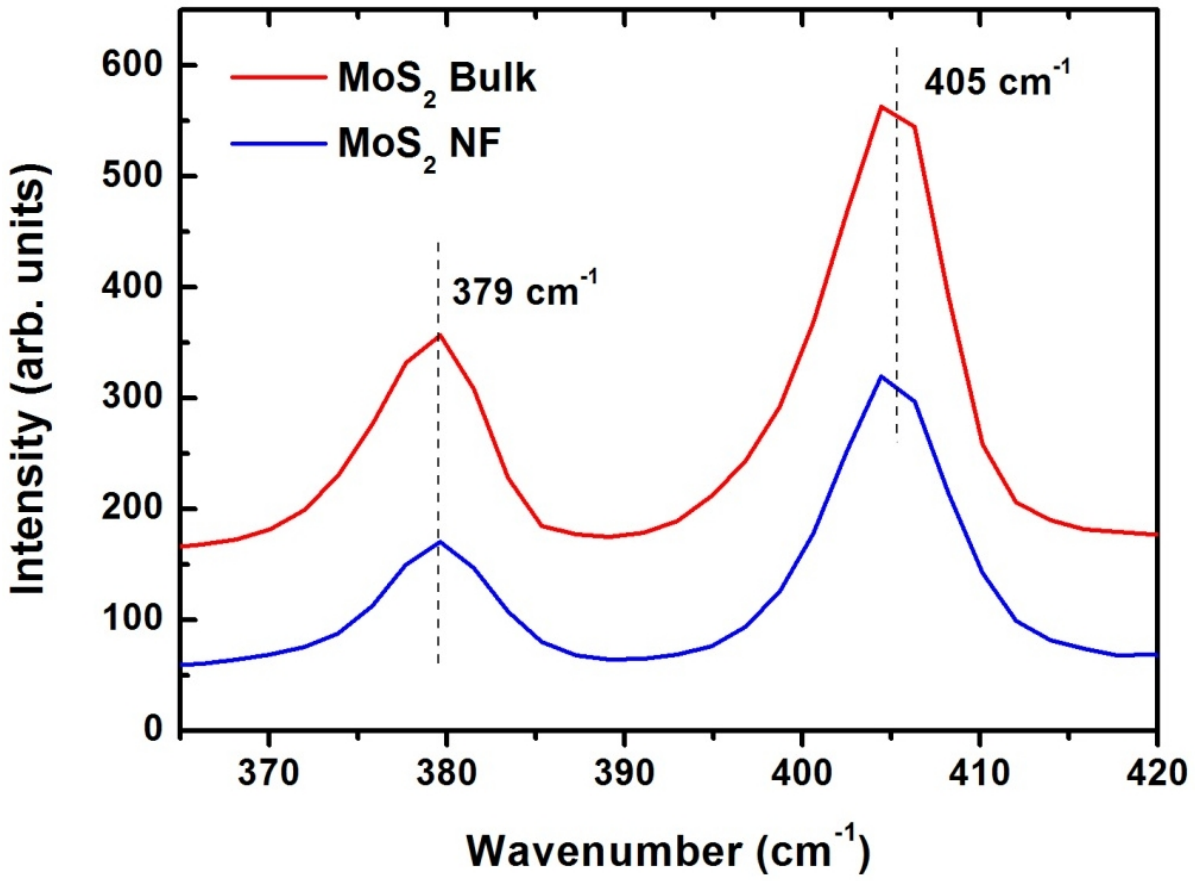

Figure S2. Raman spectra obtained from the bulk MoS_2 and the MoS_2 NFs corresponding to the Mo-S vibration mode

[Figure S3]

