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In-situ engineered $CuCo_2S_4$@$CuCo_2O_4$ heterojunction with O-S interpenetrated interface as photoanode for selective photoelectrochemical bioanalysis

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1. Experimental section

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1.1 Chemicals

L-Cysteine (L-Cys) was bought from Aladdin Biological Co., Ltd (Shanghai). Cupric chloride ($CuCl_2 \cdot 2H_2O$), cobaltous chloride ($CoCl_2 \cdot 6H_2O$), urea ($CO(NH_3)_2$), ammonium fluoride (NH_4F) and sodium sulfide (Na_2S) were analytical purity and bought from Sinopharm Company (Shenyang). The compound amino acid injections bought in local pharmacies.

1.2 Apparatus

The crystalline phase of $CuCo_2O_4$ and $CuCo_2S_4$@$CuCo_2O_4$ was investigated by X-ray diffraction (XRD, Siemens D5000, Germany). The microstructure of $CuCo_2O_4$ and $CuCo_2S_4$@$CuCo_2O_4$ were investigated in field emission scanning electron microscope equipped with an energy dispersive spectroscopy (EDS) detector (HITACHI SU8000, Japan, SEM) and transmission electron microscopy (TecnaiG220, USA, TEM). Electronic state of $CuCo_2O_4$ and $CuCo_2S_4$@$CuCo_2O_4$ were acquired by X-ray photoelectron spectroscopy (Thermo ESCALAB 250Xi, USA, XPS). The UV-Vis diffuse reflectance spectra of $CuCo_2O_4$ and $CuCo_2S_4$@$CuCo_2O_4$ were acquired by a UV2550 (UV-Vis DRS, Shimadzu Scientific Instruments Inc. Japan).

1.3 Sample preparation

To confirm the feasibility, the proposed $CuCo_2S_4$@$CuCo_2O_4$/CC PEC sensor was employed to analyze L-Cys in human urine, serum and compound amino acid injections. Prior to analysis, the urine and serum samples were centrifuged at 4000 rpm for 5 min and filtered by nylon membrane filters (0.22 μm), the supernatant liquid was appropriately diluted with 0.1 M PB (pH 7.0) before detection. The compound amino acid injection was used directly without any purification.

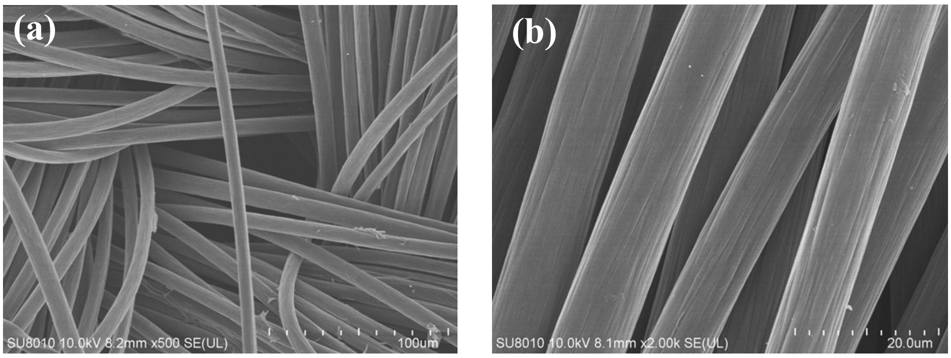

Fig. S1 The SEM images of carbon cloth

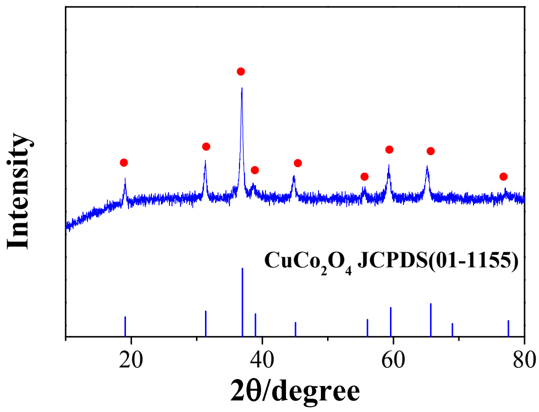

Fig. S2 The XRD of the $CuCo_2O_4$.

