

## Electronic Supplementary Information

One-pot fabrication of double Z-scheme  $\text{CeCO}_3\text{OH/g-C}_3\text{N}_4/\text{CeO}_2$  photocatalyst for  
nitrogen fixation under solar irradiation

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**Table S1** The content of elements in CN and 2Ce-CN.

Element content (wt. %)	CN	2Ce-CN
Ce	0	13.2
C	34.8	26.1
N	61.7	44.0
O	4.1	13.68
H	2.0	1.8
C/N	0.56	0.59

**Table S2** The binding energy summary of XPS.

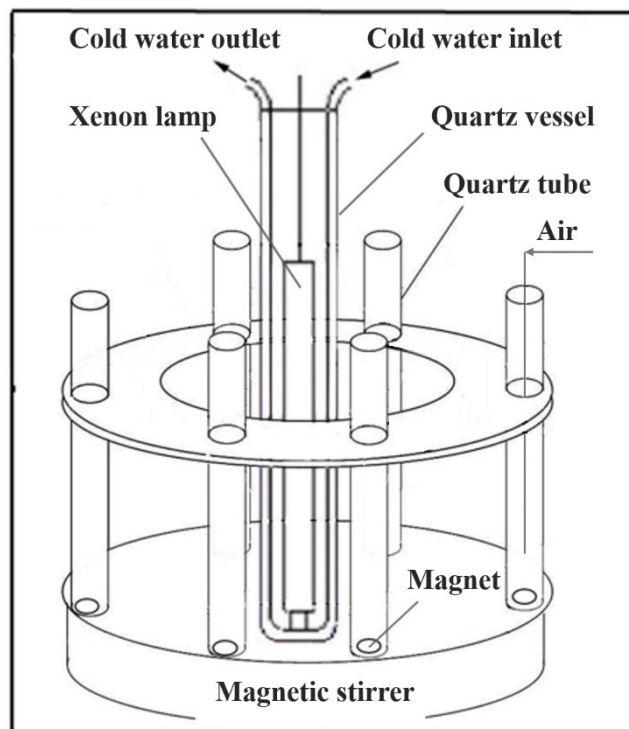
Peak	Binding Energy (eV)				
	CN	CeO <sub>2</sub>	CeCO <sub>3</sub> OH	2Ce-CN	
Ce	v	-	882.3	-	-
	v <sub>0</sub>	-	-	882.1	882.0
	v <sub>1</sub>	-	884.7	885.8	885.6
	v <sub>2</sub>	-	888.8	-	-
	v <sub>3</sub>	-	898.1	-	897.8↓
	u	-	900.8	-	-
	u <sub>0</sub>	-	-	900.2	900.4↑
	u <sub>1</sub>	-	903.3	904.2	904.0
	u <sub>2</sub>	-	907.3	-	-
	u <sub>3</sub>	-	916.6	-	916.1↓
O	Ce-O	-	529.4	-	529.0↓
	O <sub>2</sub> <sup>-</sup> / O <sup>-</sup>	-	531.2	-	-
	CO <sub>3</sub> <sup>2-</sup>	-	-	531.6	531.6
	H <sub>2</sub> O	-	-	532.2	532.2
C	CO <sub>3</sub> <sup>2-</sup>	-	-	289.9	289.9
	N-C=N	288.4	-	-	288.4
	C <sub>Calibration</sub>	284.8	-	284.8	284.8
N	C-N=C	398.8	-	-	398.6↓
	N-(C) <sub>3</sub>	399.7	-	-	399.5↓
	C-N-H	400.9	-	-	400.9

**Table S3** BET and pore volume information of CN, CeCO<sub>3</sub>OH, CeO<sub>2</sub>, CeO<sub>2</sub>-CN, and 2Ce-CN.

Samples	CN	CeCO <sub>3</sub> OH	CeO <sub>2</sub>	CeO <sub>2</sub> -CN	2Ce-CN
BET Surface Area (m <sup>2</sup> /g)	7.24	17.43	9.34	14.74	61.14
Pore Volume (cm <sup>3</sup> /g)	0.056	0.017	0.047	0.086	0.208

**Table S4** Kinetic analysis of emission decay for CN, CeO<sub>2</sub>-CN, and 2Ce-CN.

Sample	CN	CeO <sub>2</sub> -CN	2Ce-CN
$\tau_1$ (ns)	1.59	1.28	3.02
Rel (%)	100	41.11	47.48
$\tau_2$ (ns)	-	4.74	7.54
Rel (%)	-	47.25	28.65
$\tau_3$ (ns)	-	25.61	37.67
Rel (%)	-	11.63	23.87
$\tau$ (ns)	1.59	5.73	12.55
$\chi^2$	1.071	1.29	1.079



