

Electronic Supplementary Information (ESI)

Co-Cu-WS_x ball-in-ball nanosphere as high-performance Pt-free bifunctional catalyst in efficient dye-sensitized solar cell and alkaline hydrogen evolution

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Materials

Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, AR), copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O, AR), ammonium metatungstate hydrate ((NH₄)₆H₂W₁₂O₄₀·xH₂O, AR) and thioacetamide (TAA, AR) were obtained from Aladdin Ltd. (China). Ammonium metatungstate hydrate was procured from Aladdin Ltd. Lithium iodide (LiI, ≥ 99.0%), iodine (I₂, ≥ 99.9%), lithium perchlorate (LiClO₄, ≥ 99.9%) were purchased from Macklin Ltd. (China). The commercial N719 dye and Pt/C (20 wt%) powder were received from Solaronix Ltd. (Switzerland). The fluorine-doped SnO₂ (FTO) glasses, purchased from Nippon Sheet Glass(15 Ω sq⁻¹, Japan), were cleaned with cleanser essence, acetone and ethyl alcohol in sequence and cut into squares of 1.5 cm × 1.5 cm.

Instruments

The surface morphologies of all samples were observed by a scanning electron microscopy (SEM, S-4800, Hitachi). Powder XRD patterns were carried out on X-ray diffraction (XRD, X'Pert PRO, Cu Kα, λ = 0.15406 nm) for the indication of crystal structure. The microstructures of Co-Ni-MoS_x YSNs were investigated through a high-resolution transmission electron microscope (HRTEM, TECNAI, G2F20, FEI), equipped with an accessory of energy-dispersive X-ray spectroscopy (EDX). X-ray photoelectron spectroscopy (XPS) analysis was conducted on a VG ESCALAB 250 (Mg Kα, USA) spectrometer to characterize the elemental composition of Co-

Ni-MoS_x YSNs. The surface area and pore-size distribution were measured by a Micromeritics ASAP-2020.

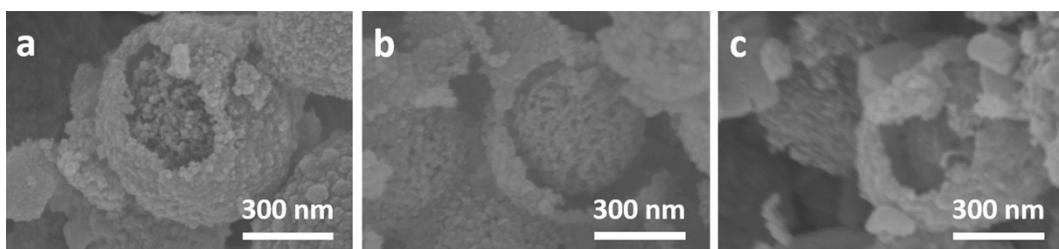


Fig. S1. SEM images of (a) cracked Co-Cu-WS_x, (b) cracked Co-WS_x, (c) cracked Co-CuS_x after the ultrasonic treatment

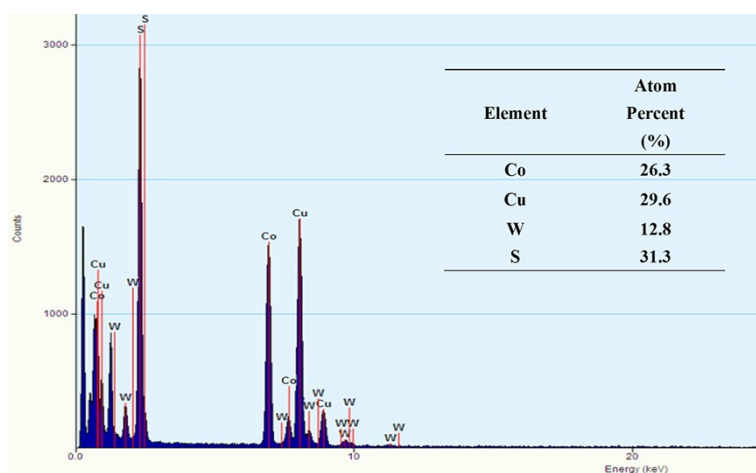


Fig. S2. EDX spectra images and main atom percent of Co-Cu-WS_x.

