Electronic Supplementary Information

$CuFeS_2$ colloidal nanocrystals as an efficient electrocatalyst for dye sensitized solar cells

Yihui Wu,[ab] Bin Zhou,[b] Chi Yang,[b] Shichao Liao,[a] Wen-Hua Zhang,[b] and Can Li*[a]

[a] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, and Dalian National Laboratory for Clean Energy, 457 Zhongshan Road, Dalian 116023, China

[b] Sichuan Research Center of New Materials, Institute of Chemical Materials, China Academy of Engineering Physics, 596 Yinhe Road, Shuangliu, Chengdu 610200, China

E-mail: canli@dicp.ac.cn

Chemicals

Copper (II) acetylacetonate ($Cu(acac)_2$, 99.99+%), oleylamine (OLA, 70%), oleic acid (OA, 90%), acetonitrile (99.8%) and and Bis(trimethylsilyl) sulfide (TMS) were purchased from Aldrich. Iron(III) chloride ($FeCl_3$, 98%), Octanoic acid (OTA, 98+%), Lauric acid (LA, 99.5%), Behenic acid (BA, 85%) and 1-Octadecene (ODE, 90%) were obtained from Alfa Aesar. Butylamine (99%), ethanol(99.7%), isopropanol (99.7%) and n-hexane (97%) were supplied by Sinopharm chemical Reagent Co., Ltd. OLA , OA, OTA, and ODE were dried under vacuum at 120 ^oC for 10 h before use.

Preparation of S sources. 1 M OLA-S and TOP-S were obtained via dissolving S powder into OLA and TOP at room temperature for 4 h, respectively.

Synthesis of $CuFeS_2$ NCs. Typically, 79 mg (0.3 mmol) of $Cu(acac)_2$, 49 mg (0.3 mmol) of $FeCl_3$, 400 μL of OLA, 400 μL of OA, and 4.5 mL of ODE were first loaded into a flask of 50 mL capacity. The flask was degassed by a vacuum pump for 30 min to remove water and other low-boiling point impurities at 100 ^oC. Afterwards, the temperature was subsequently increased to 180 ^oC, followed by swift injection of 126 μL (0.6 mmol) TMS and 1 mL dried ODE solution into the flask and maintained at this temperature for 30 min to finish the reaction. Subsequently, the solution was cooled down to 60 ^oC and then precipitated with 30 mL of isopropanol and centrifuged at 8000 rpm for 5 min. The upper solution was discarded and n-hexane was added to disperse the nanocrystals. Then the product was further purified by adding a certain amount of isopropanol and centrifuging. This process was repeated for three times. The obtained nanocrystals product were dispersed into 10 mL of n-hexane as stock solution for later use.

Fabrication of photovoltaic devices

Sputtered Pt layer (~40 nm) on a FTO glass was used as the Pt CE in this study.

$CuFeS_2$ CEs were parepared as follows: 3.5 mL of the above stock solution and 2 mL 1 mg/mL carbon black dispersed in isopropanol were then ultrasonically dispersed for 30 min, resulting in $CuFeS_2$ slurry, which was subsequently sprayed at 120 ^oC onto 8 piece ($1.2\times 2\ cm^2$) of FTO substrates to form $CuFeS_2$ CE for DSSCs followed by sintering at 400 ^oC for 30 min under N_2 atomsphere.

