Supporting Information

One-step electrodeposited $Ni_3S_2/Co_9S_8/NiS$ composite on Ni foam as high-performance electrode for supercapacitor

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I. Experimental Section

1. Materials and Characterizations

Nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), Thiourea (CH_4N_2S), Potassium hydroxide (KOH), Ethanol (C_2H_5OH), Hydrochloric acid (HCl), Polyvinyl alcohol (PVA). All pharmaceutical products are analytically pure and do not require further purification.

All reagents are commercially available and used as received without further purification. Pattern X-ray diffraction was recorded using a Bruker D8 equipped with Cu-Ka radiation. X-ray photon-electron spectroscopy analysis was performed using a VG ESCALAB MK II spectrophotometer with Mg-Kα radiation (1253.6 eV). Scanning electron microscopy (SEM) test was carried out on a Hitachi S-4800 instrument at an accelerating voltage of 5 kV. The high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) patterns was performed on a FEI Talos-F200S electron microscope. The compositions of the products were examined using energy dispersive X-ray spectroscopy (EDX) attached to the EM system.

2. Pretreatment of nickel foam

Sonicate nickel foam (1×2 cm^2) in 3M HCl solution for 30 min to remove the NiO layer on the surface of the nickel foam. It is then sonicated three times with deionized water and ethanol to remove residual hydrochloric acid and organic impurities on the surface of nickel foam.

3.Preparation of Ni_3S_2/Co_9S_8/NiS-x (x = 5, 7 and 9 cycles)

Ni_3S_2/Co_9S_8/NiS-x (x = 5, 7 and 9 cycles) were deposited onto NF using the CHI760E electrochemical workstation. For electrodeposition, 0.2910 g cobalt nitrate hexahydrate, 0.2908 g nickel nitrate hexahydrate and 0.7612 g thiourea are dissolved into deionized water (50 mL) and stirred for 35 minutes as electrolyte. NF, Pt sheet and Ag/AgCl are used as the working electrode, the counter electrode and the reference electrode, respectively. The electrodeposition process is executed by using x cycles (x = 5, 7 and 9) of CV at 5 mV s^{-1} with a voltage window of

-1.2 – 0.2 V. After electrodeposition, the electrode is rinsed three times with deionized water and ethanol, respectively, and then dried in vacuum overnight at 60 °C. The Ni_3S_2/Co_9S_8/NiS-x (x = 5, 7 and 9 cycles) are loaded on the NF, masses are about 0.5, 0.8 and 1.1 mg cm^{-2} for 5, 7 and 9 cycles, respectively.

According to the relevant literatures and experiment results, the probable electrodeposition mechanism is proposed as follows. [S1 - S3] First, M^{n+} is easily reduced to transition-metal via equation (S1). Meanwhile, some M^{n+} ions can combine with TU to form $M(TU)^{n+}$ via equation (S2), while the concentration of M^{n+} decreases due to the continuous reduction of M^{n+}, resulting in the increase of dissociative TU. Then, the dissociative TU is decomposed to S^{2-} ions via equation (S3) and further produce M_xS_y with metal via equation (S4).

$$M^{n+} + ne \rightarrow M \text{ (S1)}$$

$$TU + M^{n+} \rightarrow M(TU)^{n+} \text{ (S2)}$$

$$TU + 2e \rightarrow 2S^{2-} + CN^- + NH_4^+ \text{ (S3)}$$

$$xM + yS^{2-} + yH_2O + 1/2yO_2 \rightarrow M_xS_y + 2yOH^- \text{ (S4)}$$

4. Preparation of AC electrode

Weigh a certain proportion (8:1:1) of AC, Super P and PVDF mixed and grinded evenly, mix well and add NMP dropwise to it and sonic to make it mix evenly into a homogeneous paste. The slurry is coated on NF (1×2 cm^2), and then vacuum dried at 60 °C for 5 h.

5. Assembly of Ni_3S_2/Co_9S_8/NiS-7**//AC**

3g PVA and 3g KOH are dissolved in 30 mL deionized water under vigorous agitation at 80 °C, and after obtaining a homogeneous solution, the prepared Ni_3S_2/Co_9S_8/NiS-7 and AC electrodes are soaked in solution for 5 minutes and then removed, and assembled into a supercapacitor after curing. The positive and negative electrodes are mass matched by the following equation (S5) and (S6).

$$Q+ = Q- \text{ (S5)}$$

$$m_+ / m_- = (C_{s-} \times \Delta V_-) / (C_{s+} \times \Delta V_+) \quad (S6)$$

Where m and C_s are the active material load and the specific capacitance of the electrode, respectively. The details of characterization and electrochemical measurements of products see Supplementary Information.