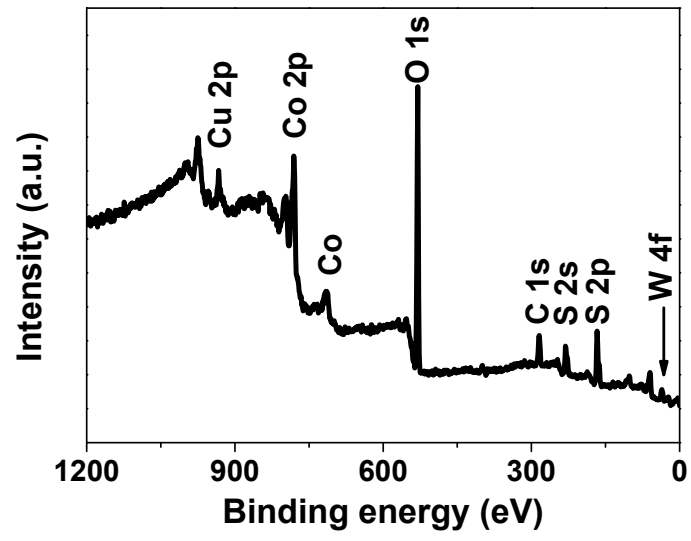


Fig. S3. XPS spectra of Co-Cu-WS_x survey spectrum.

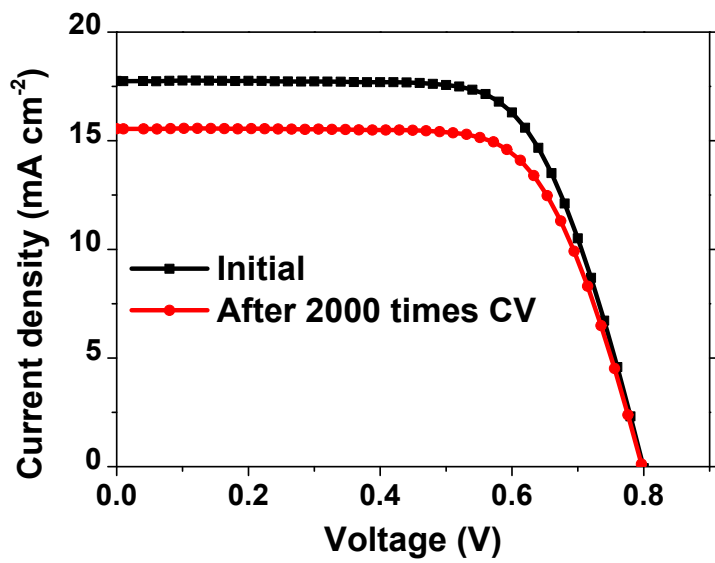


Fig. S4. J - V curves of Co-Cu-WS_x based CE before and after 2000 CV cycles.

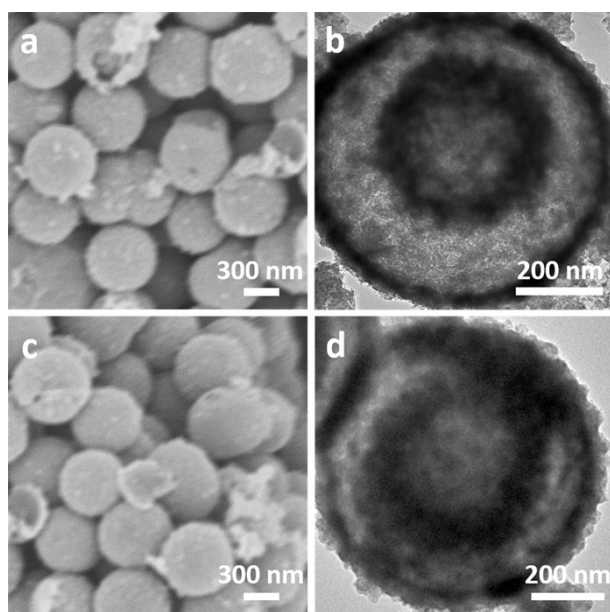


Fig. S5. (a, b) SEM/TEM images of Co-Cu-WS_x after stability tests for DSSC. (c, d) SEM/TEM images of Co-Cu-WS_x after stability tests for HER.

