Supporting Information

Ultrathin p-n type Cu_2O/CuCoCr-layered double hydroxides heterojunction nanosheets for photo-assisted aqueous Zn-CO_2 batteries

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Experimental section

Chemicals and reagents

Carbon paper(HCP 020 N, Hesen), Nafion membranes(Nafion 211, DuPont), bipolar membranes (TWBP , Astom), $Cu(NO_3)_2.3H_2O$ (AR, Alfa Aesar), $Co(NO_3)_2.6H_2O$ (AR, Alfa Aesar), $Cr(NO_3)_3.9H_2O$ (AR, Alfa Aesar), Na_2CO_3 (AR, Alfa Aesar), NaOH (AR, Alfa Aesar) were used without any pre-treatment. The absolute ethanol and deionized water were used in this work.

Preparation of CuCoCr-LDHs:

CuCoCr-LDHs were prepared via the simple co-precipitation method. In brief, 386 mg copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$), 699 mg cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$) as well as 800 mg chromium nitrate nonahydrate ($Cr(NO_3)_3.9H_2O$) were dissolved in 70 mL deionized water as solution A. 480 mg sodium hydroxide(NaOH) and 424 mg anhydrous sodium carbonate(Na_2CO_3) were dissolved in 70 mL deionized water as solution B. Simultaneously, solution A and solution B were dropped into four-necked flask and the pH value of suspension was maintained in 9-10 under 80 ℃ water bath conditions. After 8h of precipitation, washing the catalyst with ethanol and deionized water several times until its pH become neutral. Then dry the catalyst slurry in a vacuum drying oven overnight.

Preparation of Cu_2O/CuCoCr-LDHs:

Cu_2O/CuCoCr-LDHs were prepared by the precursor of CuCoCr-LDHs. Firstly, CuCoCr-LDHs were synthesized wtih the same method aforementioned. Before dried progress, dissolving the CuCoCr-LDHs slurry in a certain amount of ascorbic acid solution, the Ph value of which was adjusted through 1M NaOH solution in advance. Ascorbic acid as a reducing agent to reduce CuCoCr-LDHs in situ. After one hour of mechanical stirring, washing the catalyst with ethanol and deionized water several times until its Ph become neutral. Then dry the catalyst slurry in a vacuum drying oven overnight.

Preparation of ultrathin Cu_2O/CuCoCr-LDHs nanosheets:

Ultrathin Cu_2O/CuCoCr-LDHs nanosheets were prepared by the precursor of ultrathin CuCoCr-LDHs nanosheets. Firstly, ultrathin CuCoCr-LDHs nanosheets were synthesized wtih the similar method aforementioned. Except that before dropping solutions A and B, 20 ml formamide and a small amount of sodium nitrate were transferred to the four-necked flask, which used as a growth inhibitor to obtain ultrathin and small nanosheets. And the precipitation time decrease to 10 minutes. Then repeat the above in-situ reduction as well as washing process so that attained ultrathin Cu_2O/CuCoCr-LDHs nanosheets.

Material characterizations:

The X-ray diffraction (XRD) pattern characterization was performed on a Rigaku XRD-6000 diffractometer, using Cu Ka radiation with a scanning rate of 10.00° min^{-1}. Scanning electron microscope (SEM Zeiss Supra 55, Germany) and high resolution transmission electron microscope (HRTEM, JEOL JEM-2100F, 200 Kv, Japan) were performed to investigate the morphology of samples. XPS analysis of the samples was carried out on a Physical Electronics PHI 1600 ESCA system with an Al Kα X-ray source. Jingdao UV-3600 spectrophotometer selected to characterize the ultraviolet–visible diffuse reflectance spectra (UV–vis DRS) of the samples, and the range was 200 to 800 nm. The photoluminescence (PL) spectra were obtained on a FL-4600 fluorospectrophotometer(commercial HITACHI F-4600, Japan). The MS plots, photo response characterization, EIS and LSV were tested in the electrochemical workstation (Chenhua, Shanghai, CHI 660E) with a glassy carbon electrode with a area of 0.1256 cm^2.

