Supplementary Information for

Hollow ZIF-67 Derived Porous Cobalt Sulfide for Efficient Bifunctional Electrocatalysts for Overall Water Splitting

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1. Experimental Procedures

1.1 Synthesis of conventional ZIF-67

For the synthesis of conventional ZIF-67, $Co(NO_3)_2 \cdot 6H_2O$ (2.328 g, 8 mmol) and 2-MeIm (2.464 g, 3 mmol) were dissolved in 40 mL of MeOH to form two clear solutions, respectively. Then the solution of $Co(NO_3)_2 \cdot 6H_2O$ was poured into the mixture solution of 2-MeIm. The mixed solution stirred at room temperature for 24 h, the light purple precipitates were centrifuged, washed with MeOH several times, and dried at 60 °C.

1.2 Synthesis of unregulated CoS_2 (t-CoS_2)

For the synthesis of t-CoS_2, firstly, the conventional ZIF-67 (0.2 g) and TAA (0.9 g) was dispersed in 40 mL of MeOH to form a mixture solution. After the mixture was refluxed at 90°C for 30 min, the black precipitates were centrifuged, washed with MeOH and dried at 60°C. Then the black precipitates were placed in a tube furnace, heated to 600°C with a ramp rate of 2°C·min^{-1}, and kept for 2 h in N_2.

1.3 Synthesis of Cu_2S

The Cu_2S was prepared according to the synthetic strategy of h-CoS_2 basically，with using $Cu(NO_3)_2 \cdot 6H_2O$ to replace $Co(NO_3)_2 \cdot 6H_2O$ in the preparation of regulated ZIF-67.

1.4 Electrochemical measurements

All the electrochemical measurements were carried out on a CHI 660E electrochemical workstation (CH Instruments, Inc., Shanghai) with a standard three-electrode setup. A glassy

carbon electrode (GCE, 4 mm in diameter) used as the support for the working electrode. 5 mg of the samples and 50 μL Nafion solution (5 wt.%) were dispersed in 950 μL ethanol and sonicated for at least 30 min to form ink. Then, 10 μL of the ink was loaded onto the surface of GCE and dried at room temperature. The platinum foil and the Hg/HgO full of 1 M KOH served as counter and the reference electrodes, respectively. The electrocatalytic activity of the electrocatalysts were examined by obtaining polarization curves using linear sweep voltammetry (LSV) at room temperature. In this work, the measured potentials were converted to the reversible hydrogen electrode (RHE) scale according to the Nernst Equation: $E(RHE)=E(Hg/HgO)+0.059 \times pH+0.098$. The stability measurements were performed by cyclic voltanmmetry scanning 1000 cycles (CV, sweep rate, 100 mV/s) and long-term chronoamperometry. CV method also was used to determine the electrochemical double-layer capacitances (C_{dl}). The electrochemical surface area (ECSA) values were evaluated by cyclic voltammetry (CV) method with different scan rates (5 ~ 50 mV s^{-1}) at non-Faradaic region. The capacitive current density ($\Delta J= J_{anodic} - J_{cathodic}$) has linear relationship against the scan rate and the value of the linear slop is considered as twice of electrochemical double layer capacitance (C_{dl}). For comparison, 5 mg of commercial noble based catalyst (Pt/C and RuO_2) was dispersed to a solution containing 950 μL ethanol and 50 μL Nafion. The obtained suspension was ultrasonicated to obtain a uniform catalyst ink. Subsequently, 10 μL of the ink solution was pipetted on the surface of GCE. Finally, the samples were dried at room temperature. The electrochemical impedance spectroscopy (EIS) measurements were performed from 10^5 Hz to 0.01 Hz with an amplitude of 5 mV.

