Supplementary Materials for

Band structure modulated 2D/2D ZnIn₂S₄@amorphous polymeric g-C₃N₄ S-scheme heterojunction for efficient photocatalytic reduction of CO₂

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Contents

- Chemicals and Characterizations
- **Supplementary Table S1-S3**
- Supplementary Fig. S1-S16

Chemicals and Characterizations

Chemicals: Urea (H₂NCONH₂), ammonium formate (CH₅NO₂), ethanol (CH₃CH₂OH), triethanolamine (TEOA), thioacetamide (TAA), indium chloride tetrahydrate (InCl₃·4H₂O), zinc chloride (ZnCl₂), acetonitrile (CH₃CN), cobalt (II) chloride (CoCl₂), and 2,2'-Bipyridyl (C₁₀H₈N₂, bpy) were purchased from Aladdin Reagent Co., Ltd. All chemicals and solvents were used as-received. Deionized water with a resistivity of 18.25 MΩ cm was obtained from the Smart-S15UVF integral system. High-purity carbon dioxide (99.999%) and argon gas (99.999%) were purchased from Chongqing Ruike Gas Co. Ltd.

Characterizations: The morphologies were characterized by a transmission electron microscopy (TEM, JEOL-JEM-2100F). The crystal structure was analyzed by X-ray diffraction (XRD, Cu Ka radiation source, D8 Advanced, Bruker, Germany). The Fourier transform infrared (FT-IR) spectra were used to characterize the surface functional groups by a Nicolet IS 50-FTIR spectrometer (Thermo Scientific). The chemical compositions and surface states were analyzed by the X-ray photoelectron spectroscopy (XPS, Thermo SCIENTIFIC ESCALAB 250Xi). The energy band structures were characterized by the ultraviolet photoelectron spectrometer (UPS, Thermo ESCALAB 250Xi). The diffuse reflectance spectra were recorded on a UV-vis spectrophotometer (UV-2700, Shimadzu, Japan). The pore structure and adsorption property were measured using nitrogen adsorption and desorption isotherms (Micromeritics ASAP 2460). The room-temperature electron paramagnetic resonance spectra were measured by an electron paramagnetic resonance (EPR, JES-FA 200, JEOL, Japan, 100 kHz, 1.0 mW). The photoluminescence (PL) spectra were measured by a fluorescence spectrophotometer (FLS1000 Photoluminescence Spectrometer, Edinburgh Instruments Ltd.). The In and Zn concentrations were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent ICP-OES730).

In-situ FTIR experiments: The *in-situ* Fourier transform infrared spectroscopy (FTIR) experiments were carried out on a Shimadzu IRTracer-100, equipped with a DLATGS detector cooled by liquid nitrogen and a homemade reaction chamber was utilized. Typically, $Co(bpy)_{3}^{2+}/ZIS@APCN$ was put on the crucible. The samples were degassed at 20 °C by the Ar gas for 30 min. Then, pure CO₂ carried with TEOA aqueous solution was selected as the gas source to simulate the photocatalytic reaction condition. After 30 min adsorption in the dark at room temperature, the specimen chamber-loaded samples were irradiated with an Xe lamp and infrared absorbance spectra were recorded every 1 min.

Photoelectrochemical measurements: The photoelectrochemical measurements were performed in a three-electrode cell by an electrochemical workstation (CHI-760E, Shanghai Chenhua Instrument Co., Ltd, China). During the photocurrent measurement, an Ag/AgCl electrode was used as the reference electrode and a Pt foil acted as the counter electrode. The working electrodes were prepared by depositing the prepared photocatalysts on the fluoride tin oxide (FTO) conductive glass. A quartz cell filled with 0.5 M Na₂SO₄ (pH = 6.8) was used in the measurements. For the electrochemical impedance spectroscopy (EIS) measurements, the amplitude of the sinusoidal wave was 5 mV, and the frequency ranged from 0.05 Hz to 100 kHz.

Apparent quantum yield (AQY): The wavelength-dependent apparent quantum yield (AQY) of CO₂ photoreduction by ZIS@APCN was calculated using different monochromatic light sources. The AQY was defined as the ratio of the total number of electrons participating in reduction reactions to the total number of incident photons. Therefore, the AQY could be calculated by the equation as follows:

$$AQY(\%) = \frac{2 \times Y_{CO} + 2 \times Y_{H_2}}{number of incident \ eletrons} \times 100\%$$

where Y_{CO} and Y_{H2} represent the yields of CO and H₂ within a certain period of time, respectively. The number of incident electrons was calculated by the following equation:

number of incident eletrons =
$$\frac{PS\lambda t}{N_A hc}$$

where the irradiation area (*S*) was 9.62 cm², *t* is the irradiation time, λ is the irradiation wavelength number (365, 400, 420, and 450 nm), N_A is the Avogadro constant (6.022×10²³ mol⁻¹), *h* is the Planck constant (6.63×10⁻³⁴ J·s) and *c* is the speed of the light (3×10⁸ m s⁻¹). The average light intensity (*P*) was measured to be 1.53 mW·cm⁻² for 365 nm, 10.61 mW·cm⁻² for 400 nm, 48.80 mW·cm⁻² for 420 nm, and 50.2 mW·cm⁻² for 450 nm.

