Electronic Supplementary Information

Stabilizing $CuGaS_2$ by CdS through interfacial Z-scheme charge transfer for enhanced photocatalytic CO_2 reduction under visible light

Shimiao Wu,‡[a] Hong Pang,‡[d] Wei Zhou,‡[d, e] Baopeng Yang,[a] Xianguang Meng,*[, b] Xiaoqing Qiu,[c] Gen Chen,[a] Ligang Zhang,[a] Shengyao Wang,[f] Xiaohe Liu,[a] Renzhi Ma,[d] Jinhua Ye,[d] and Ning Zhang *[, a]

[a] *School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, China*

E-mail: nzhang@csu.edu.cn (N. Zhang)

[b] *Hebei Provincial Key Laboratory of Inorganic Nonmetallic Materials, College of Materials Science and Engineering, North China University of Science and Technology, Tangshan, Hebei 063210, P. R. China*

E-mail: mengxg_materchem@163.com (X. Meng)

[c] *College of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410083, P. R. China*

[d] *International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*

[e] *Department of Applied Physics, School of Science, Tianjin University, P. R. China*

[f] *College of Science, Huazhong Agricultural University, Wuhan 430070, P. R. China*

‡ These authors contributed equally to the work.

Experimental section

Chemicals and Materials

Cuprous sulphide (Cu_2S, AR grade) and Nafion *D-521 dispersion (5 % w/w in water and 1-propanol, ≥0.92 meq/g exchange capacity) were purchased from Alfa Aesar chemical Co. Ltd. Cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$, AR grade), Sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$, AR) and Potassium sulfate (K_2SO_4, AR grade) were purchased from Sinopharm Chemical Reagent Co. Ltd. Gallium(III) sulfide (Ga_2S_3, AR grade) was produced from Adamas-beta Ltd. All reagents were used without further purification. Deionized water (DI) was used for the synthesis of all samples.

Materials synthesis

$CuGaS_2$ was prepared by a solid-state reaction. In a typical synthesis, Ga_2S_3 (1.4 mmol) was well mixed and grinded with Cu_2S (1.0 mmol). Then the mixture was sealed into a quartz ampoule tube with evacuated, which was calcined at 1073 K for about 10 h. $CuGaS_2$ coated with CdS ($CuGaS_2$/CdS) composites with different mass ratios such as 2:1, 1:1, and 1:2 were prepared as follows: $CuGaS_2$ (0.4 g, 0.2 g, and 0.1 g) were mixed in solution of $Cd(NO_3)_2$ (3.27 g/L, 100 mL) under ultrasonic dispersion. After adding Na_2S solution (1.08 g/L, 100 mL), the suspensions were stirred for 0.5 h. Precipitates were vacuum freeze-dried after washing three times with deionized water. CdS nanoparticle is synthesized as same procedure as $CuGaS_2$/CdS without addition of $CuGaS_2$.

Characterizations

The crystalline phase of these as-prepared products was determined by X-ray diffraction (XRD, Rigaku MiniFlex 600, CuKa radiation). Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and scanning transmission electron microscopy (STEM) images were recorded by FEI Tecnai G2 F20 field emission transmission electron microscopy operated at 200 kV. The X−ray photoelectron spectroscopy spectra (XPS) were performed using a Thermo Fisher ESCALAB 250Xi spectrophotometer. Diffuse reflectance spectra were obtained with a UV-vis spectrometer with an integrating sphere (Shimazu, UV-2600) and were converted from reflectance to absorbance by the Kubelka-Munk method. The photoluminescence (PL) measurements were performed on a fluorescence spectrometer (JASCO FP-6500) with excitation wavelength of 320 nm.

