Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supporting Information

Construction of S-scheme $Bi_2S_3/CdIn_2S_4$ heterojunction for the photocatalytic generation of methyl formate

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1. Preparation of working electrode

The production process of the working electrode is as follows: the FTO conductive glass was subjected to a 30-minute water treatment to eliminate surface impurities, followed by drying in a vacuum drying oven at 80 °C. Subsequently, the prepared catalyst (5 mg) was dissolved in a mixture of naphthol (50 μL) and anhydrous ethanol (950 μL). After 20 minutes of ultrasonic dispersion, a solution of 100 μL was carefully dripped onto the FTO conductive glass in a repetitive manner, ensuring that the coating area remained within 1 cm^2. The electrode was ultimately obtained through vacuum drying at 80°C for a duration of 12 hours.

Table S1. Comparison of the S_{BET}, pore volume (V_p) and average pore size (d_p) for diverse samples.

Samples	S_{BET} (m^2/g)	V_p (cm^3/g)	d_p (nm)
Bi_2S_3	16.26	0.041	10.08
$CdIn_2S_4$	41.98	0.147	14.02
$Bi_2S_3/CdIn_2S_4$	30.39	0.185	24.41

Table S2. The photocatalytic conversion rate of Bi_2S_3, $CdIn_2S_4$ and $Bi_2S_3/CdIn_2S_4$ to MF under different conditions in methanol.[a]

Samples	visible light [b]	simulated sunlight [b]	
	CO_2	N_2	CO_2
Bi_2S_3	63	25	186
$CdIn_2S_4$	1561	2154	3250
$Bi_2S_3/CdIn_2S_4$	1956	2365	5464

a Reaction condition was described in Photocatalytic activity measurement.

b The unit of the generation rate was $\mu mol \cdot h^{-1} \cdot g^{-1}$.

