

Supporting information

Construction of Z-scheme heterojunction between Zn-doped UiO-66-NH₂ and CeO₂ towards highly selective photoreduction of CO₂ to CH₄

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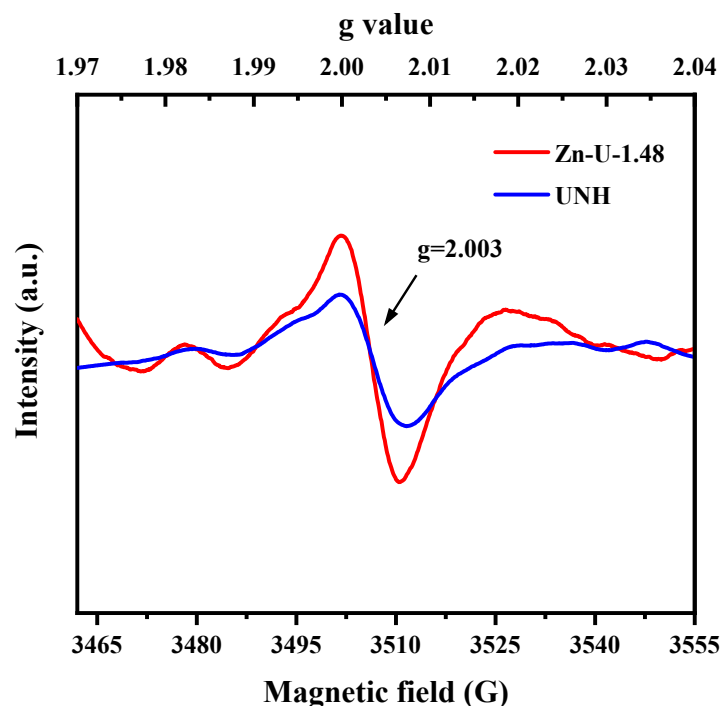


Fig. S1. EPR spectra of pure UNH and Zn-doped Zn-U-1.48.

The XRD and XPS characterizations of the samples Zn-U/C-1.0 and Zn-U/C-1.96 are shown in **Fig. S2**. It can be observed that the crystallinity of the composites is significantly decreased compared with pure UNH in **Fig. S2(a)**. Meanwhile, the intensity of the 7.2° (111) characteristic peak of Zn-U/C-1.96 decreased with the increase of x from 1.0 to 1.96. Therefore, we can conclude that the crystallinity of Zn-U/C- x is also gradually destroyed when the input amount of ZnO/CeO₂ increases.

The Ce-N-O bond is the main evidence for the formation of heterojunction, and therefore the representation on XPS is mainly changes in the binding energy of Ce 3d and N1s. As seen in **Fig. 5**, for Zn-U/C-1.48, there is a significant positive shift in its Ce 3d binding energy compared to ZnO/CeO₂. And as seen from **Fig. S2(b)**, for Zn-

U/C-1.96, the change of Ce 3d binding energy is smaller compared to ZnO/CeO₂, which suggests that the Ce in Zn-U/C-1.96 favors the existence in the form of CeO₂ alone, resulting in a weaker binding to UNH. Meanwhile, from the N1s spectra as shown in Fig. S2(c), the peak intensities of the N-O species occurred to be decreased with the increase of the compound amount, which also indicate the weakening of the interaction between CeO₂ and UNH.

In conclusion, the decrease in crystallinity and the changes in the binding energy and peak intensity of Ce, N demonstrate that too high amount of ZnO/CeO₂ composite is detrimental to the formation of a compact heterojunction structure.