6. Electrochemical characterization

Electrochemical measurements such as cyclic voltammetry (CV), galvanostat charge and discharge (GCD), and electrochemical impedance spectroscopy (EIS) were studied on the CHI760E Electrochemical Workstation (Shanghai Chenhua Instrument Co., Ltd.). In the three-electrode system, the prepared electrode was used as the working electrode, the platinum sheet (1×1 cm^2) as the counter electrode, the Ag/AgCl electrode as the reference electrode, and the electrolyte was 3 M KOH solution. Cyclic voltammetry (CV) analysis was performed using a potential window from −0.2 to 0.6 V recorded at different scan rates from 5 to 100 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was performed under open circuit conditions between 100 kHz and 0.01 Hz frequencies. Galvanostatic charge/discharge studies were performed between a potential window of 0 to 0.4 V with current densities ranging from 1 to 10 A g^{-1}. Then, the specific capacitance (C_s, F g^{-1}) is calculated according to the GCD using the following equation (S7):

$$C_s = (I \times \Delta t) / (m \times \Delta V) \quad (S7)$$

where I is the current (A), Δt is the discharge time (s), m is the electrode active material loading (g), and ΔV is the discharge voltage range (V).

The energy density (E, Wh kg^{-1}) and power density (P, W kg^{-1}) of the assembled asymmetric supercapacitor are calculated using eq. (S8) and (S9):

$$E = C_s \times (\Delta V)^2 / (2 \times 3.6) \quad (S8)$$

$$P = (3600 \times E) / \Delta t \quad (S9)$$

Notes and references

S1 C. W. Su, J. M. Li, W. Yang and J. M. Guo, *J. Phys. Chem. C*,2013, **118**, 767–773.

S2 J. Y. Lin, J. H. Liao and S. W. Chou, *Electrochim. Acta*, 2011, **56**, 8818–8826.

S3 Y. L. Sun, C. Q. Huang, J. L. Shen, Y. J. Zhong, J. Q. Ning and Y. Hu, *J. Colloid Interface Sci.*, 2020, **558**, 1–8.

II Supplementary Structural Section

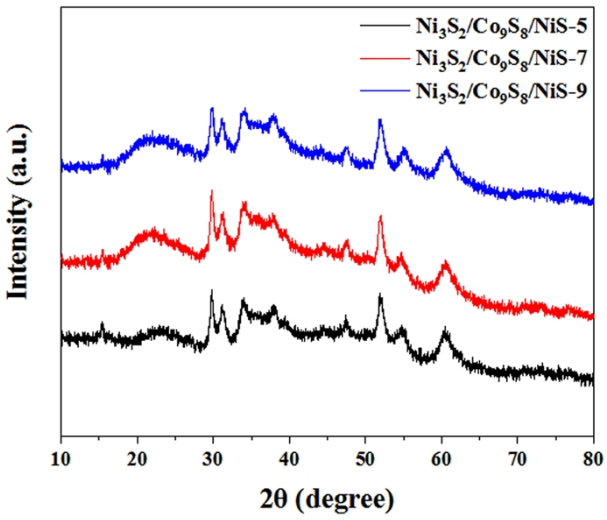

Fig. S1 XRD patterns of Ni_3S_2/Co_9S_8/NiS-7 (x = 5,7 and 9 cycles).

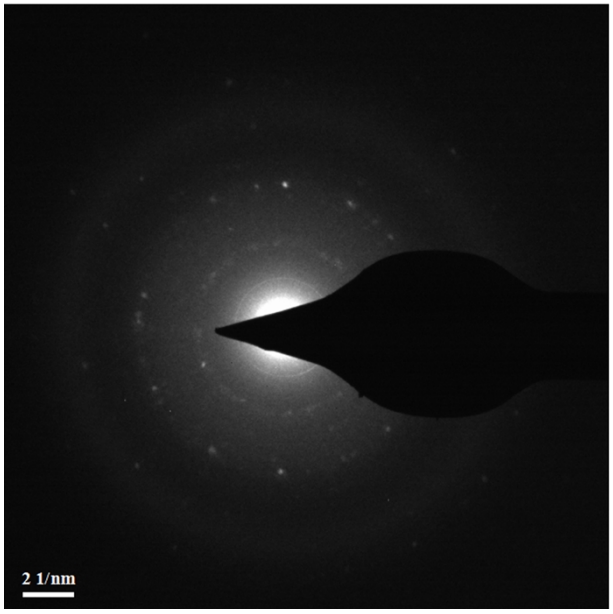

Fig. S2 The SAED patterns of Ni_3S_2/Co_9S_8/NiS-7.

