

Electronic Supplementary Information

Bridge-type interface optimization on a dual-semiconductor heterostructure toward high performance overall water splitting

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Characterization Techniques.

Scanning electron microscope (SEM). The morphology of samples was investigated using a scanning electron microscope (Zeiss SUPRA 55) with an accelerating voltage of 20 kV.

Transmission electron microscope (TEM). The TEM images were recorded on JEOL JEM-2010 equipment with an accelerating voltage of 200 kV.

X-ray diffraction (XRD). The XRD patterns were collected on a Bruker D8 Advance X-Ray Diffractometer using a Cu K α source, at a scan rate of 10°/min.

Photoelectrochemical property. The electrode for photocurrent measurement was fabricated as follow: (1) 50 mg of Cu₂O@ZnCr-LDH photocatalyst was dispersed in ethanol (10 ml) by supersonic treatment for 1 h to produce a uniform suspension; (2) the suspension (~1 mL) was spread onto an ITO substrate (~3 cm × 1 cm) and dried to obtain the working electrode. The photocurrent measurement was operated in 0.5 M Na₂SO₄ solution, under a Xe lamp (300 W) illumination ($\lambda > 420$ nm) for all the samples. The data were collected by a CHI 660E electrochemistry workstation (Shanghai Chenhua Instrument Co., Ltd.) with a standard three-electrode system. Saturated calomel electrode (SCE) and platinum filament were used as reference and counter electrode, respectively. The bias voltage was set at 0.1 V vs. SCE with direct current.

Electrochemical impedance spectroscopy (EIS). The EIS test was carried out using the same three-electrode system as that in the photocurrent measurement; and was evaluated by applying an AC voltage at ~0.1 V with frequency ranging from 0.1 to 100 kHz.

Elemental analysis. The Cu content of samples was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with a Shimadzu ICPS-7500 instrument.

Photoluminescence measurement. The fluorescence spectra were collected on a RF-5301PC fluorospectrophotometer with the 360 nm excitation light. The width of both the excitation and emission slit is 5 nm.

Figures and Tables

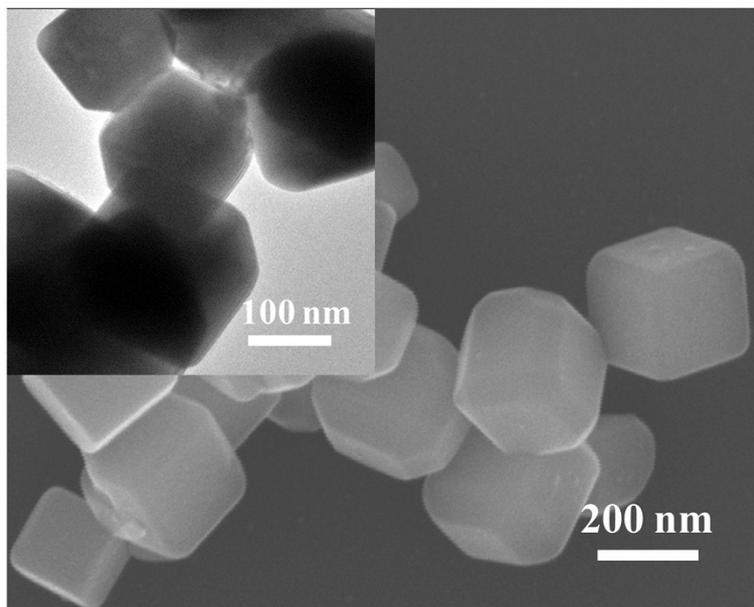


Fig. S1 SEM and TEM (inset) images of the Cu₂O nanocubes.