Preparation of photoelectrode:

5 mg catalyst powder, 485 μL ethanol, 485 μL deionized water and 30 μL 5% nafion-117 solution were mixed as catalyst ink. When using a glassy carbon electrode for testing, take 5 μL of catalyst ink and drop it on the glassy carbon electrode devised with rotating ring-disk electrode (RRDE) During the photoelectric reduction of CO_2 and photo-assisted Zn-CO_2 batteries test, the 1 mL catalyst ink (including 5 mg catalyst) was evenly dropped on the 1×3cm FTO, the catalyst area was 1×2 cm.

Photoelectrochemical CO_2RR measurements:

The CO_2RR testing was carried out in a gastight H-type electrolytic cell separated by a nafion 117 member. In both chambers, 0.5M $KHCO_3$ and 0.1M KOH were used as cathode and anode electrolyte, respectively. A three-electrode system, in which ultrathin Cu_2O/CuCoCr-LDHs used as work electrode, Ag/AgCl (3.5M KCl) and Pt (2cm × 2cm) plate as reference and counter electrode with an electrochemical station(CHI 660E) was adopt to electrochemical measurements. Photoelectrochemical CO_2 reduction was performed at ambient temperature and CO_2 (99.999%) was bumped into cathode for 30min before potentiostatic photoelectrochemical CO_2 reduction. The gaseous products were detected by gas chromatography(GC7970, Nickel conversion furnace and N_2 as a carrier gas) equipped with a flame ionization detector and a column(TDX-01). Bruker Avance Ⅲ 400MHz HD spectrometer with ^{1}H NMR measurements was used to analyst the liquid products and the Dimethyl sulfoxide (DMSO) was used as an internal standard in this process for quantifying the liquid products under electrolysis at each given potential. 300W xenon lamp was severed as photo source in all photo assisted systems in this study. In this study, the potentials were converted by the following equation[1]:

$$\textbf{E vs RHE=E vs.Ag/AgCl + 0.0592 pH +0.197}$$

Photo-assisted aqueous Zn-CO_2 batteries

The photo-assisted aqueous Zn-CO_2 batteries was comprised of Cu_2O/CuCoCr-LDHs cathode and Zn plates (2 × 5cm) anode separated by bipolar member. Simultaneously, a quartz window was used for light illumination. In both chambers, 0.5 M $KHCO_3$ and 1.0 M KOH added 0.02 M $(CH_3COO)_2Zn$ selected as cathode electrolyte and anode electrolyte, respectively. The battery performance test is carried out on battery test system (LANHE CT2001A).