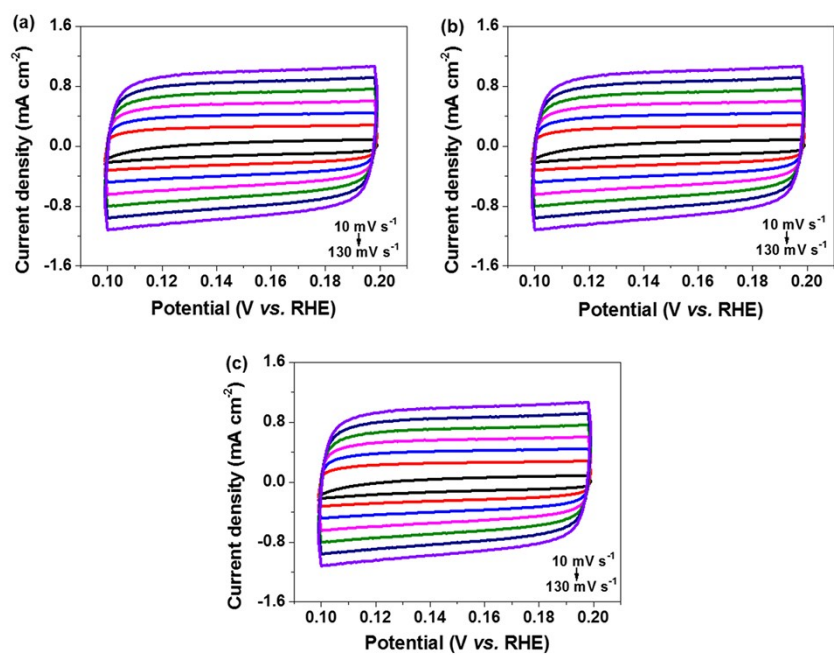


Figure S6. Cycle voltammograms of (a) Co-Cu-WS_x, (b) Co-WS_x and (c) Co-CuS_x at different scan rates (10, 30, 50, 70, 90, 110 and 130 mV s⁻¹) in 1.0 M KOH.

Table S1. Comparisons of DSSC performances for Co-Cu-WS_x with other typical non-noble metal-based catalysts.

Catalyst	η (%)	η_{Pt} (%)	η/η_{Pt}	Reference
Co-Cu-WS _x	9.61	8.24	1.17	This work
CuS/WS ₂	8.21	7.97	1.03	1
Co ₃ S ₄ nanosheet/rGO	8.08	7.62	1.06	2
WO _x @WS ₂ @carbon	7.71	7.34	1.05	3
Co ₃ S ₄ /ECs	9.23	8.38	1.10	4
MoS ₂ /Co ₃ S ₄	6.77	7.14	0.95	5
CoS on om-SnO ₂	7.50	5.80	1.29	6
carbon-coated WS ₂	5.50	5.60	0.98	7
WS ₂ /MWCNTa	7.36	7.54	0.98	8
WS ₂	7.73	7.64	1.01	9

Table S2. Comparison of HER performance in alkaline medium for as-obtained samples with other non-noble metal-based catalysts.

Catalyst	Onset potential (mV)	η_{10} (mV)	Tafel slope (mV decade ⁻¹)	Reference
Co-Cu-WS _x	25.5	82.5	53.8	This work
Co ₃ S ₄ HNSs	—	221	111	10
Co ₃ S ₄ /MoS ₂ /Ni ₂ P	60	—	98	11
Co ₃ S ₄ @MoS ₂	—	136	74.	12
MoS ₂ /Co ₃ S ₄	—	225	115.3	13
γ -Cu ₂ S/CF	105	190	98.9	14
NiO@Ni/WS ₂ /CC	40	—	43	15
Co ₃ S ₄ /CoP	38	86	45	16
NiS ₂ /MoS ₂ HNW	—	204	65	17
WS ₂ /SNCF	96	157	66	18

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