Supporting Information

Hollow CuSe nanocubes as bifunctional electrocatalyst for energy-saving overall urea-water electrolysis

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Experimental Section

Chemicals

Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) and sodium hydroxide were purchased from Sinopod Group Chemical Reagent Co., LTD. Polyvinylpyrrolidone (PVP), selenium dioxide (SeO_2), ascorbic acid, DL-tartaric acid, D (+) glucose, selenium powder, sodium citrate, copper citrate were purchased from Shanghai Aladdin Biochemical Technology Co., LTD. Urea (CH_4N_2O) was from Tianjin Zhiyuan chemical reagent Co., Ltd. Potassium hydroxide (KOH) was purchased from Jindong Tianzheng Fine Chemical Reagent Factory. Pt/C (20 wt.%, Pt on Vulcan XC-72R) and Nafion (5 wt%) were obtained from Aldrich. All reagents are analytically pure and used directly without further purification and all aqueous solutions were prepared with ultrapure water (18.2 MΩ·cm) obtained from a Millipore system.

Physical Characterizations

The morphology and microstructure were observed by transmission electron microscope (TEM Tecnai G2 F20). The Crystalline phase of the synthesized sample was tested by Y-2000 X-ray diffractometer (XRD) with the 2θ ranges from 10° to 80° at a scanning rate of 10° min^{-1}.

Electrochemical Measurements

Electrochemical HER performance was tested on an electrochemical workstation (CHI 660e) in 1 M KOH solution at room temperature, using a standard three-electrode system. The synthesized catalyst was selected as the working electrode, Hg/HgO electrode as the reference electrode, and carbon rod as the counter electrode. The

polarization curves were recorded by linear sweep voltammetry (LSV) technique at 5 $mV \cdot s^{-1}$ with iR correction. In addition, the current density is calculated on the basis of the actual electrode area (0.5 × 0.5 cm^2) immersed in the electrolyte. All of the measured potentials were showed versus reversible hydrogen electrode (RHE) following the equation: $E_{RHE}=E_{Hg/HgO}$ + 0.098 V+0.059 pH. According to the reported electrochemical method, the electrochemical active surface area (ECSA) of the catalyst modified electrode was calculated by double-layer capacitor (C_{dl}). The cyclic voltammograms (CVs) were tested with different rates from 20 to 100 $mV \cdot s^{-1}$. Electrochemical impedance spectroscopy (EIS) was performed at a current density of 10 $mA \cdot cm^{-2}$. All impedance data have been fitted. For long-term stability tests, which were carried out at 10 $mV \cdot s^{-1}$. The long-term durability test of CuSe/NF electrode was tested by constant current electrolysis.

