Supporting Information

for

Localized surface plasma resonance enhanced visible-light-driven CO_2 photoreduction in Cu nanoparticles loaded ZnInS solid solutions

Hai–Bo Huang,[ab] Kai Yu,[a] Ning Zhang,[a] Jian–Ying Xu,[a] Xu–Teng Yu,[a] Heng–Xin Liu,[a] Hai–Lei Cao,[a] Jian Lü*[ab] and Rong Cao*[b]

[a]Fujian Provincial Key Laboratory of Soil Environmental Health and Regulation, College of Resources and Environment, Fujian Agriculture and Forestry University, Fuzhou 350002, P.R. China; [b]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, P.R. China; [§]University of Chinese Academy of Sciences, Beijing 100049, P.R. China.

*Corresponding authors. E–mail: jian_lu_fafu@163.com (J.L.); rcao@fjirsm.ac.cn (R.C.).

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Table Caption

Table S1. The products of photoreduction CO_2 and the Cu element content of the ZIS-Cu(x) samples.

Table S2. The activity of photoreduction CO2 over the ZIS-Cu2 and other samples in the reported literature.

Figure Caption

Fig. S1. XPS survey spectra of ZIS-Cu(x) samples.

Fig. S2. (a) SEM; (b) TEM and (c) HR–TEM images; and (d) element mapping of the ZIS sample.

Fig. S3. (a) UV–vis DRS of ZIS-Cu(x); and (b) K–M plots of ZIS; (c) room–temperature photoluminescence (PL) spectra of ZIS-Cu(x) samples; and (d) Mott–Schottky plots of ZIS.

Fig. S4. (a) Cycling runs for the photoreduction CO_2 reaction of ZIS-Cu2; (b) PXRD patterns of ZIS-Cu2 before and after cycling reactions; (c) EIS Nyquist plots of ZIS–Cu(x); and (d) absorption spectra of DPD/POD reagent of the ZIS-Cu2 after reaction.

Fig. S5. High–resolution XPS spectra of (a) Zn 2p, (b) In 3d, (c) S 2p and (d) Cu 2p of ZIS-Cu2 before and after cycling reactions.

Table S1

Photocatalysts	Cu contents (%)	CH_4 selectivity (%)
ZIS	N.A.	2.77
ZIS-Cu1	1.14	24.3
ZIS-Cu2	1.26	71.1
ZIS-Cu3	2.41	46.7
ZIS-Cu5	2.85	58.3
ZIS-Cu7	3.25	12.4

Table S2

Photocatalysts	Light source	Main Product	Selectivity(%)	Yields ($\mu mol\ h^{-1}\ g^{-1}$)	Ref.
Cu/TiO_2	solar simulator 150W	CO	N.A.	CO 25 CH_4 4.4	[7]
Cu/GO-1	300W halogen lamp	CH_4	41.2	1.08	[11]
Cu/C_3N_4-6	350W(Xe)	CO	N.A.	49.43	[6]
$g-C_3N_4$–Pt	$\lambda = 254$ nm 8 W (Hg)	CH_4	37.5	0.24	[4]
$Pt/g-C_3N_4/NaNbO_3$	$\lambda > 420$nm 300W (Xe)	CH_4	N.A.	6.4	[5]
$Pt-Cu_2O/TiO_2$	300 nm $<\lambda<$ 400 nm 300W (Xe)	CH_4	N.A.	CO 0.05 CH_4 1.42	[9]
Ag/TiO_2	300W (Xe)	CH_4	N.A.	1.40	[10]
$Ag–TiO_2$	$\lambda \geq 420$nm 300W (Xe)	CH_4	N.A.	2.89	[8]
One-Unit-Cell $ZnIn_2S_4$	AM1.5G 300W (Xe)	CO	N.A.	33.2	[12]
$V_{Zn}–ZnIn_2S_4$	AM1.5G 300W (Xe)	CO	N.A.	276.7	[13]
$ZnIn_2S_4/TiO_2$	AM1.5G 300W (Xe)	CH_4	N.A.	1.13	[14]
RGO–CdS	$\lambda \geq 420$nm 300W (Xe)	CH_4	N.A.	CH_4 2.51	[3]
$CdS@CeO_2$	$\lambda \geq 420$nm 300W (Xe)	CH_3OH	N.A.	CH_4 0.87 CH_3OH 137.5	[1]
$CdS–WO_3$	$\lambda \geq 420$nm 300W (Xe)	CH_4	N.A.	CH_4 1.02	[2]
ZIS-Cu2	$\lambda \geq 420$nm 300W (Xe)	CH_4	71.1	CH_4 13.0 CO 3.63	This work