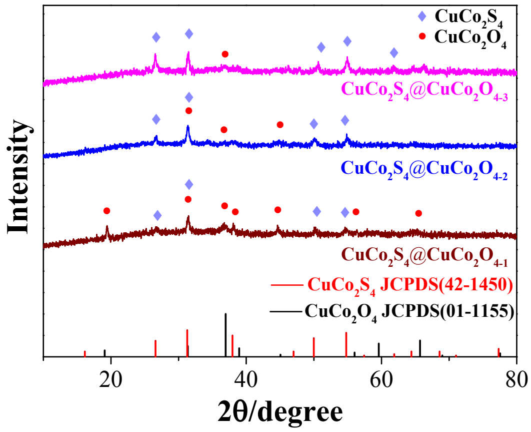

Fig. S3 The XRD of $CuCo_2S_4@CuCo_2O_{4-1}$/CC, $CuCo_2S_4@CuCo_2O_{4-2}$/CC and $CuCo_2S_4@CuCo_2O_{4-3}$/CC

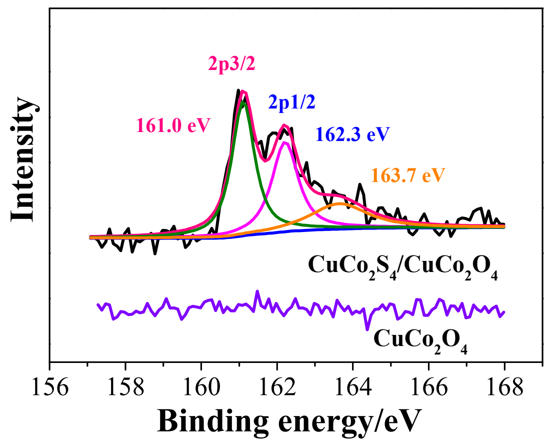

Fig. S4 XPS spectra of S

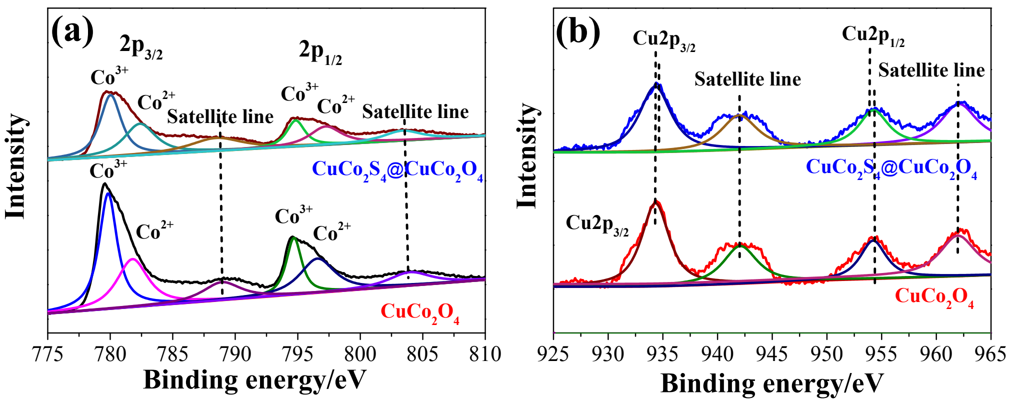

Fig. S5 XPS spectra of Co (a) and Cu (b)