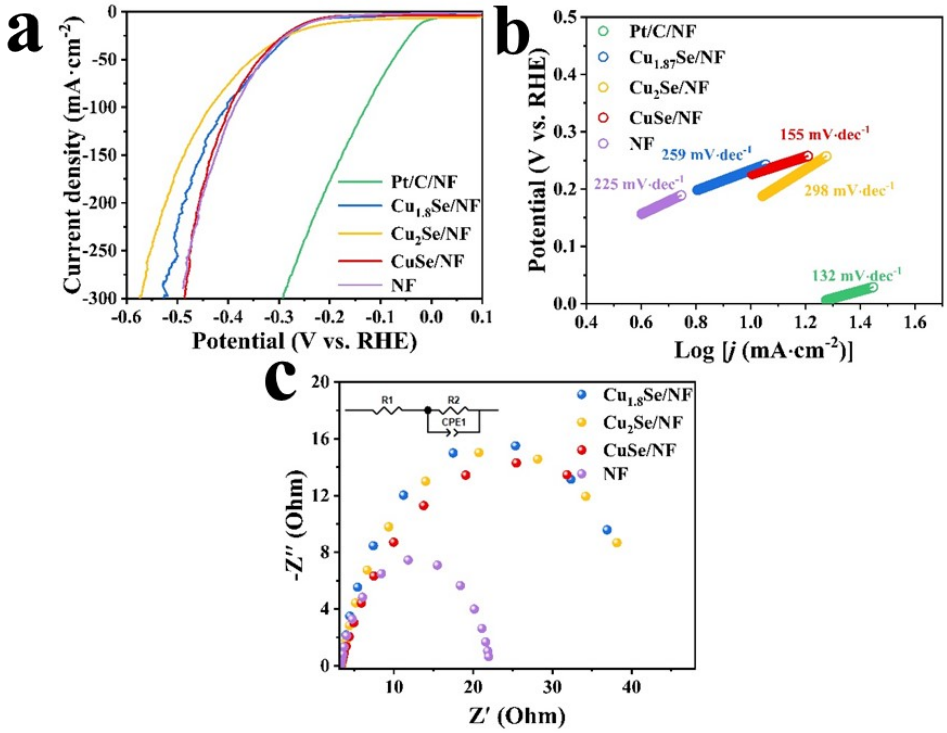

Fig. S1 (a) LSV curves towards the HER of Pt/C/NF, $Cu_{1.8}Se$/NF, Cu_2Se /NF, CuSe/NF and NF in 1.0 M KOH; (b) Tafel slopes towards the HER in 1.0 M KOH; (c) EIS curves at 10 $mA \cdot cm^{-2}$ towards the HER in 1.0 M KOH.

Table S1 Comparison of HER properties of CuSe/NF with other catalysts.

Catalyst	j (mA cm^{-2})	η (mV)	Ref.
CuSe/NF	10	199	This work
Zn-$MoSe_2$	10	182	[1]
Cu_2Se@NiFe-LDHNS	10	205	[2]
Cu_3P/Cu_2Se	10	166	[3]
Cu-Ni_3S_2/NF	10	188	[4]
NiCo-WSe_2	10	205	[5]

