Supporting information

Extrinsic Pseudocapacitive Ultrathin 2D MoS_2 Nanoflakes Clamped 1D Sb_2S_3 Nanorods: An Advanced Heterostructured Anode for High-Energy Ammonium Ion Hybrid Capacitors

Supriya J. Marje[a], Harshitha B. Tyagaraj[a], Seung-Kyu Hwang[b], Kugalur Shanmugam Ranjith[a], Ebrahim Alhajri[c], Nilesh R. Chodankar[c], Yun Suk Huh[b]*, Young-Kyu Han[a]**

[a]Department of Energy and Material Engineering, Dongguk University-Seoul, Seoul, 04620, South Korea

[b]Department of Biological Engineering, Inha University, Incheon, 22212, South Korea

[c]Mechanical Engineering Department, Khalifa University, Abu Dhabi, 127788 United Arab Emirates

Experimental section:

Sb_2S_3/MoS_2 electrode preparation:

Synthesized Sb_2S_3/MoS_2 was well mixed with carbon black and polyvinylidene fluoride (PVDF) in a weight ratio of 8:1:1, and a few drops of ethanol were added to make a slurry. The slurry was coated on CC substrates and dried for 12 h at 120°C. An identical procedure was followed for Sb_2S_3 and MoS_2 electrode preparation using Sb_2S_3 and MoS_2, respectively.

Material Characterizations:

A detailed morphological study of the prepared samples was performed using a scanning electron microscope (FE-SEM, Hitachi, Japan) and a high-resolution transmission electron microscope (FE-TEM, JEM-2100F, JEOL, Japan). X-ray diffraction (XRD, X'Pert-PRO MRD, Philips, The Netherlands) with Cu Kα irradiation was used to investigate the structural characteristics of the prepared samples. BET surface area analysis was performed using N_2 adsorption/desorption isotherms obtained using a TriStar II fully automatic physisorption analyzer (Micromeritics, GA, USA). The chemical environment and valence states were examined by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, K-alpha, USA).

Electrochemical measurements:

Electrochemical analyses were performed on Zive SP6 instrument. A three-electrode cell was fabricated using as-prepared active material, Pt plate, and SCE as the working, counter, and reference electrodes, respectively. In addition, a two-electrode system was fabricated using MnO_2 as the cathode and Sb_2S_3/MoS_2 as the anode. Both cell types were fabricated in 1 M $(NH_4)_2SO_4$ electrolyte. Cycling performance was investigated using a Wonatech battery cycler (WBCS3000M1) with a three and two-electrode system.

Formulae used for calculations:

Specific capacitance (C_s) (F g^{-1}) is derived from Galvanostatic charge-discharge (GCD) analysis as follows,

$$C_s = \frac{I \times \Delta t}{w \times \Delta V} \quad \text{(S1)}$$

where I, Δt, w, and ΔV are current density, discharge time, mass of active material, and potential window, respectively.

Cathode and anode charges were balanced using the mass balance theory as per the following equation for the two-electrode cell,

$$\frac{m_+}{m_-} = \frac{C_- \times \Delta V_-}{C_+ \times \Delta V_+} \quad \text{(S2)}$$

where, $m_{(+\ or\ -)}$, $\Delta V_{(+\ or\ -)}$, and $C_{(+\ or\ -)}$ are the mass of active material (g), potential window (V), and specific capacitance (F g^{-1}) of cathode and anode, respectively.

