Supporting Information

Assembling CeO_2 nanoparticles on ZIF-8 via hydrothermal method to promote CO_2 photoreduction performances

Yuxin Zhang, Feifan Lang*, Yujie Zhao, Hongwei Hou*

Green Catalysis Center and College of Chemistry, Zhengzhou University, Zhengzhou, 450000, P. R. China
E-mail: houhongw@zzu.edu.cn; flang_cn@foxmail.com

CeO_2 content calculation. The CeO_2 content for the ZIF-8@CeO_2 composites was measured using thermogravimetric analysis.

For the ZIF-8:

$$\frac{m(ZnO)}{m(ZIF{-}8)} = 37.54\%$$

m(ZnO)=0.3754×m(ZIF-8)

For the ZIF-8@CeO_2:

$$\frac{m(ZnO) + m(CeO2)}{m(ZIF{-}8) + m(CeO2)} = 59.81\%$$

$$\frac{0.3754 \times m(ZIF{-}8) + m(CeO2)}{m(ZIF{-}8) + m(CeO2)} = 59.81\%$$

0.3754×m(ZIF-8) + m(CeO_2) = 0.5981×(m(ZIF-8) + m(CeO_2))

0.4019×m(CeO_2) = 0.2227×m(ZIF-8)

m(CeO_2) = 0.55×m(ZIF-8)

$$\frac{m(CeO2)}{m(ZIF{-}8@CeO2)} = \frac{m(CeO2)}{m(ZIF{-}8) + m(CeO2)} = \frac{0.55 \times m(ZIF{-}8)}{m(ZIF{-}8) + 0.55 \times m(ZIF{-}8)} = \frac{0.55}{1 + 0.55} = 35\%$$

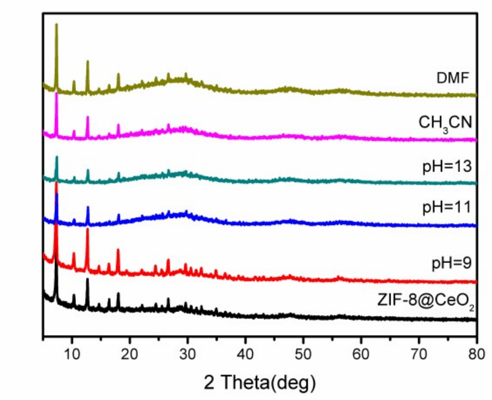

Fig. S1 XRD patterns of the sample ZIF-8@CeO_2 in water with varied pH, or common solvents.

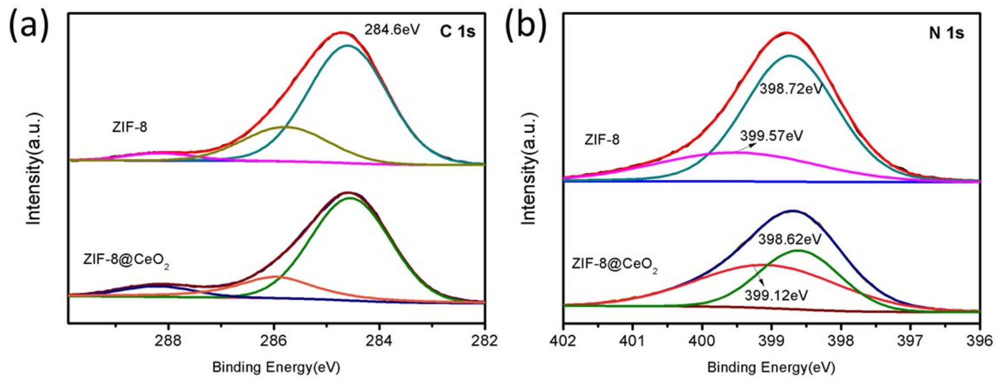

Fig. S2 High-resolution XPS spectra of (a) C 1s and (b) N 1s for samples respectively.

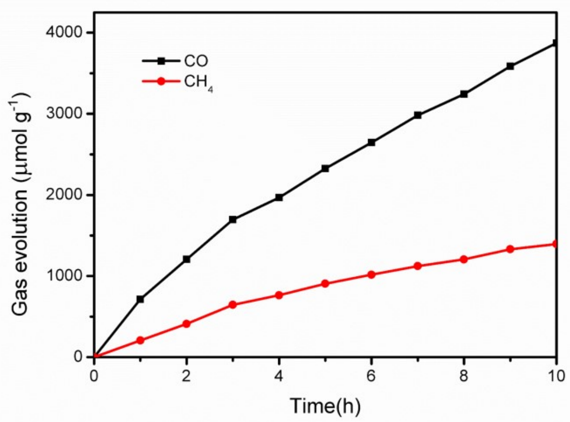

Fig. S3 The long-time performance test of the ZIF-8@CeO_2.