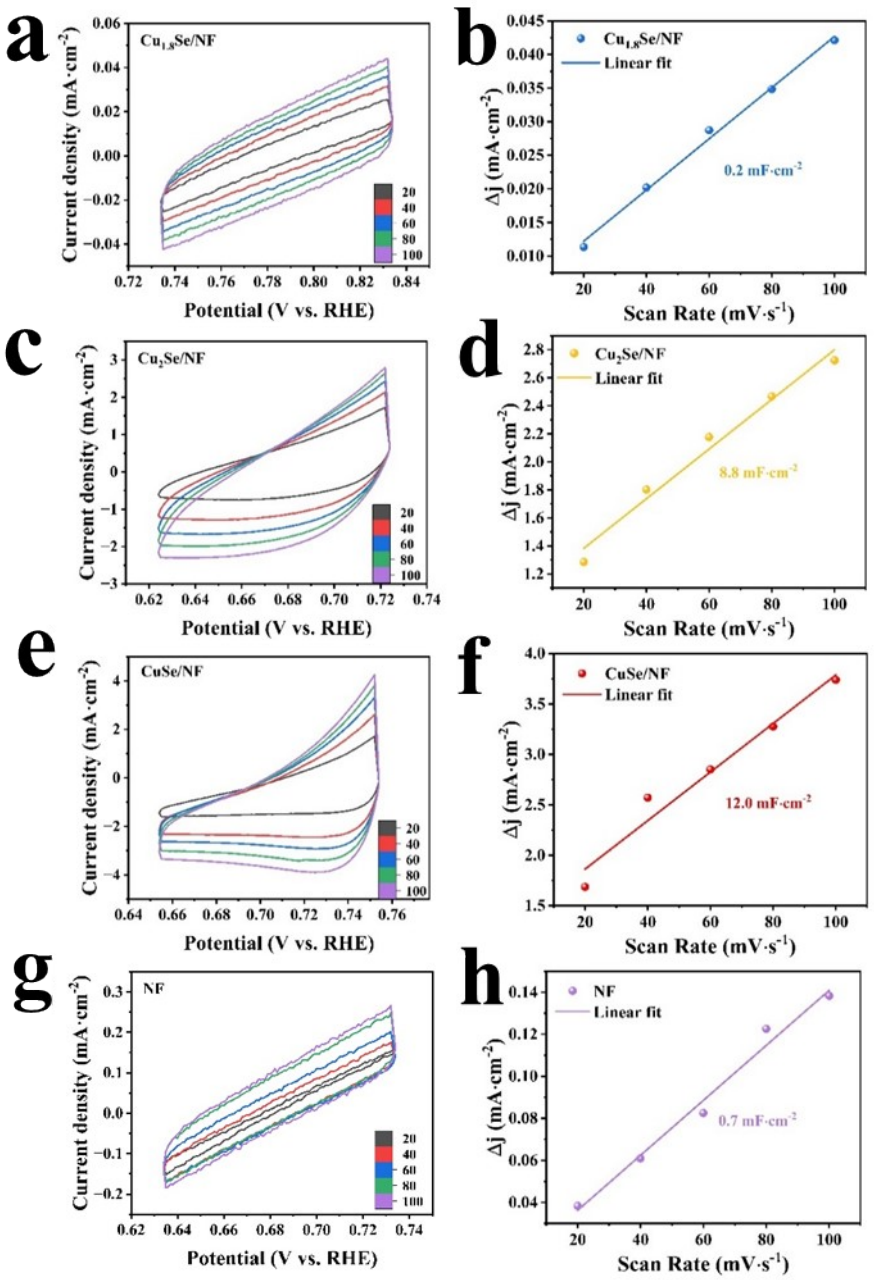

Fig. S2 Cyclic voltammograms at scan rates from 20-100 mV·s^{-1}. Samples measured in a non-Faradaic region at different scan rates in 1 M KOH + 0.5 M urea electrolyte: (a, b) $Cu_{1.8}Se$/NF, (c, d) Cu_2Se/NF, (e, f) CuSe/NF and (g, h) NF.

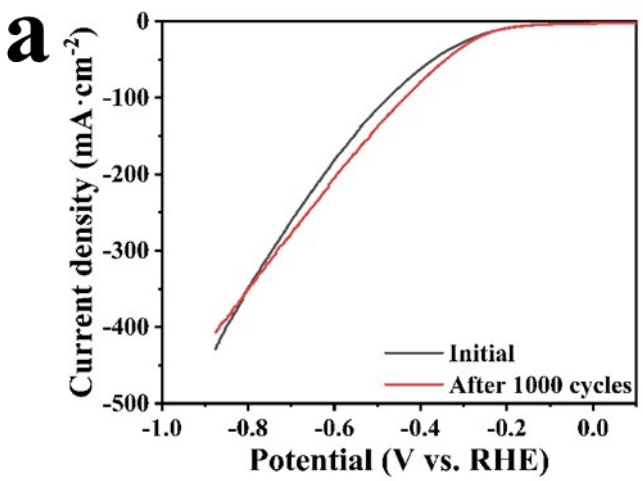

Fig. S3 (a) Polarization curves of CuSe/NF for the HER before and after 1000 CV cycles in 1 M KOH + 0.5 M urea.