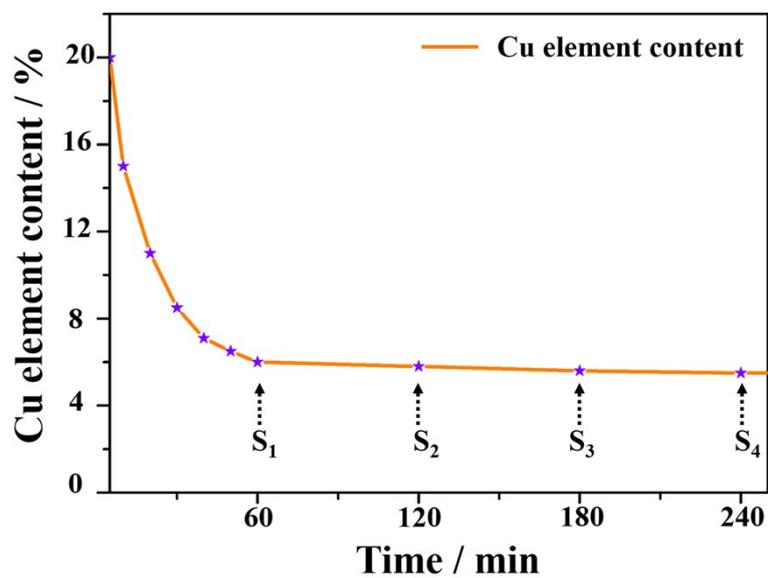


Fig. S2 Cu content (wt.%) of Cu₂O@ZnCr-LDH samples measured by ICP-AES with different synthesis time.

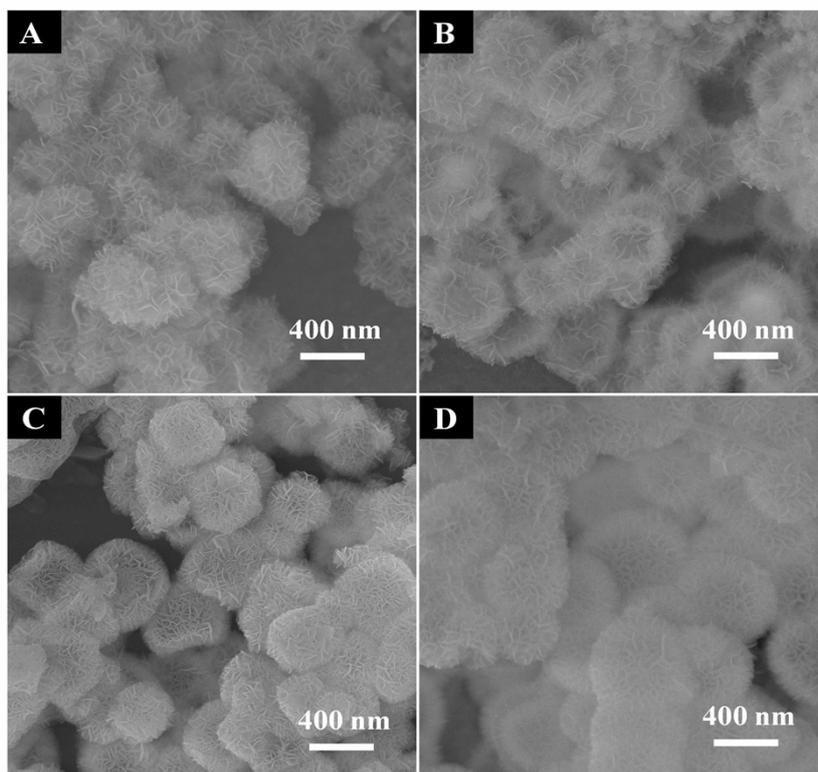


Fig. S3 SEM images of $\text{Cu}_2\text{O}@\text{ZnCr-LDH}$ samples: (A) S_1 , (B) S_2 , (C) S_3 and (D) S_4 .