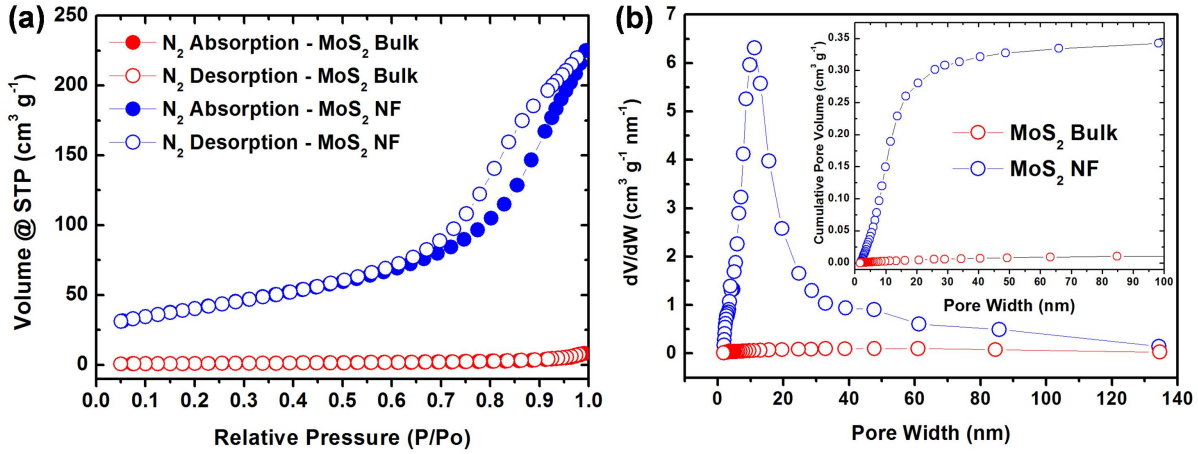

Figure S3. (a) Nitrogen adsorption/desorption isotherms obtained at 77 K, (b) pore size distribution, and cumulative pore volume (inset) of the bulk MoS_2 and the MoS_2 NFs

[Figure S4]