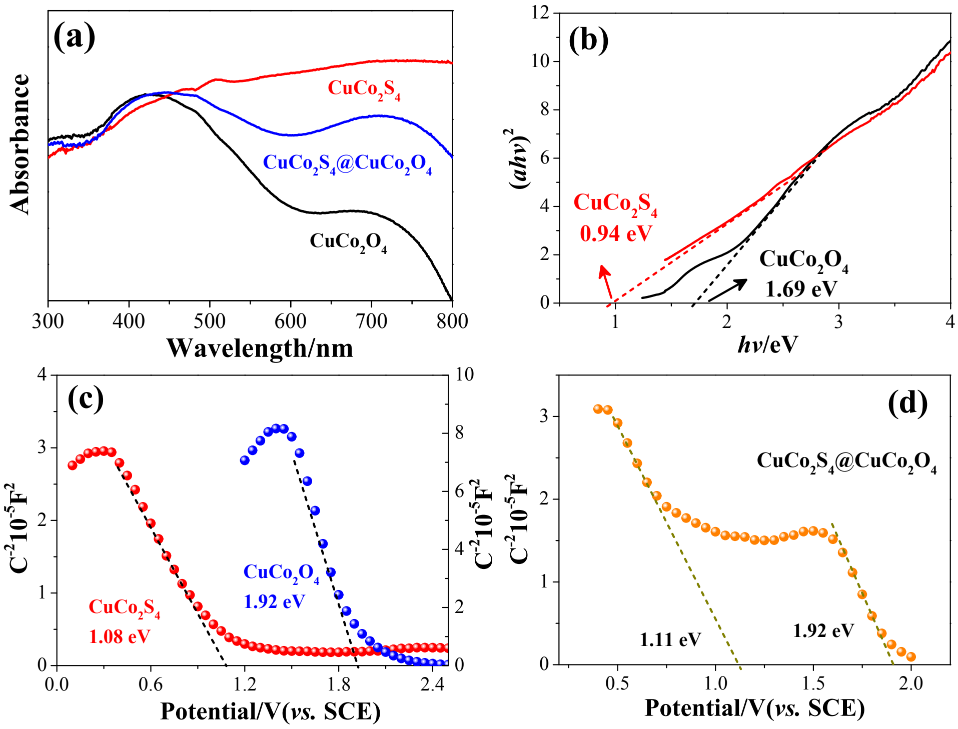

Fig. S6 UV-Vis DRS (a); plots of $(ahv)^2$ versus photo energy(b); M-S curve of $CuCo_2O_4$ and $CuCo_2S_4$(c); M-S curve of $CuCo_2S_4$@$CuCo_2O_4$(d)

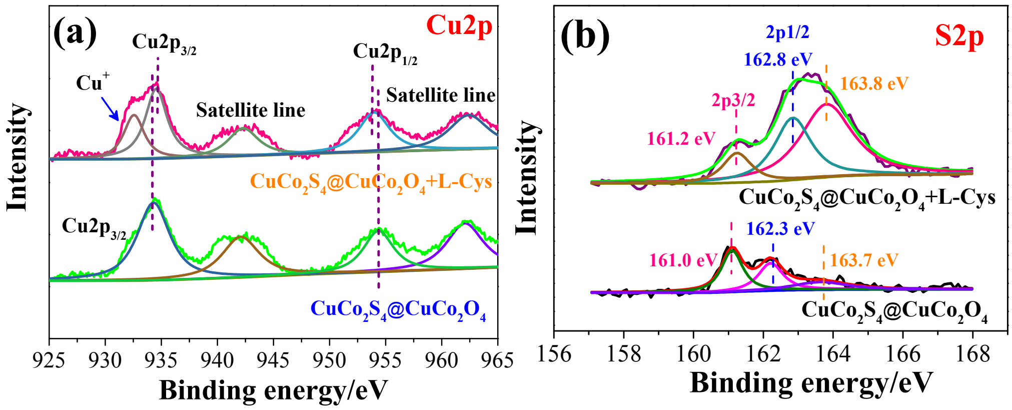

Fig. S7 Cu (a), S (b) XPS spectra of $CuCo_2S_4@CuCo_2O_4$ and $CuCo_2S_4@CuCo_2O_4$-L-Cys

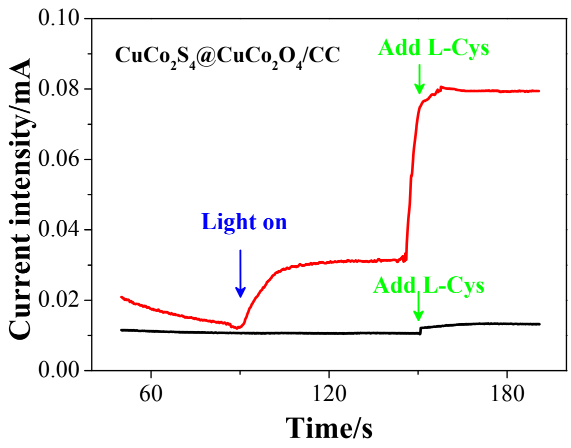

Fig. S8 The influence of light irradiation for the response of $CuCo_2S_4@CuCo_2O_4$ to 0.5 μM L-Cys

