

## Supplementary Information

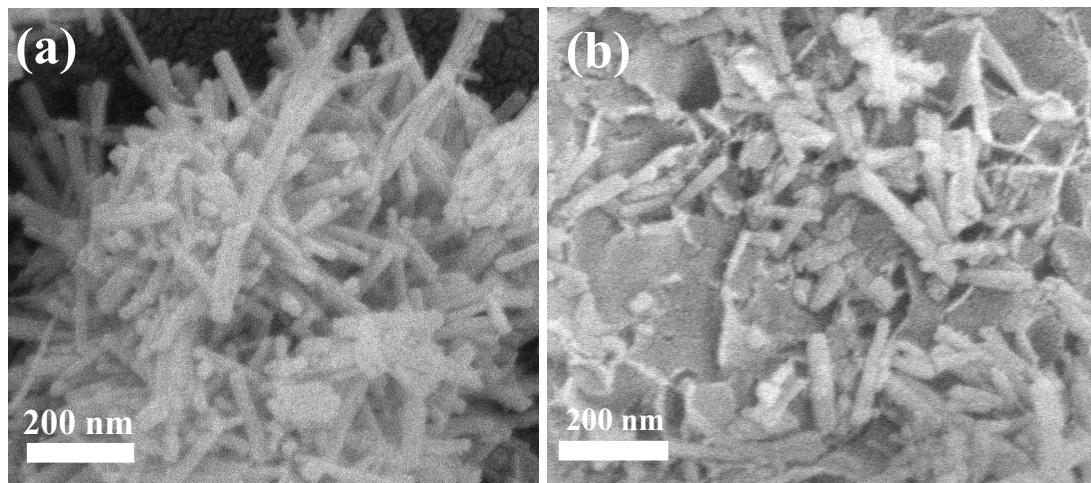
### Surface plasmon resonance and structure defects synergistic effect of ZnCdS<sub>2</sub>/NiMoO<sub>4</sub>@Cu Z-scheme heterojunction for enhanced photocatalytic CO<sub>2</sub> reduction to CH<sub>4</sub>

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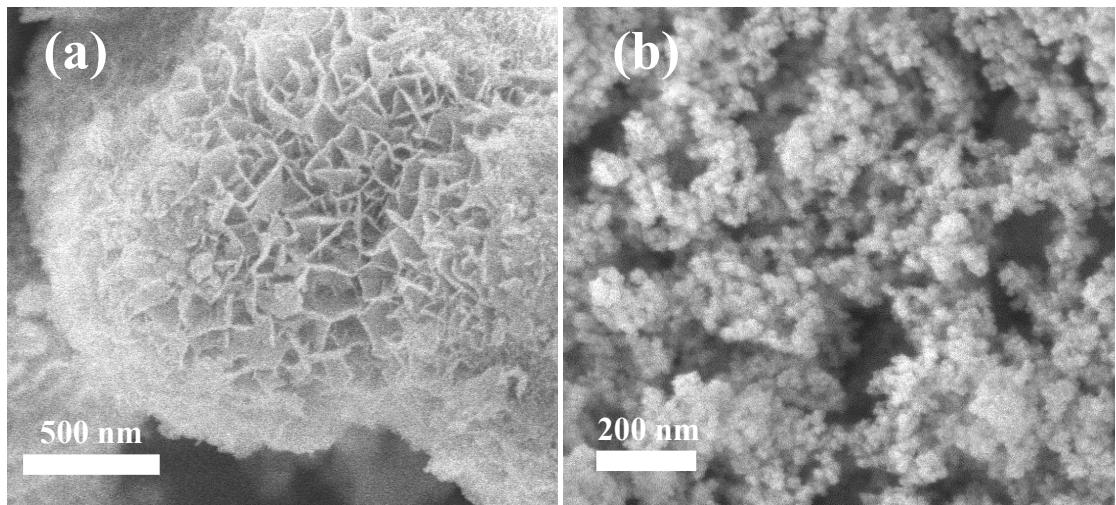
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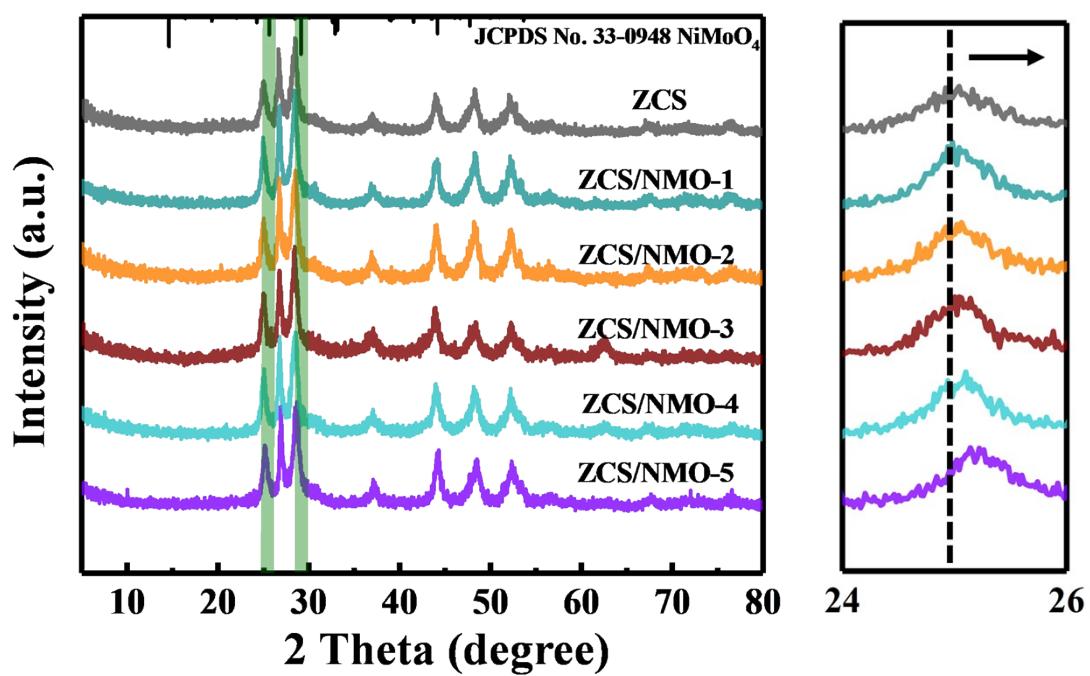
E-mail: [sunbojing@ctgu.edu.cn](mailto:sunbojing@ctgu.edu.cn) (Bojing Sun); [dfhouok@126.com](mailto:dfhouok@126.com) (Dongfang Hou); [lidongsheng1@126.com](mailto:lidongsheng1@126.com) (Dong-sheng Li).