Fig. S1

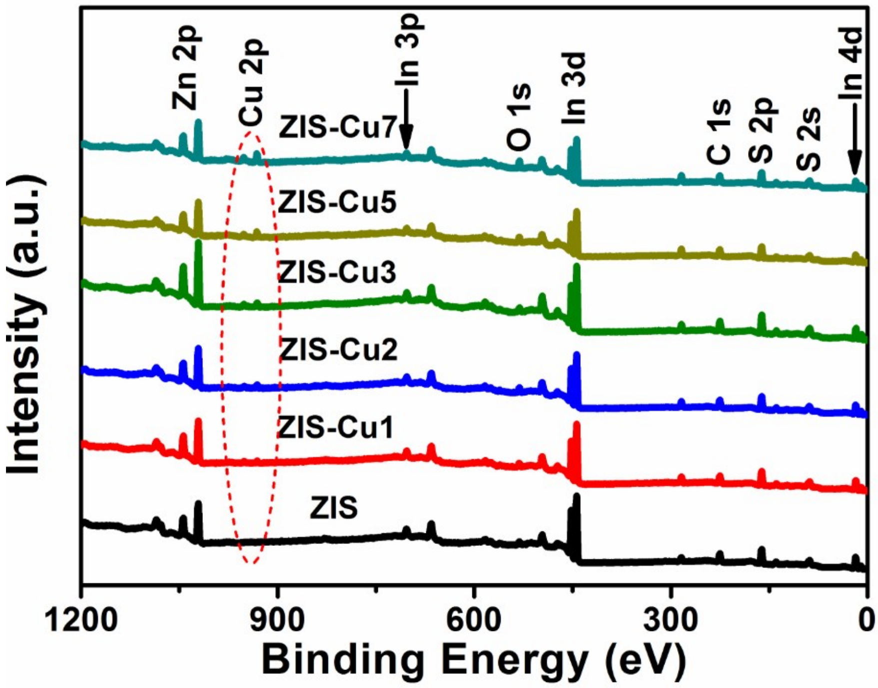

Zn 2p
Cu 2p
In 3p
O 1s
In 3d
C 1s
S 2p
S 2s
In 4d
ZIS-Cu7
ZIS-Cu5
ZIS-Cu3
ZIS-Cu2
ZIS-Cu1
ZIS
Intensity (a.u.)
1200
900
600
300
0
Binding Energy (eV)