Energy (E) (Wh kg^{-1}) and power density (P) (kW kg^{-1}) were calculated using the following formulae;

$$E = \frac{0.5 \times C_s \times (\Delta V)^2}{3.6} \quad \text{(S3)}$$

And

$$P = \frac{E \times 3.6}{\Delta t} \quad \text{(S4)}$$

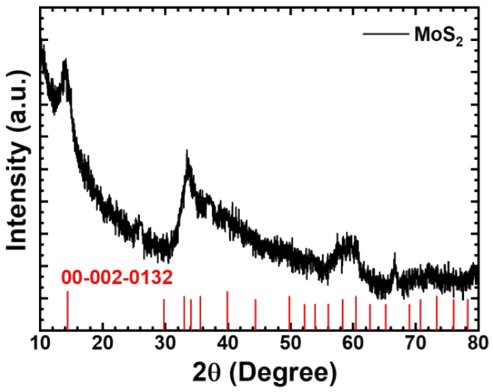

Fig. S1 XRD pattern of MoS_2 powder.

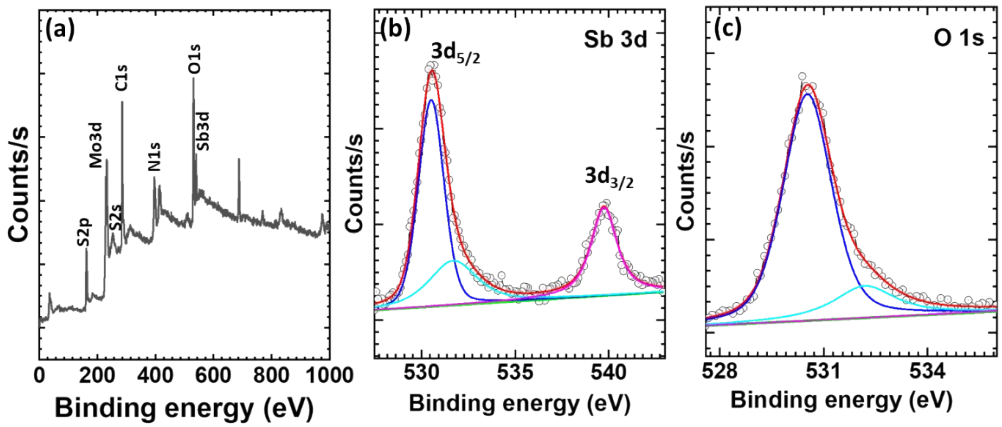

Fig. S2 XPS (a) full scan, high-resolution (b) Sb 3d and (c) O 1s spectra of Sb_2S_3/MoS_2.

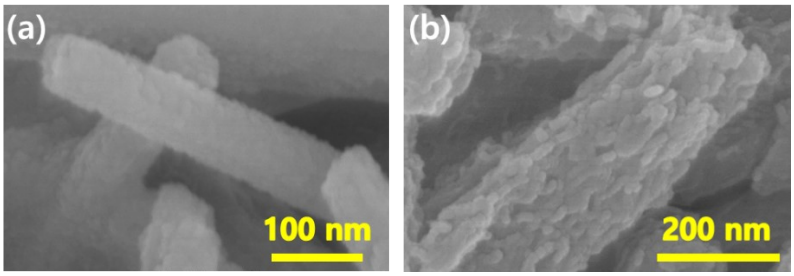

Fig. S3 SEM images of (a) Sb_2S_3 and (b) Sb_2S_3/MoS_2.