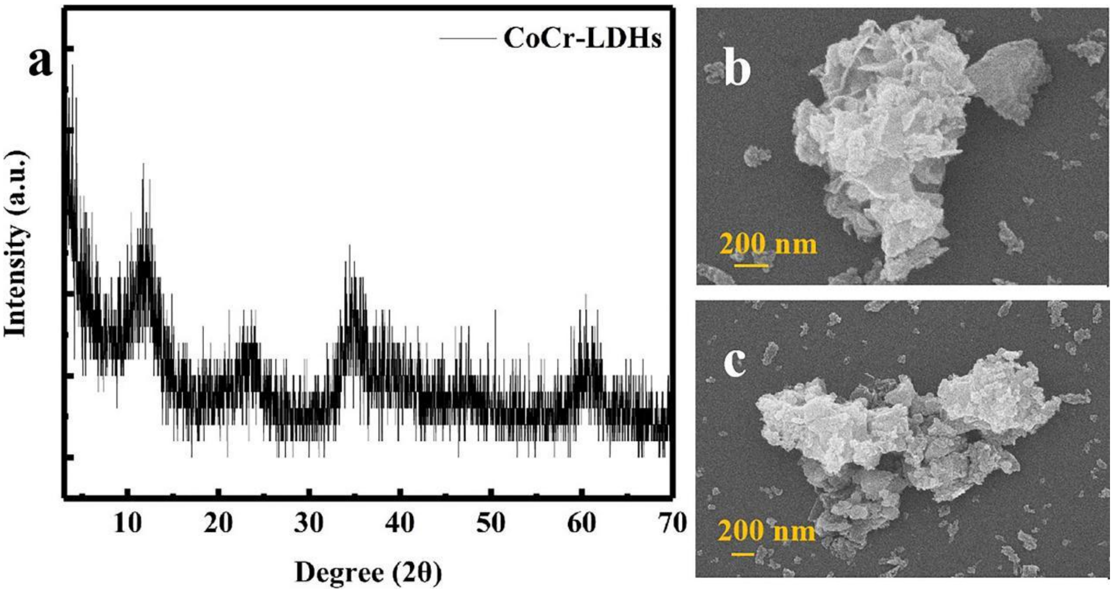

Figure S1 The sample of CoCr-LDHs. a) XRD; b, c) SEM images

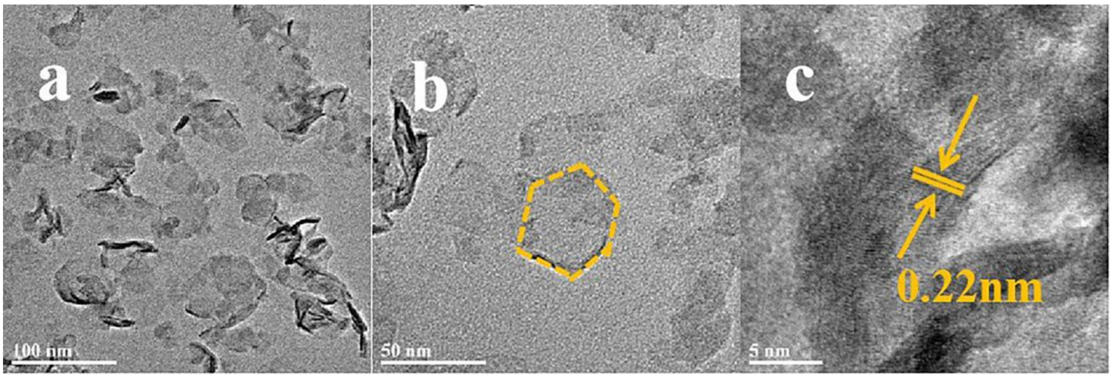

Figure S2. a-c) HRTEM of CuCoCr-LDHs

Table S1 EDS of CuCuCr-LDHs

Element	Weight%	Atomic%
Cr K	27.46	30.76
Co K	38.40	37.95
Cu K	34.14	31.29
Totals	100.00	

Table S2 EDS of U-Cu_2O/CuCuCr-LDHs

Element	Weight%	Atomic%
O K	27.51	57.81
Cr K	22.21	14.36
Co K	29.76	16.98
Cu K	20.52	10.85
Totals	100.00	