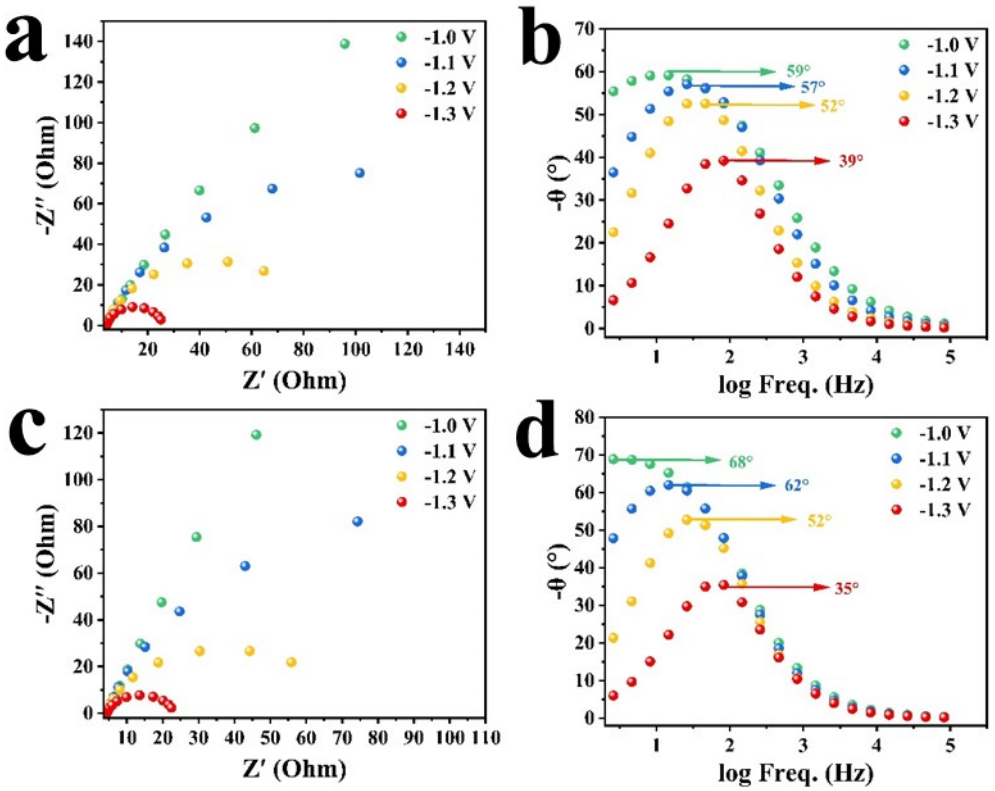

Fig. S4 Nyquist and Bode plots at different potentials (-1.0, -1.1, -1.2, and -1.3 V vs. SCE) for (a, b) $Cu_{1.8}Se$/NF and (c, d) Cu_2Se/NF in 1 M KOH + 0.5 M urea electrolyte.

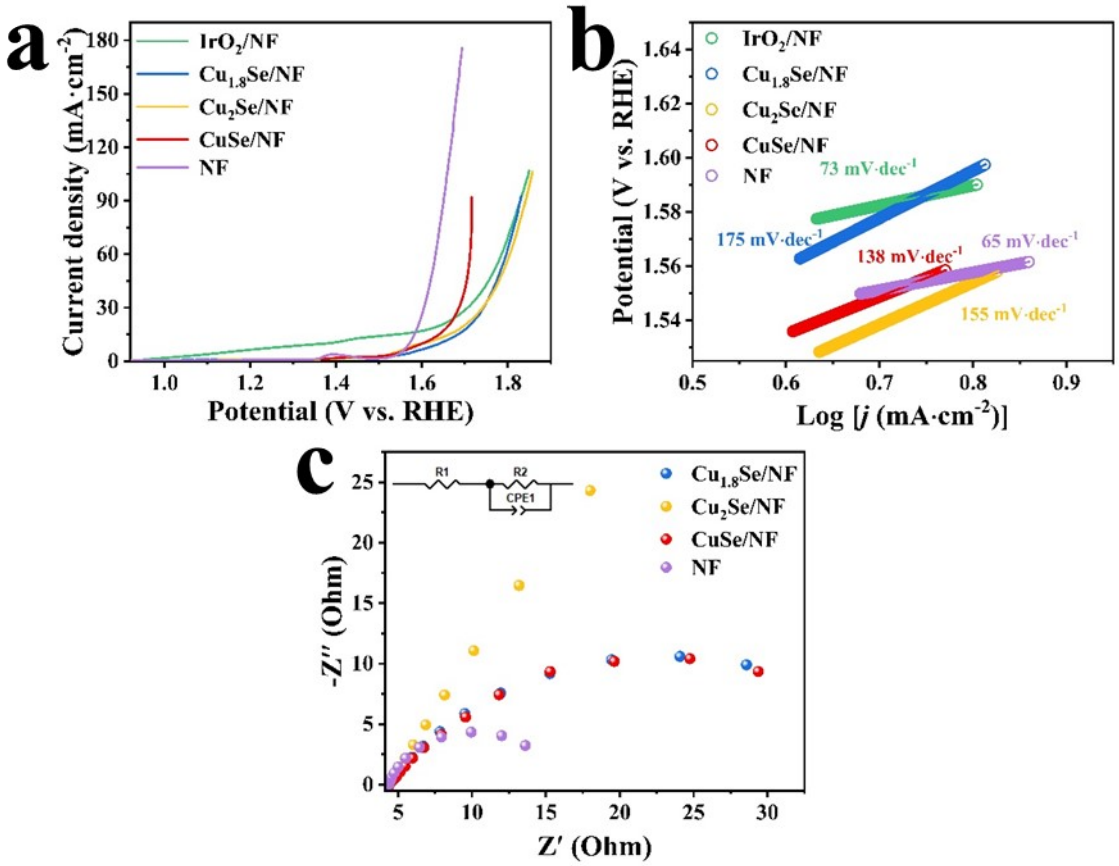

Fig. S5 (a) LSV curves towards the OER of Pt/C/NF, $Cu_{1.8}Se$/NF, Cu_2Se /NF, CuSe/NF and NF in 1.0 M KOH; (b) Tafel slopes towards the OER in 1.0 M KOH; (c) EIS results at 10 mA·cm^{-2} towards the OER in 1.0 M KOH.