Photocatalytic evaluations

Photocatalytic CO_2 reduction was conducted in a closed gas circulation system connecting a side-irradiation cell with a Pyrex window. A photocatalyst powder (0.2 g) was dispersed in 200 mL of deionized water. Afterwards, K_2SO_3 and $KHCO_3$ were dissolved into the reaction suspension with the concentration of 0.1M and 0.5M respectively. Finally, the reaction system was evacuated and high-purity CO_2 (99.99%) was injected until the reaction suspension was saturated. The final pressure of CO_2 in the gas space of cell is around 99 kPa. A 300W Xe-lamp equipped with cut-off filter L42 (HOYA) was used as the light source. The CO in the reaction system were sampled and measured with a gas chromatograph (GC-2014, Shimadzu, N_2 carrier) equipped with a flame ionization detector (FID) according to the standard curves. The amount of evolved hydrogen was determined by on-line gas chromatography (Shimazu, GC-2014C, Ar carrier) with a TCD detector according to the standard curve.

In isotope tracing experiment, $^{13}CO_2$ was injected to the evacuated reaction system and pre-absorbed by reaction solution only containing 0.1 g $CuGaS_2/CdS$-2:1 and 0.1 mol/L K_2SO_3. In such an evaluation, $KHCO_3$ was not added to the reaction solution to maintain the purity of ^{13}C isotope in carbon source. Isotope tracing experiments for the identification of ^{13}CO were performed by gas chromatography-mass spectrometry (GC-MS, JMS-K9, JEOL Co., Japan).

Photoelectrochemical measurement

Photoelectrochemical experiments were carried out on a Bio Logic VMP-3 (Bio Logic Science Instruments, Claix, France) electrochemical workstation in a three-electrode cell at room temperature. The Ag/AgCl (3.5 M KCl filled) electrode was used as reference electrode, graphite electrode was acted as counter electrode. The ITO electrode modified with catalyst was used as the working electrode. The catalyst ink was prepared by dispersing a 20 mg catalyst in 1 mL ethanol and 1mL deionized water to form ethanol/water solution. Subsequently, 20 μL Nafion solution (Nafion D-521 5% w/w in water and 1-propano, Alfa Aesar Co. Ltd.) was added to the ink as a proton conducting binder to ensure good adhesion onto the ITO electrode. To form a homogeneous solution, the catalyst ink was ultrasonic dispersed for 30 min and vigorous stirred for 12 h at room temperature. The surface of ITO electrode (1 cm^{-2}) was coated with 100 μL of the catalyst ink to make the catalyst on the working electrode was about 1 mg cm^{-2}. The pasted catalyst on the working electrode was dried at 60 °C in vacuum for further use. All photoelectrochemical measurements were carried out in 0.1 M K_2SO_4 electrolyte solution. A

300W Xe-lamp equipped with cut-off filter L42 (HOYA) was used as the light source. Current−potential curves was recorded with a scan rate of 1 mV s^{-1}. During the measurements, the distance between Xe lamp and photoelectrochemical cell was about 5 cm and the photoelectrodes were illuminated from the backside from the as prepared ITO/catalyst photoelectrodes.

Apparent quantum efficiency

The apparent quantum efficiency (AQE) was measured under the same photocatalytic reaction condition with irradiation light at 420 nm by using combined band-pass (Vacuum & Optical instruments) and cut-off filters (HOYA) and 300 W Xe lamp, and the AQE was calculated according to the following equations:

$$\mathrm{AQE}\ (H_2) = N(H_2) \times 2/N(\mathrm{Photons}) \times 100\%$$

$$\mathrm{AQE}\ (\mathrm{CO}) = N(\mathrm{CO}) \times 2/N(\mathrm{Photons}) \times 100\%$$

$$\mathrm{AQE}\ (CO_2) \approx \mathrm{AQE}\ (\mathrm{CO})$$

The apparent quantum efficiency of H_2 and CO are 0.86% and 0.005%, respectively.

Computational methods

In this work, all calculations were performed using Vienna ab-initio Simulation Package (VASP) based on density functional theory. The generalized gradient approximation was used for the exchange-correlation energy. A plane-wave expansion for the basis set with a cutoff energy of 450 eV was chosen for calculations. A supercell model including 96 atoms was built for the simulation of CdS/$CuGaS_2$ heterostructure. The Gamma point centered Monkhorst k-point meshes (1 × 1 × 1) were used for the Brillouin-zone integrations of heterostructure model. The total energy converges within an error of 1×10^{-5} eV/atom, and all atoms were relaxed until the residual force was less than 0.01 eV/Å during crystal relaxation.

