Electronic Supplementary Information (ESI)

Synthesis of hexagonal and cubic ZnIn$_2$S$_4$ nanosheets for the photocatalytic reduction of CO$_2$ with methanol

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Experimental Details

Synthesis of ZnIn$_2$S$_4$ microspheres: In a typical synthesis procedure, Zn(NO$_3$)$_2$·6H$_2$O (0.150 g), In(NO$_3$)$_3$·4.5H$_2$O (0.391 g), citric acid (CA, 0.1 g) and thiourea (TU, 0.308 g) were dissolved in 40 mL of deionized water and transferred to a 70 mL Teflon liner. The Teflon liner was sealed in the stainless steel autoclave and heated at 180°C for 18 h. After being cooled to room temperature, the yellow precipitate was collected by centrifugation and washed with ethanol and the distilled water for three times, respectively. And then it was dried at 60°C to obtain the ZnIn$_2$S$_4$ microspheres.

Figure S1. SEM image of the ZnIn$_2$S$_4$ samples obtained via hydrothermal method.
**Figure S2.** TEM image of the hexagonal ZnIn$_2$S$_4$ nanosheets.

**Figure S3.** XPS spectra of the hexagonal ZnIn$_2$S$_4$ nanosheets: high-resolution In3d, Zn2p, and S2p spectra.
Figure S4. SEM image of ZnIn$_2$S$_4$-DETA precursor suggesting a sheet-like structure.

Figure S5. XPS spectra of the cubic ZnIn$_2$S$_4$ nanosheets.
**Figure S6.** HRTEM image of cubic ZnIn$_2$S$_4$ nanosheets.

**Figure S7.** SEM image of ZnIn$_2$S$_4$ microspheres.

**Tab. S1** The BET result of as-prepared samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hexagonal ZnIn$_2$S$_4$</th>
<th>Cubic ZnIn$_2$S$_4$</th>
<th>Microspheres ZnIn$_2$S$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$</td>
<td>28.65</td>
<td>25.84</td>
<td>42.16</td>
</tr>
</tbody>
</table>
Figure S8. Time course of photocatalytic MF production over hexagonal (a) and cubic (b) ZnIn$_2$S$_4$ nanosheets.

Figure S9. Relative concentration of CO$_2$ (the peak at 2343 cm$^{-1}$) as a function of time using hexagonal ZnIn$_2$S$_4$ nanosheets in the dark (black), using cubic ZnIn$_2$S$_4$ nanosheets under light irradiation (red), and using hexagonal ZnIn$_2$S$_4$ nanosheets under light irradiation (green).