

Supplementary Information

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**P-type conducting transparent characteristics of  
delafossite Ca doped CuScO<sub>2</sub> prepared by  
hydrothermal synthesis**

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### **Experimental sections:**

#### **Preparation of Ca-doped CuScO<sub>2</sub>**

All chemicals in these experiments were purchased from Sinopharm Chemical Reagent Co., Ltd with analytical grade and used without further purification. Pure CuScO<sub>2</sub> crystals were prepared according to our previous work (Deng, Y.; Xiong, D.; Gao, H.; Wu, J.; Verma, S. K.; Liu, B.; Zhao, X., Hydrothermal synthesis of delafossite CuScO<sub>2</sub> hexagonal plates as an electrocatalyst for the alkaline oxygen evolution reaction. *Dalton Transactions*, 2020, 49 (11), 3519-3524.). Typically, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Sc(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O, EG (ethylene glycol), and NaOH were dissolved sequentially in 70 ml deionized water at room temperature. Afterward, the solution was loaded into a 100 mL Teflon-lined autoclave reactor and the reaction was carried out in an oven at different temperatures for 24 hours. Subsequently, the autoclave reactor was cooled naturally to room temperature. The precipitates were washed several times with deionized water and ethanol, then dried at 60 °C for 12 hours for further characterization.

Ca-doped CuScO<sub>2</sub> was synthesized based on the preparation of pure CuScO<sub>2</sub>. Typically, 15 mmol Cu (NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, 15 mmol Sc (NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O and 15x mmol Ca (NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (The values of x are 1%, 3%, and 5%) were dissolved sequentially in 70 ml deionized water at room temperature, 0.5 ml ethylene glycol, and 2.00 g NaOH was added to the above solution, and the reaction took place at 240 °C for 24 hours. Finally, the as-obtained CuScO<sub>2</sub>-based samples were washed several times with deionized water and ethanol, then dried at 60 °C for 12 hours for further characterization.

#### **Materials Characterization**

The crystal phase of samples was characterized by the powder X-ray diffraction (XRD, D8 Advance). The microstructure, morphology, and composition of as-synthesized CCO based samples were observed using the transmission electron microscopy (TEM, FEI Titan ChemiSTEM operating at 200 keV) coupled with energy-dispersive X-ray spectroscopy (EDX), and the field-emission scanning electron microscopy (FESEM, QUANTA FEG 450). The surface chemical states of CuScO<sub>2</sub>-based powders were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo

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Escalab 250Xi), and the C 1s line (284.80 eV) corresponding to the surface adventitious carbon (C-C line bond) has been used as the reference binding energy. The absorption spectra were measured in the range of 200-800 nm using UV-VIS-NIR spectroscopy (Lambda 750 S). Electrical conductivity was measured using the four-probe configuration (Tektronix 6517B), the dry powder of CuScO<sub>2</sub>-based samples was pressed into a sheet with 0.8 cm diameter and 0.5 cm thickness using a tablet press machine (769YP-15A), and the temperature of the tableting samples was controlled by a temperature-controlled stage (Linkam HFS600E-PB2) from 0 to 300 °C with the heating rate of 2 °C min<sup>-1</sup>. The Mott-Schottky measurements were carried out by an electrochemical analyzer (CS2350H, Wuhan Corrtest Instruments Corp., China), and the applied potential ranges from 0.67 to 0.97 V vs.SCE at the frequency of 1 kHz in 1.0 M KOH (pH~13.5) solution. For the Mott-Schottky measurements, Ca doped CuScO<sub>2</sub> working electrodes (active areas: 1 × 1 cm<sup>2</sup>) were prepared through traditional doctor blade method at room temperature.