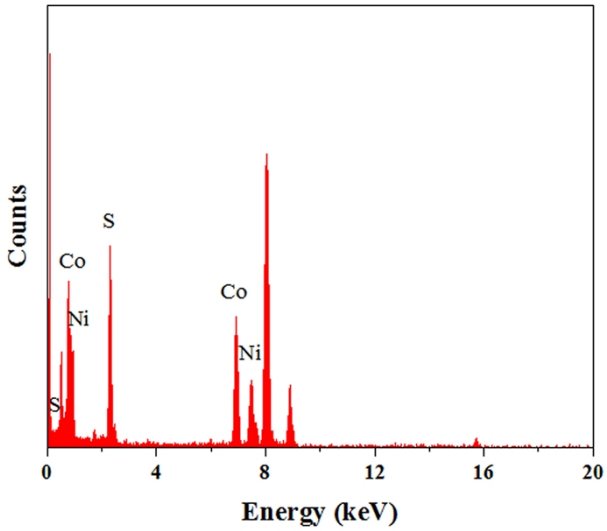

Fig. S3 EDX spectrum of the Ni_3S_2/Co_9S_8/NiS-7.

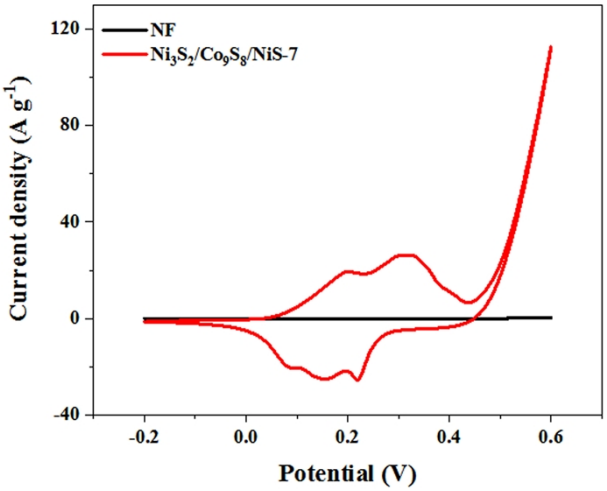

Fig. S4 The CV curves of NF and Ni_3S_2/Co_9S_8/NiS-7 at 5 mV s^{-1}.

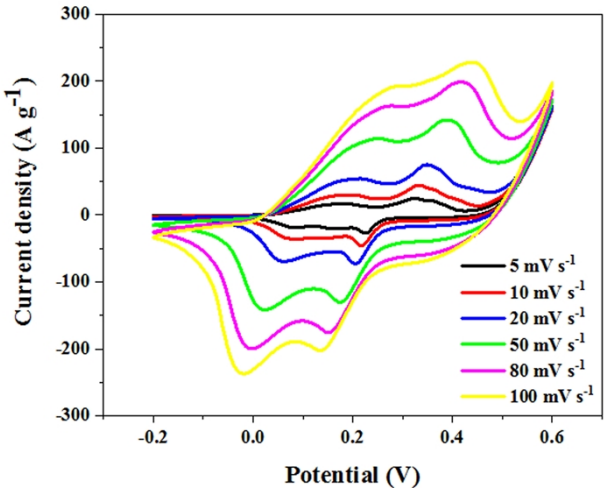

Fig. S5 CV curves of Ni_3S_2/Co_9S_8/NiS-5.