Table S2 Comparison of UOR properties of CuSe/NF with other catalysts.

Catalyst	j (mA cm^{-2})	η (V)	Ref.
CuSe/NF	10	1.38	This work
$NiCo_2S_4$@Ni_3Se_2	10	1.396	[6]
Cu_3P@CuO_x	10	1.37	[7]
Se-CoS_2 NW/CF	10	1.46	[8]
NiMoSe	10	1.39	[9]
Cu_3P-NW/CF	10	1.43	[10]

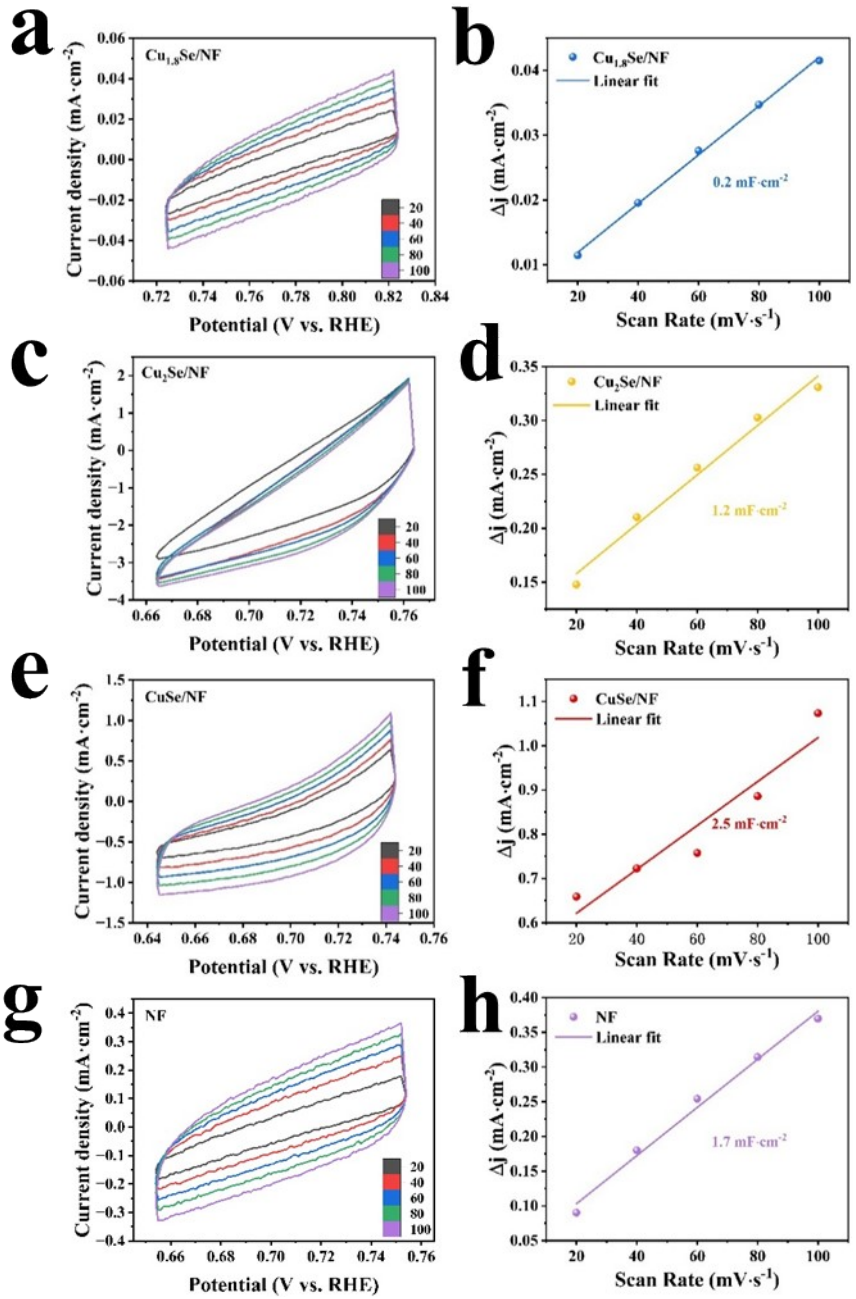

Fig. S6 Cyclic voltammograms at scan rates from 20-100 $mV \cdot s^{-1}$. Samples measured in a non-Faradaic region at different scan rates in 1 M KOH + 0.5 M urea electrolyte: (a, b) $Cu_{1.8}Se$/NF, (c, d), Cu_2Se/NF (e, f), CuSe/NF and (g, h) NF.