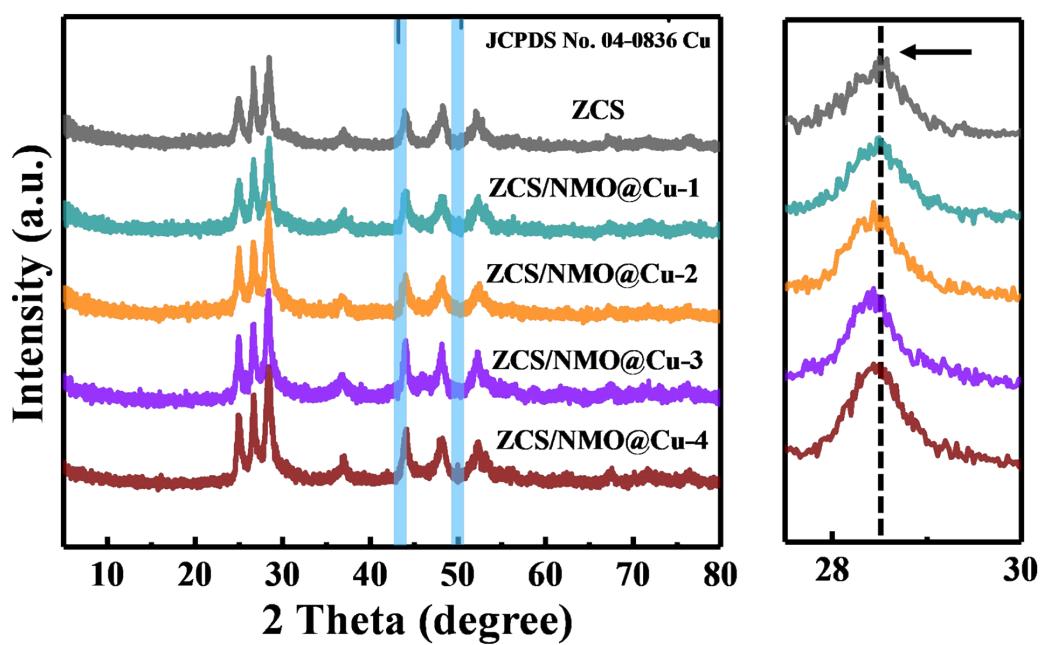
**Fig. S1. a-b** The SEM images of ZCS and ZCS/NMO.