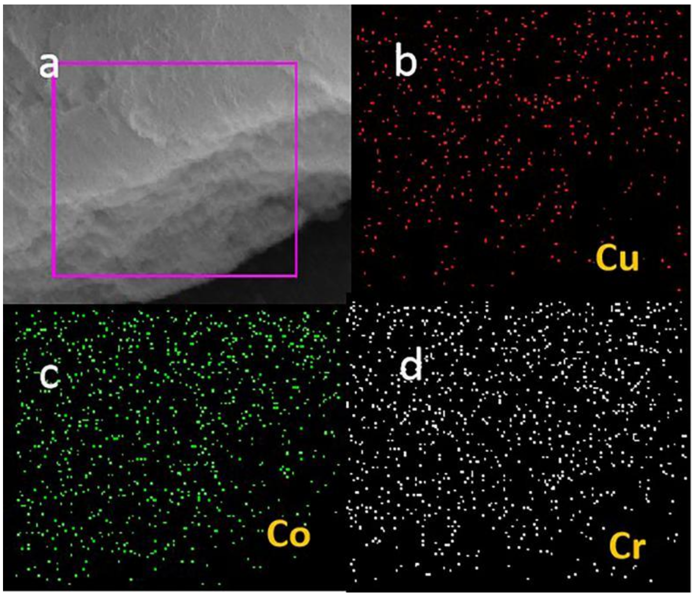

Figure S3. a-c) mapping of CuCoCr-LDHs

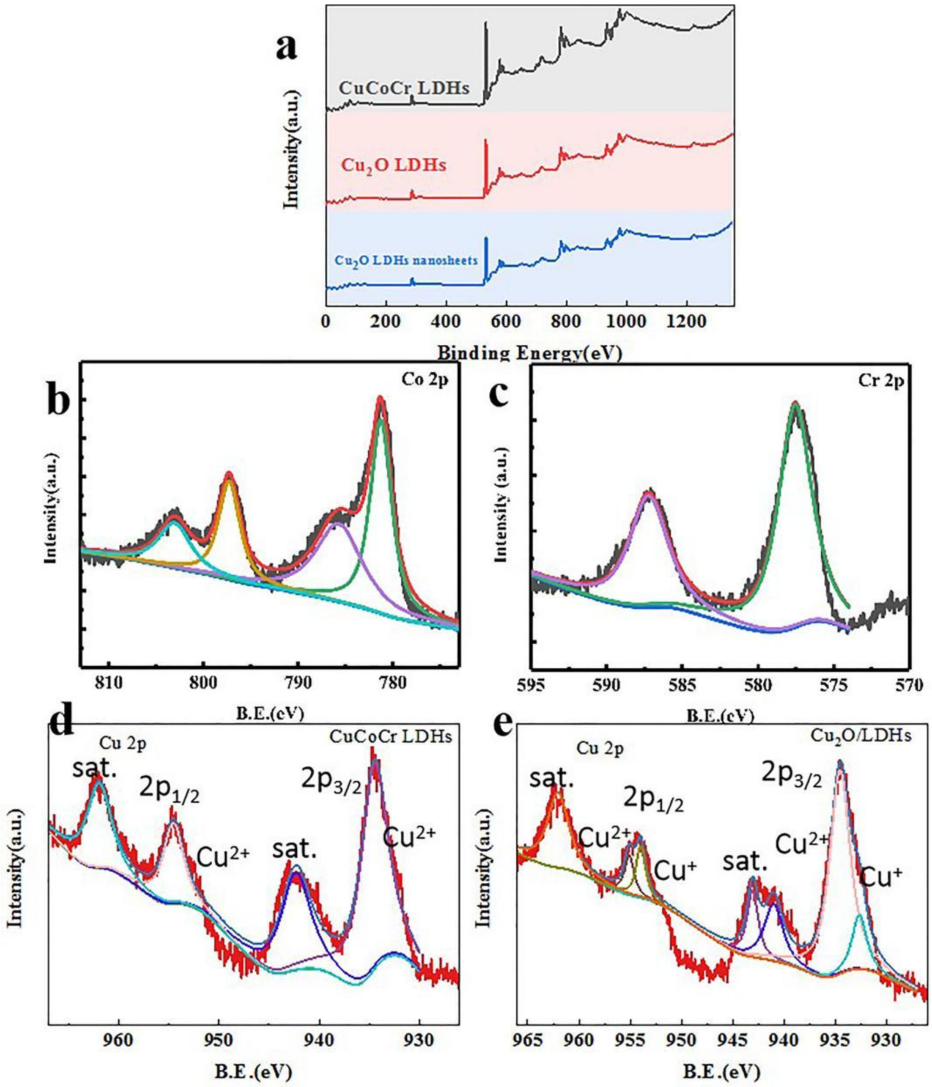

Figure S4 XPS of samples. a) full spectrum. b) Co 2p of U-Cu$_2$O/CuCoCr-LDHs. c) Cr 2p of U-Cu$_2$O/CuCoCr-LDHs. d) Cu 2p of CuCoCr-LDHs. e) Cu 2p of Cu$_2$O/CuCoCr-LDHs.