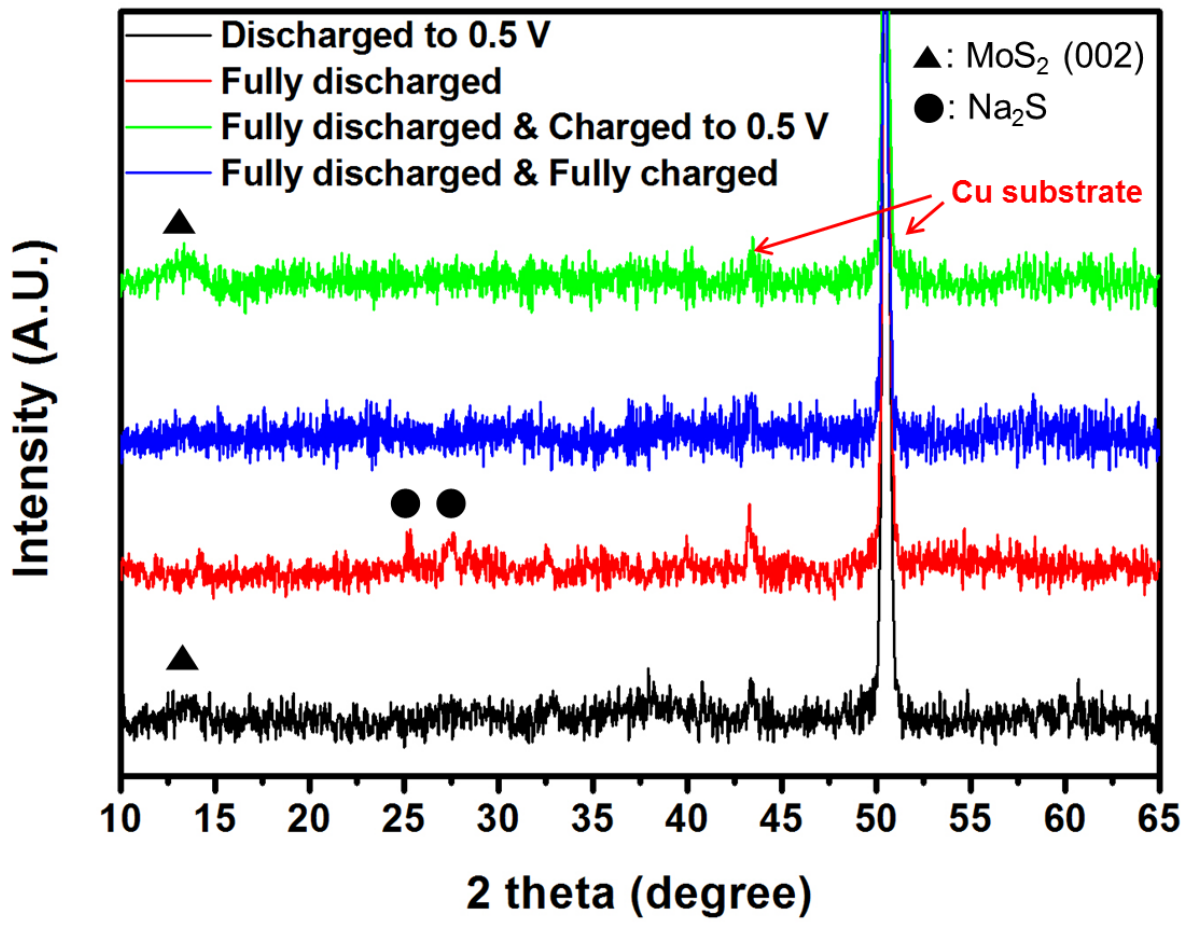

Figure S4. *Ex-situ* X-ray diffraction patterns of the MoS_2 NFs collected at various states during the charge and discharge process

[Figure S5]

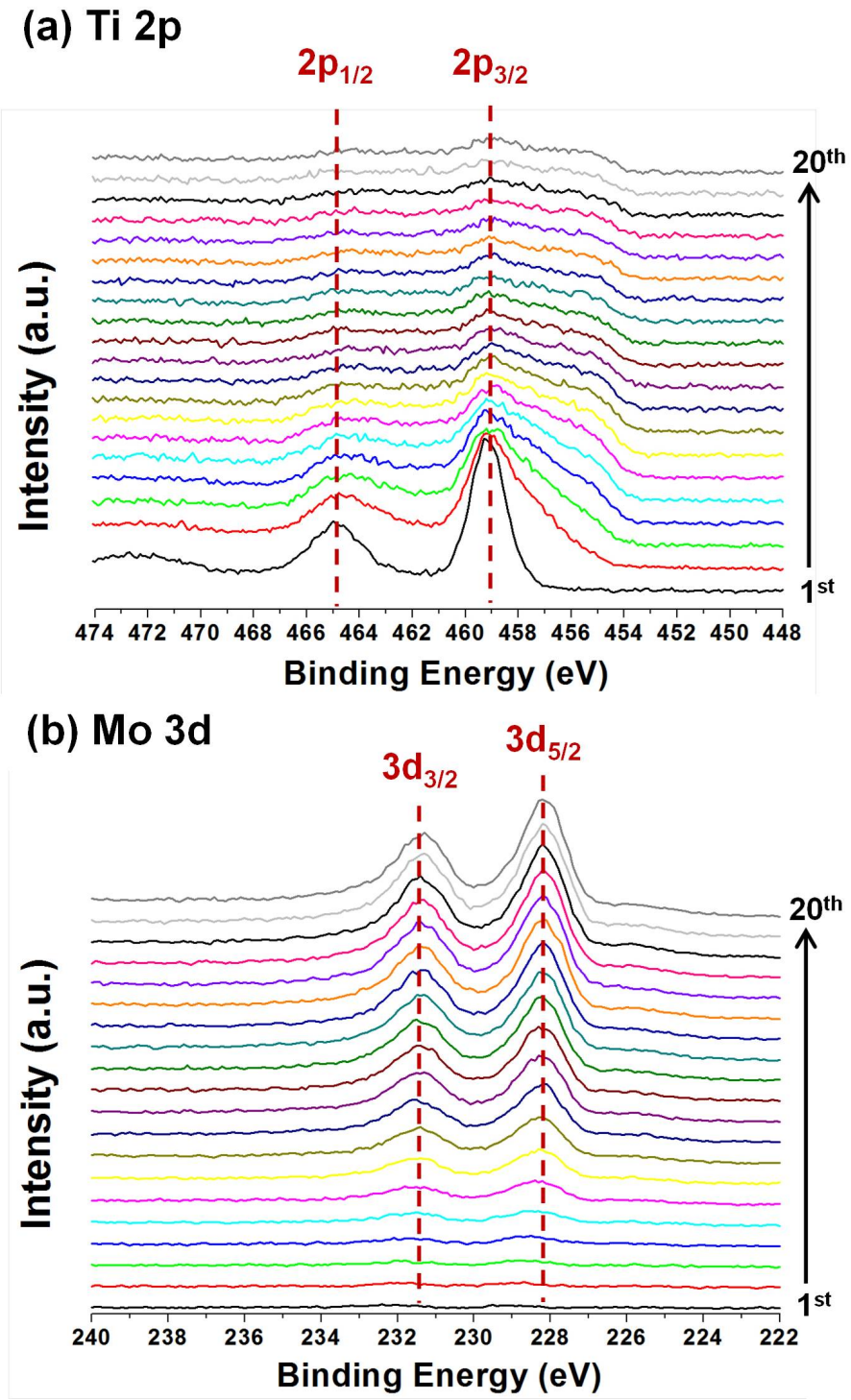

Figure S5. X-ray photoelectron spectra collected in the (a) Ti 2p and (b) Mo 3d regions obtained from the TiO_2-coated MoS_2 NF electrode. The XPS spectra of the electrodes were collected at a depth profile of 20 cycles.