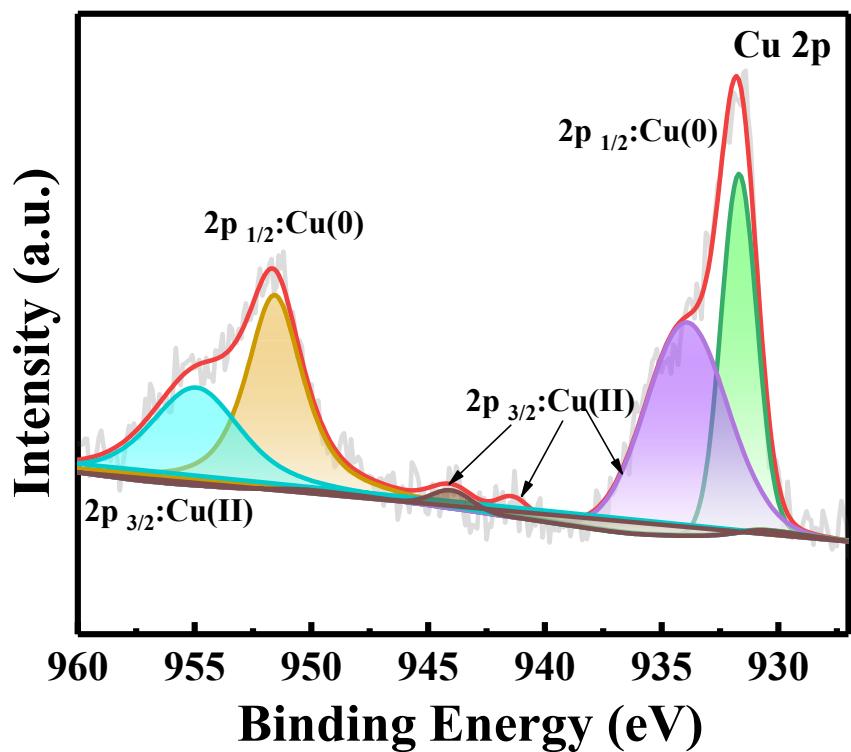
**Fig. S2. a-b** The SEM images of  $\text{NiMoO}_4$  and Cu.



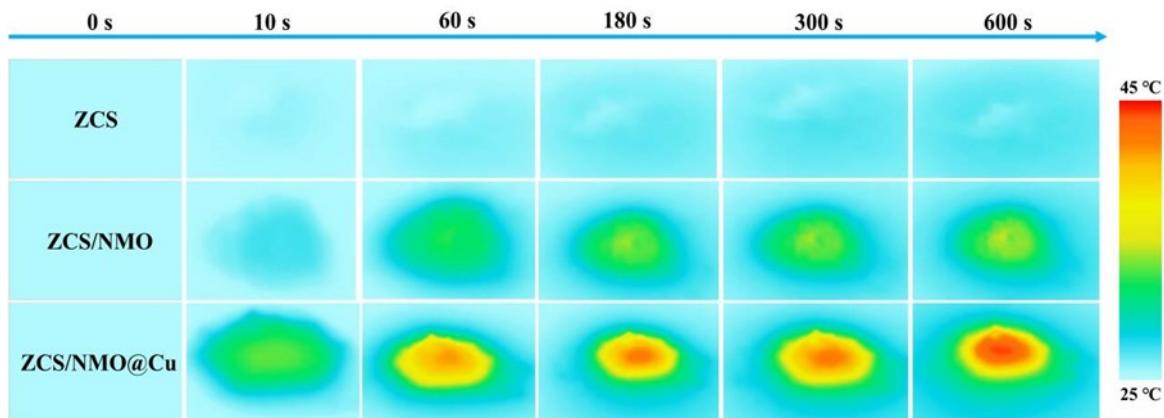
**Fig. S3.** The XRD patterns and magnified patterns of ZCS and ZCS/NMO-X