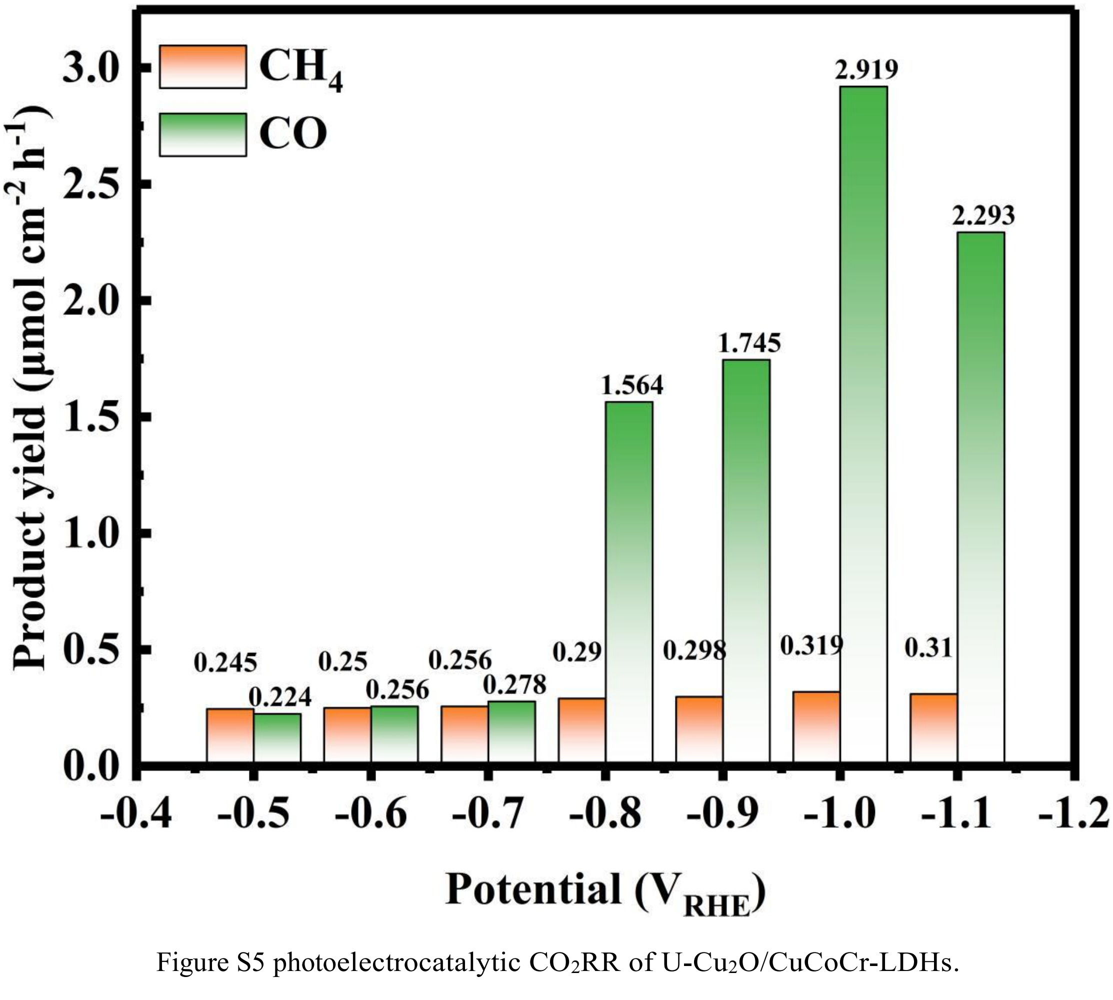

Figure S5 photoelectrocatalytic CO_2RR of U-Cu_2O/CuCoCr-LDHs.