The overall water splitting electrolyze configuration was assembled using two identical transition metal chalcogenides electrodes and measured in a two-electrode cell in 1 M KOH solution with a carbon fiber cloth(CFC) as the carrier (the catalyst loading is 2 mg · cm^{-2}).
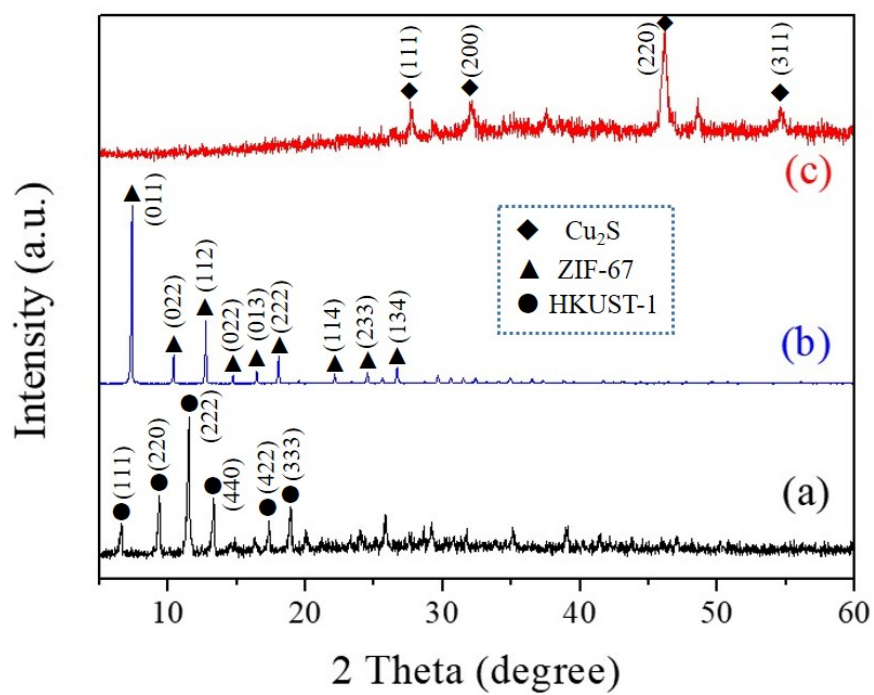
Fig.S1 XRD pattern of (a) as-obtained HKUST-1, (b) regulated ZIF-67, and (c) Cu$_2$S

Note for c：The diffraction lines at 27.6°, 32.1°, 46.1° and 54.7° are indexed to the

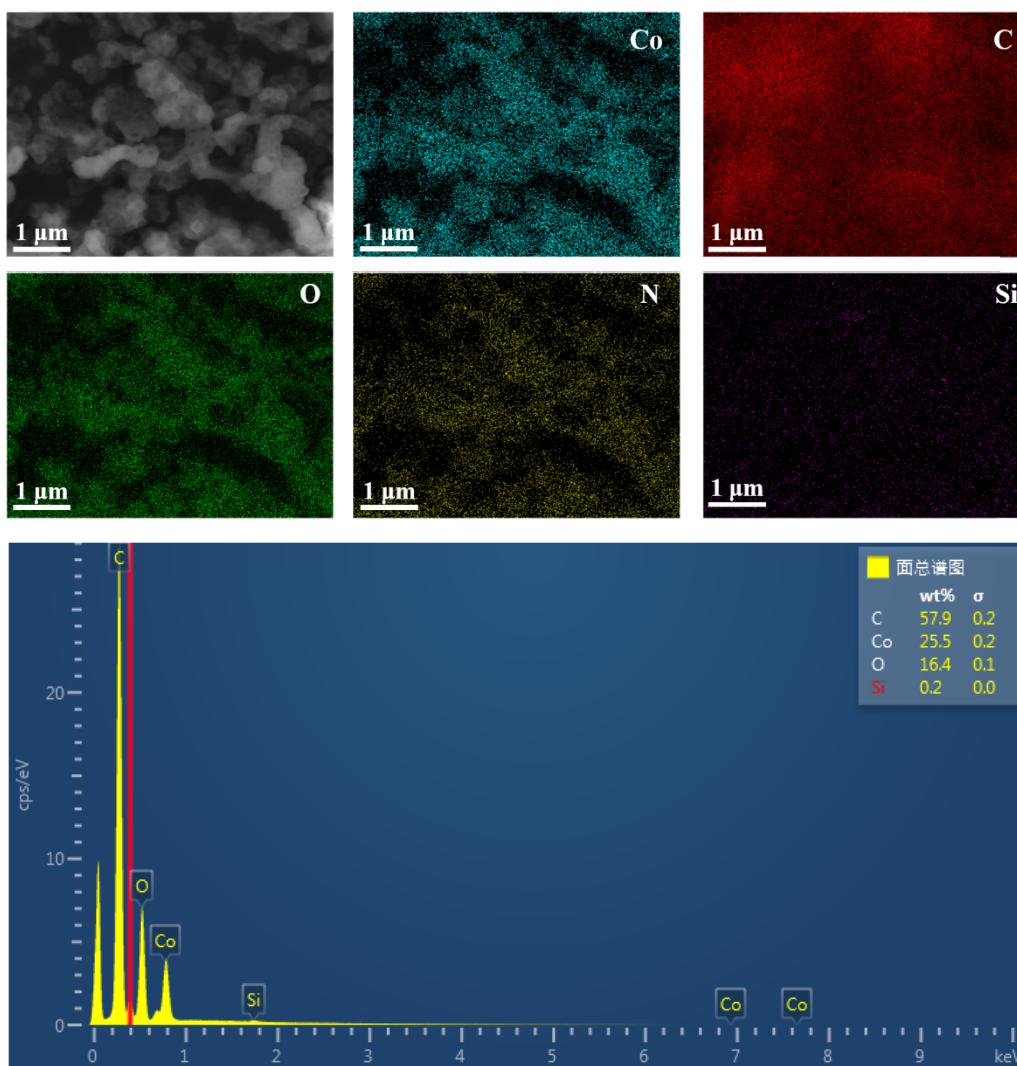(111), (200), (220) and (311) planes of Cu$_2$S (JCPDS # 53-0522), respectively.