The commercial TiO_2 photoanodes (Ying kou Opvtech New Energy Co., Ltd) were first annealed at 500 ^oC for 30 min. After being cooled to 70 °C, the TiO_2 photoanodes were immersed in a 0.5 mM ethanol solution of N719 dye (Solaronix SA, Switzerland) for 24 h. The TiO_2 photoanodes were assembled with various CEs to fabricated DSSCs. The dye-sensitized TiO_2 photoanode and the CE were separated by a hot-melt Surlyn film (60 μm thick) and sealed through hot-pressing. The redox electrolyte (0.1 M LiI, 0.05 M I_2, 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide, and 0.5 M 4-tert-butylpyridine in anhydrous acetonitrile) was injected into the interspace between the photoanode and CE. Finally, the holes on the back of the CE were sealed with a Surlyn film covered with a thin glass slide under heat. The as-assembled DSSCs with an active area of 0.16 cm^2 were used for photovoltaic performance tests. A dummy cell was assembled with two identical counter electrodes in a sandwich fashion containing the same electrolyte as used in the assembled DSSCs. The as-assembled symmetrical cell was used for the electrochemical impedance spectroscopy and Tafel polarization measurements.

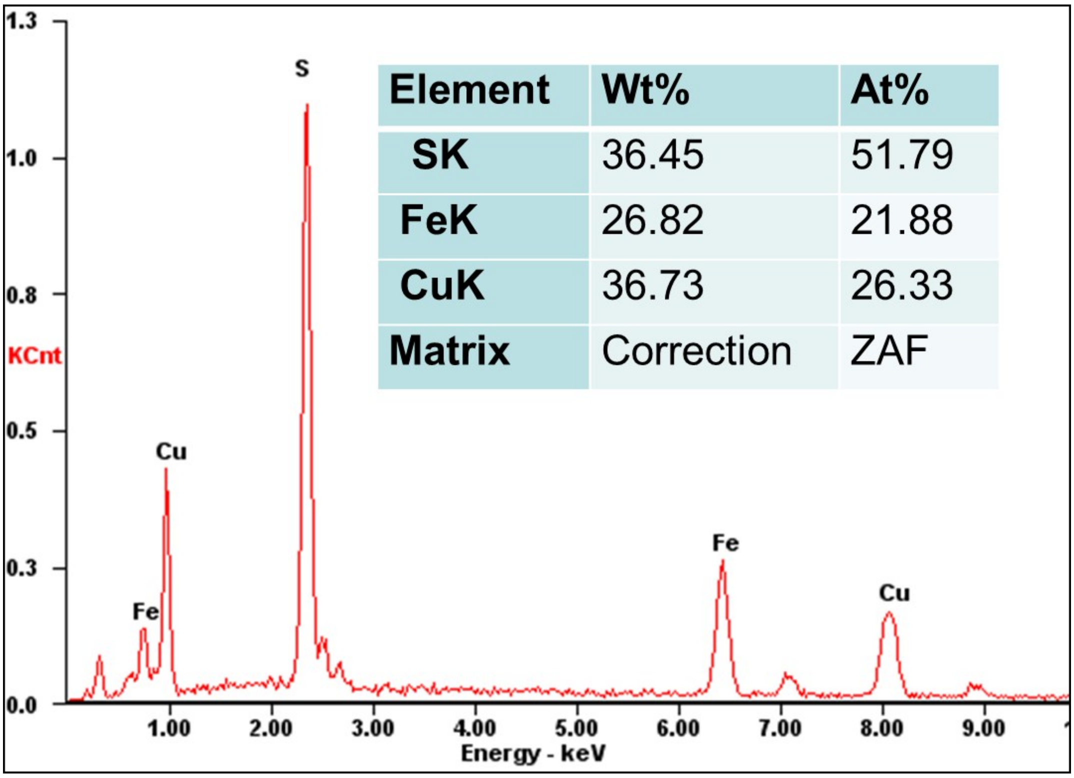
Characterization

X-ray diffraction (XRD) analyses were performed on a Rigaku RINT D/Max-2500 powder diffraction system using Cu Kα radiation source (λ = 1.541 Å) operating at 40 kV and 200 mA with a scanning rate of 5°/ min in the 2θ range of 20-70° at a step size of 0.02 s. The TEM images showing the morphology of the NCs were obtained on a FEI TECNAI G^2 spirit microscope, operating at an accelerating voltage of 100 kV. HRTEM images and selective area electron diffraction (SAED) patterns were obtained with a JEOL 4000EX transmission electron microscopes with an accelerating voltage of 300 kV. Element analysis as an ensemble measurement was conducted on FEI Quanta 200F scanning electron microscope equipped with energy dispersive spectroscopy (EDS) detector. UV-Vis-NIR absorption spectra of NCs suspensions in toluene were acquired in 1 cm path length