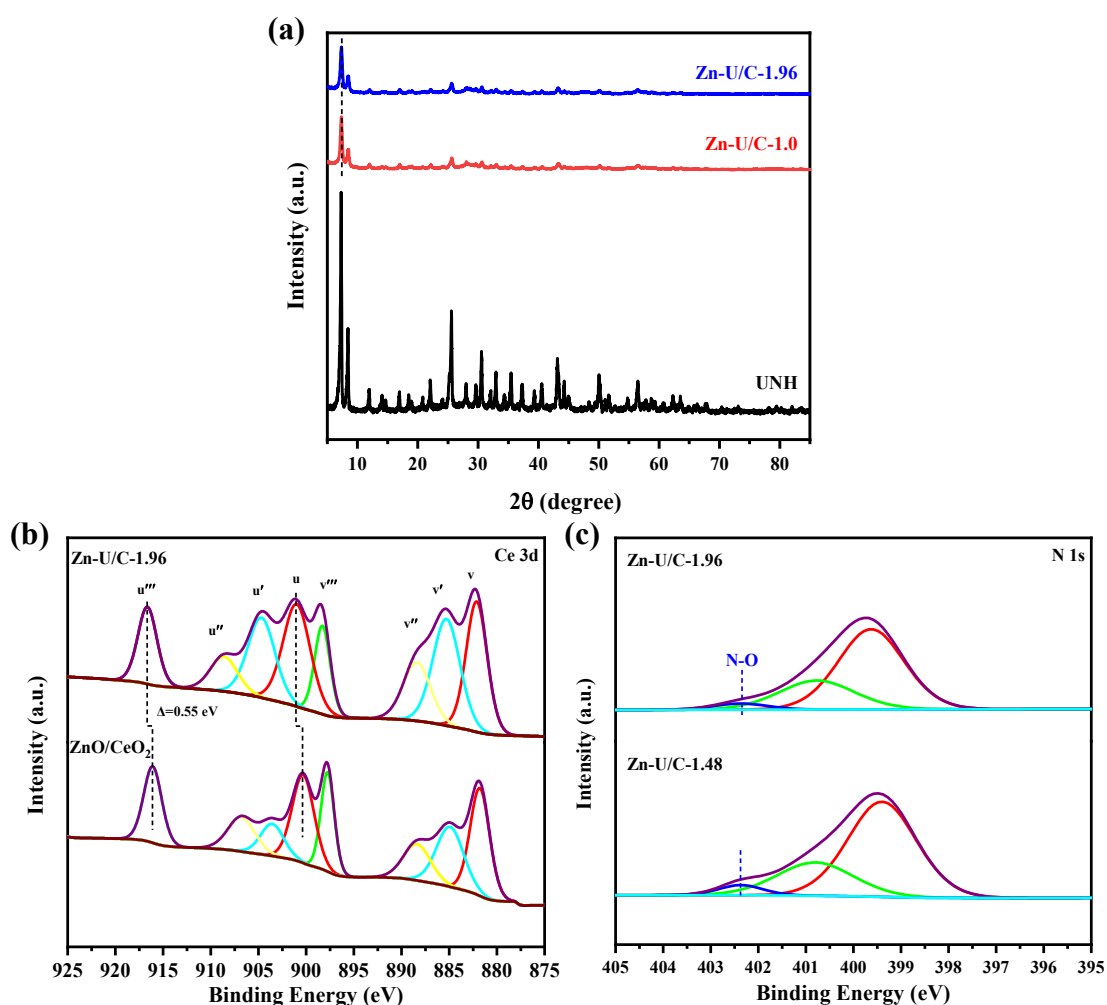


Fig. S2. XRD patterns(a) of pure UNH, Zn-U/C-1.0 and Zn-U/C-1.96, Ce 3d spectra (b) and N 1s spectra (c) of ZnO/CeO₂, Zn-U/C-1.48 and Zn-U/C-1.96.

In order to investigate the effect of the ratio of Zn to Ce in ZnO/CeO₂ on the performance, the mass ratio $m(\text{ZnO}/\text{CeO}_2): m(\text{UNH}) = 1.48$ is kept constant in the experiments, and ZnO/CeO₂ with different values of Zn/Ce molar ratios y ($y = 6.39, 9.17, \text{ and } 11.73$) are obtained by varying the incorporation of ZnO. The catalytic performance of the as-prepared catalysts is shown in **Fig. S3**. It shows a slight decrease in both CO and CH₄ yields of the catalyst material at $y=6.39$ compared to the sample with molar ratio $y=9.17$, with the most apparent decrease in performance when the ratio $y=11.73$, which demonstrates that the Zn to Ce ratio in the material is optimal for the molar ratio of Zn to Ce of $y=9.17$ (the optimal catalyst in this work).