Combining these two equations, the AQY (%) values for monochromatic light was calculated. For example, the AQY (%) @365 nm is shown here: $Y_{CO} = 2.55 \ \mu mol \cdot g^{-1}$, $Y_{H2} = 0.6 \ \mu mol \cdot g^{-1}$, t=1 h.

$$AQY(\%) = \frac{(2 \times 2.55 + 2 \times 0.6) \times 10^{-6}}{1} \times \frac{6.02 \times 10^{23} \times 6.63 \times 10^{-34} \times 3 \times 10^{8}}{1.53 \times 10^{-3} \times 9.62 \times 365 \times 10^{-9} \times 1 \times 3600} \times 100\% = 3.91\%$$

Similarly, AQY values for 400 nm, 420 nm, 450 nm were calculated as 1.07%, 0.17%, and 0.06%, respectively.

Supplementary Table S1-S3

Samples	In (wt.%)	Zn (wt.%)	APCN content in ZIS@APCN (wt.%)
ZIS@APCN-15	36.11	9.42	34.33
ZIS@APCN-20	32.44	8.40	41.07
ZIS@APCN-25	25.95	6.79	52.79
ZIS@APCN-30	22.46	5.88	59.13

Table S1 ICP-OES results

Table S2 Elemental analysis by EDS					
Element	Weight (%)	Atom (%)			
С	29.07	39.86			
Ν	45.14	53.07			
S	7.89	4.10			
Zn	3.87	0.97			
In	13.95	2.00			
Total	100	100			

Table S2 Elemental analysis by EDS

Samples	BET surface area	Pore size	Pore volume
	$m^2 \cdot g^{-1}$	nm	cm ³ ·g ⁻¹
APCN	40.46	12.98	0.13
ZIS	63.39	11.18	0.17
ZIS@APCN	73.14	14.69	0.26
BCN	37.68	13.48	0.12
ZIS@BCN	55.75	15.40	0.21

Table S3 Specific surface area and pore structure

Table S4 Performance comparison

Catalyst	Co-catalyst/ photosensitizer	CO yield rate (µmol·g ⁻¹ ·h ⁻¹)	CO Selectivity	Ref.
ZIS@APCN	Co(bpy) ₃ ²⁺	1425	81.6%	This work
ZnIn ₂ S ₄ / HCNT	$Co(bpy)_3^{2+}$	883	93%	[1]
In_2S_3 -Cd In_2S_4	$Co(bpy)_3^{2+}$	825	~72.36%	[2]
2Ag-In-S QDs	$Co(bpy)_3^{2+}$	460	74.61%	[3]
Covalent organic framework/single Ni sites	Ru ^(a)	966	96%	[4]
UCN670-2	$Co(bpy)_3^{2+}$	1287	91.4%	[5]
PCN/ZnIn ₂ S ₄	$Co(bpy)_3^{2+}$	832	87.8%	[6]
CdS HMCHPs	$Co(bpy)_3^{2+}$	1337	70.3%	[7]
B-CN-CdS	$Co(bpy)_3^{2+}$	250	84.8%	[8]
ZnIn ₂ S ₄ @CNO	Co(bpy) ₃ ²⁺	253.8	Not mentioned	[9]
$TiO_{2-x}/g-C_3N_4$	$Co(bpy)_3^{2+}$	388.9	83%	[10]
d-PCN-NSs	$Co(bpy)_3^{2+}$	1310	90%	[11]
L-g-C ₃ N ₄	Co(bpy) ₃ ²⁺	263.5	82.2%	[12]

 $\overline{(a) \text{ Ru repsents } [\text{Ru}(\text{bpy})_3]\text{Cl}_2.}$

■ Supplementary Fig. S1-S16



Fig. S1 TEM images of (a) BCN and (b) APCN and pore size distribution.



Fig. S2 Elemental-mapping images of pure ZnIn₂S₄.



Fig. S3 EDS result on ZIS@APCN-20.



Fig. S4 XRD patterns of BCN and APCN.



Fig. S5 Pore size distributions.



Fig. S6 UPS results of BCN.



Fig. S7 Band structures of BCN, APCN and ZIS.



Fig. S8 AQY and DRS spectra of ZIS@APCN-20.



Fig. S9 Raw data of ¹³C isotope tracing experiment acquired via GC-MS: (a) ¹²CO₂ to ¹²CO and (b) ¹³CO₂ to ¹³CO.



Fig. S10 Time-dependent CO/H₂ production rates with re-introducing TEOA.



Fig. S11 TEM images of ZIS@APCN-20 after reactions.



Fig. S12 (a) XRD patterns and (b) FTIR results before and after reactions.



Fig. S13 XPS spectra of ZIS@APCN-20 after reactions.



Fig. S14 Steady state PL spectra.



Fig. S15 Schematic illustration of charge transport in type-II heterojunction.



Fig. S16 UPS result of ZIS@APCN-20.



Fig. S17 In situ DRIFTS spectra of ZIS@APCN-20 under dark condition.



Fig. S18 Adsorption Spectra of Co(bpy)₃²⁺, ZIS@APCN and Co(bpy)₃²⁺/ ZIS@APCN.

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