## Supplementary Information

### Supplementary Table:

**Table S1.** Detailed reaction conditions employed to synthesize CuScO<sub>2</sub> crystals.

No.	Cu (mmol)	Sc (mmol)	NaOH (g)	EG (ml)	Temperature (°C)	Time (h)
1	4	4	2	1	150	24
2	4	4	2	1	180	24
3	4	4	2	1	210	24
4	4	4	2	1	240	24
5	4	4	2	1	260	24
6	5	4	2	1	240	24
7	6	4	2	1	240	24
8	7	4	2	1	240	24
9	8	4	2	1	240	24
10	5	4	2	0.50	240	24
11	5	4	2	0.25	240	24
12	5	4	2	0.15	240	24
13	5	4	0.50	0.25	240	24
14	5	4	1	0.25	240	24
15	5	4	3	0.25	240	24
16	18.75	15	2	0.25	240	24
17	15	15	2	0.25	240	24
18	15	15	2	0.50	240	24

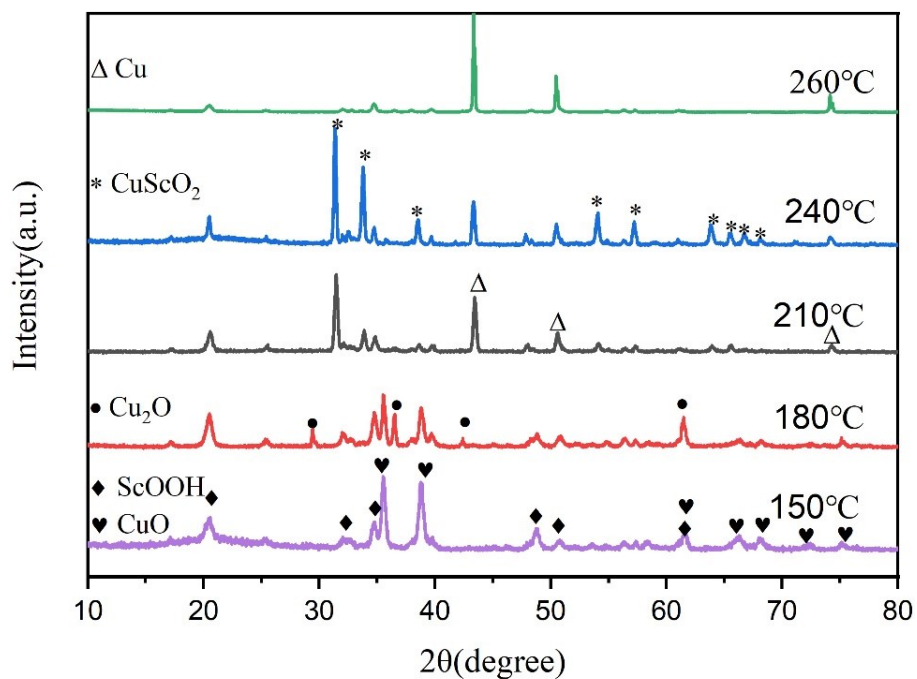
**Table S2.** Calculated chemical compositions of Ca-doped CSO from XPS results

Samples	Cu/Sc	Ca/Cu	Ca/(Ca+Cu)	Ca/(Ca+Sc)
1% Ca-CSO	0.83	0.00803	0.008	0.006
3% Ca-CSO	0.80	0.02656	0.026	0.020
5% Ca-CSO	0.7625	0.04918	0.047	0.036