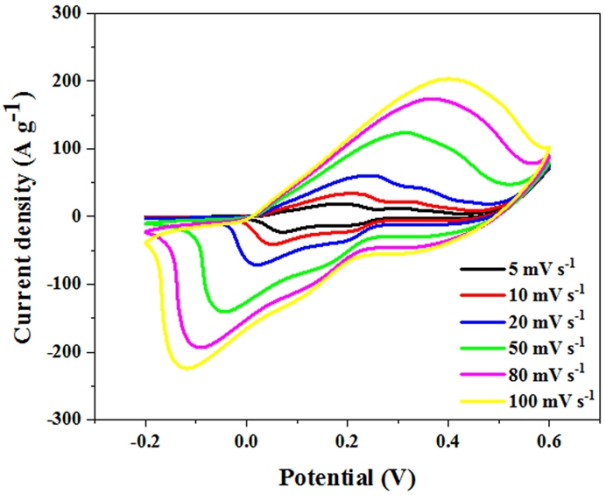

Fig. S6 CV curves of Ni_3S_2/Co_9S_8/NiS-9.

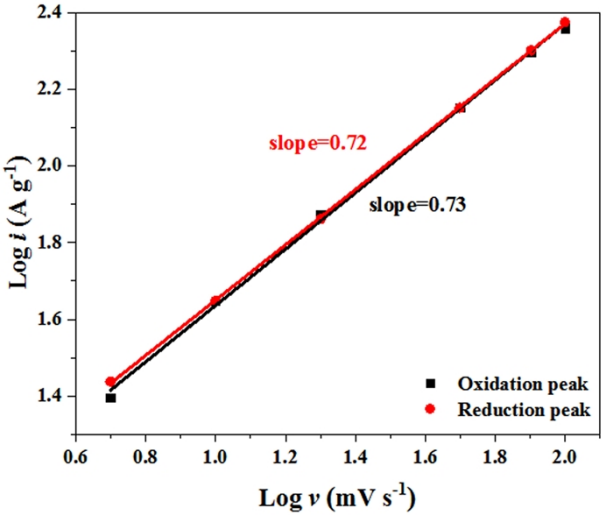

Fig. S7 Straight line relationship of log*i* and log*v* of Ni_3S_2/Co_9S_8/NiS-5 electrode.

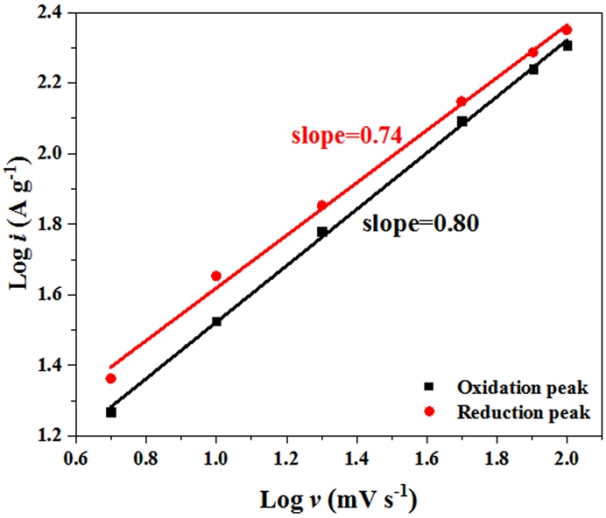

Fig. S8 Straight line relationship of log*i* and log*v* of Ni_3S_2/Co_9S_8/NiS-9 electrode.

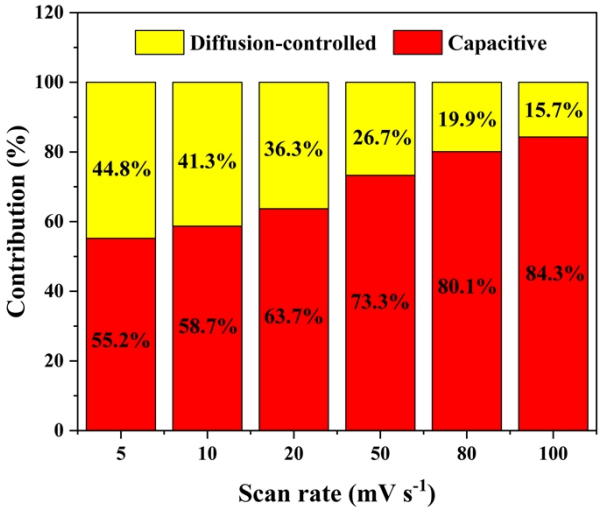

Fig. S9 Normalized contribution ratio of capacitive capacities at different scan rates of Ni_3S_2/Co_9S_8/NiS-5 electrode.