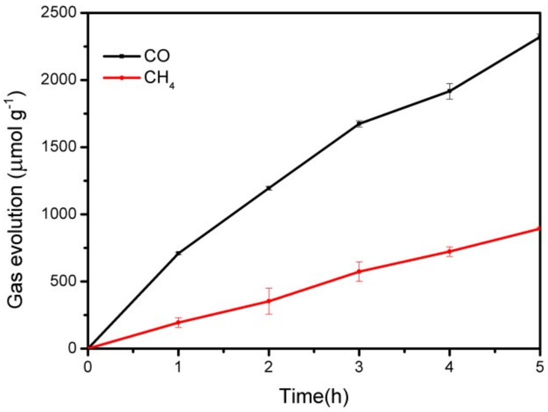

Fig. S4 The error bar of ZIF-8@CeO_2 performance test.

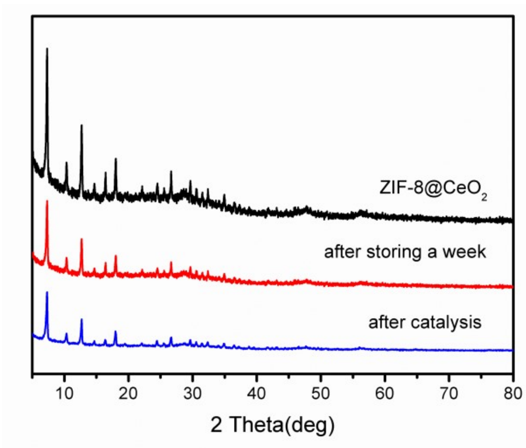

Fig. S5 XRD patterns of the sample pristine ZIF-8@CeO_2, ZIF-8@CeO_2 after storing without protecting from natural light and ZIF-8@CeO_2 after catalysis.

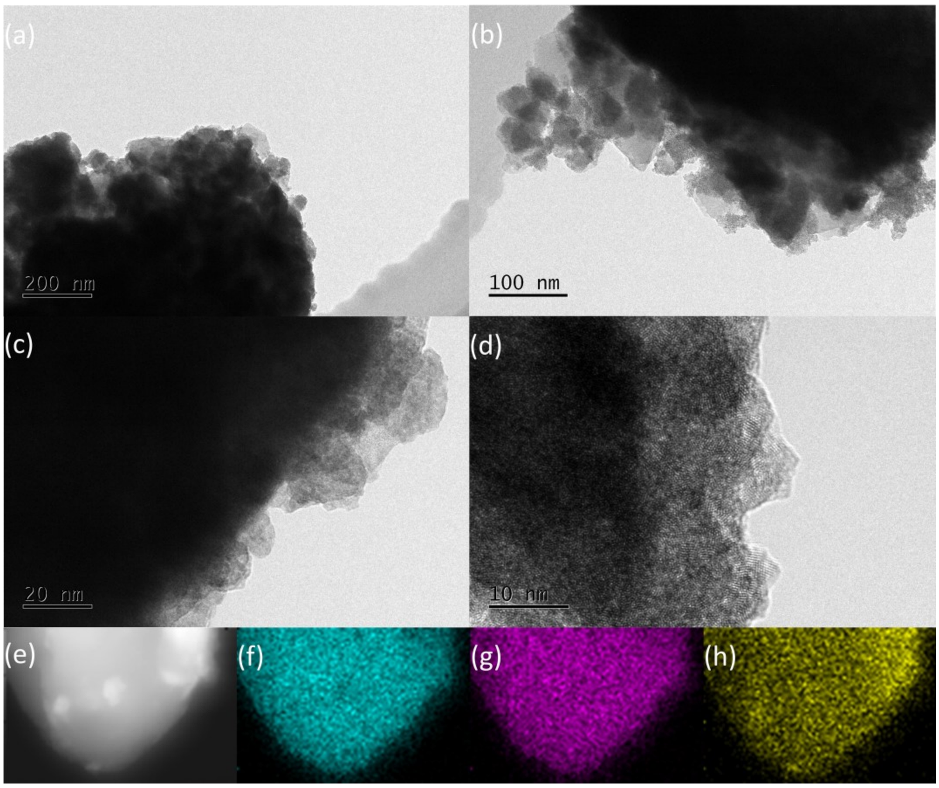

Fig. S6 (a) and (b) The TEM image of the used ZIF-8@CeO_2 composite, (c) and (d) High-magnification TEM image of the used ZIF-8@CeO_2, (e) Scanning TEM image and EDS mapping analysis of (f) Zn (blue), (g) Ce (purple) and (h) O (yellow) of the used ZIF-8@CeO_2.

