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## **Electronic Supplementary Information**

## Photothermal-coupled solar photocatalytic CO<sub>2</sub> reduction with high efficiency and selectivity on MoO<sub>3-x</sub>@ZnIn<sub>2</sub>S<sub>4</sub> coreshell S-scheme heterojunction

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**Fig. S1** XRD patterns of the prepared  $MoO_{3-x}$  and  $MoO_3$  samples.



Fig. S2 EPR spectra of the prepared  $MoO_{3-x}$ ,  $MoO_3$  and MO@ZIS-3 samples.



Fig. S3 XPS spectra of the prepared  $MoO_3$  sample: (a) the XPS survey spectrum, and the XPS core-level spectra of (b) Mo 3*d* and (c) O 1*s*.



Fig. S4 (a-b) SEM images of the prepared  $MoO_3$  sample. (c-d) SEM images, (e-f) TEM images, (g) HRTEM image, and (h) SAED patterns of the prepared  $MoO_{3-x}$  sample.



Fig. S5 EDS spectra of the prepared (a)  $MoO_3$  and (b)  $MoO_{3-x}$  samples.



**Fig. S6** (a) Electron image, (b) EDS layered image, and the corresponding EDS elemental mapping images of (c) Mo and (d) O of the prepared  $MoO_{3-x}$  sample.



Fig. S7 (a-b) SEM images, (c-d) TEM images, (e) HRTEM image, and (f) SAED patterns of the prepared  $ZnIn_2S_4$  sample.



Fig. S8 EDS spectrum of the prepared  $ZnIn_2S_4$  sample.



Fig. S9 (a) Electron image, and the corresponding EDS elemental mapping images of (b) Zn,(c) In, and (d) S of the prepared ZnIn<sub>2</sub>S<sub>4</sub> sample.



Fig. S10 EDS spectrum of the prepared MO@ZIS-3 sample.



**Fig. S11** UV-Vis-NIR absorption spectra of the prepared  $MoO_{3-x}$  and  $MoO_3$  samples.



Fig. S12 Product yields and  $CH_4$  selectivity of the prepared MO@ZIS-3 photocatalyst under different temperatures.



**Fig. S13** (a) CH<sub>4</sub> production and (b) CO production as a function of irradiation time under full-spectrum illumination for the prepared MO@ZIS-3 photocatalyst over five runs of cycling tests. (c) Product yields and (d) the corresponding catalyst surface temperatures during the five cycles of tests.



Fig. S14 XRD patterns of the MO@ZIS-3 catalyst before and after five runs of photocatalytic  $CO_2$  reduction.



Fig. S15 SEM images of (a-b) the pristine MO@ZIS-3 photocatalyst and (c-d) that after five runs of photocatalytic  $CO_2$  reduction.

Sample	Zinc element content (wt %)	Indium element content (wt %)	Sulfur element content (wt %)
Before catalysis	6.15	21.81	12.20
After catalysis	6.06	21.49	12.01

 Table S1 Contents of Zn, In and S elements in the MO@ZIS-3 catalyst before and after five

 cycles of photocatalytic experiments.



Fig. S16 Transient photocurrent responses of the prepared  $MoO_{3-x}$ , MO@ZIS-3 and  $ZnIn_2S_4$  samples under UV-Vis and UV-Vis-IR illumination.