Fig. S2

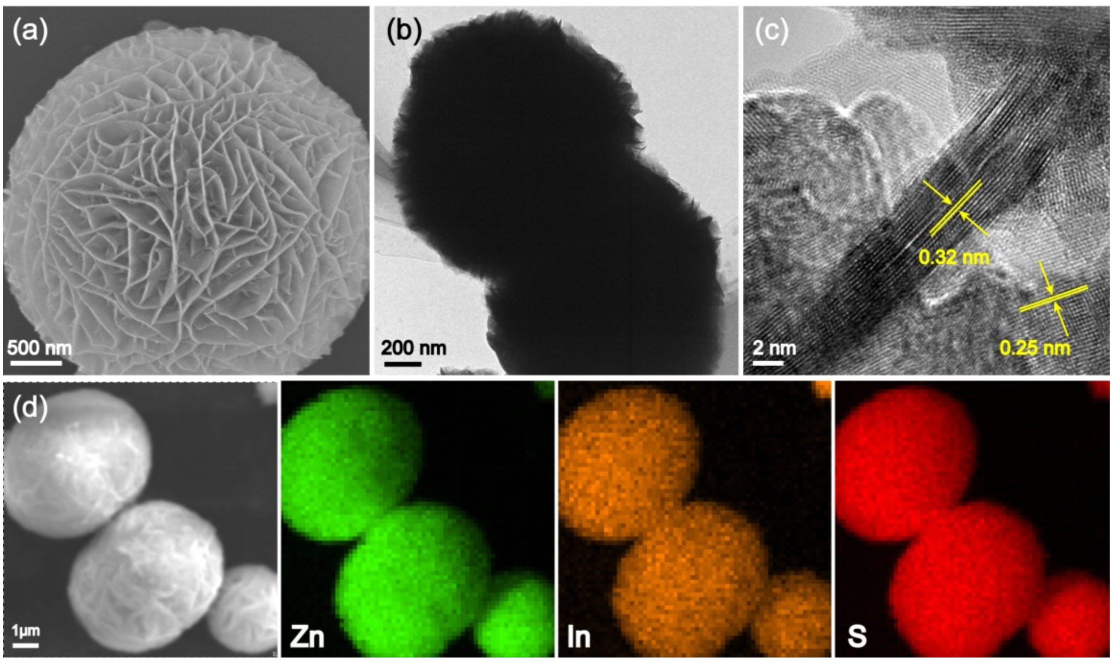

(a)
500 nm
(b)
200 nm
(c)
0.32 nm
0.25 nm
2 nm
(d)
1μm
Zn
In
S

Fig. S3

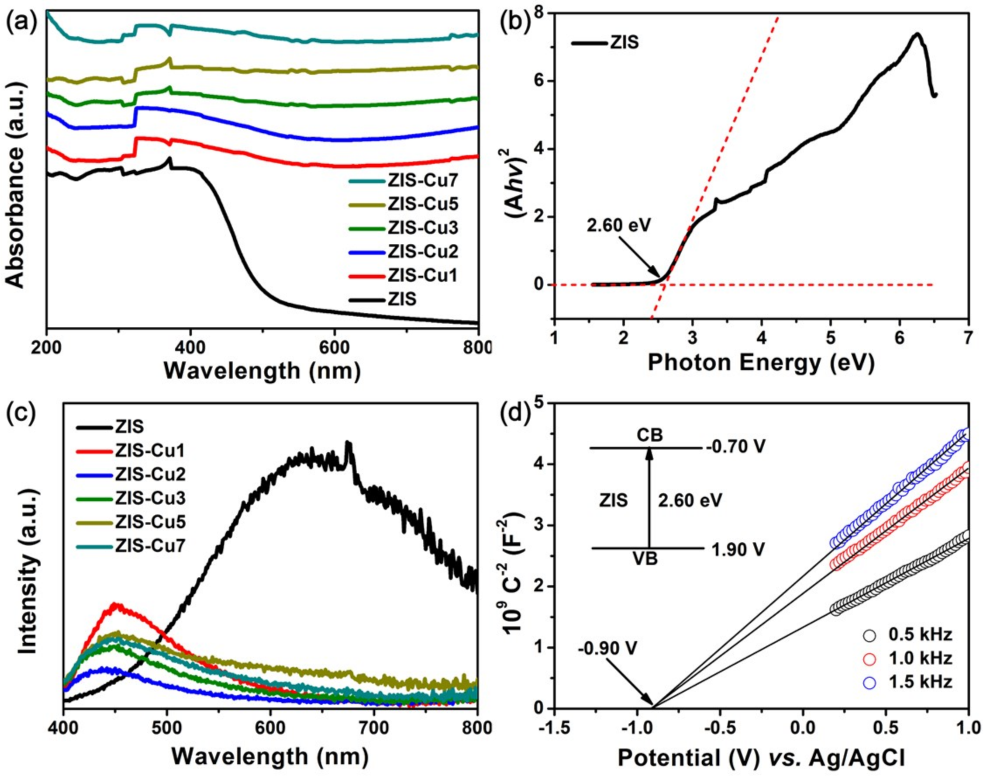

(a)
Absorbance (a.u.)
Wavelength (nm)
ZIS-Cu7
ZIS-Cu5
ZIS-Cu3
ZIS-Cu2
ZIS-Cu1
ZIS
(b)
ZIS
2.60 eV
$(Ah\nu)^2$
Photon Energy (eV)
(c)
ZIS
ZIS-Cu1
ZIS-Cu2
ZIS-Cu3
ZIS-Cu5
ZIS-Cu7
Intensity (a.u.)
Wavelength (nm)
(d)
CB
-0.70 V
ZIS
2.60 eV
VB
1.90 V
-0.90 V
0.5 kHz
1.0 kHz
1.5 kHz
10^9 C^{-2} (F^{-2})
Potential (V) vs. Ag/AgCl