Additional figures and captions

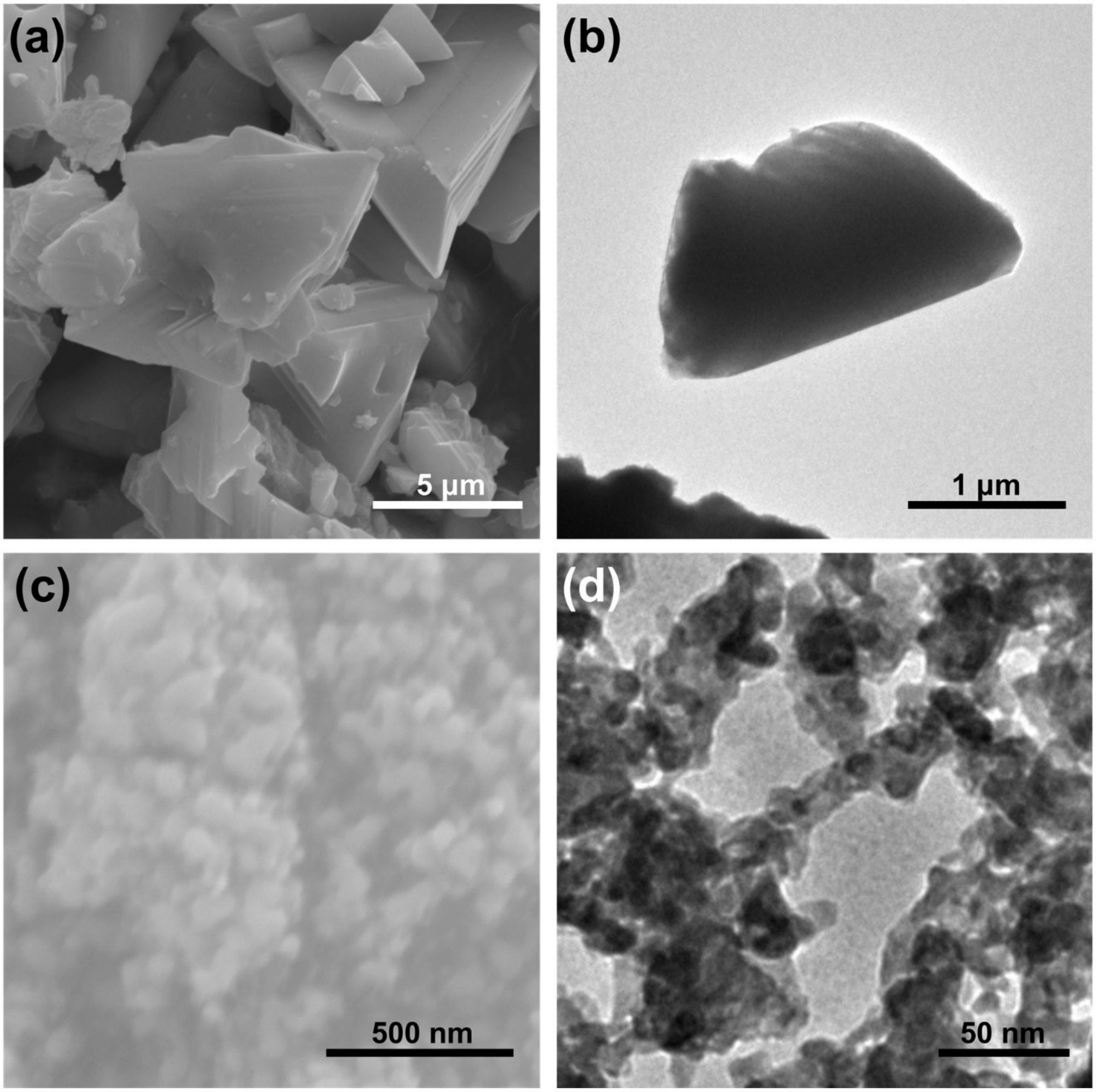

Fig. S1 (a) The SEM image, (b) TEM image of $CuGaS_2$; (c) the SEM image, (d) TEM image of CdS.