quartz cuvettes using a Cary 5000 spectrophotometer. Cyclic voltammetry (CV) for the I^-/I_3^- system was measured in an anhydrous acetonitrile solution consisting of 0.1 M $LiClO_4$, 10 mM LiI, and 1 mM I_2, and conducted over the potential range from -0.25 V to 0.85 V at different scanning rates, using a electrochemical workstation (CHI760C, Chenhua, Shanghai) in a three-electrode electrochemical system. The resultant CEs acted as the working electrode, a Pt foil as the counter electrode, and a saturated calomel electrode as the reference electrode. The symmetrical dummy cells assembled with two identical CEs filled with the same electrolyte as used in the DSSCs were used for the electrochemical impedance spectroscopy (EIS) measurements and Tafel polarization tests. EIS experiments were carried out using an electro-chemical workstation (IM6 Zahner, Germany) at 0 V with a frequency range of 100 mHz ~1 MHz and a potential modulation of 20 mV under dark conditions. The resultant impedance spectra were analyzed with an appropriate equivalent circuit by means of Z-view software. The Tafel polarization curves were measured at a scanning rate of 10 mV s^{-1}. Photovoltaic measurement was recorded with a Newport Oriel class AAA solar simulator (model 92250A-1000) equipped with a class A 300 W xenon light source powered by a Newport power supply (model 69907). The power output of the lamp was calibrated to 1 Sun (AM1.5G, 100 mW cm^{-2}) using a certified Si reference cell (SRC−1000−TC−QZ, VLSI standard, S/N 10510-0031). The current-voltage characteristics of each cell were recorded with a Keithley digital source meter (model

2400). Photovoltaic performance was measured using a metal mask displayed a square geography with the diameter of 3 mm.

Table S1. Electrochemical parameters of the dummy cells.

CEs	*Rs(Ω cm^2)*	*Rct(Ω cm^2)*	*Z_N(Ω cm^2)*	*Epp (mV)*	J_{Ox}-A/|J_{Red}-A|
Pt	3.88	1.44	0.59	149	1.09
$CuFeS_2$	3.84	0.39	0.63	104	0.96



Element	Wt%	At%
SK	36.45	51.79
FeK	26.82	21.88
CuK	36.73	26.33
Matrix	Correction	ZAF

Fig. S1 EDAX spectrum of $CuFeS_2$ NCs.