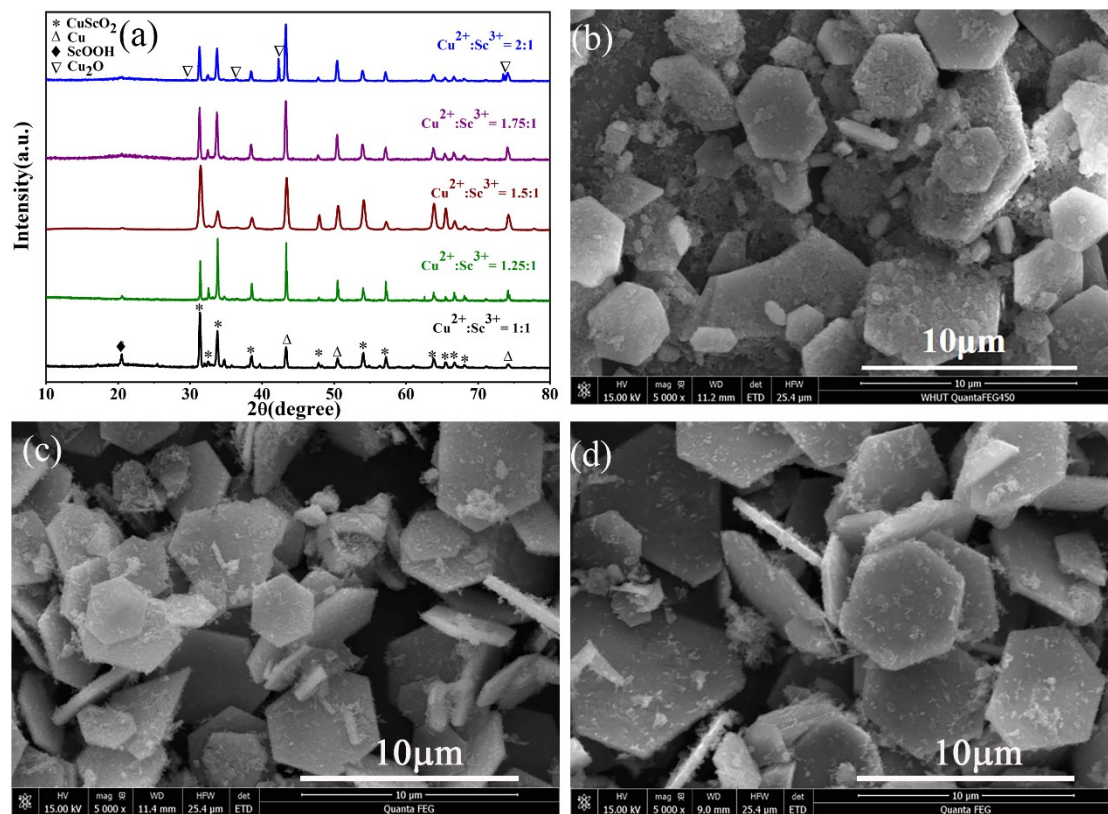
**Table S3.** The lattice parameters of CSO based samples.

Composition	a (Å)	c (Å)
Pure CSO	3.2228(2)	17.071(3)
1% Ca-CSO	3.2231(2)	17.108(3)
3% Ca-CSO	3.2233(2)	17.114(2)
5% Ca-CSO	3.2236(2)	17.125(3)

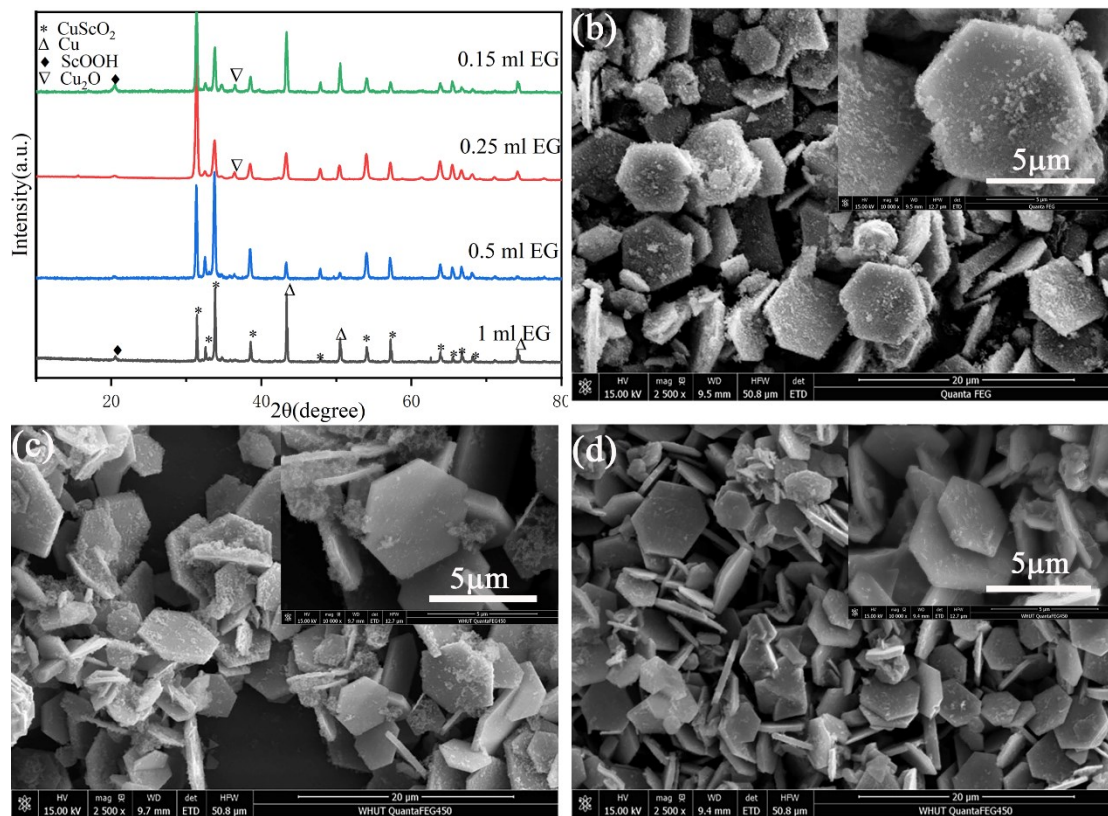
## Supplementary Figures:



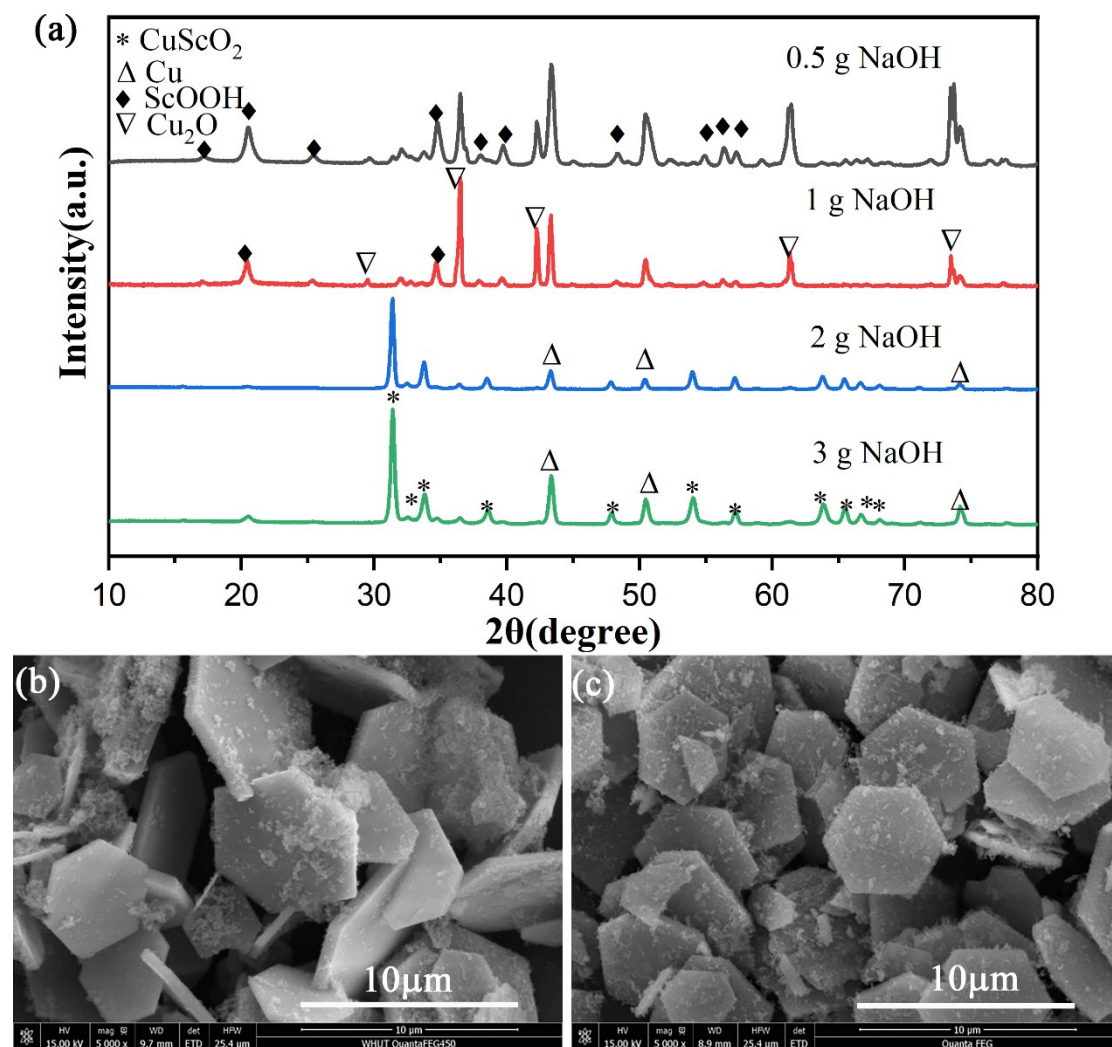
**Fig. S1.** XRD patterns of hydrothermal products at different temperatures (150, 180, 210, 240, and 260°C).