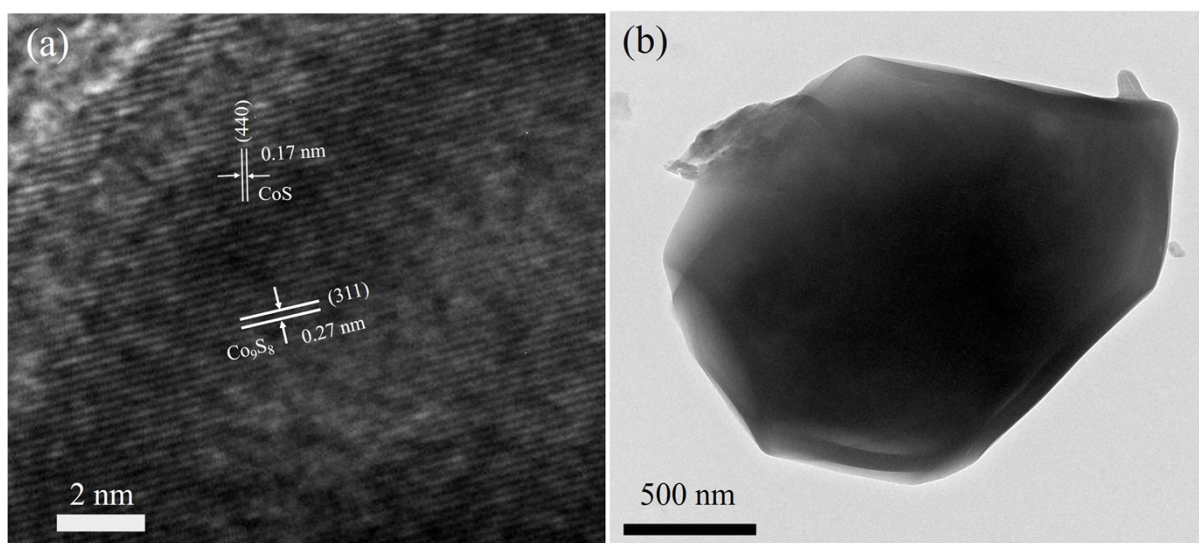Fig.S2 EDS elemental mapping images of the regulated ZIF-67. (Silicon may be an unexpected impurity in the test.)