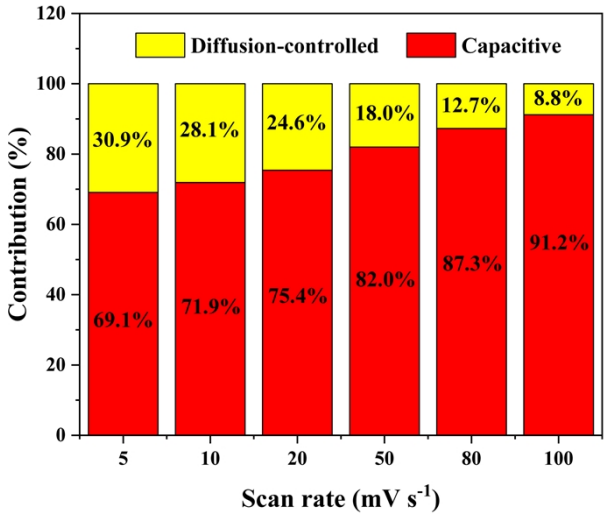

Fig. S10 Normalized contribution ratio of capacitive capacities at different scan rates of Ni_3S_2/Co_9S_8/NiS-9 electrode.

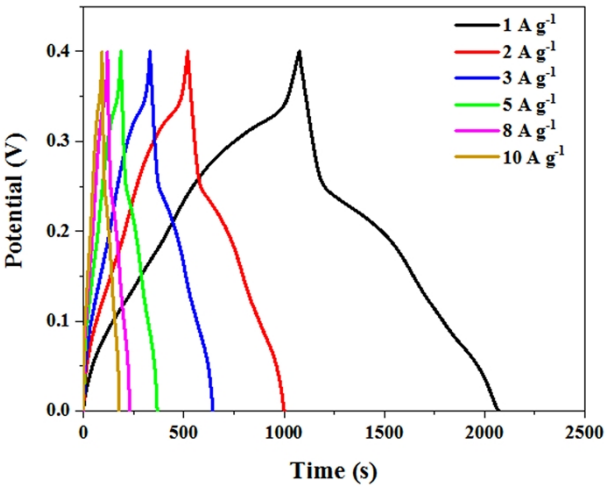

Fig. S11 GCD curves of Ni_3S_2/Co_9S_8/NiS-5 electrode at different current densities.

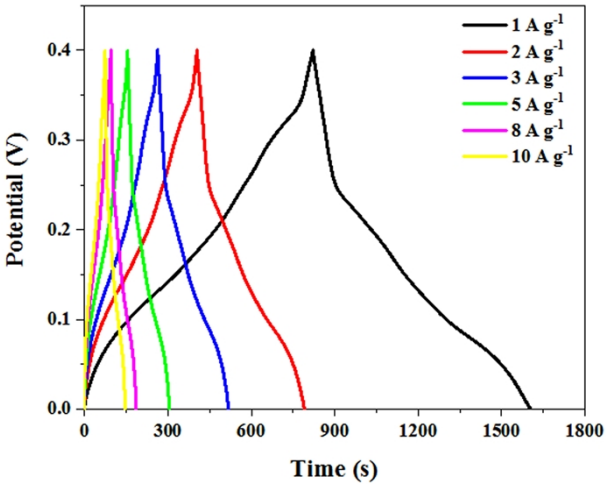

Fig. S12 GCD curves of Ni_3S_2/Co_9S_8/NiS-9 electrode at different current densities.

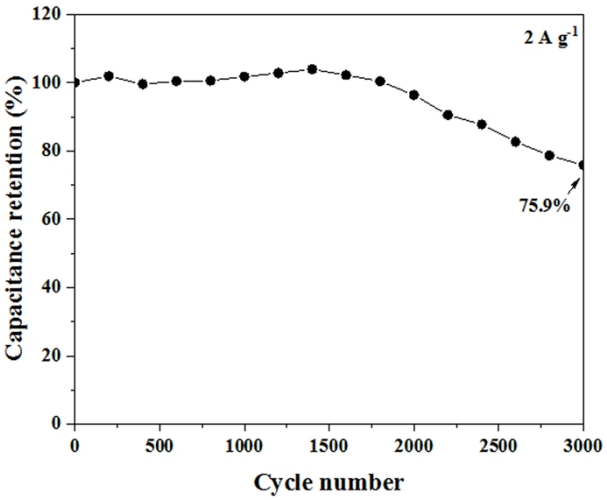

Fig. S13 Cycling stability of Ni_3S_2/Co_9S_8/NiS-5.