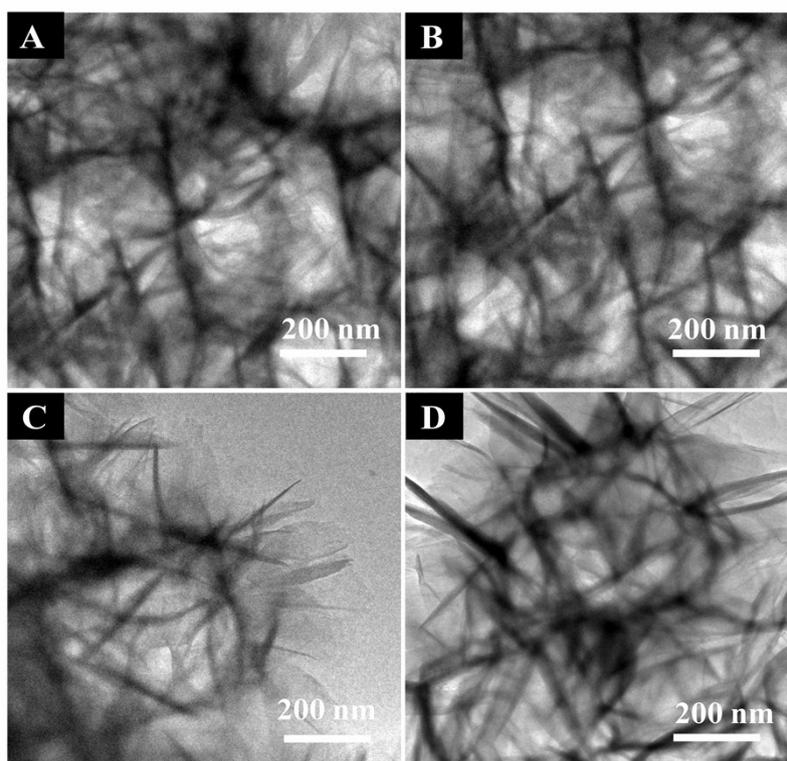


Fig. S4 TEM images of $\text{Cu}_2\text{O}@\text{ZnCr-LDH}$ samples: (A) S_1 , (B) S_2 , (C) S_3 and (D) S_4 .

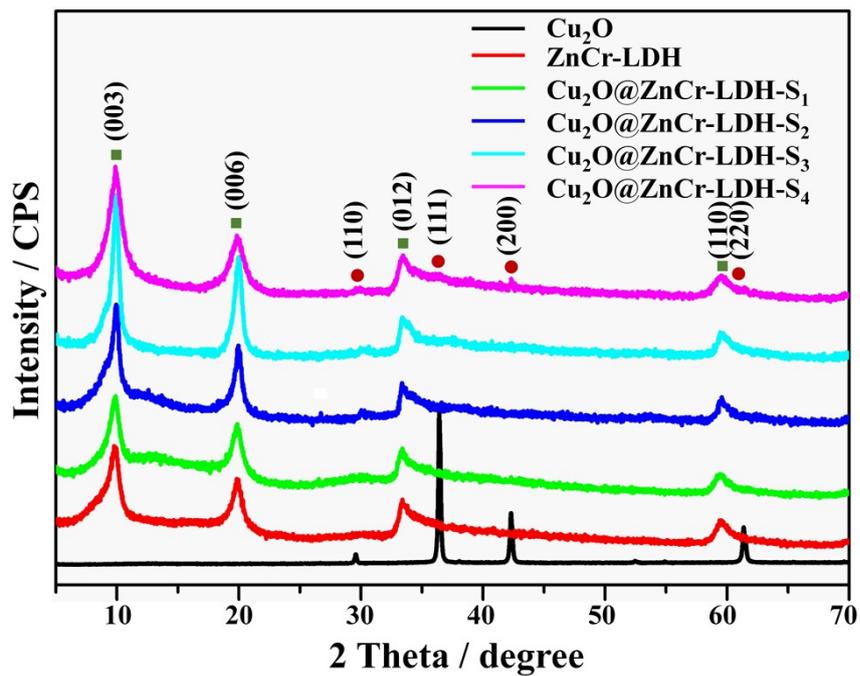


Fig. S5 XRD patterns of Cu_2O , ZnCr-LDH and $\text{Cu}_2\text{O}@ZnCr\text{-LDH}$ samples (S_1 – S_4).