Fig. S4

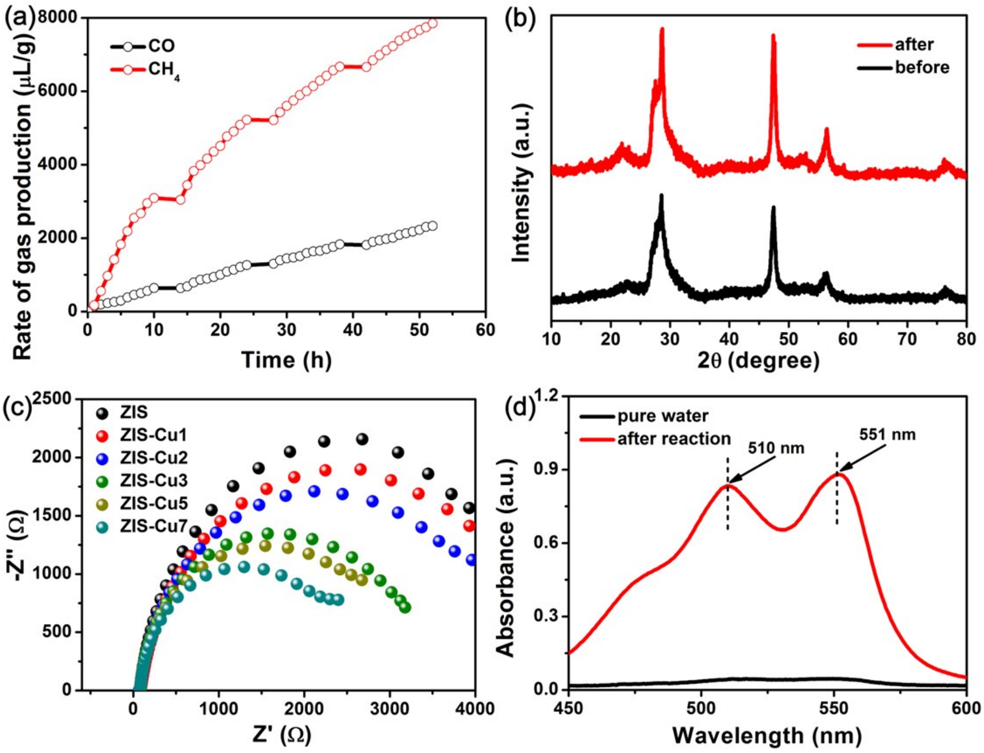
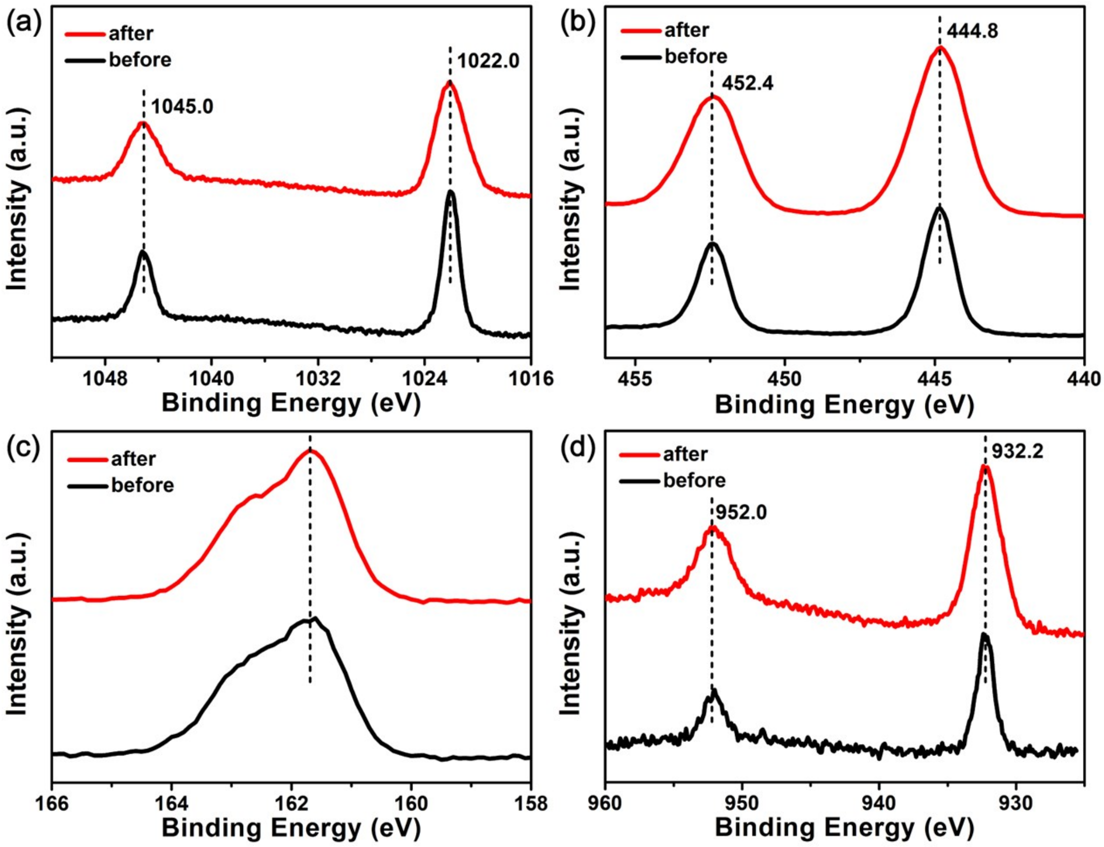

(a)
CO
CH_4
Rate of gas production (μL/g)
Time (h)
(b)
after
before
Intensity (a.u.)
2θ (degree)
(c)
ZIS
ZIS-Cu1
ZIS-Cu2
ZIS-Cu3
ZIS-Cu5
ZIS-Cu7
-Z'' (Ω)
Z' (Ω)
(d)
pure water
after reaction
510 nm
551 nm
Absorbance (a.u.)
Wavelength (nm)

Fig. S5



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