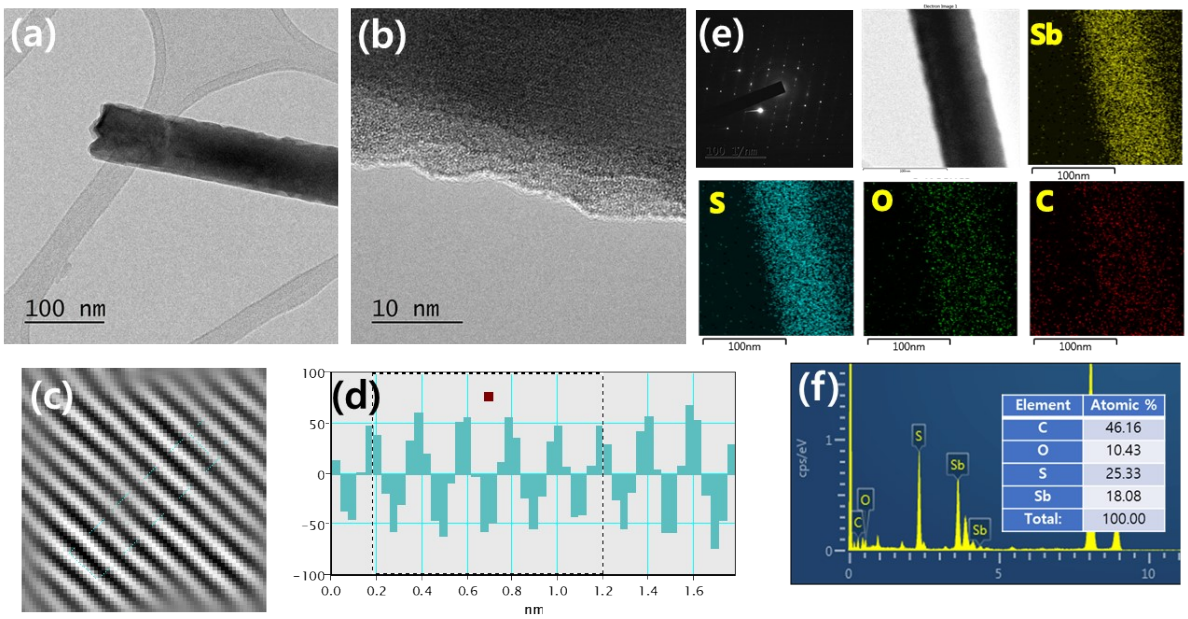

Fig. S4 HR-TEM images and elemental mapping of Sb_2S_3.

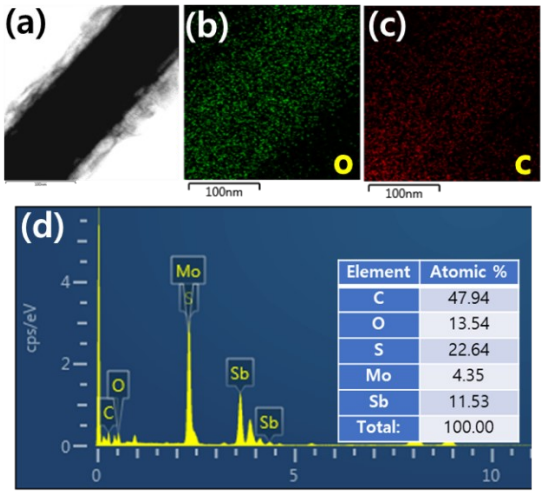

Fig. S5 Elemental mapping of Sb_2S_3/MoS_2.