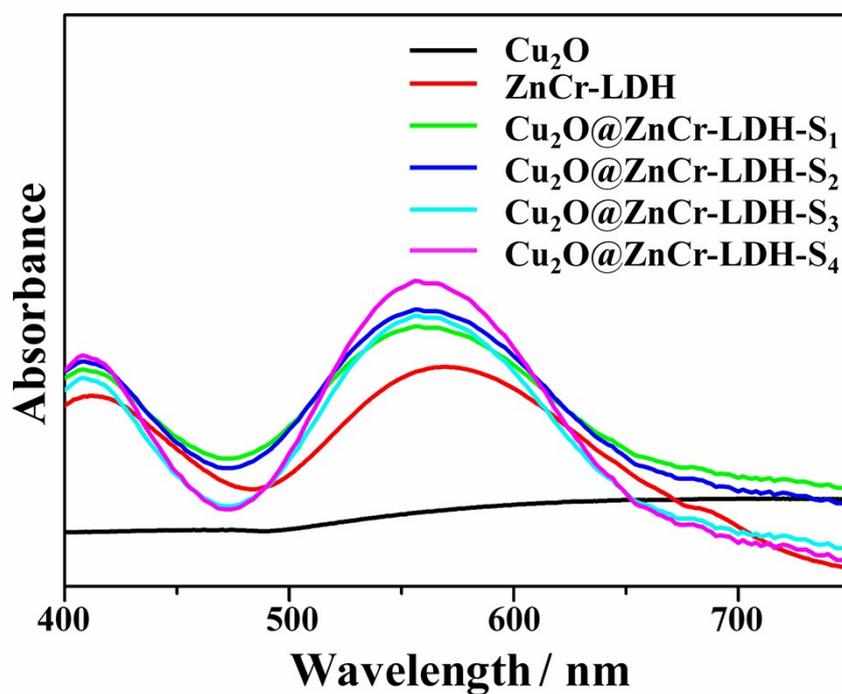


Fig. S6 Diffuse reflection spectra of Cu_2O , ZnCr-LDH and $\text{Cu}_2\text{O}@ZnCr\text{-LDH}$ samples (S_1 – S_4).

Calculation details of apparent quantum efficiency (AQE):

$$\begin{aligned} \text{AQE (\%)} &= \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100\% \\ &= \frac{\text{Number of generated hydrogen molecules} \times 2}{\text{Number of incident photons}} \times 100\% \end{aligned}$$

Table S1. Apparent quantum efficiency (AQE) of samples under visible light irradiation ($\lambda > 420$ nm; photocatalytic reaction time: 1 h)

Sample	H ₂ /μmol	O ₂ /μmol	AQE/%
Sample S ₁	0.90	0.44	0.20
Sample S ₂	1.32	0.74	0.29
Sample S ₃	2.13	1.05	0.47
Sample S ₄	3.42	1.63	0.76