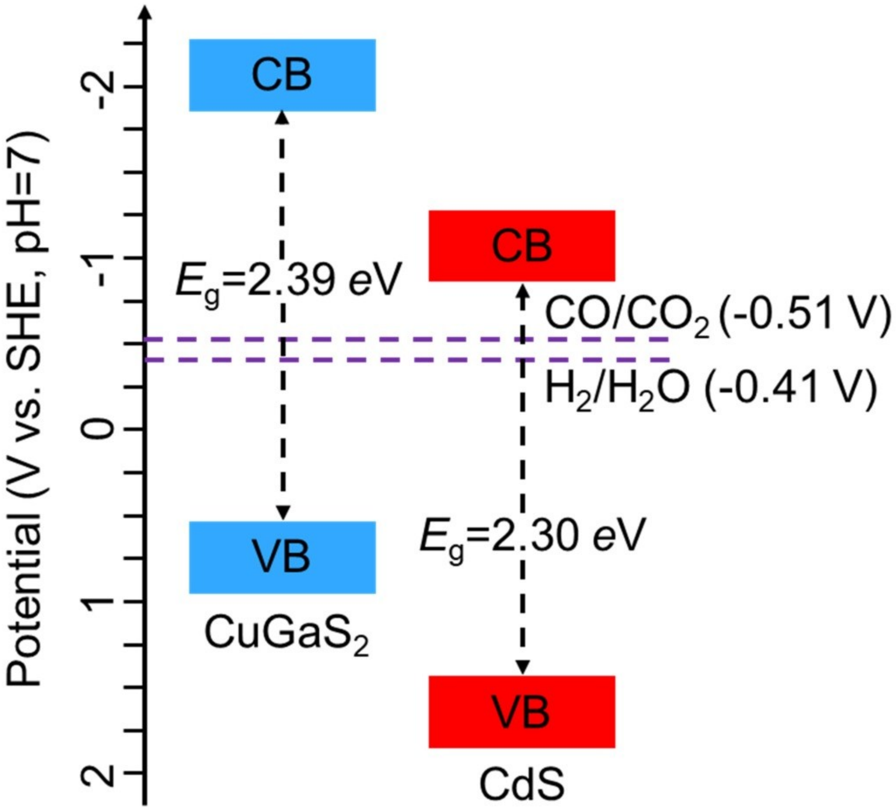

Fig. S2 Scheme of relatively energy band positions for $CuGaS_2$ and CdS.[1,2]