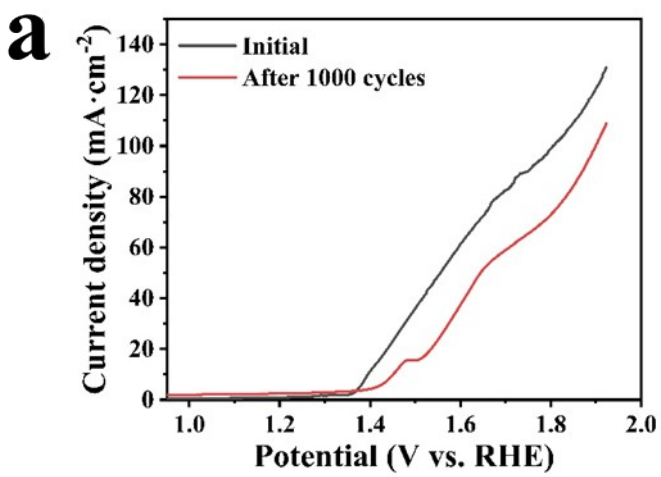

Fig. S7. (a) Polarization curves of CuSe/NF for the UOR before and after 1000 CV cycles.

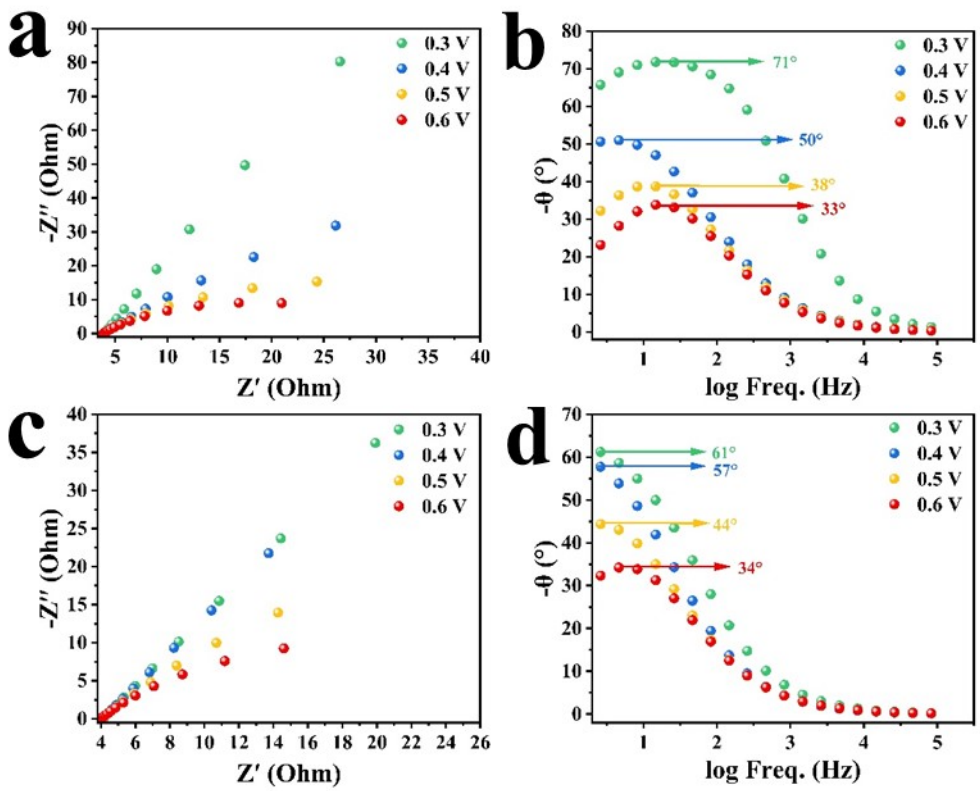

Fig. S8 Nyquist and Bode plots at different potentials (0.3, 0.4, 0.5, and 0.6V vs. SCE) for (a, b) $Cu_{1.8}Se$/NF and (c, d) Cu_2Se/NF in 1 M KOH + 0.5 M urea electrolyte.

Reference

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