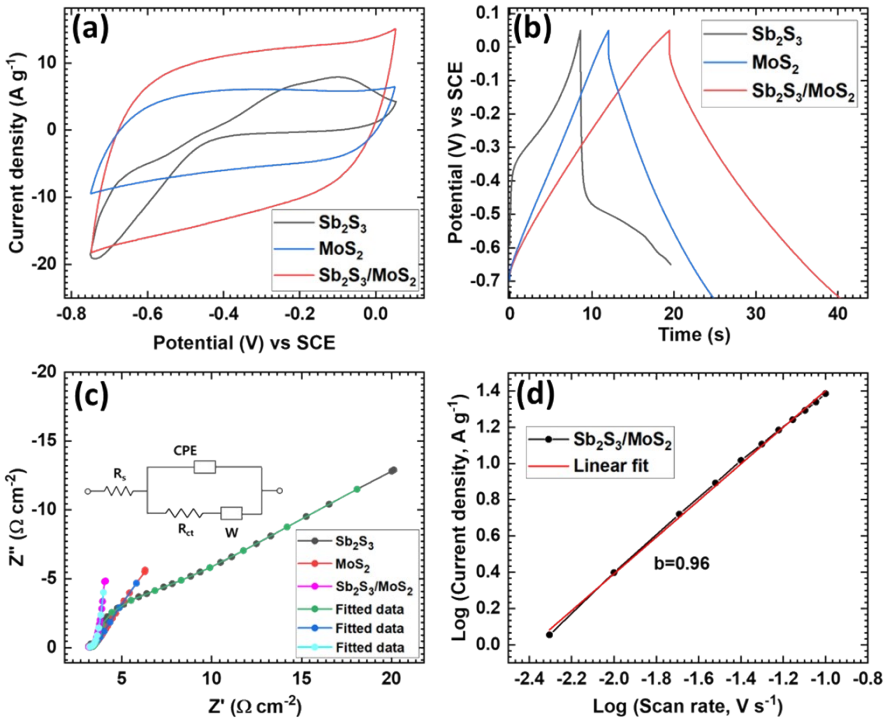

Fig. S6 (a) Comparative CV curves and (b) GCD curves of Sb_2S_3, MoS_2 and Sb_2S_3/MoS_2 electrodes. (c) Nyquist plots (inset: fitted circuit) of Sb_2S_3, MoS_2 and Sb_2S_3/MoS_2 electrodes. (d) The plot of log (current density) versus log (scan rate) to determine the 'b' value of Sb_2S_3/MoS_2 electrode.

Table S1. Electrochemical impedance spectroscopic fitted circuit parameters for Nyquist plots of Sb_2S_3, MoS_2 and Sb_2S_3/MoS_2 electrodes.

Sample Name	R_s (Ω cm^{-2})	R_{ct} (Ω cm^{-2})	CPE (mF)	n	W (Ω cm^{-2})
Sb_2S_3	3.31	4.15	19.8	0.92	0.57
MoS_2	3.15	0.31	9.3	0.72	0.34
Sb_2S_3/MoS_2	3.12	0.16	6.2	0.54	0.23
After stability Sb_2S_3/MoS_2	3.13	1.45	0.6	0.55	0.39

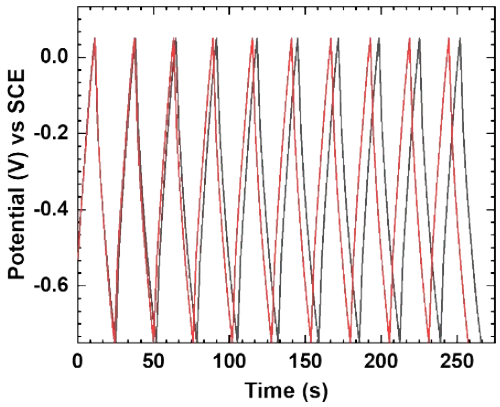

Fig. S7. Initial (black) and final (red) 10 GCD cycles of Sb_2S_3/MoS_2 electrode stability test.