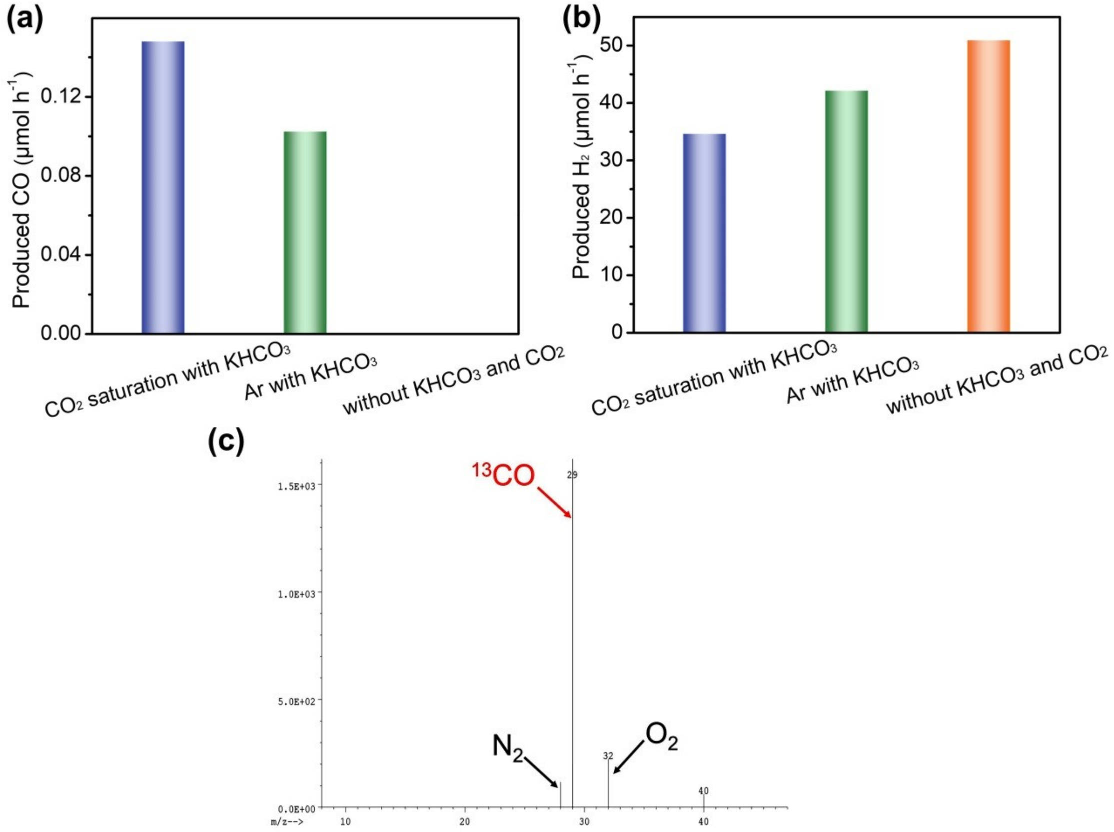

Fig. S3 (a) CO and (b) H_2 evolution rate over control experiments by using Ar instead of CO_2 and in the absent of $KHCO_3$; (c) Mass spectrum of ^{13}CO produced in isotope tracing experiment in presence of $^{13}CO_2$ and H_2O.

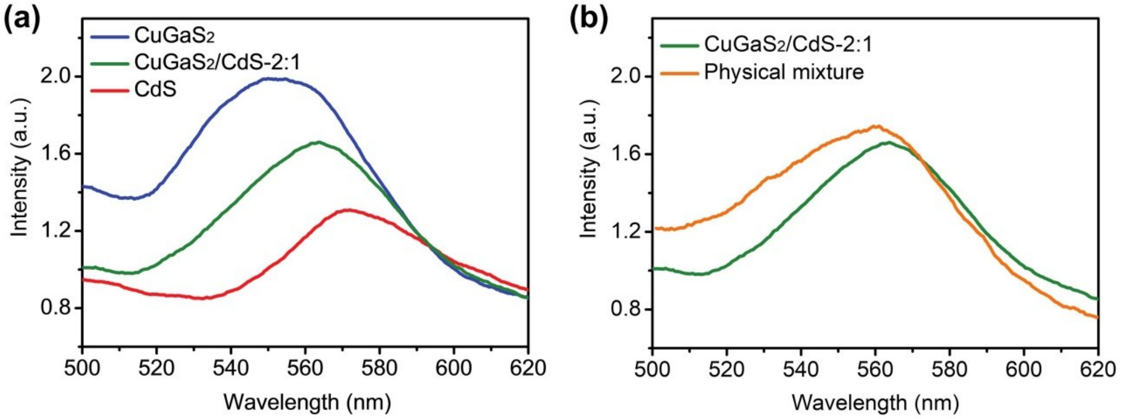

Fig. S4 (a) Photoluminescence spectra of $CuGaS_2$, $CuGaS_2$/CdS-2:1 and CdS; (b) photoluminescence spectra of $CuGaS_2$/CdS-2:1 and physical mixture of $CuGaS_2$ and CdS with ratio of 2:1.