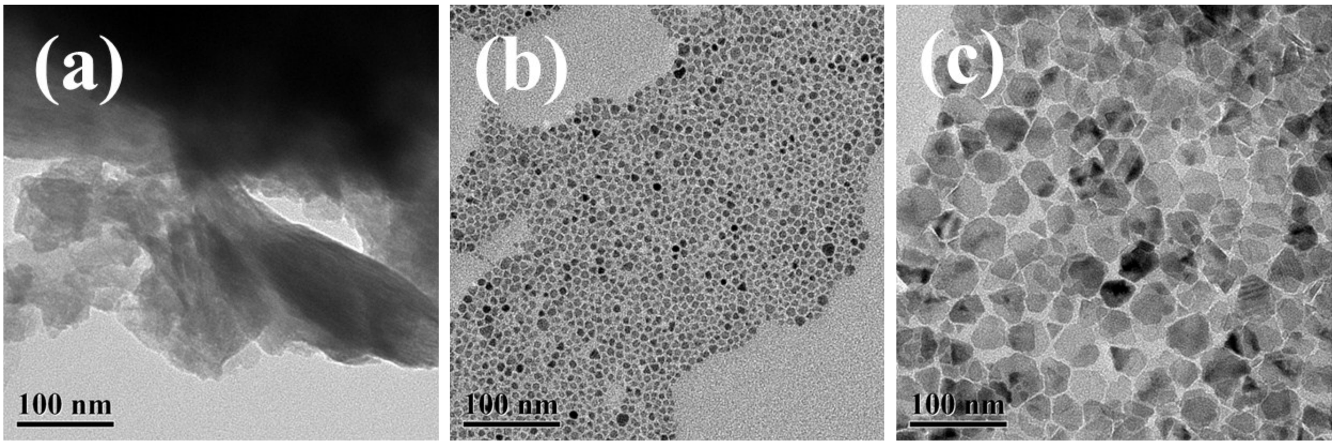


Fig. S2 TEM images of $CuFeS_2$ NCs obtained with different S sources: (a) TOP-S, (b) TMS, and (c) OLA-S.

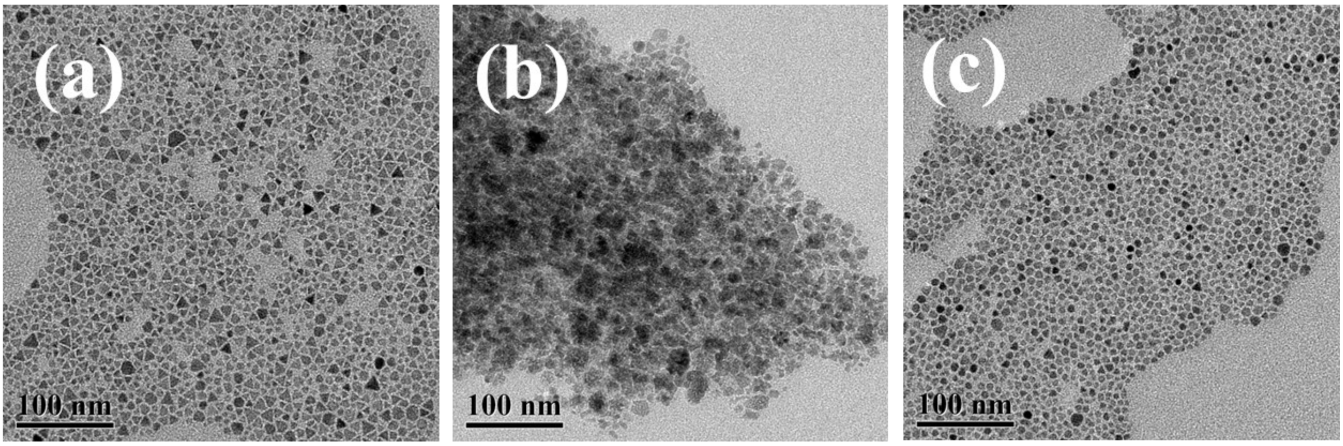


Fig. S3 TEM images of $CuFeS_2$ NCs obtained with adding different surfactants: (a) OLA, (b) OA, and (c) OLA and OA.