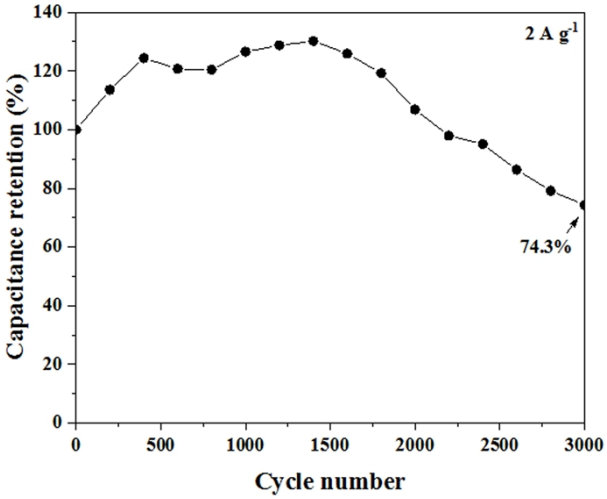

Fig. S14 Cycling stability of Ni_3S_2/Co_9S_8/NiS-9.

Table S1 Comparison of specific capacitance performance of similar materials.

Material	Current density (A g^{-1})	Capacitance (F g^{-1})	Ref.
Ni_3S_2/CoAl-LDH/rGO	1	2457.5	49
$MgCo_2O_4$ @Ni_3S_2	1	1123.9	50
Co_9S_8@NiO	1	1627	51
$MnCo_2S_4$/Co_9S_8	1	1058	52
$MnCo_2S_4$/Co_9S_8	1	1100.5	53
NiS/NiO	0.5	1260	54
NiS/CMS	1	1594	55
$CoMoO_4$/MoO_3@CuCoNi-S	1	2600	56
Ni_3S_2/Co_9S_8/NiS-7	1	2785.3	This work

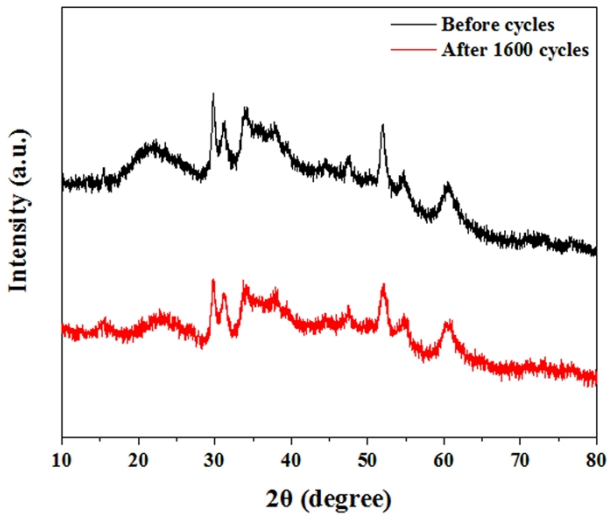

Fig. S15 XRD of before and after 1600 cycles for Ni_3S_2/Co_9S_8/NiS-7 electrode.

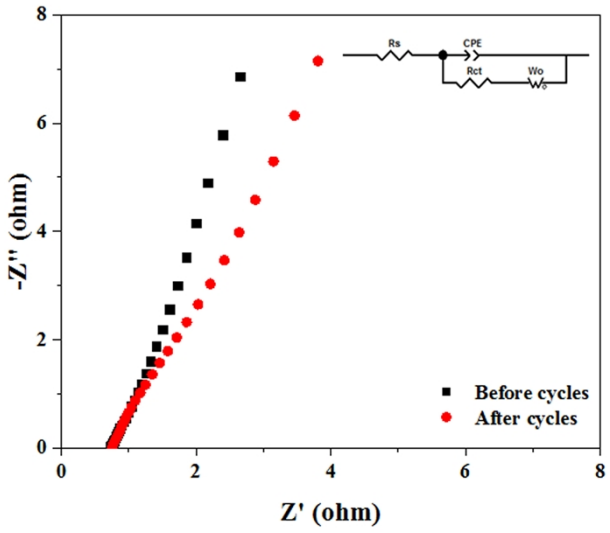

Fig. S16 Nyquist plots of before and after cycles for Ni_3S_2/Co_9S_8/NiS-7 electrode.