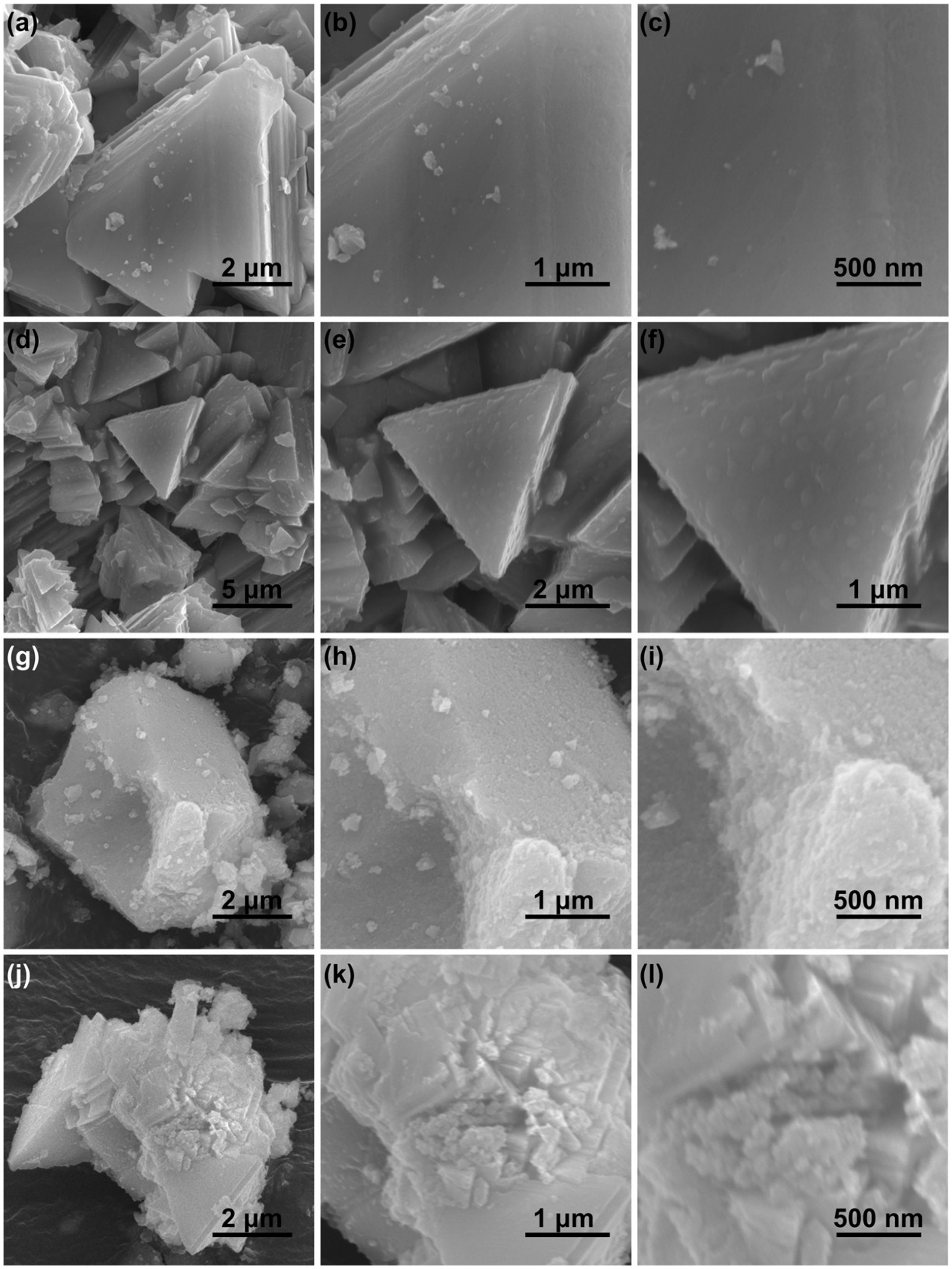

Fig. S5 (a, b, c) SEM image of $CuGaS_2$ before reaction; (d, e, f) SEM image of $CuGaS_2$ after reaction; (g, h, i) SEM image of $CuGaS_2$/CdS-2:1 before reaction; (j, k, l) SEM image of $CuGaS_2$/CdS-2:1 after reaction;