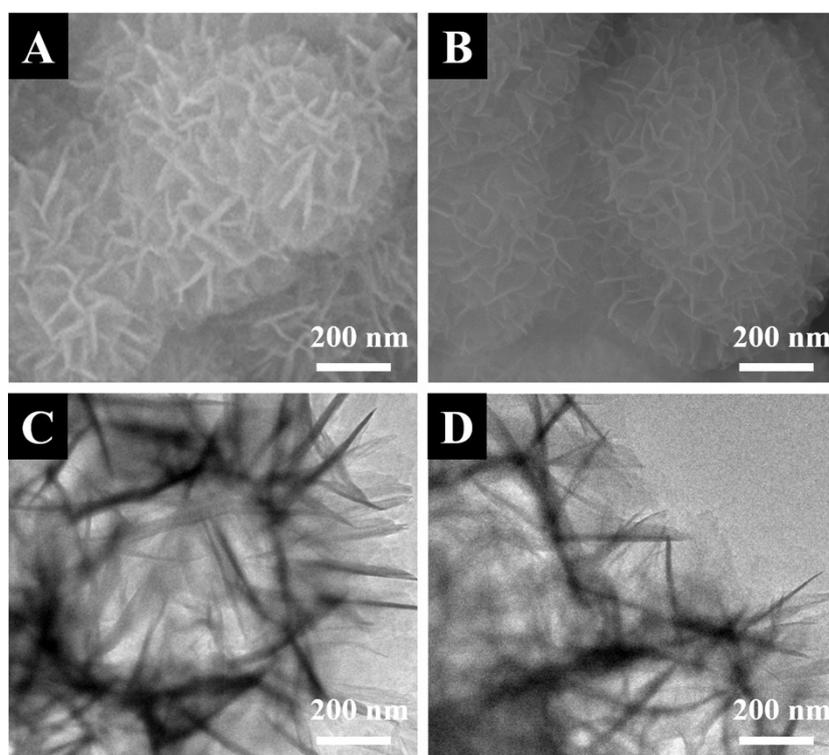


Fig. S7 SEM and HR-TEM images of the Cu₂O@ZnCr-LDH-S₄ sample: (A) and (C) the fresh sample; (B) and (D) the used sample after photocatalytic reaction for 25 h.

Table S2. Local structure obtained from EXAFS refinement at Cu K-edge^a

Sample	Atomic pair	CN	R (Å)	r -parameter S/O	σ^2 (Å ² ·10 ³)	ΔE^0 (eV)	R factor %
S ₄	Cu-O	0.52(18)	1.96(2)	5.15	4.3(6)	1.1(4)	0.94
	Cu-S	2.68(12)	2.23(1)				
	Cu-Cu	0.00	-				
S ₃	Cu-O	0.70(17)	1.96(2)	3.73	5.2(1.0)	-1.1(5)	1.28
	Cu-S	2.61(28)	2.23(1)				
	Cu-Cu	0.93(42)	3.08(3)				
S ₂	Cu-O	0.92(16)	1.95(2)	2.33	2.6(5)	-0.8(7)	1.37
	Cu-S	2.14(12)	2.22(1)				
	Cu-Cu	1.58(48)	3.08(2)				
S ₁	Cu-O	1.34(18)	1.97(2)	1.22	3.6(7)	0.5(4)	1.47
	Cu-S	1.63(21)	2.23(1)				
	Cu-Cu	2.69(54)	3.09(2)				
Cu ₂ O	Cu-O	1.90(8)	1.85(1)	-	3.2(5)	-2.9(2)	2.11
	Cu-Cu	11.92(69)	3.03(1)				
	Cu-O	5.47(77)	3.56(1)				
CuO	Cu-O	4.03(12)	1.95(1)	-	3.4(4)	-0.1(2)	0.87
	Cu-Cu	4.13(29)	2.90(1)				
	Cu-Cu	4.08(46)	3.08(1)				
Cu	Cu-Cu	11.46(27)	2.54(1)	-	7.6(2)	-5.9(2)	1.02
	Cu-Cu	8.56(76)	3.58(1)				
	Cu-Cu	25.21(89)	4.45(1)				

^a CN: coordination number; R : atomic distance; σ^2 : Debye-Waller factor; ΔE^0 : shift of the threshold energy; R factor: goodness of fit. S_0^2 : 0.8305, was obtained from the experimental EXAFS fit of CuO reference by fixing CN as the known crystallographic value and was fixed to all the samples. Uncertainties are given by the number in brackets on the last digit, *i.e.*, 0.52(18) represents 0.52 ± 0.18 , 1.96(2) means 1.96 ± 0.02 , and 10.8(4.0) is 10.8 ± 4.0 .