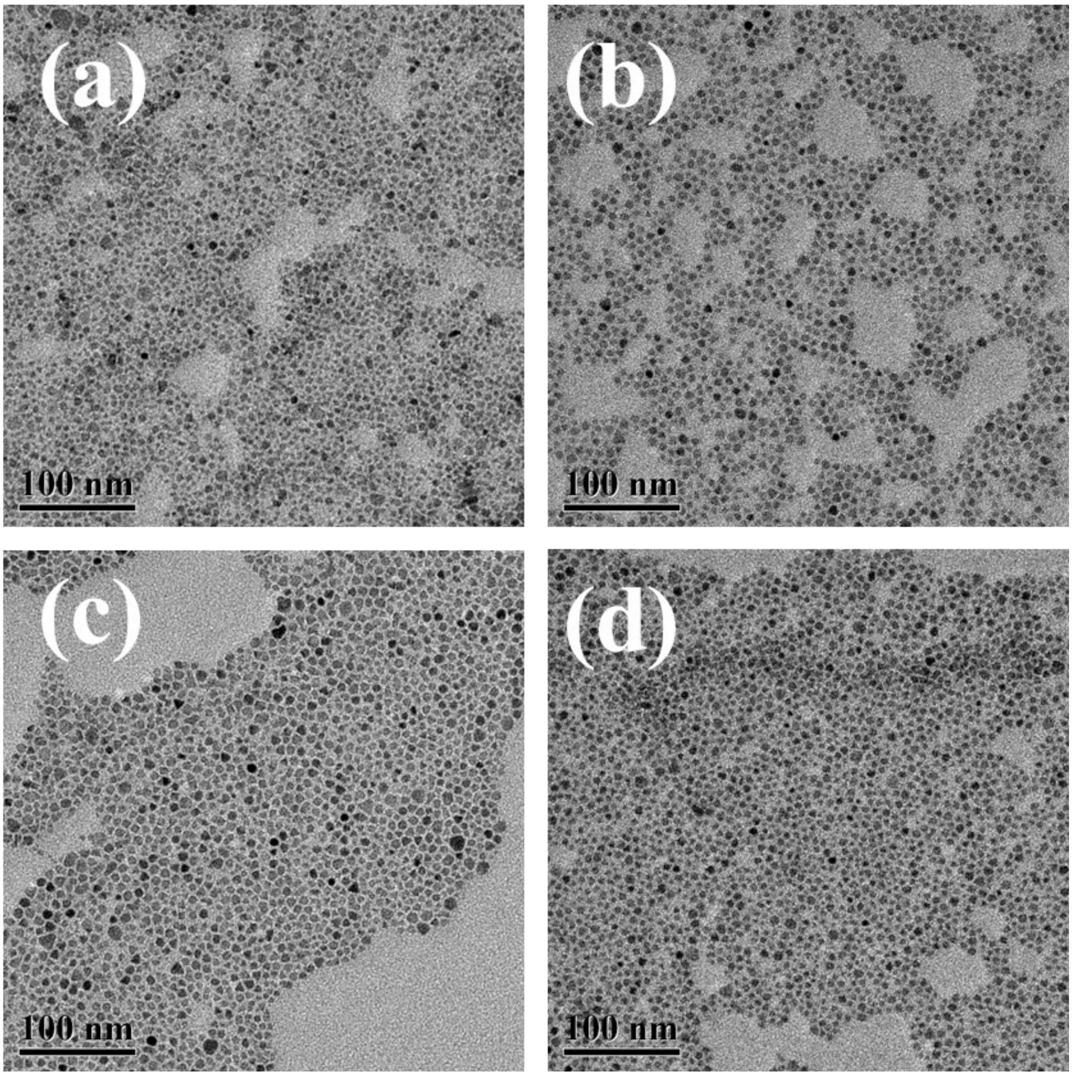


Fig. S4 TEM images of $CuFeS_2$ NCs obtained with adding different organic acid: (a) OLA and OTA, (b) OLA and OA, (c) OLA and LA, and (d) OLA and BA.