TableS3 catalytic cathode for Zn-CO2 batteries[2].

cathode	Discharge voltage	Charge voltage	Ref.
Nano Au	0.15 V (10 mA cm^{-2})	NM	[3]
Cu_3P@C	-1.5 V (0 mA)	NM	[4]
Ir@Au	0.69 V (0.1 mA)	2.25 V (0.01 mA)	[5]
NiPG	0.47 V (0.25 mA)	2.58 V (0.25 mA)	[6]
SiNC	0.47 V (0.25 mA)	NM	[7]
U-CU_2O/CuCoCr-LDHs	1.22 V (0.025 mA cm^{-2})	2.07 V (0.025 mA cm^{-2})	This work

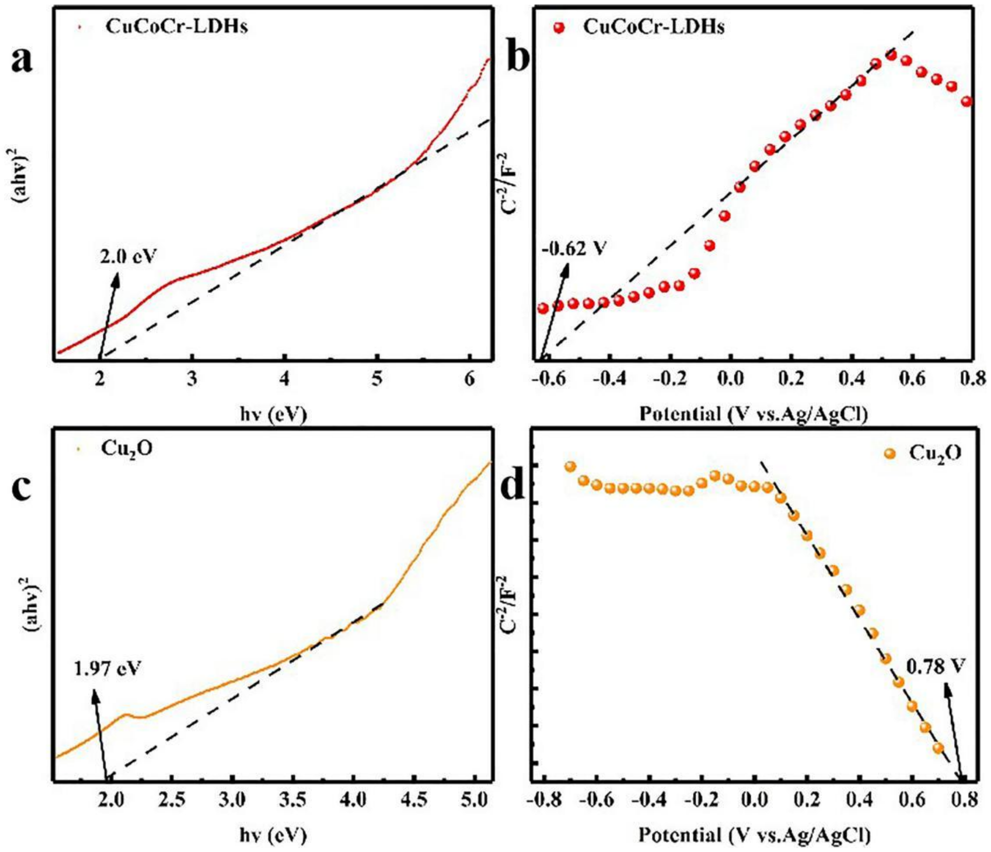

Figure S6 a,) the band gap of CuCoCr-LDHs; b) the MS plots of CuCoCr-LDHs; c) the band gap of pure Cu_2O; d) the MS plots of Cu_2O.

Reference

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