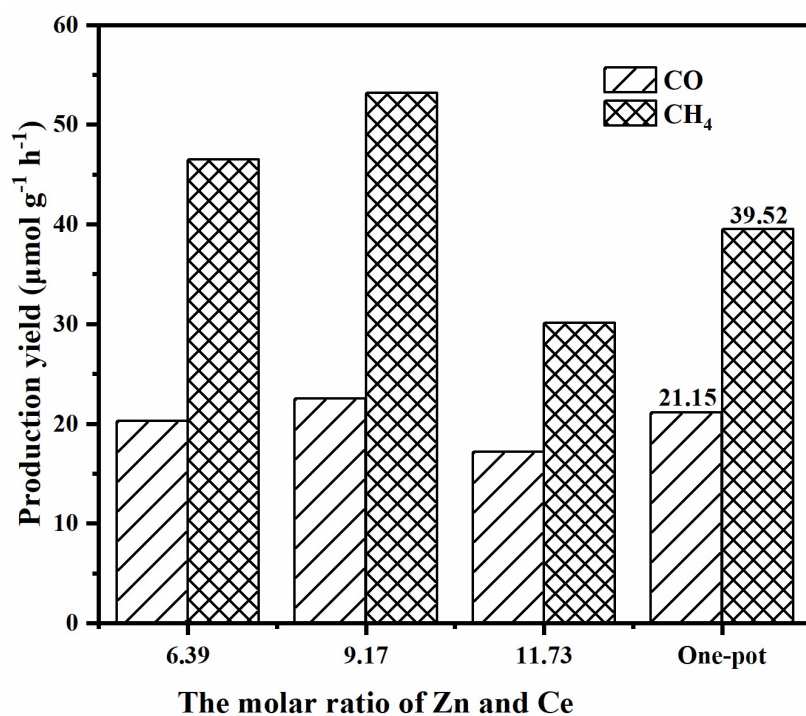


Fig. S3. Effect of Zn/Ce ratio and preparation method on Zn-U/C-1.48 catalyst performance.

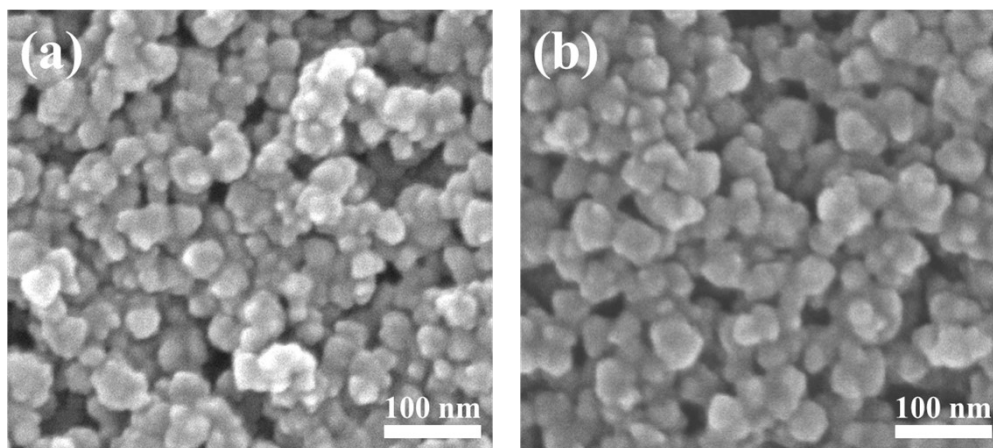
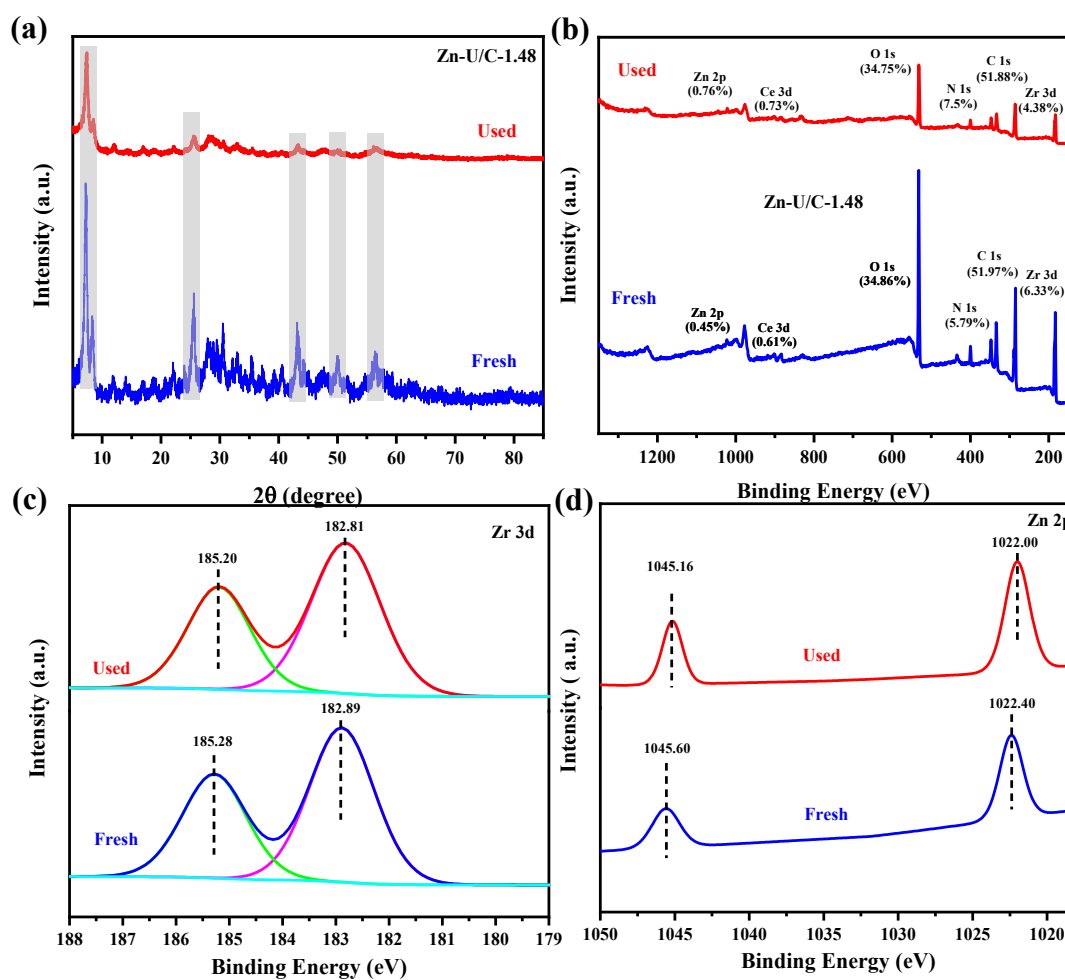