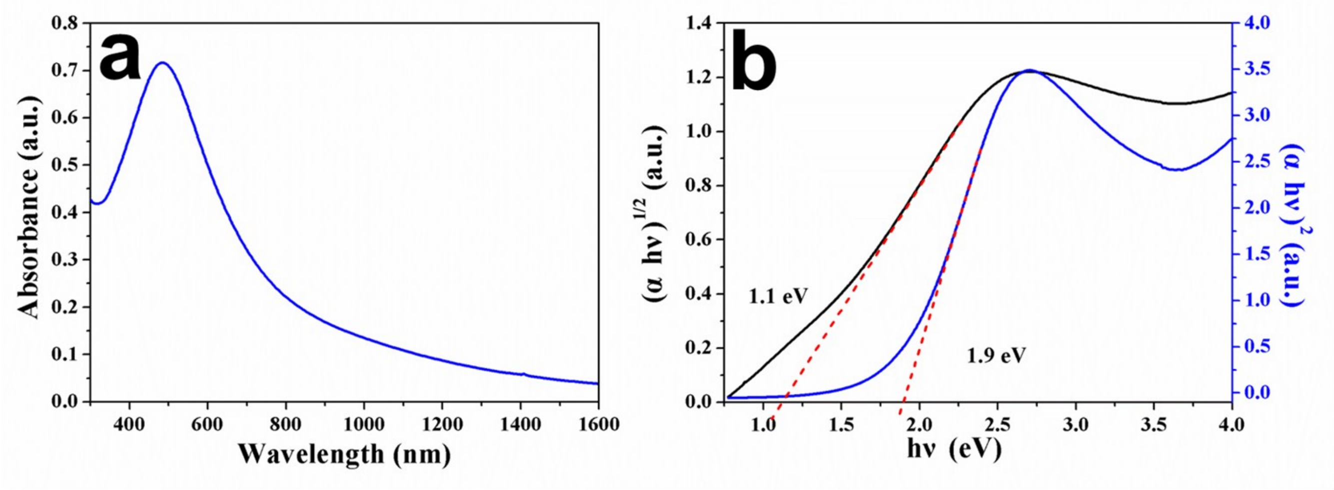


Fig. S5 (a) UV-vis-NIR absorption spectrum and (b) band gaps of $CuFeS_2$ NCs.