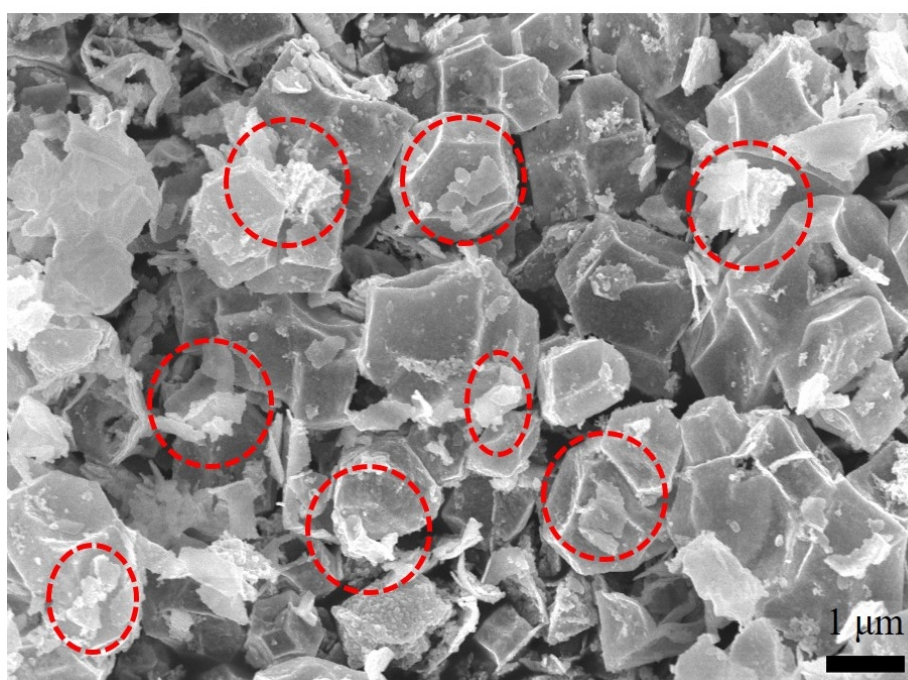Fig. S3 (a) HRTEM image of h-Co_xS_y catalyst, (b) TEM image of t-Co_9S_8
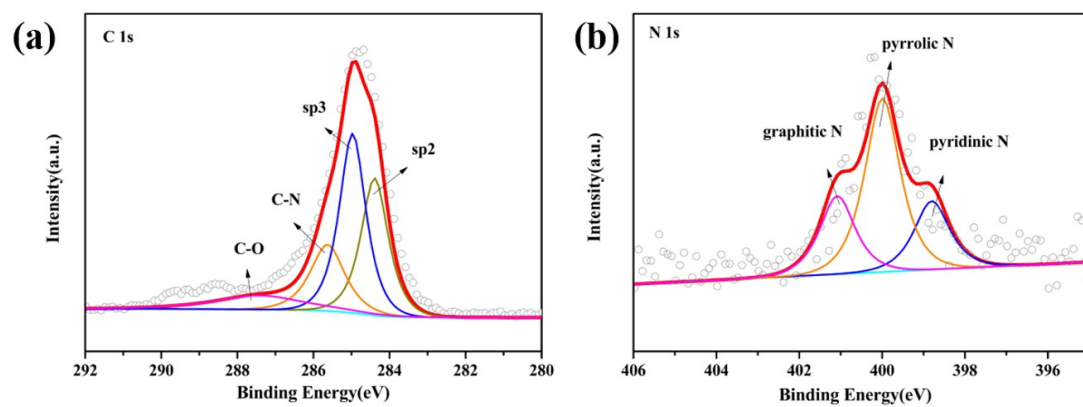

Fig. S4 SEM of t-Co_9S_8 catalyst

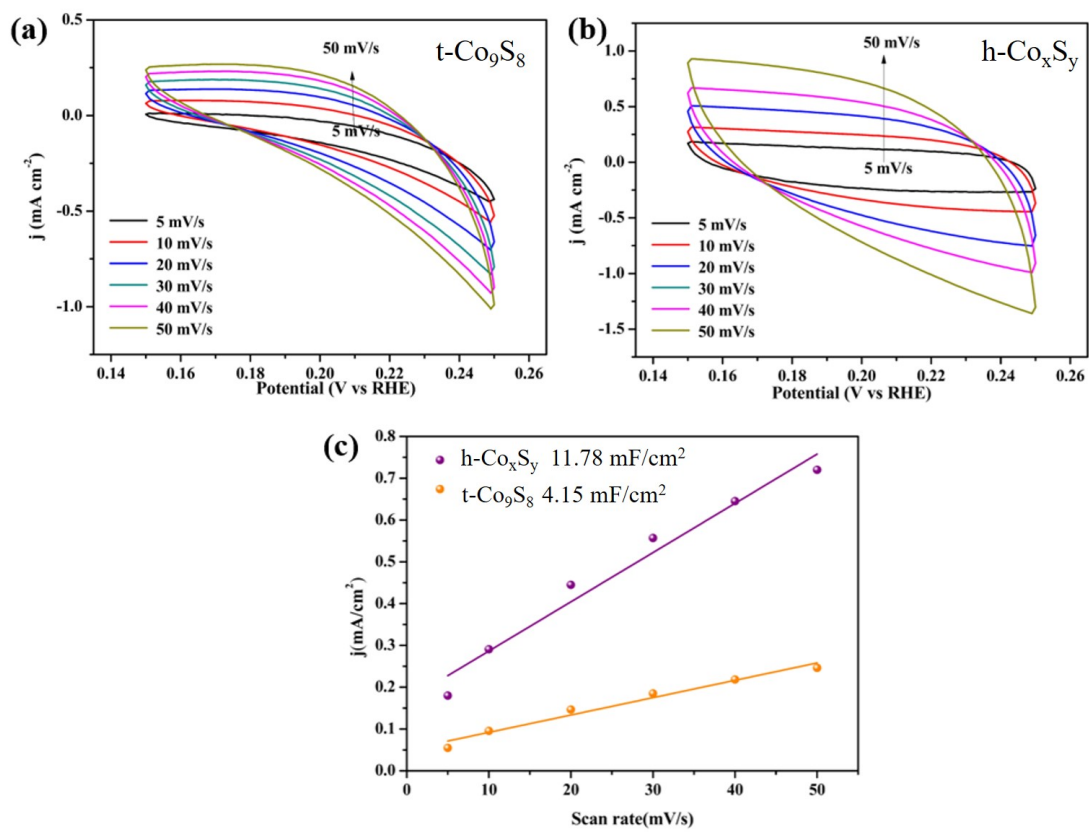Fig.S5 Deconvoluted C 1s (a) and N 1s (b) XPS profiles of h-Co$_x$S$_y$ catalyst