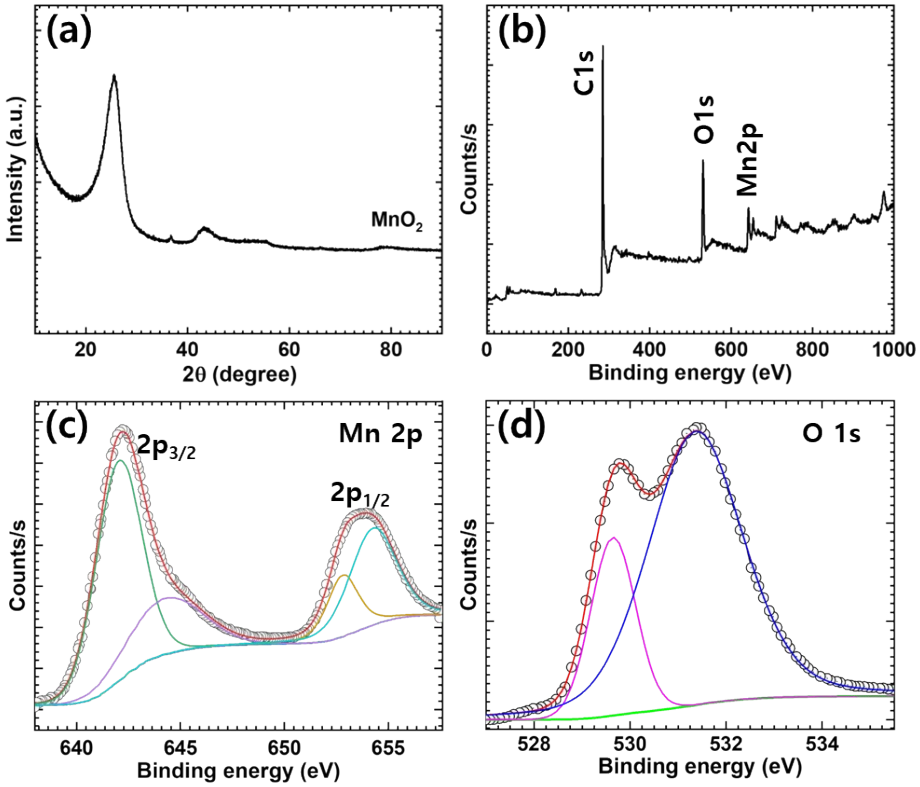

Fig. S8 (a) XRD pattern of MnO_2 on CC. XPS (b) full scan, (c) high-resolution Mn 2p and (d) O 1s spectra of MnO_2.

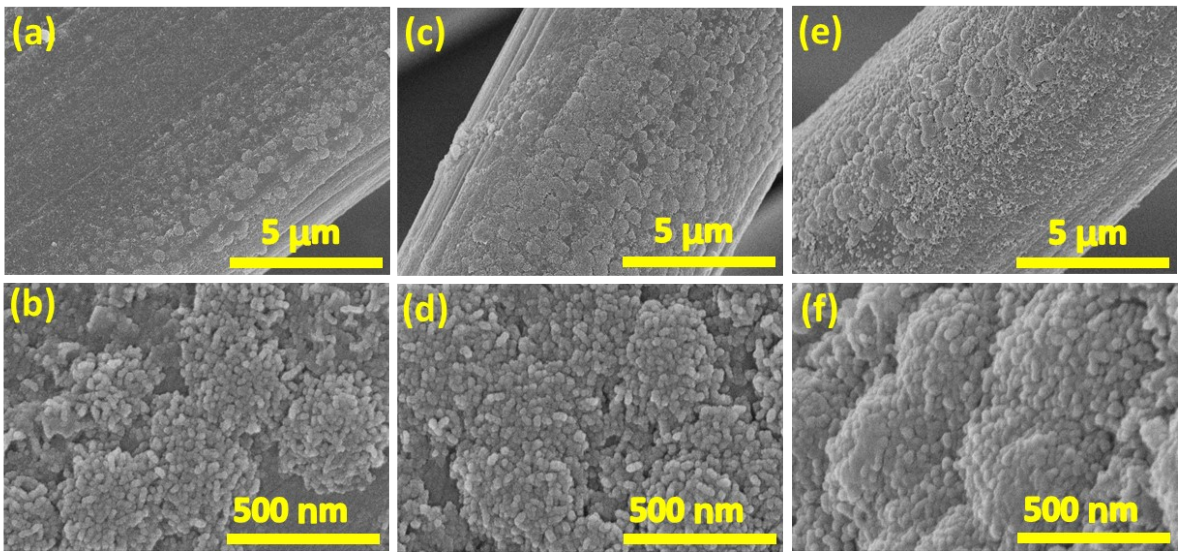

Fig. S9 SEM images of (a,b) Mn-50, (c,d) Mn-100, and (e,f) Mn-200.