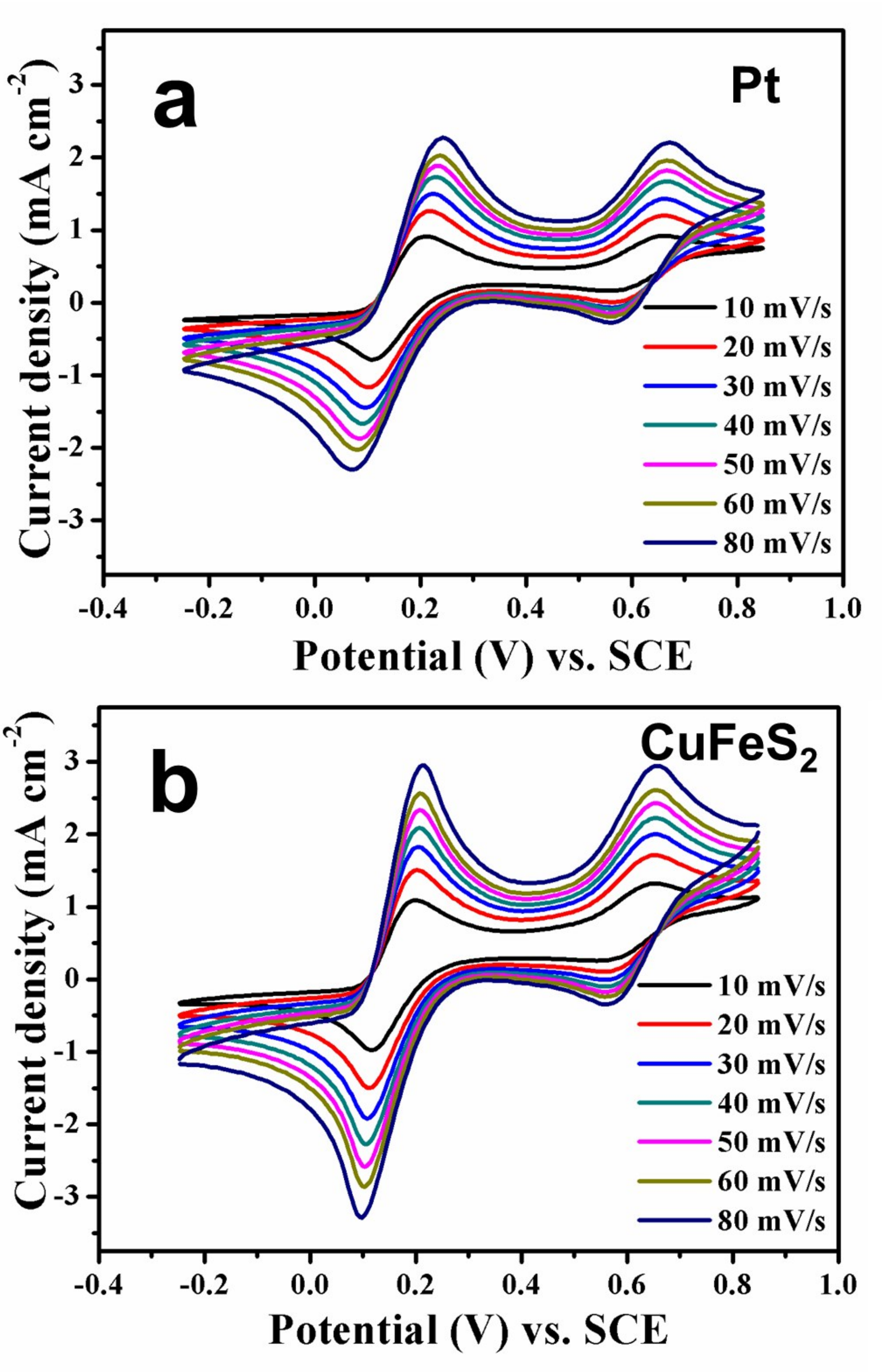


Fig. S6 The cyclic voltammograms of Pt (a) and CuFeS$_2$ (b) electrodes at different scanning rates.