[Figure S6]

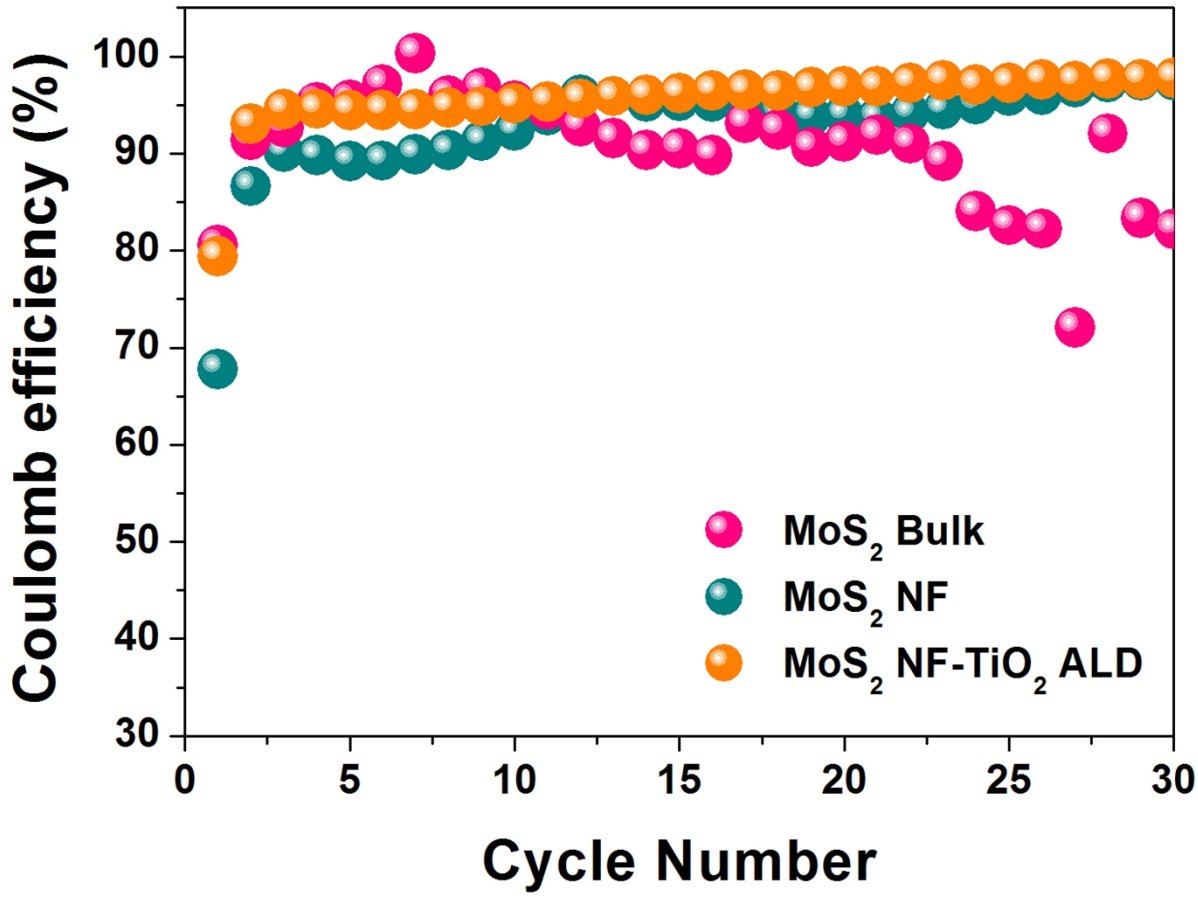

Figure S6. Coulomb efficiencies of the bulk MoS_2 electrode, the MoS_2 NF electrode, and the TiO_2-coated MoS_2 NF electrode during charge/discharge cycling in a voltage window between 3.0 and 0.01 V at a current density of 100 mA/g.

