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## **Supporting information**

## Fabrication of the direct Z-scheme heterojunction of UiO-66-NH<sub>2</sub> and tubular g-C<sub>3</sub>N<sub>4</sub> for stable photocatalytic reduction of CO<sub>2</sub> to CO and CH<sub>4</sub>

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**Schematic S1.** The schematic of the photocatalytic reactor and the CO<sub>2</sub> reduction experiment conducted.



Fig. S1. SEM images of TCN (a) and SCN (b).

	Atomic%					
	С	N O		Zr		
UNH	53.98	5.36	33.93	6.74		
T/U-0.65	51.51	31.37	15.6	1.52		

Table S1. XPS elemental content of UNH and T/U-0.65.

500 Quantity Adsorbed (cm<sup>3</sup>/g STP) 400 UNH 300 200 T/U-0.65 100 TCN 0 0.2 0.0 0.4 0.6 0.8 1.0 Relative Pressure (P/P<sub>0</sub>)

Fig. S2. N<sub>2</sub> adsorption-desorption isotherms of TCN, pure UNH and T/U-0.65.

	$S_{BET}$ (cm <sup>2</sup> /g)	$V_{total}(cm^{3}/g)$	V <sub>mic</sub> (cm <sup>3</sup> /g)	V <sub>mes</sub> (cm <sup>3</sup> /g)
TCN	58	0.27	0.014	0.13
UNH	1172	0.69	0.44	0.25
T/U-0.65	592	0.68	0.20	0.48

Table S2.  $S_{BET}$  and pore volume data for TCN, pure UNH and T/U-0.65.



Fig. S3. Mott-Schottky curves of SCN (a), TCN (b) and pure UNH (c).



Fig. S4. XRD patterns (a) and TEM images (b, c) of fresh and used T/U-0.65 catalyst.

Catalysts	CO and CH <sub>4</sub> yields (µmol g <sup>-1</sup> h <sup>-1</sup> )	S <sub>CH4</sub> (%)	Reaction time(h)	Reducing agent	References
UiO-66-NH <sub>2</sub> /Cu <sub>2</sub> O/Cu- 0.39	CO: 4.54	0	12	H <sub>2</sub> O	1
f-MoS <sub>2</sub> @UiO-66-NH <sub>2</sub>	CO : 23.16 CH <sub>4</sub> : 27.18	82.44	25	H <sub>2</sub> O, MeCN	2
8%NU66/CIS	CO : 11.24 CH <sub>4</sub> : 2.92	51	18	H <sub>2</sub> O	3
NH <sub>2</sub> -UiO-66/CuZnS	CO : 22.85	0	14	water vapor	4
UNH/Ce (HCOO) <sub>3</sub> - 1.80	CO : 16.45 CH <sub>4</sub> : 29.4	84	15	H <sub>2</sub> O, TEOA	5
NU/CC-1.6-90	CO : 20.6 CH <sub>4</sub> : 14	73	15	H <sub>2</sub> O, TEOA	6
UiO-66(NH <sub>2</sub> )/HGN	CO: 31.6 CH <sub>4</sub> : 1.82	18.7	48	H <sub>2</sub> O, TEOA	7
T/U-0.65	CO: 4.33 CH <sub>4</sub> : 14.68	93.1	40	H <sub>2</sub> O, TEOA	This work

 Table S3. Comparison of CO2 photoreduction performance over some reported catalysts and this work.

## References

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