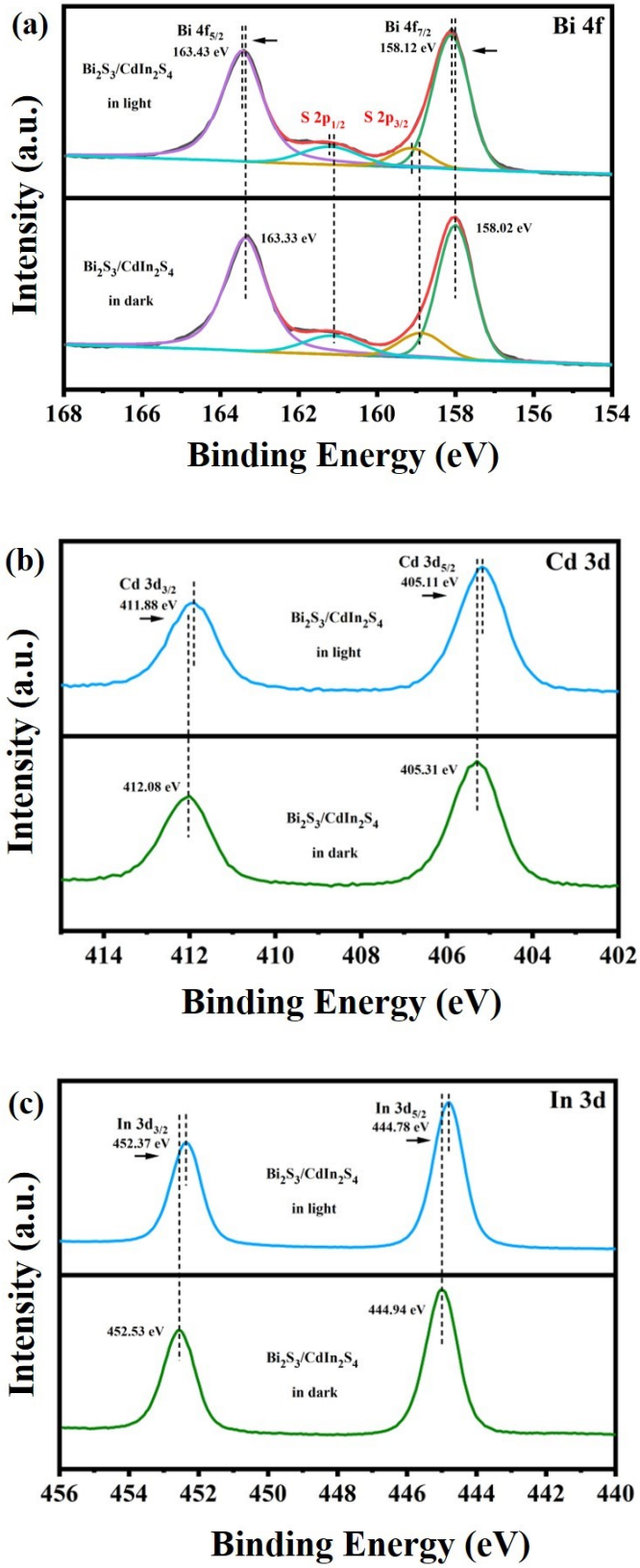

Fig. S1. XPS spectra of $Bi_2S_3/CdIn_2S_4$ in dark or in light; (a) Bi 4f peaks; (b) Cd 3d peaks; (c) In 3d peaks.

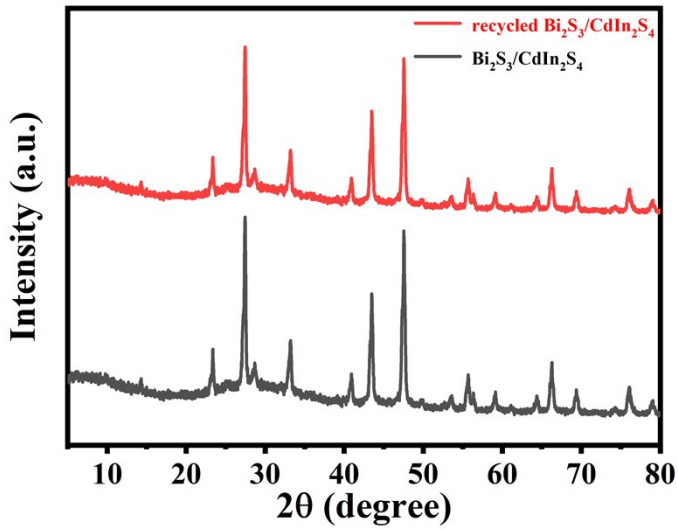

Fig. S2. XRD of recycled $Bi_2S_3/CdIn_2S_4$.