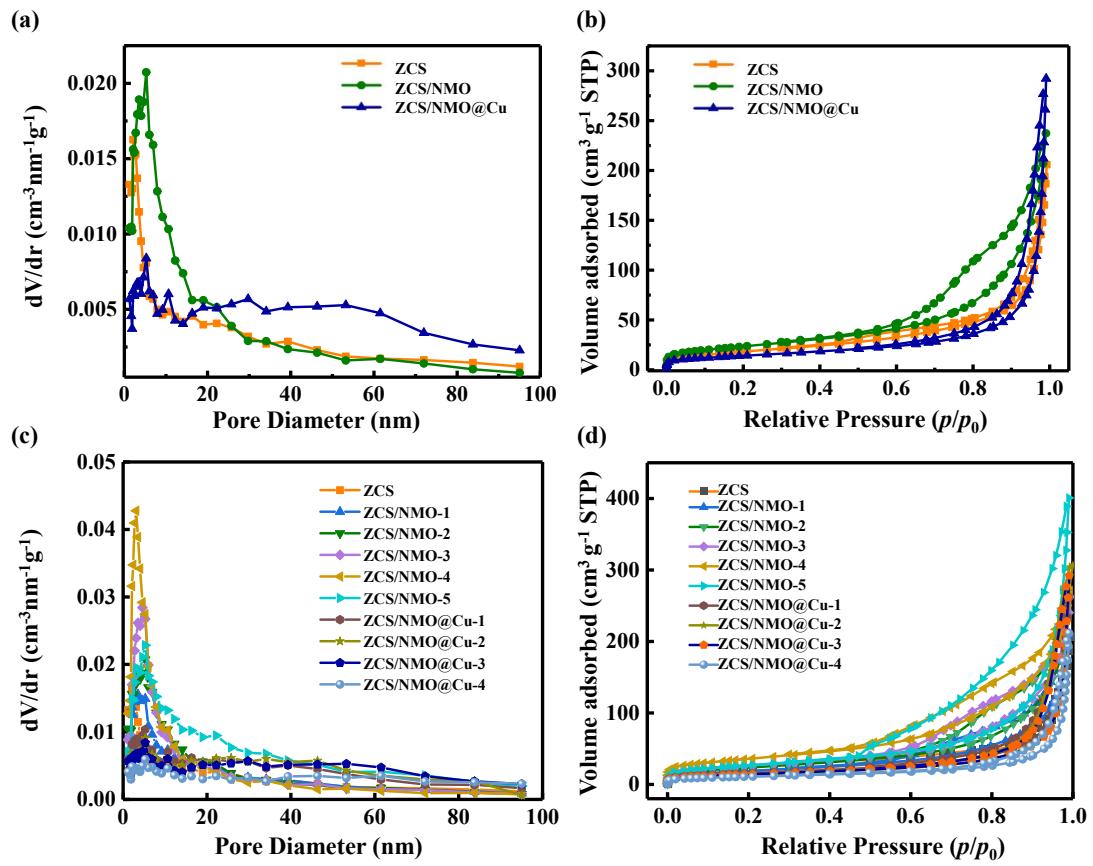
**Fig. S4.** The XRD patterns and magnified patterns of ZCS and ZCS/NMO@Cu-X



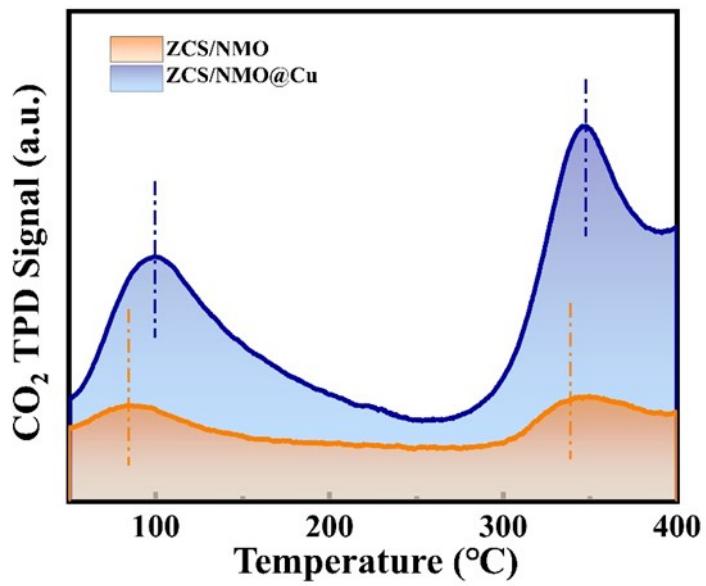
**Fig. S5.** High resolution XPS spectra of Cu 2p of ZCS/NMO@Cu



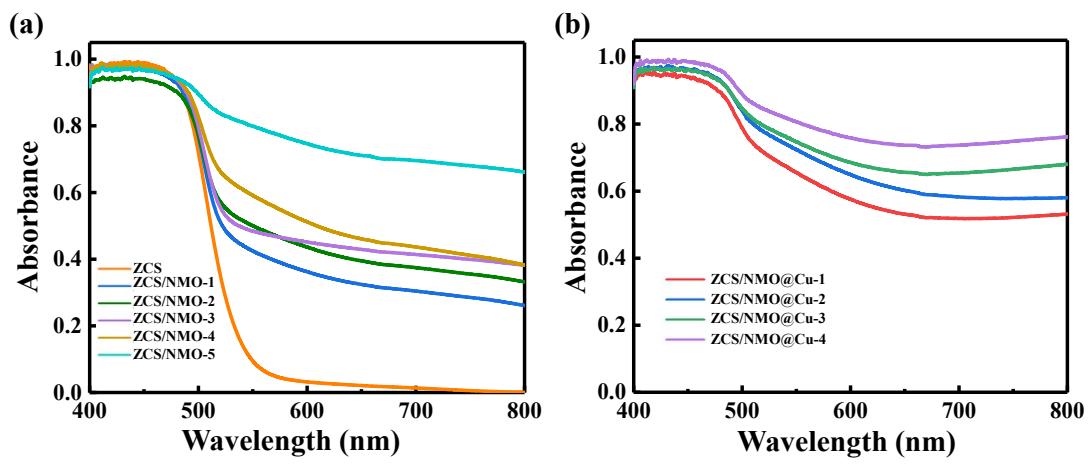
**Fig. S6.** Photothermal maps of ZCS, ZCS/NMO, and ZCS/NMO@Cu under near-infrared light irradiation at different times.