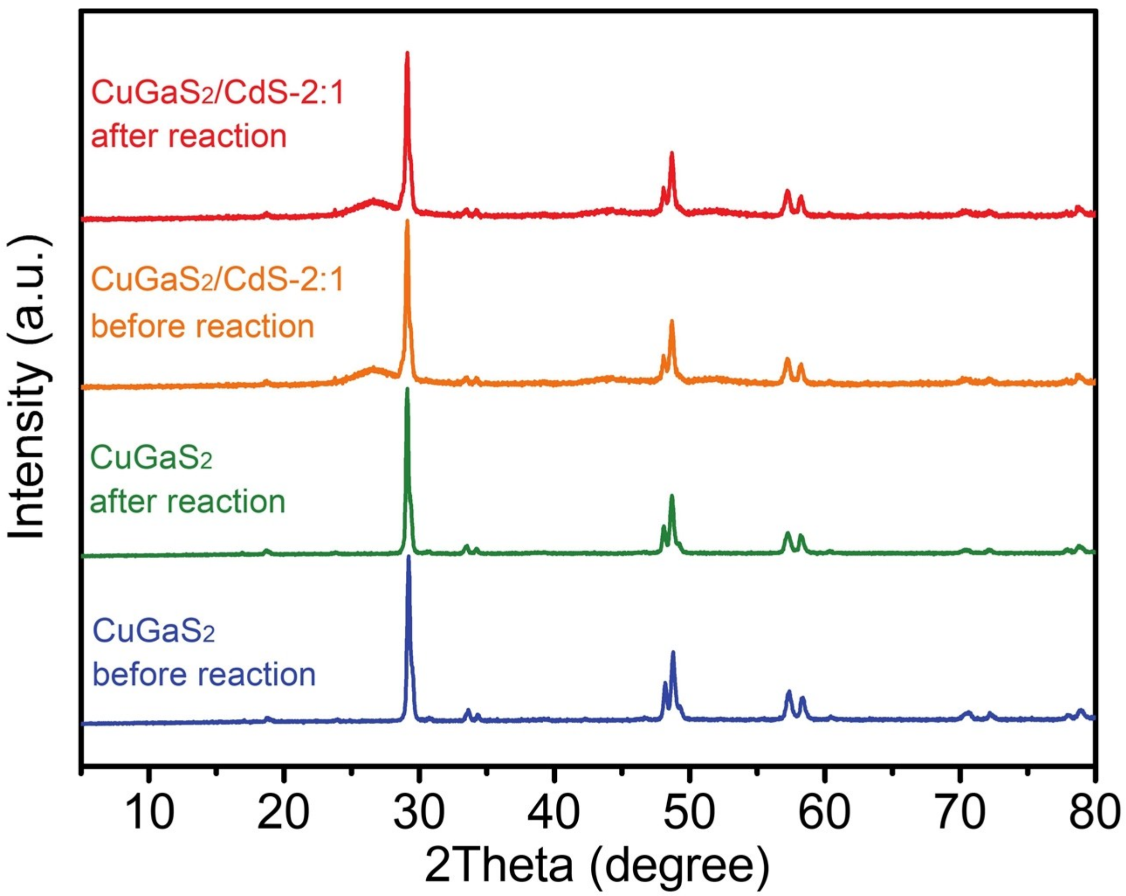

Fig. S6 XRD patterns of as synthesized $CuGaS_2$, $CuGaS_2$/CdS-2:1 before and after reaction.