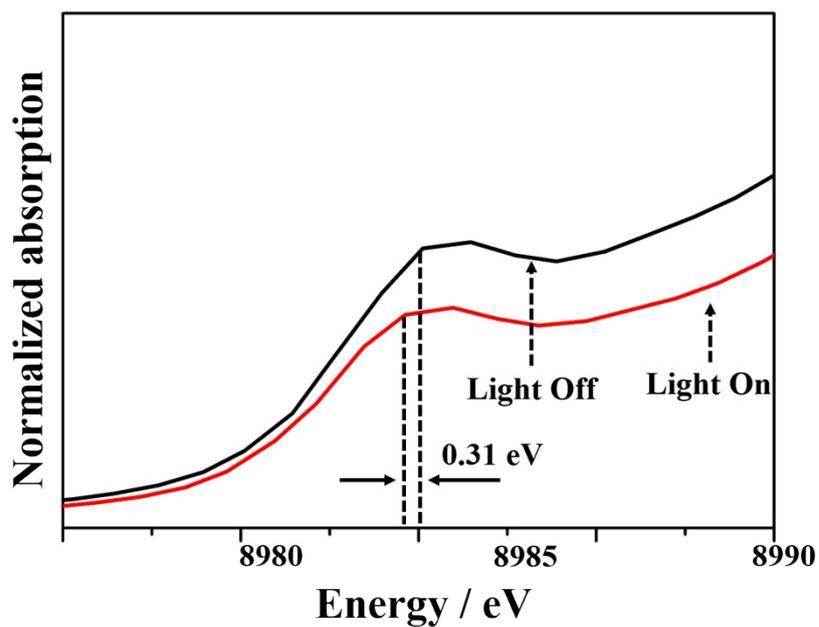


Fig. S8 Transient Cu K-edge XAS data of the $\text{Cu}_2\text{O}@Zn\text{Cr-LDH-S}_4$ collected after photocatalysis.

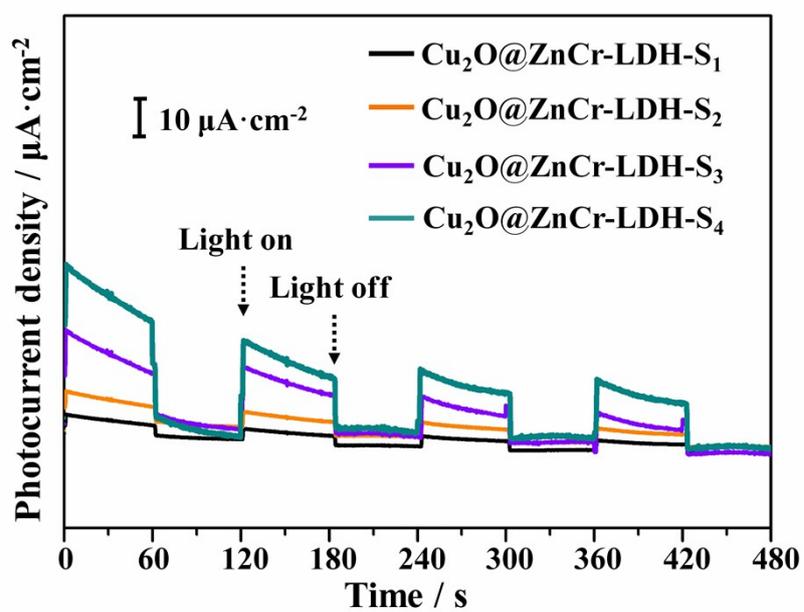


Fig. S9 Current-potential curves of $\text{Cu}_2\text{O}@Zn\text{Cr-LDH}$ samples (S_1 – S_4).