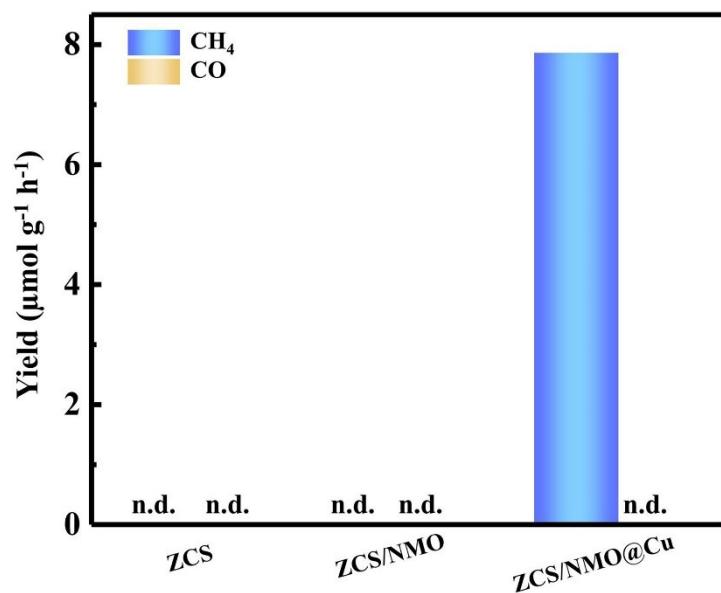
**Fig. S7.** **a** Pore size distribution of ZCS, ZCS/NMO and ZCS/NMO@Cu. **b** Nitrogen sorption isotherms of ZCS, ZCS/NMO and ZCS/NMO@Cu. **c** Pore size distribution of ZCS, ZCS/NMO-X and ZCS/NMO@Cu-X. **d** Nitrogen sorption isotherms of ZCS, ZCS/NMO-X and ZCS/NMO@Cu-X.



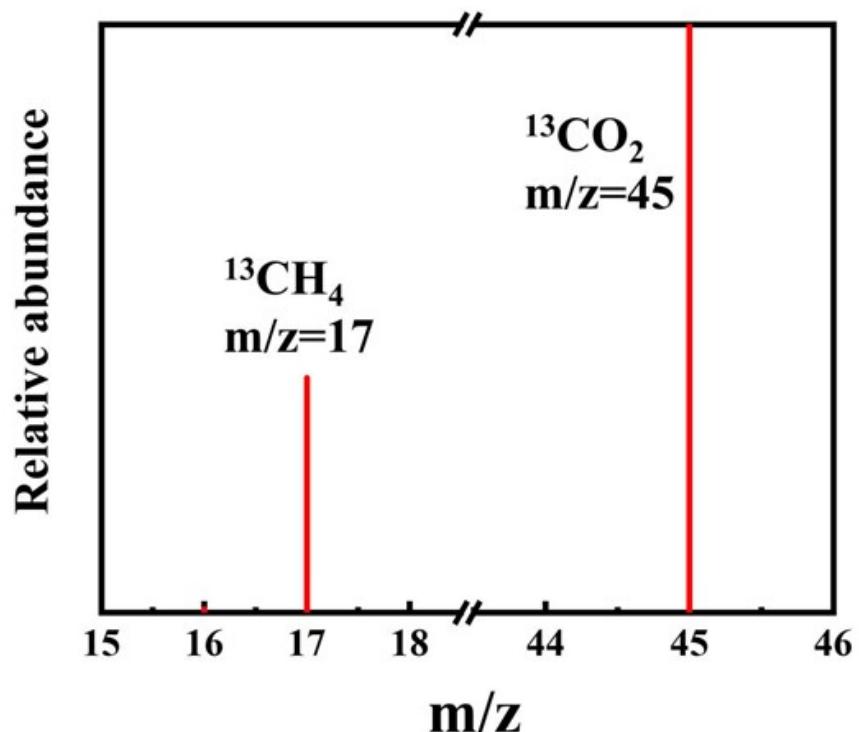
**Fig. S8.** CO<sub>2</sub> TPD profiles of ZCS/NMO and ZCS/NMO@Cu.