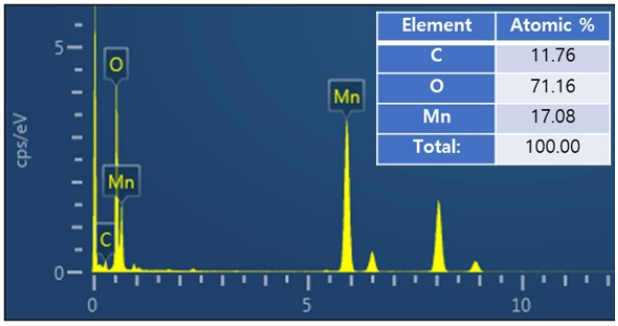

Fig. S10 Elemental mapping of MnO_2 (Mn-150).

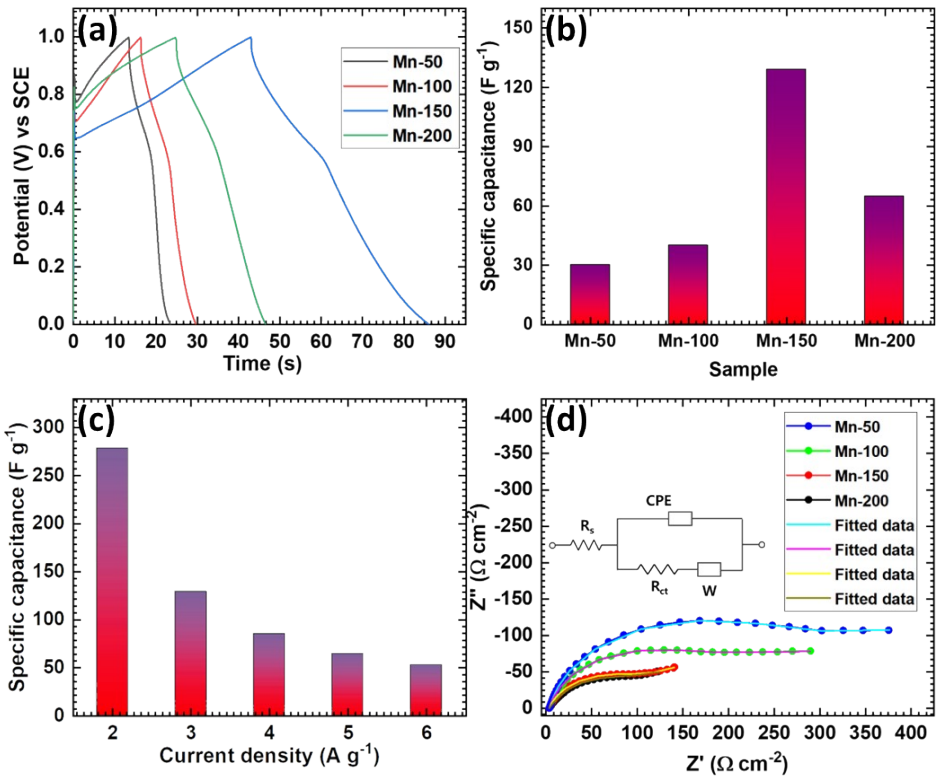

Fig. S11 Comparative (a) GCD curves of Mn series electrodes and (b) specific capacitance extracted from GCD curves. (c) calculated specific capacitance at various current densities of the Mn-150 electrode. (d) Nyquist plots of Mn series electrodes with fitted data (inset: fitted circuit).

Table S2. Electrochemical impedance spectroscopic fitted circuit parameters for Nyquist plots of Mn series electrodes.