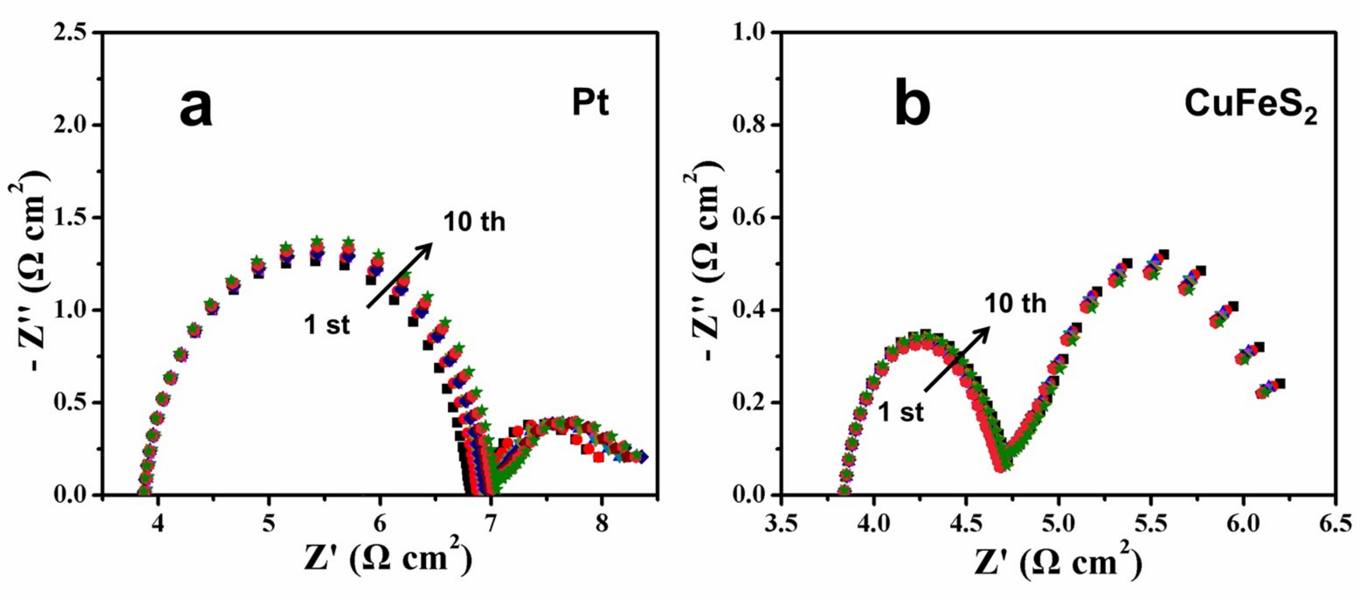


Fig. S7 Nyquist plots of EIS for the symmetrical cells with (a) sputtered Pt and (b) $CuFeS_2$ electrodes. The cells were first subjected to Tafel scanning (from 0 V→0.5 V→-0.5 V →0 V at a scanning rate of 10 mV s^{-1}), followed by 60 s relaxation at 0 V, and then EIS measurement was performed at 0 V from 0.1 Hz to 1 MHz. This sequential electrochemical test was repeated 10 times.

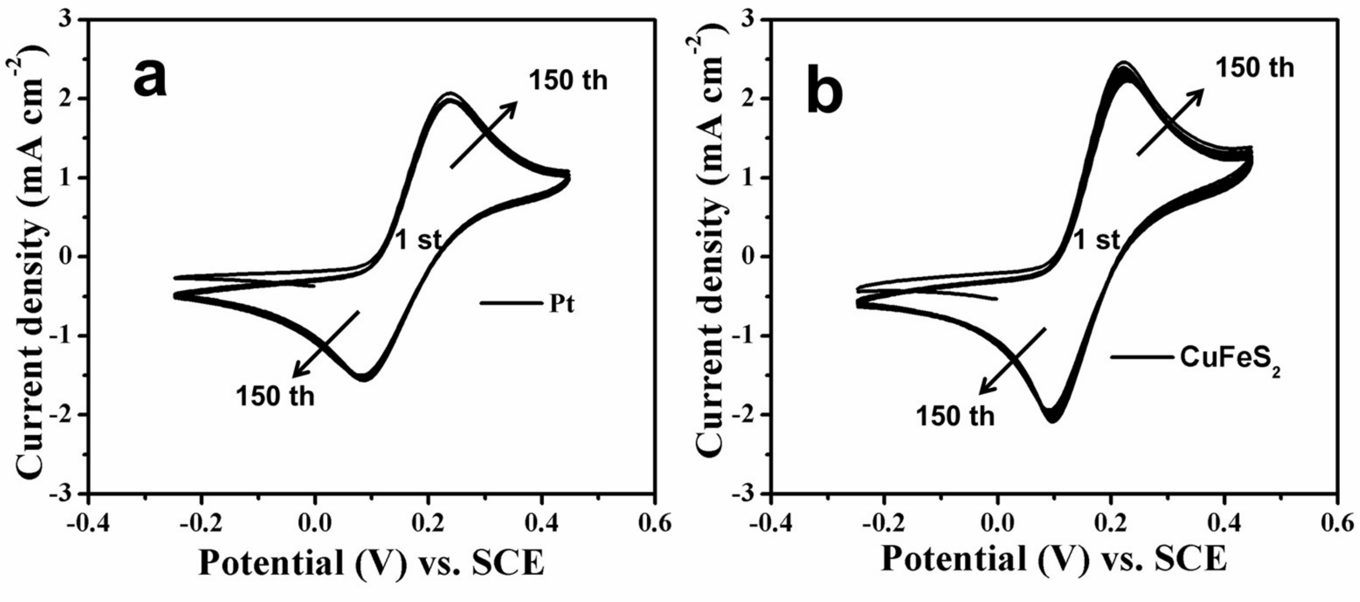


Fig. S8 A total of 150 consecutive cyclic voltammograms for the I^-/I_3^- system at a scanning rate of 50 mV s^{-1} for (a) sputtered Pt and (b) $CuFeS_2$ CEs.