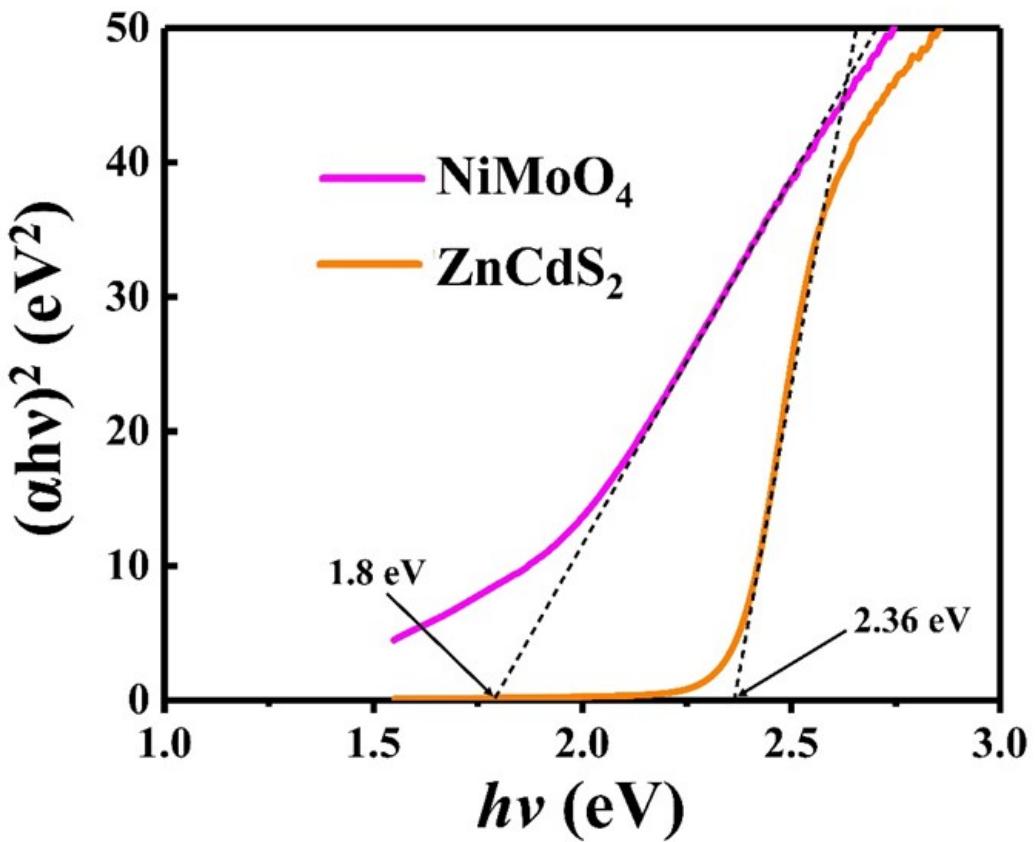
**Fig. S9.** **a** UV-vis absorption spectra of ZCS and ZCS/NMO-X. **b** UV-vis absorption spectra of ZCS/NMO@Cu-X



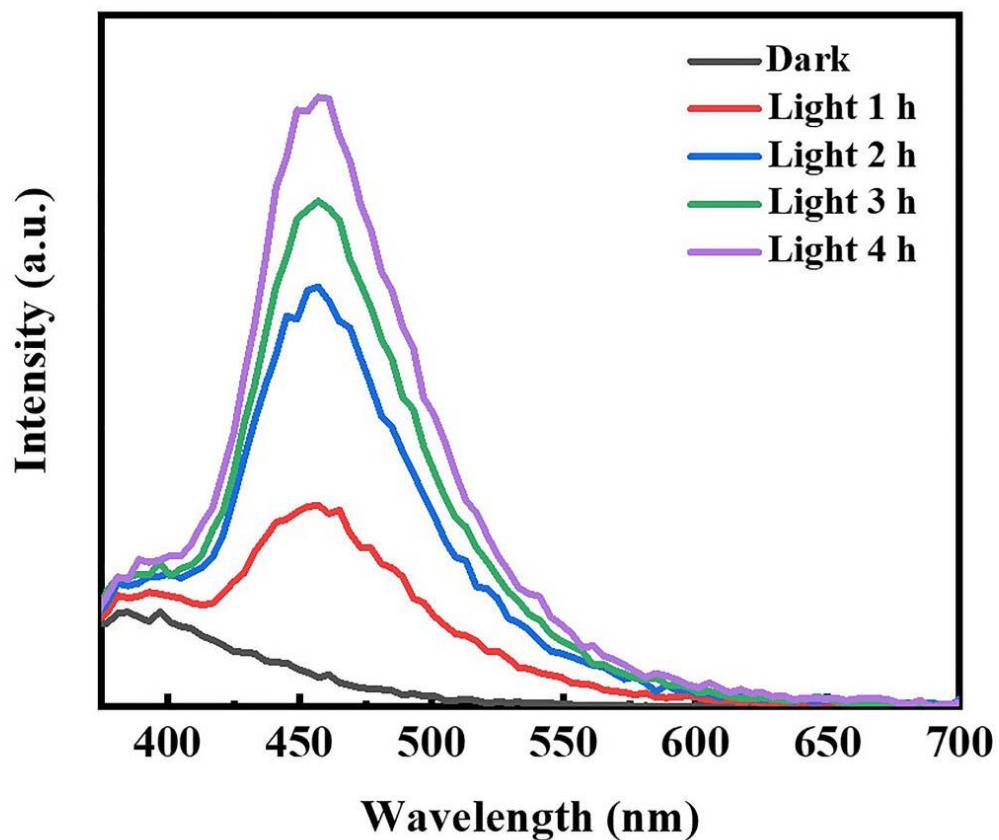
**Fig S10.** CO<sub>2</sub> reduction performance under near-infrared light irradiation.