Sample Name	R_s (Ω cm^{-2})	R_{ct} (Ω cm^{-2})	CPE (mF)	n	W (Ω cm^{-2})
Mn-50	3.65	278.3	0.8	0.81	0.59
Mn-100	3.52	205	0.8	0.78	0.34
Mn-150	3.37	98	1.4	0.79	0.33
Mn-200	3.35	80.49	2.7	0.81	0.24

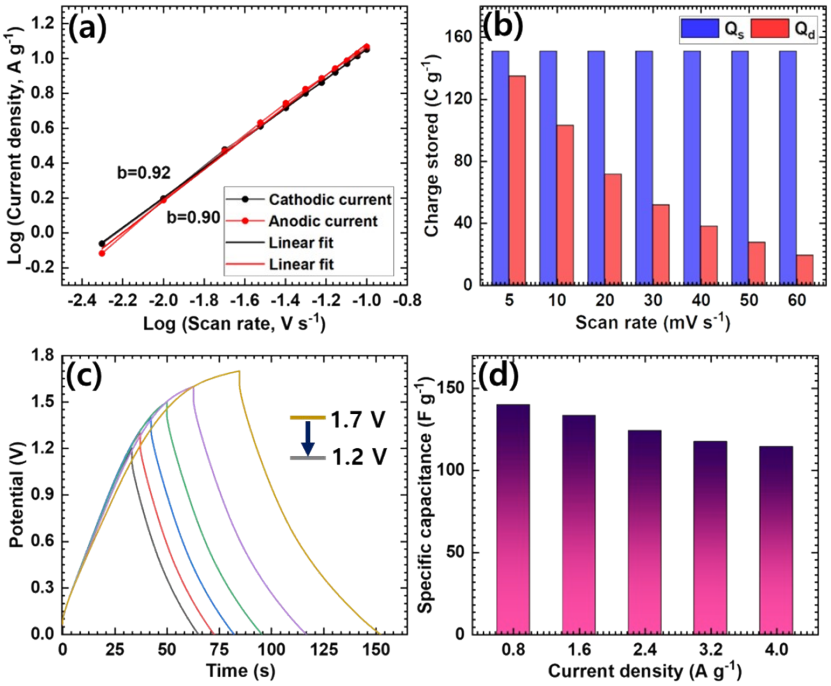

Fig. S12 (a) The plot of log (current density) versus log (scan rate) to determine the 'b' value. (b) Surface and diffusive charges stored at different scan rates for the AIHC. (c) GCD curves of AIHC at different voltage windows and (d) calculated specific capacitance at various current densities of the AIHC.

Table S3. Electrochemical impedance spectroscopic fitted circuit parameters for Nyquist plots of AIHC.

	R_s (Ω)	R_{ct} (Ω)	CPE (mF)	n	W (Ω)
Before stability	5.48	0.5	5.4	0.98	0.34
After stability	5.41	5.6	0.68	0.88	0.42

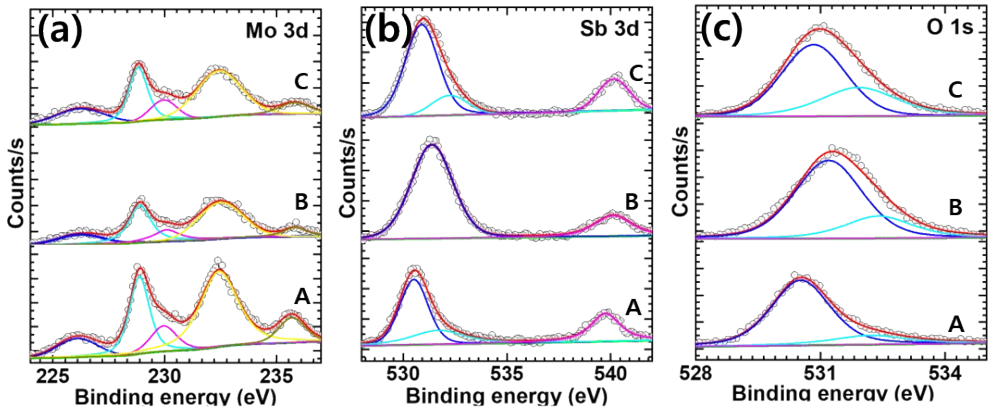

Fig. S13 High-resolution (a) Mo 3d, (b) Sb 3d and O 1s spectra at different charging/discharging states of Sb_2S_3/MoS_2 electrode.