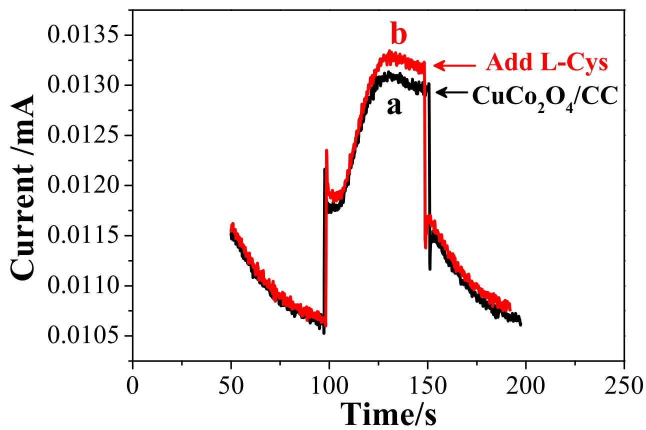

Fig. S9 The i-t response of $CuCo_2O_4$ without (a) and with 0.5 μM L-Cys (b)

The reproducibility of the $CuCo_2S_4@CuCo_2O_{4-2}/CC$ was evaluated. Five independently$CuCo_2S_4@CuCo_2O_{4-2}/CC$ electrodes were fabricated and applied to the detection of L-Cys under the same condition. The relative standard deviation (RSD) value is less than 4.1%, demonstrating a good reproducibility. The repeatability of the $CuCo_2S_4@CuCo_2O_{4-2}/CC$ sensor were study by using the same electrode for 10 repeated experiments, and the RSD value was about 3.7%, suggesting excellent repeatability. As shown in Fig. S7, the photocurrent of $CuCo_2S_4@CuCo_2O_{4-2}/CC$ shows little change after 10 repeated lights on-off illumination cycles. The results indicate the formation of $CuCo_2S_4@CuCo_2O_{4-2}/CC$ integration electrode with interpenetrated interface is beneficial to the transfer of photogenerated carriers and avoid $CuCo_2S_4@CuCo_2O_{4-2}$ falling off from the CC substrate, which is effective to enhance the stability and durability of PEC sensor.

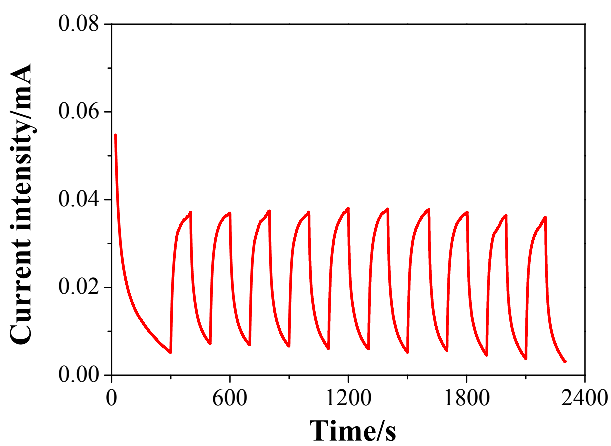

Fig. S10 The photocurrent stability of the $CuCo_2S_4@CuCo_2O_{4-2}/CC$

The application ability of the $CuCo_2S_4@CuCo_2O_{4-2}$/CC PEC sensor was evaluated by assaying L-Cys in human serum, urine and injection samples. As shown in Table S1, the recoveries are in the range from 90.0 to 117.0%, and the RSD value was about 5.2%, showing a satisfactory result.

Table S1 Analytical result of L-Cys in the real samples

Sample	Spiked (μmol L^{-1})	Found (μmol L^{-1})	R%	RSD%
Compound amino acid injections	0	2.32	—	3.2
	0.1	2.41	90.0	5.2
	5	7.18	97.2	4.7
	25	27.35	101.2	3.6
Urine	0.1	0.117	117.0	4.0
	5	5.08	101.6	4.8
	25	24.67	98.7	3.5
Serum	0.1	0.091	91.0	3.9
	5	4.73	94.6	4.5
	25	24.95	99.8	3.3

[a] Mean of three measurement