Fig S4. SEM images of fresh and used Zn-U/C-1.48 catalyst.



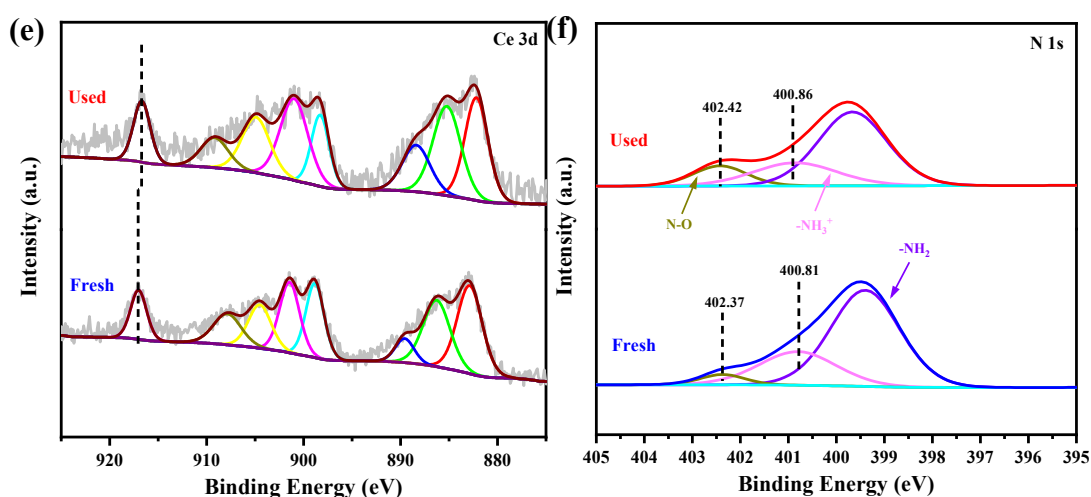


Fig S5. XRD patterns (a) and XPS survey spectra (b), Zr 3d spectra (c), Zn 2p spectra (d), Ce 3d spectra (e) and N 1s spectra (f) of fresh and used Zn-U/C-1.48 catalyst.

Table S1. Comparison of CO₂ photoreduction performance over some reported catalysts and this work.

Catalysts	CO and CH ₄ yields ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	R_{electron} ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	S_{CH_4} (%)	Reducing agent	References
UiO-66-NH ₂ /Cu ₂ O/Cu-0.39	CO: 4.54	9.08	0	H ₂ O	1
f-MoS ₂ @UiO-66-NH ₂	CO: 23.16 CH ₄ : 27.18	263.78	82.44	H ₂ O, MeCN	2
8%NU66/CIS	CO: 11.24 CH ₄ : 2.92	45.84	51	H ₂ O	3
NH ₂ -UiO-66/CuZnS	CO: 22.85	45.7	0	water vapor	4
UNH/Ce (HCOO) ₃ -1.80	CO: 16.45 CH ₄ : 29.4	268.14	84	H ₂ O, TEOA	5
NU/CC-1.6-90	CO: 20.6 CH ₄ : 14	152.8	73	H ₂ O, TEOA	6
UiO-66(NH ₂)/HGN	CO: 31.6 CH ₄ : 1.82	77.8	18.7	H ₂ O, TEOA	7
Zn-U/C-1.48	CO: 22.52 CH ₄ : 53.18	470.51	90.42	H ₂ O, TEOA	This work

References

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