.

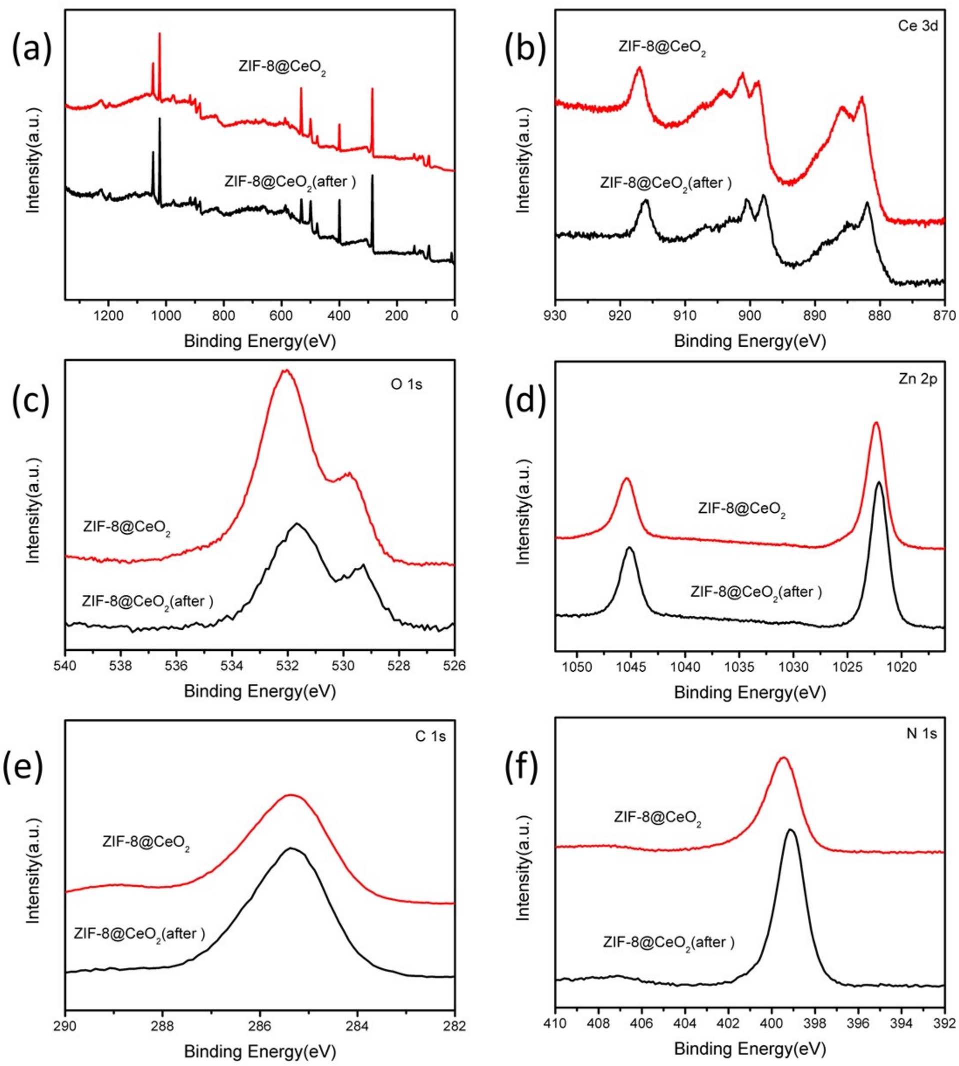

Fig.S7 XPS spectra of ZIF-8@CeO_2 before and after photocatalytic CO_2 reduction reactions.

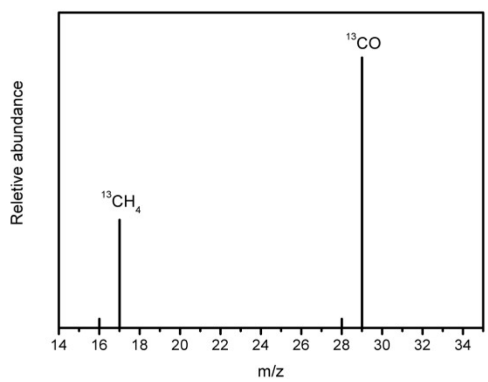

Fig.S8 The mass spectra of $^{13}CH_4$ and ^{13}CO generated under $^{13}CO_2$ atmosphere.