**Fig. S2.** XRD pattern (a) and SEM images (b, 1:1; c, 1.25:4; d, 1.75:1) of products with different  $\text{Cu}^{2+}/\text{Sc}^{3+}$  ratios obtained at 240 °C for 24 hours.

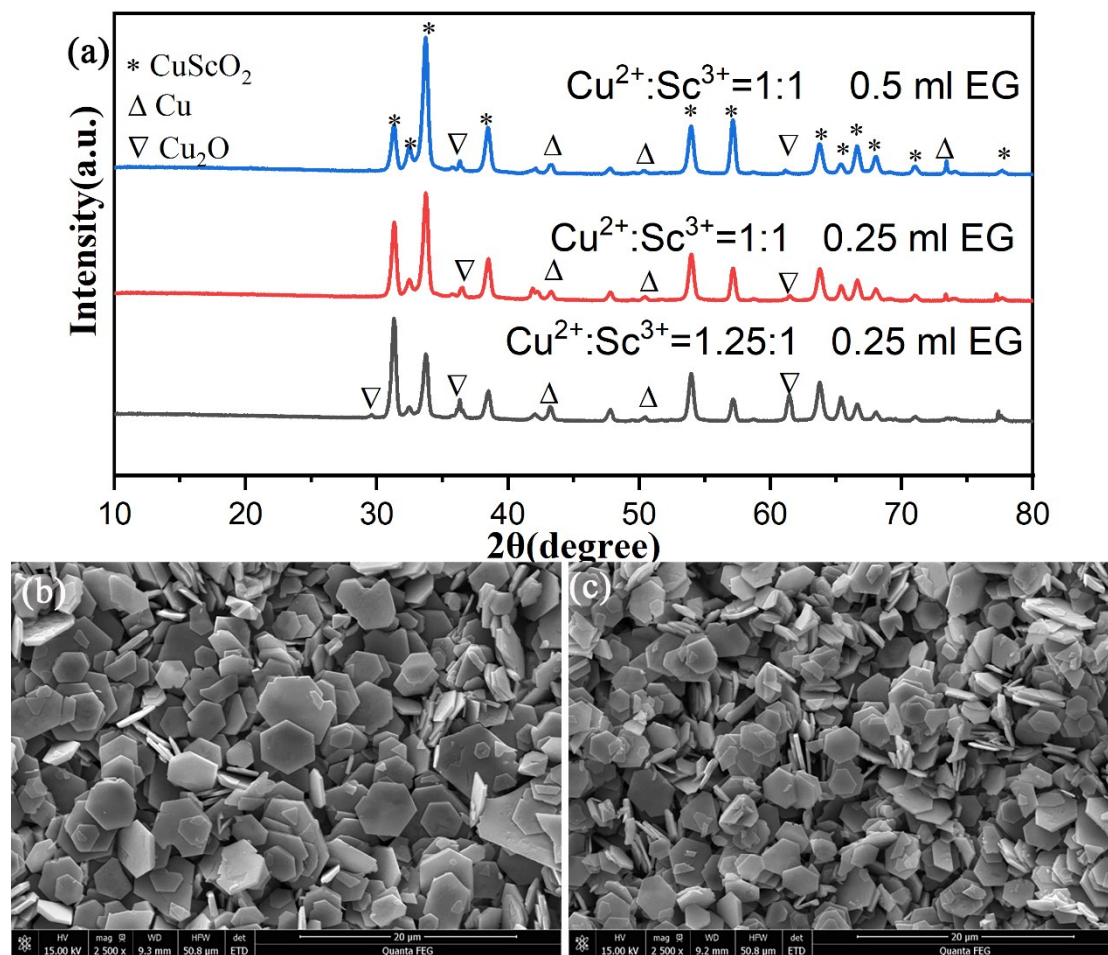


**Fig. S3.** XRD pattern (a) and SEM images (b, 0.15 ml; c, 0.25 ml; d, 0.5 ml) of products obtained by hydrothermal synthesis with different EG additions.