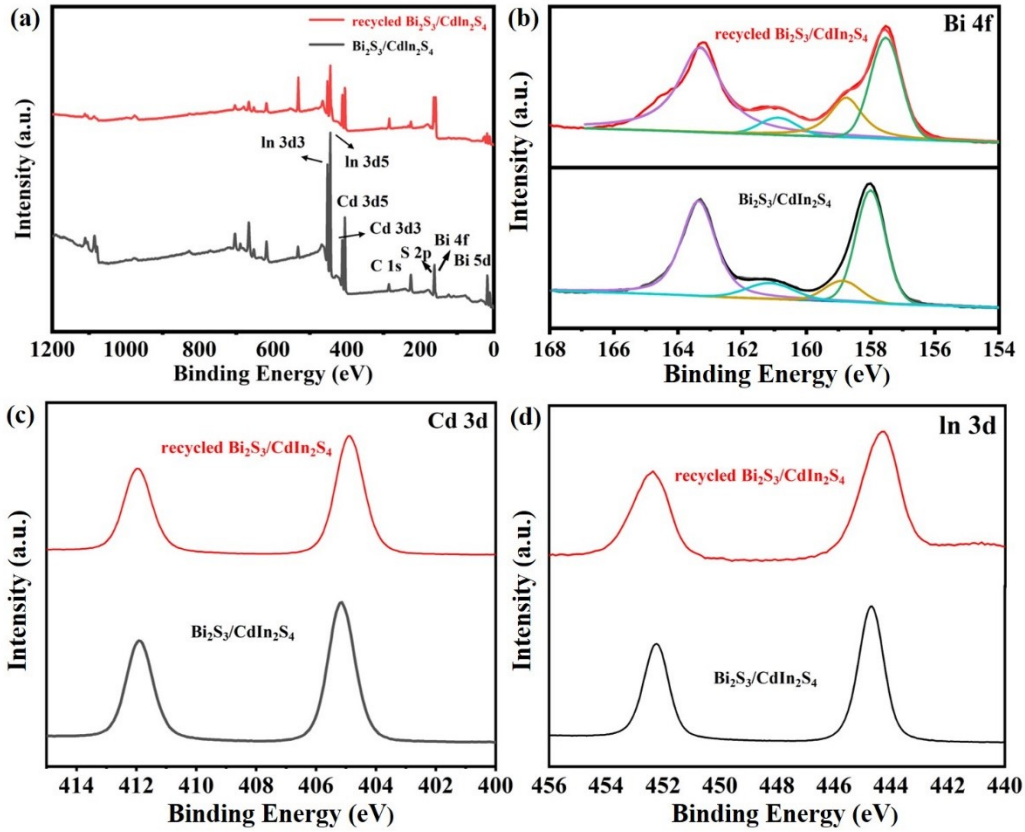

Fig. S3. XPS spectra of $Bi_2S_3/CdIn_2S_4$ before and after cyclic reactions.

Table S3. Comparison of the reaction conditions and photocatalytic activity with other catalysts for CO_2/methanol reduction to MF.

Photocatalysts	Light sources	Reaction conditions/	Main Product	Photocatalytic efficiencies	Ref.
$Bi_2S_3/CdIn_2S_4$	350 W Xe lamp (λ > 200 nm)	25 °C, Liquid-solid, CO_2, methanol	MF	5464 μmol g^{-1} h^{-1}	This work
Bi_2S_3 microspheres	250 W high pressure mercury lamp (UV-vis light)	25 °C, Liquid-solid, CO_2, methanol	MF	175 μmol g^{-1} h^{-1}	1
$CdIn_2S_4$ (from thioacetamide)	250 W high pressure mercury lamp (UV-vis light) (λ > 365 nm)	25 °C, Liquid-solid, CO_2, methanol	MF	3604 μmol g^{-1} h^{-1}	2
Bi_2S_3-$ZnIn_2S_4$ (2 wt%)	250 W high-pressure mercury lamp (UV-vis light)	25 °C, Liquid-solid, CO_2, methanol	MF	299.43 μmol g^{-1} h^{-1}	3
0.5 wt% Pd/TiO_2	300 W Xe lamp (UV light)	25 °C, Liquid-solid, CO_2, methanol	MF	1367.22 μmol g^{-1} h^{-1}	4
hexagonal $ZnIn_2S_4$	250 W high pressure mercury lamp (λ > 365 nm)	25 °C, Liquid-solid, CO_2, methanol	MF	762.36 μmol g^{-1} h^{-1}	5
0.3 % Ni/ZnS	250 W high pressure mercury lamp (λ > 365 nm)	25 °C, Liquid-solid, CO_2, methanol	MF	121.4 μmol g^{-1} h^{-1}	6
TiO_2/NCC-EDA(54 g L^{-1})	300 W Xenon light with UV cut-off filter (λ > 420 nm)	Room temperature, Liquid-soild, CO_2, H_2O	MF	62.14 μmol g^{-1} h^{-1}	7
MXene/GO/PDI	350 W Xe lamp (λ > 200 nm)	25 °C, Liquid-solid, CO_2, methanol	MF	771.1 μmol g^{-1} h^{-1}	8
CuO/TiO_2（AB）	250 W Hg lamp (λ > 365 nm)	25 °C, Liquid-solid, CO_2, methanol	MF	450 μmol g^{-1} h^{-1}	9

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