Table S1 Ce 3d XPS data CeO_2 and ZIF-8@CeO_2.

Sample	Ce^{3+}/ (Ce^{3+} + Ce^{4+})	Ce^{4+}/ (Ce^{3+}+Ce^{4+})
CeO2	18.96%	81.04%
ZIF-8@CeO_2	22.76%	77.24%

Table S2 A series of control experiments based on reaction conditions[a]

Catalyst	Solvent	Sacrificial agent	Source of radiation	Reaction	CO/μmol g^{-1} h^{-1}	CH_4/μmol g^{-1} h^{-1}
ZIF-8	H_2O	TEOA	200nm<λ<800nm	CO_2	378.86	138.64
ZIF-8	H_2O	TEOA	in the dark	CO_2	n.d[a]	n.d
ZIF-8	H_2O	TEOA	200nm<λ<800nm	Ar	n.d	n.d
ZIF-8	H_2O	—	200nm<λ<800nm	CO_2	11.80	n.d
ZIF-8	H_2O	TEA	200nm<λ<800nm	CO_2	10.78	n.d
ZIF-8	CH_3CN	TEOA	200nm<λ<800nm	CO_2	9.48	n.d
—	H_2O	TEOA	200nm<λ<800nm	CO_2	122.73	38.39
MOF-808	H_2O	TEOA	200nm<λ<800nm	CO_2	275.68	109.05
MIL-101(Cr)	H_2O	TEOA	200nm<λ<800nm	CO_2	427.52	137.20
ZIF-67	H_2O	TEOA	200nm<λ<800nm	CO_2	378.63	136.89

[a]Not detectable.

Table S3 A series of control experiments of ZIF-8@CeO_2 based on reaction conditions.

Catalyst	Solvent	Sacrificial agent	Source of radiation	Reaction	CO/μmol g^{-1} h^{-1}	CH_4/μmol g^{-1} h^{-1}
ZIF-8@CeO_2	H_2O	TEOA	200nm<λ<800nm	CO_2	465.01	181.27
ZIF-8@CeO_2	H_2O	TEOA	in the dark	CO_2	n.d[a]	n.d
ZIF-8@CeO_2	H_2O	TEOA	200nm<λ<800nm	Ar	n.d	n.d
Physical mixture of ZIF-8 and CeO_2	H_2O	TEOA	200nm<λ<800nm	CO_2	306.04	114.79

[a]Not detectable.

Table S4 The CO_2 photoreduction performance compared with reported works.

Photocatalyst	Light source/ Solvent/ Sacrificial agent	Major products evolution rate	Reference
CeO_2@ZIF-8	H_2O/TEOA=5:1	CO 465.01 μmol g^{-1} h^{-1} CH_4 181.27 μmol g^{-1} h^{-1}	This study
TiO_2/AuCu/ZIF-8	H_2O	CO 82.99μmol g^{-1} h^{-1} CH_4 3.91 μmol g^{-1} h^{-1}	*Nano Energy 62 (2019) 426–433*
ZIF-8@TiO_2	H_2O(g)	CO 10.512 μmol g^{-1} h^{-1} H_2 7.2 μmol g^{-1} h^{-1}	*Applied Catalysis B: Environmental 270 (2020) 118856*
CeO_2/ATP	NaOH solution /CH_3CN	CO 309.44 μmol g^{-1} h^{-1} CH_4 184.33 μmol g^{-1} h^{-1}	*Catal. Sci. Technol., 2019, 9, 3788–3799 | 3795*
Co-ZIF-9/TiO_2	H_2O(g)	CO 17.58 μmol g^{-1} h^{-1} CH_4 1.98 μmol g^{-1} h^{-1} H_2 2.6 μmol g^{-1} h^{-1}	*J. Mater. Chem. A, 2016, 4, 15126–15133*
TiO_2/UiO-66	H_2O(g)	CO 1.9 μmol g^{-1} h^{-1} CH_4 17.9 μmol g^{-1} h^{-1}	*Applied Catalysis B: Environmental 270 (2020) 118856*
ZnO/ZIF-8	H_2O	CH_3OH 6843 μmol g^{-1} h^{-1}	*Journal of CO2 Utilization 43 (2021) 101373*
Ni@CdS⊂Zn/Co-ZIF-8	H_2O/TEOA	CO 307.9 μmol g^{-1} h^{-1} H_2 1731.4 μmol g^{-1} h^{-1}	*ACS Appl. Mater. Interfaces 2022, 14, 28123−28132*