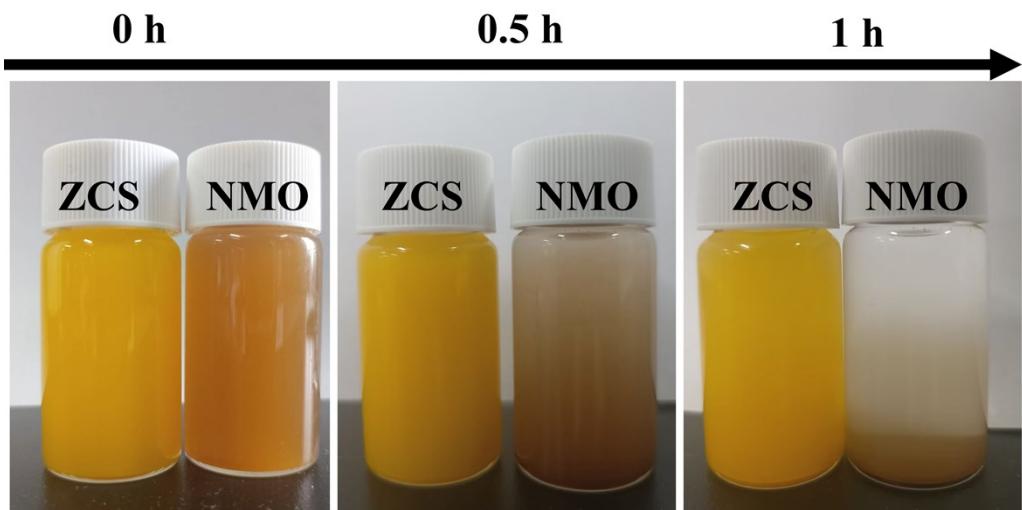
**Fig S11.** Mass spectra of  $^{13}\text{CH}_4$  generated from the isotopic  $^{13}\text{CO}_2$  photoreduction.



**Fig S12.** Band gap spectra of  $\text{ZnCdS}_2$  and  $\text{NiMoO}_4$ .



**Fig S13.** Fluorescence spectra of ZCS/NMO@Cu under visible irradiation.



**Fig S14.** Static experiment of ZCS and NMO.

**Table S1** Specific surface areas and pore volume of ZCS, ZCS/NMO-X and ZCS/NMO@Cu-X.

Sample	Surface area (m <sup>2</sup> /g)	Mean pore diameter (nm)	Pore volume (cm <sup>3</sup> /g)
ZCS	<b>68.43</b>	<b>17.10</b>	<b>0.29</b>
ZCS/NMO-1	<b>68.6</b>	<b>18.82</b>	<b>0.32</b>
ZCS/NMO-2	<b>85.45</b>	<b>17.10</b>	<b>0.37</b>
ZCS/NMO-3	<b>95.05</b>	<b>15.71</b>	<b>0.37</b>
ZCS/NMO-4	<b>128.97</b>	<b>12.48</b>	<b>0.40</b>
ZCS/NMO-5	<b>97.7</b>	<b>25.15</b>	<b>0.61</b>
ZCS/NMO@Cu-1	<b>56.19</b>	<b>28.71</b>	<b>0.40</b>
ZCS/NMO@Cu-2	<b>49.11</b>	<b>34.56</b>	<b>0.42</b>
ZCS/NMO@Cu-3	<b>51.29</b>	<b>34.05</b>	<b>0.44</b>
ZCS/NMO@Cu-4	<b>38.46</b>	<b>32.79</b>	<b>0.32</b>

**Table S2** Comparison of photocatalytic CO<sub>2</sub> conversion to CH<sub>4</sub> performance of our photocatalysts with previously reported system of similar catalytic materials.