Fig. S6 CV curves of t-Co$_9$S$_8$ (a) and h-Co$_x$S$_y$ (b) with various scan rates in 1.0 M KOH, (c) Corresponding double layer capacitances (C$_{dl}$).
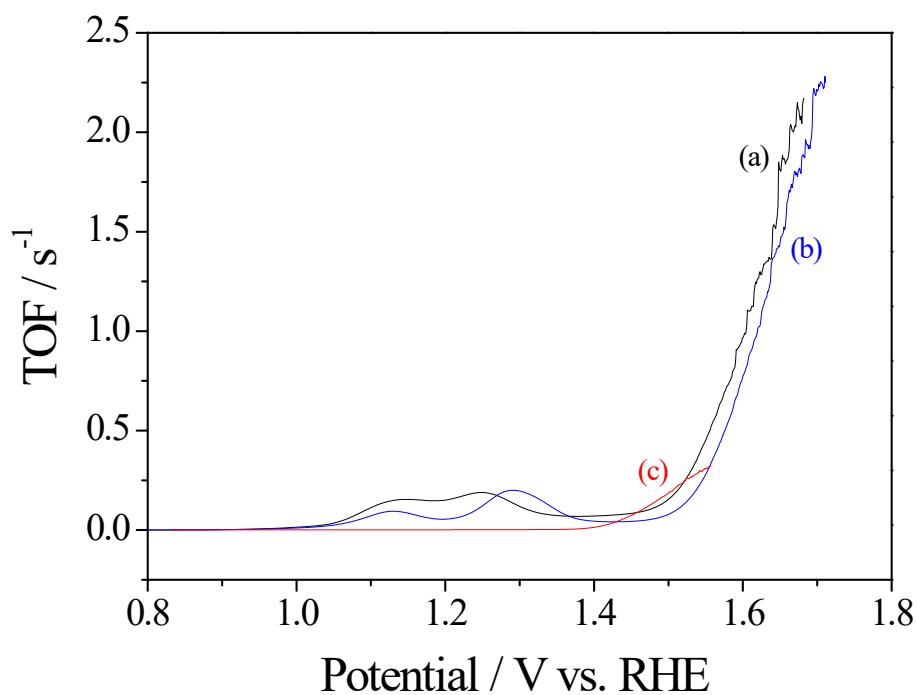
Fig.S7 The OER TOF curves of (a) h-Co$_x$S$_y$, (b) t-Co$_9$S$_8$, and (c) RuO$_2$