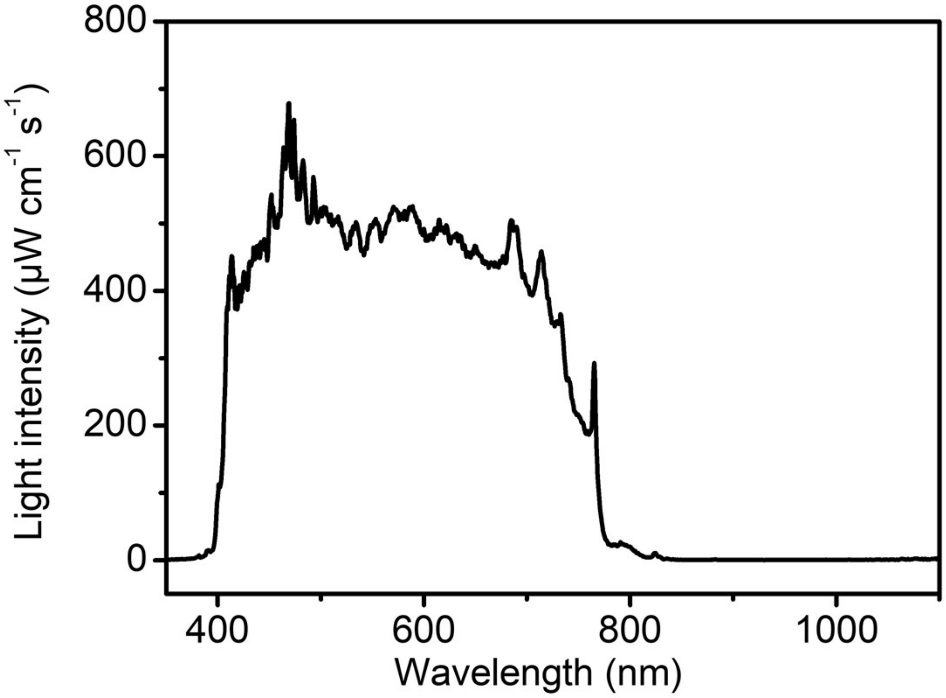

Fig. S7 The light intensity of irradiation by using 420 nm cut-off filters and filters.

Table S1 CO_2 reduction or water splitting on various metal sulfide photocatalysts in the presence of electron donors

Entry	Photocatalyst	Electron donor	Activity (mol h^{-1})			Ref
			H_2	CO	HCOOH	
1	$ZnGa_2S_4$[a]	K_2SO_3+Na_2S	0.4	0	0	3
2	ZnS[a]	K_2SO_3	Trace	Trace	0	4
3	CdS[a]	K_2SO_3	0.45	Trace	0	5
4	ZnS (Pb 1.0%)[a]	Na_2S	47	0.02	0.96	6
5	ZnS (Ni 1.0%)/[Ru(dpbpy)][b]	TEOA	0.61	0.22	0.80	7
6	$CuGaS_2$[a]	K_2SO_3	11	0.25	Trace	8
7	$CuGaS_2$-RGO-TiO_2[c]	water	28.8	0.15	0	8
8	$CuGaS_2$-TiO_2[c]	water	8.4	0.02	0	8
9	$CuGaS_2$(Thin flim)[d]	water	0.85	0.01	0	9
9	$Cu_{0.3}Ga_{0.3}Zn_{1.4}S_2$-$BiVO_4$ /[Ru(dpbpy)][b]	water	0.125	0.11	0	10
10	$CuGaS_2$-CdS[a]	K_2SO_3	34.60	0.15	0	This work

Light source: a 300 W Xe-lamp, [a] λ>420 nm, [b] λ>390 nm, [c] λ>330 nm; [d] simulated sunlight (AM1.5G)

Table S2 The ratio of Cu^+ and Cu^{2+} before and after photocatalytic reaction over $CuGaS_2$ and $CuGaS_2$/CdS-2:1 determined by the Cu 2p XPS spectra.

Catalyst	Before reaction		After reaction	
	Ratio of Cu^+	Ratio of Cu^{2+}	Ratio of Cu^+	Ratio of Cu^{2+}
$CuGaS_2$	100%	0	67.5 %	32.5 %
$CuGaS_2$/CdS-2:1	100%	0	93.7 %	6.3 %

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