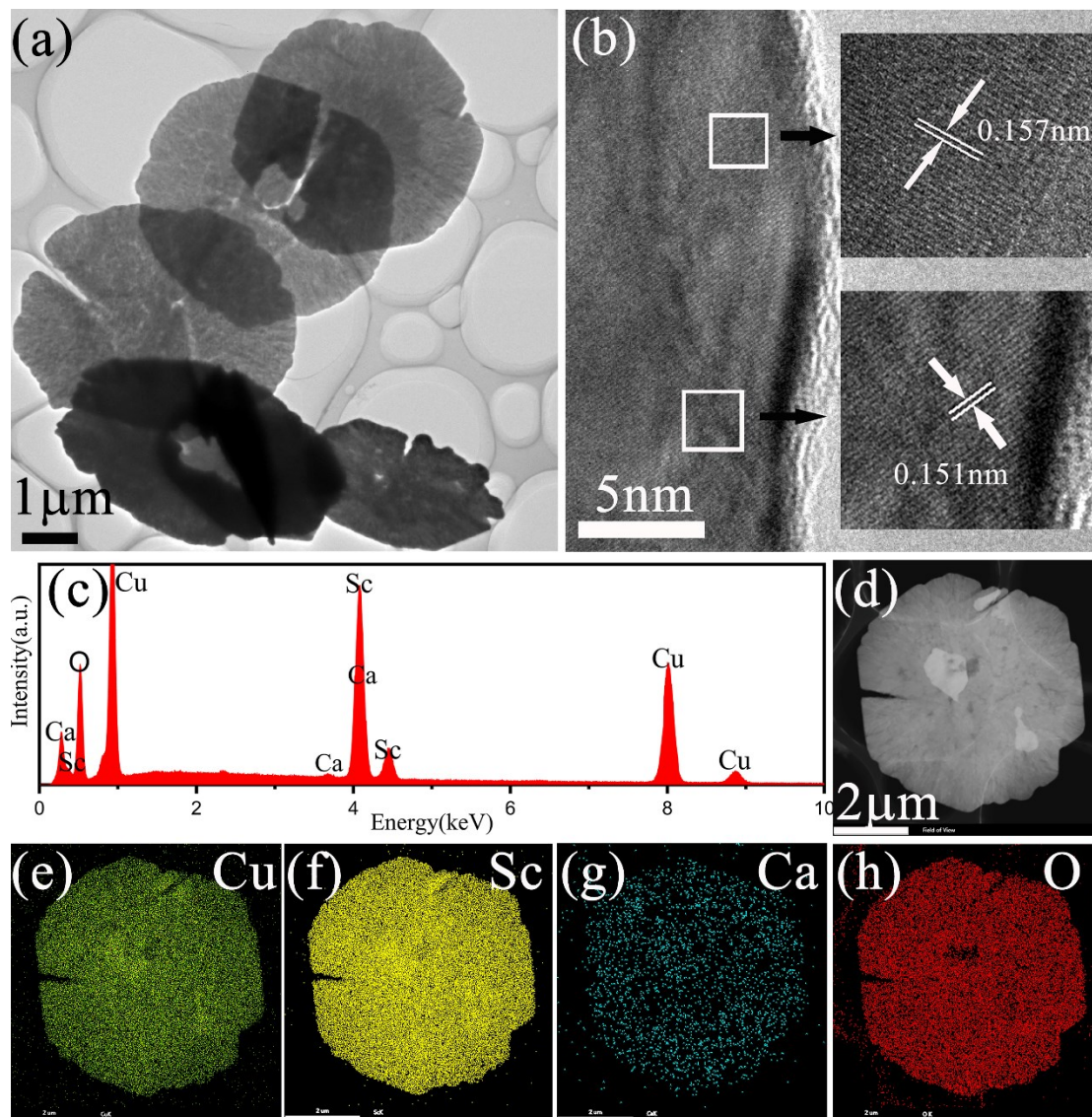


**Fig. S4.** XRD pattern (a) and SEM images (b, 2 g; c, 3 g) of products obtained by hydrothermal synthesis with different NaOH additions.