TOF values for the OER electrocatalysts were calculated using the following equation:

$$TOF = (J \times A)/(4 \times n \times F) \qquad (1)$$

In the above equation, J is the current density, A is the area of the glassy carbon electrode, F is the faraday constant (a value of 96485 C/mol), n is the number of moles of the electrocatalysts that deposited onto the glassy carbon electrode, all the atoms are considered to be active in this calculation (As the Co$_9$S$_8$ phase is the major component for the case of h-Co$_x$S$_y$, we consider that the h-Co$_x$S$_y$ only contains Co$_9$S$_8$ phase at the calculation process of n).
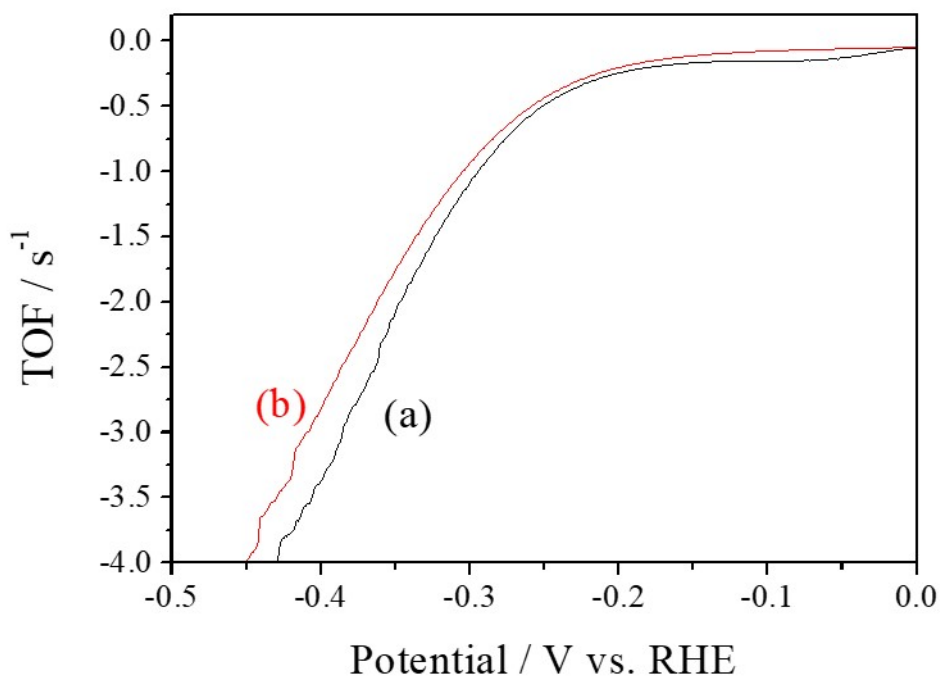
Fig.S8 The HER TOF curves of (a) h-Co$_x$S$_y$ and (b) t-Co$_9$S$_8$

TOF values for the OER electrocatalysts were calculated using the following equation:

$$TOF = (J \times A)/(2 \times n \times F) \qquad (2)$$

In the above equation, J is the current density, A is the area of the glassy carbon electrode, F is the faraday constant (a value of 96485 C/mol), n is the number of moles of the electrocatalysts that deposited onto the glassy carbon electrode, all the atoms are considered to be active in this calculation.
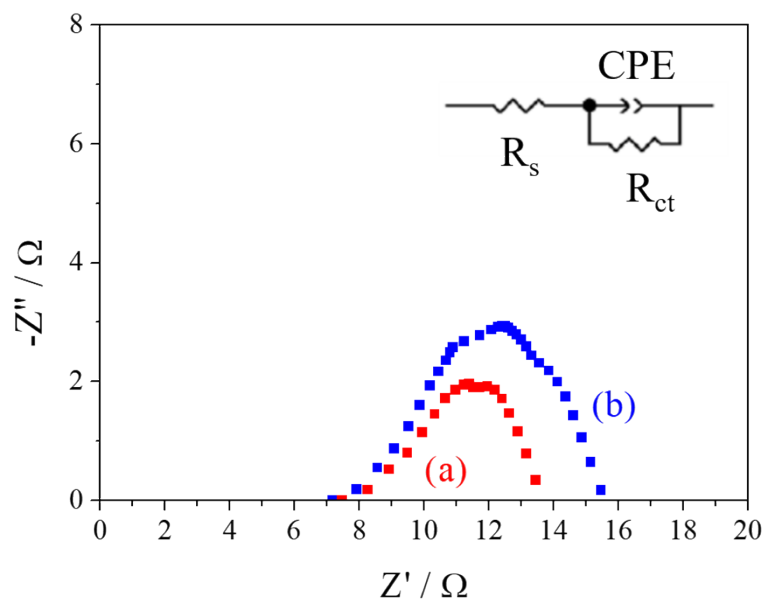
Fig.S9 Nyquist plots of (a) h-Co$_x$S$_y$, (b) t-Co$_9$S$_8$ at -0.32V versus RHE