Catalyst	Light Source	CH <sub>4</sub> yield	Selectivity	Ref
UiO-66/Co <sub>9</sub> S <sub>8</sub>	300W Xe lamp, AM 1.5	240.9 μmol·g <sup>-1</sup> ·h <sup>-1</sup>	~100%	1
CuSnInS <sub>4</sub>	300W Xe lamp, >420 nm	5.83 μmol·g <sup>-1</sup> ·h <sup>-1</sup> ,	67.3%	2
Vs-CuIn <sub>5</sub> S <sub>8</sub>	300W Xe lamp, >420 nm	8.7 μmol·g <sup>-1</sup> ·h <sup>-1</sup> ,	~100%	3
Bi <sub>2</sub> WO <sub>6</sub> /ZnIn <sub>2</sub> S <sub>4</sub>	300W Xe lamp, >420 nm	5.12 μmol·g <sup>-1</sup> ·h <sup>-1</sup> ,	94.5%	4
C <sub>60</sub> /CuS@ZnIn <sub>2</sub> S <sub>4</sub>	300W Xe lamp (>400 nm), H <sub>2</sub> O	43.6 μmol·g <sup>-1</sup> ·h <sup>-1</sup> ,	~100%	5
ZnIn <sub>2</sub> S <sub>4</sub> /N-doped graphene	300W Xe lamp, >420 nm	1.01 μmol·g <sup>-1</sup> ·h <sup>-1</sup>	42.4%	6
TiO <sub>2</sub> -Cu <sub>2</sub> ZnSnS <sub>4</sub>	400 W Xe lamp, ≥420 nm	1.01 μmol·g <sup>-1</sup> ·h <sup>-1</sup>	0.05%	7
Cu-ZnIn <sub>2</sub> S <sub>4</sub> /ZIF-67	300W Xe lamp, 400-780 nm	22.27 μmol·g <sup>-1</sup> ·h <sup>-1</sup>	94.7%	8
NH <sub>2</sub> -B-TiO <sub>2</sub> - Cu <sub>x</sub> S	300W Xe lamp, >420 nm	3.34 μmol·g <sup>-1</sup> ·h <sup>-1</sup>	16%	9
BiOBr/CdIn <sub>2</sub> S <sub>4</sub>	300W Xe lamp, >420 nm	1.50 μmol·g <sup>-1</sup> ·h <sup>-1</sup>	16.7%	10
SnS <sub>2</sub>	150W halogen lamp, AM 1.5	0.13 μmol cm <sup>-2</sup>	92%	11

CuS@SnS <sub>2</sub>	300W Xe lamp, $\geq 400$ nm	77.5 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	35.6%	12
MoO <sub>3</sub> /MoS <sub>2</sub> /CuS	300W Xe lamp, $>420$ nm	44.64 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	85.5%	13
MoS <sub>2</sub> /SnS <sub>2</sub> /r-GO	8W mercury lamp, H <sub>2</sub> O	50.548 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	42.4%	14
In <sub>2</sub> S <sub>3</sub> /WS <sub>2</sub>	400W Xe lamp, $>420$ nm	16 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	47%	15
Co-ZnS/MoS <sub>2</sub> /graphene	350W Xe lamp, $>420$ nm	23.4 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	$\sim 100\%$	16
MS/In <sub>2</sub> S <sub>3</sub>	300W Xe lamp, $>420$ nm	68.41 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	80.3%	17
BiOI/MoS <sub>2</sub> /CdS	300W Xe lamp, $>420$ nm	46.22 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	55.6%	18
ZnFe <sub>2</sub> O <sub>4</sub> /ZnO/CdS	300W Xe lamp, $>420$ nm	105.9 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	28.5%	19
ZnCdS <sub>2</sub> /NiMoO <sub>4</sub> @Cu	300W Xe lamp, $>420$ nm	92.17 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	$\sim 100\%$	<b>This work</b>

**Table S3** Time-resolved fluorescence spectra of ZCS, ZCS/NMO-X and ZCS/NMO@Cu-X

Samples	$\tau_1$ (ns)	A <sub>1</sub>	$\tau_2$ (ns)	A <sub>2</sub>	$\tau$ (ns)
ZCS	<b>1.87</b>	<b>49.48</b>	6.33	<b>50.52</b>	<b>4.12</b>
ZCS/NMO	<b>0.85</b>	<b>18.83</b>	<b>4.17</b>	<b>81.17</b>	<b>3.55</b>
ZCS/NMO@Cu	<b>1.91</b>	<b>43.91</b>	<b>6.20</b>	<b>56.09</b>	<b>4.32</b>

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