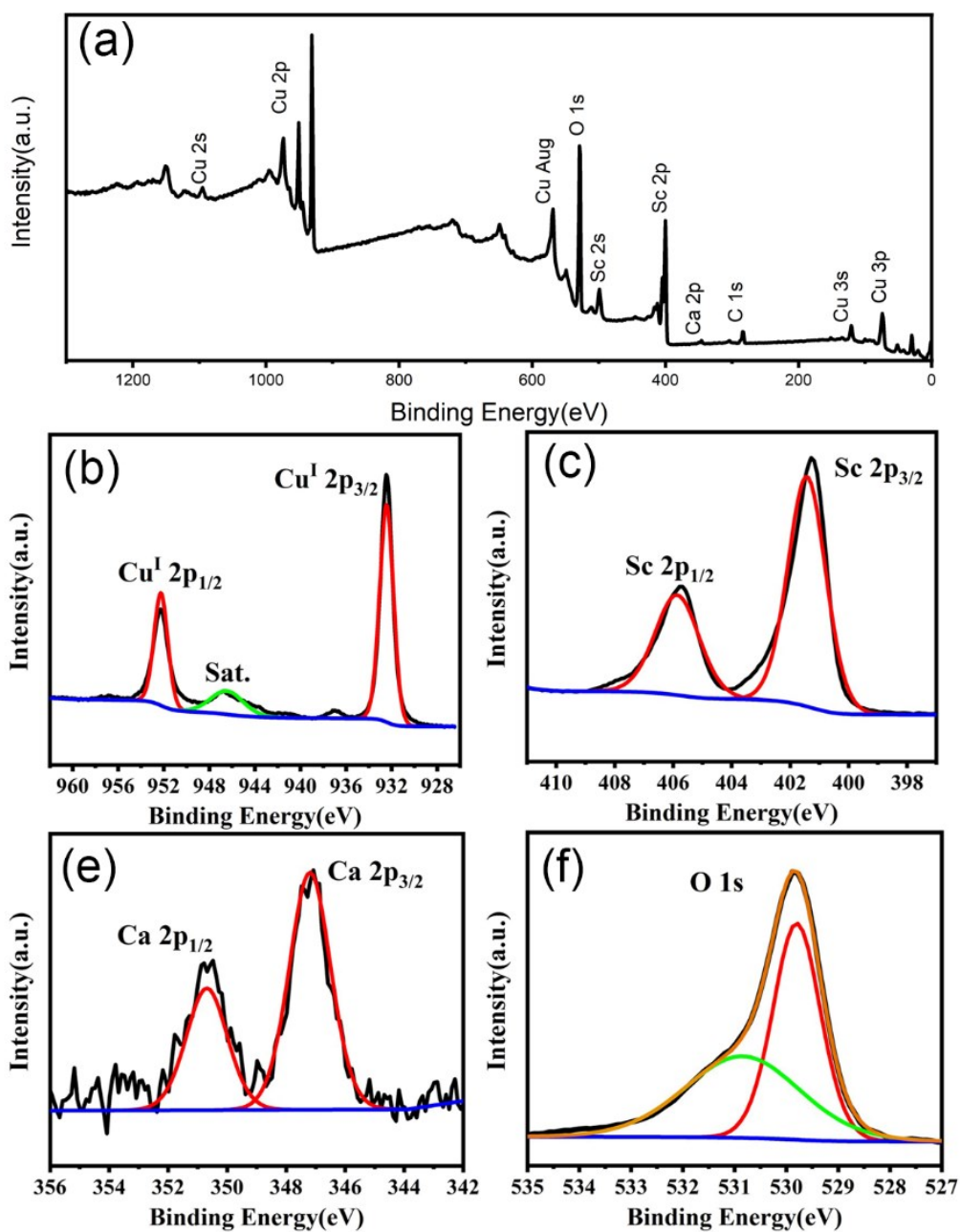




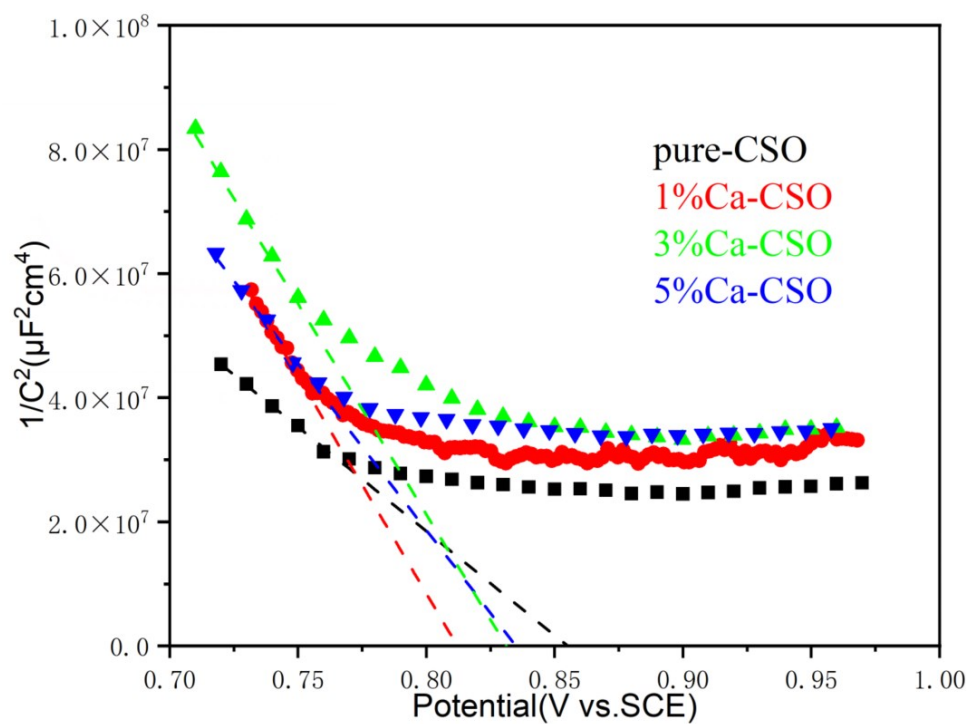
**Fig. S5.** XRD pattern (a) and SEM images (b,  $\text{Cu}^{2+}/\text{Sc}^{3+} = 1:1$ , 0.25 ml EG; c,  $\text{Cu}^{2+}/\text{Sc}^{3+} = 1:1$ , 0.5 ml EG) of products obtained by hydrothermal synthesis with 15 mmol concentration of reactant.



**Fig. S6.** TEM (a), HRTEM (b), EDX spectrum (c), HAADF-STEM (d), and elemental maps (e, Cu; f, Sc; g, Ca; h, O) of 5% Ca-doped CSO particles. The insets in (b) are two zoomed views of two lattice fringe.



**Fig. S7.** XPS fully scanned spectra (a), high resolution XPS spectra for Cu 2p (b), Sc 2p (c), Ca 2p (d) and O 1s (e) of 5% Ca doped CuScO<sub>2</sub> powders.



**Fig. S8.** Mott-Schottky plots of these Ca-doped CSO samples.