[Figure S7]

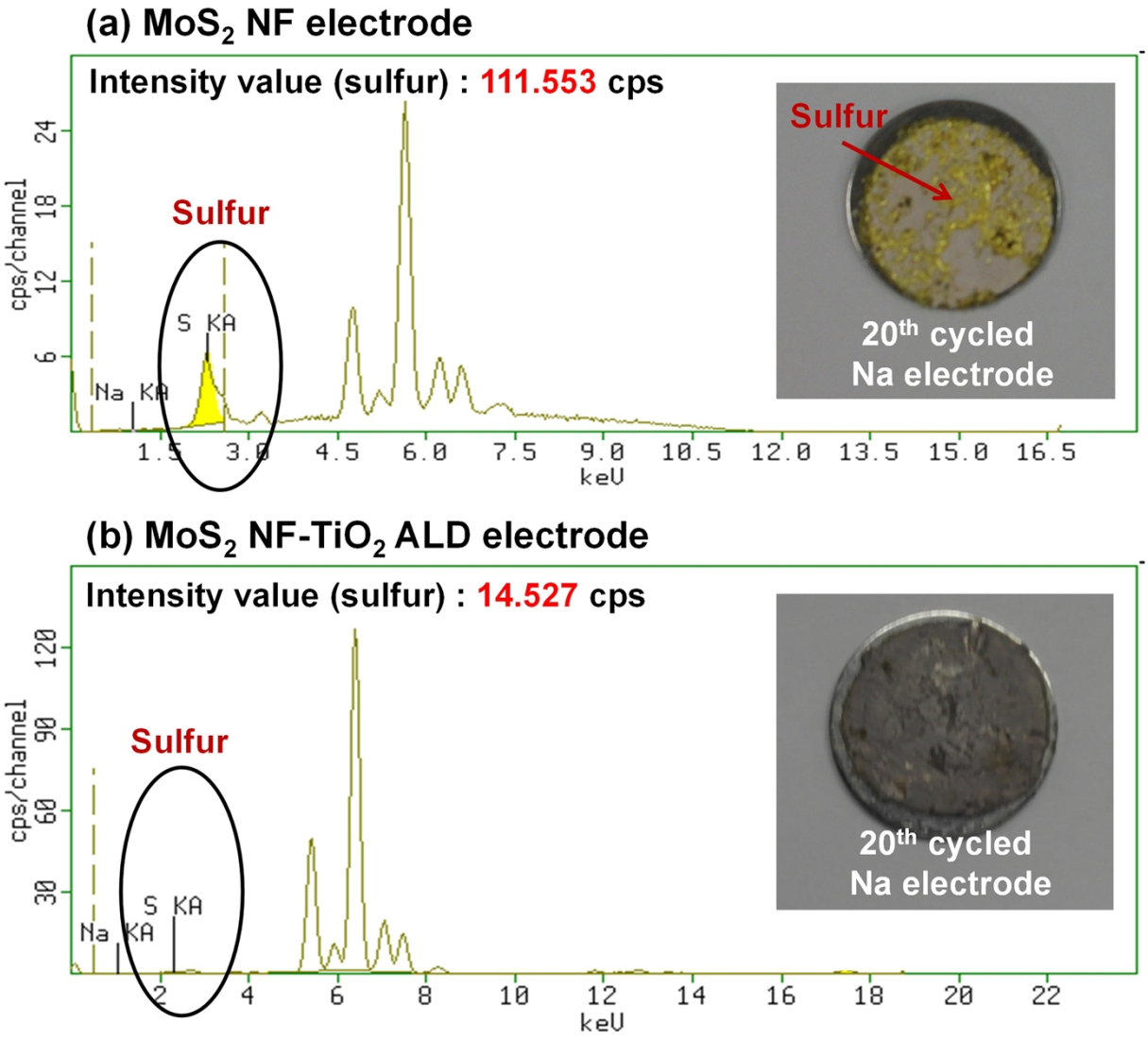

Figure S7. *Ex-situ* X-ray fluorescence analysis of the MoS_2 NF electrode and the TiO_2-coated MoS_2 NF electrode collected after the 20th cycle. The inset figures are *ex-situ* SEM images of a sodium metal electrode loaded onto a stainless steel spacer in a 2032 coin cell.