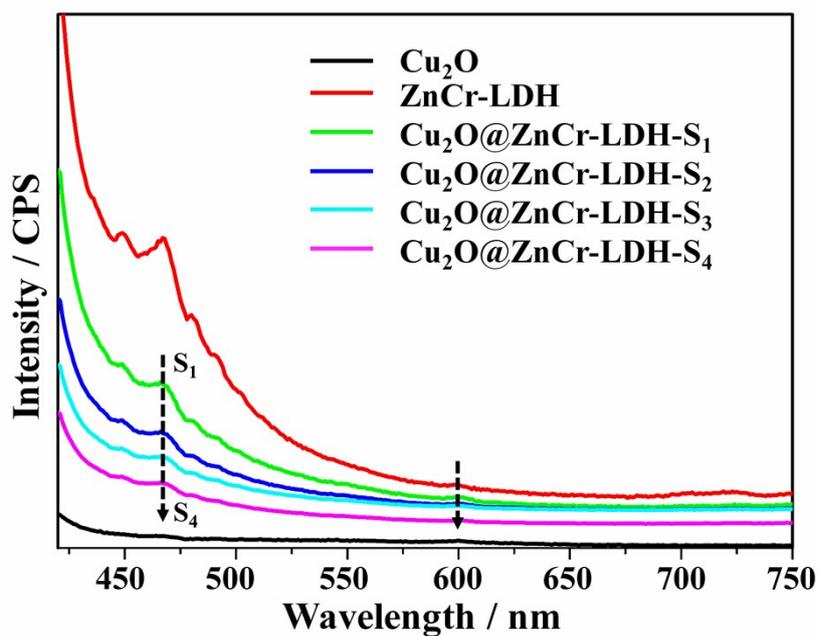


Fig. S10 Photoluminescence (PL) spectra of Cu_2O , ZnCr-LDH and $\text{Cu}_2\text{O}@ZnCr\text{-LDH}$ samples (S_1 – S_4).

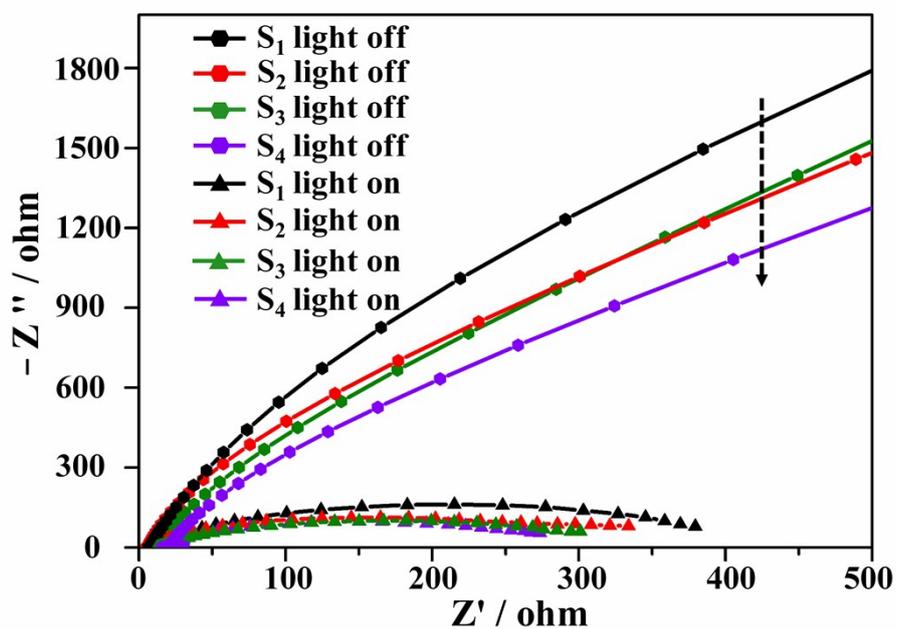
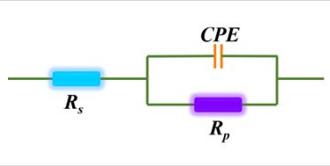


Fig. S11 Nyquist plots of $\text{Cu}_2\text{O}@ZnCr\text{-LDH}$ samples (S_1 – S_4) with and without light irradiation.

Table S3. Resistance of Cu₂O@ZnCr-LDH samples (S₁–S₄) under light irradiation obtained by fitting of EIS data

	R_s (Ω)	R_p (Ω)	CPE (F)
Sample S ₁	10.65	416	2.4659 E-5
Sample S ₂	7.723	354	3.5906 E-5
Sample S ₃	6.503	302	4.3796 E-5
Sample S ₄	5.422	263	7.3422 E-5

R_s is uncompensated resistance;

R_p is charge-transfer resistance;

CPE is constant phase element.