**Fig. S1** Photocatalytic nitrogen fixation reaction device

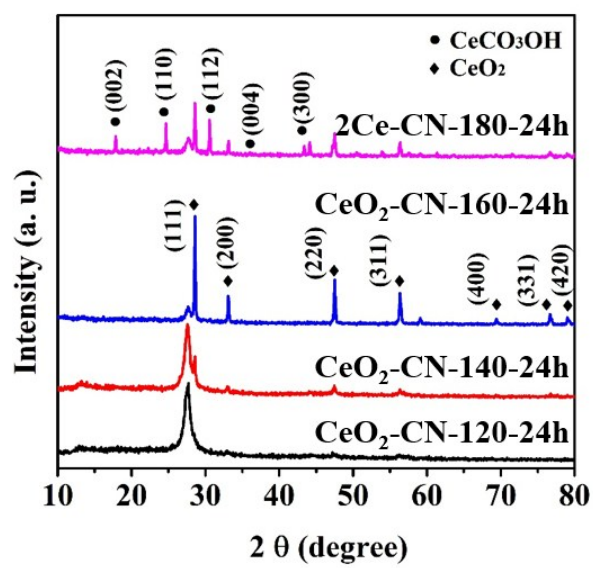
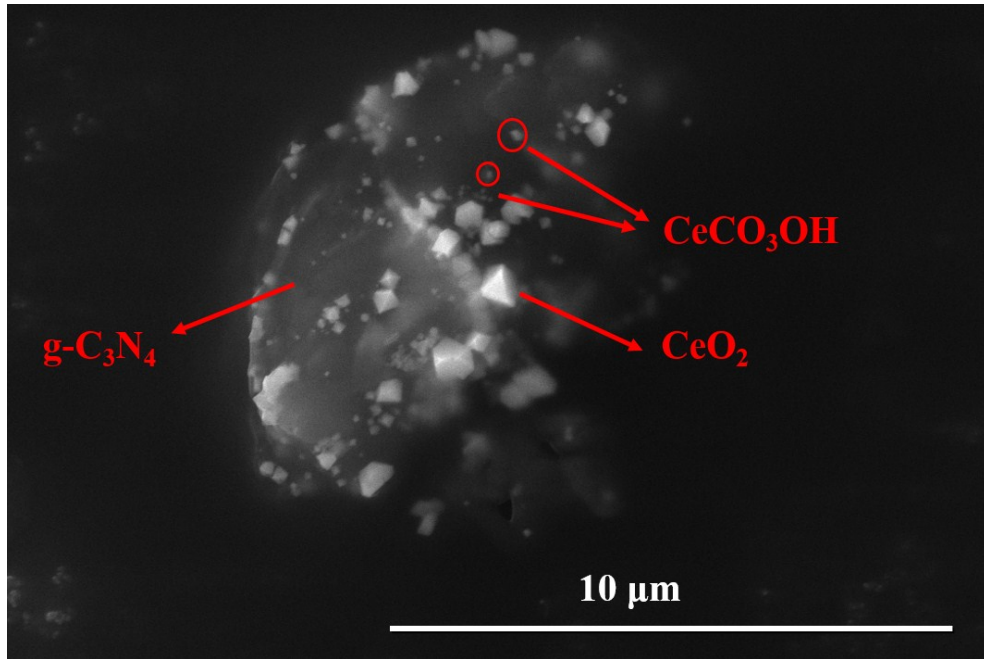
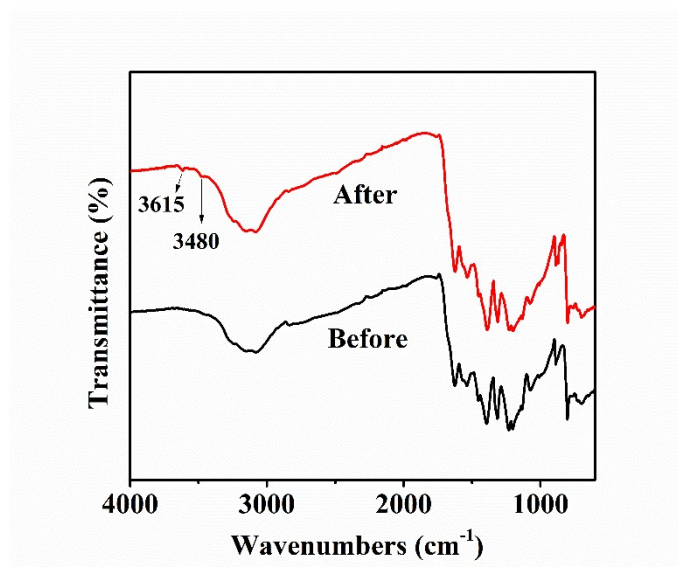


Fig. S2 XRD diffraction patterns of CeO<sub>2</sub>-CN and 2Ce-CN prepared in different temperature.

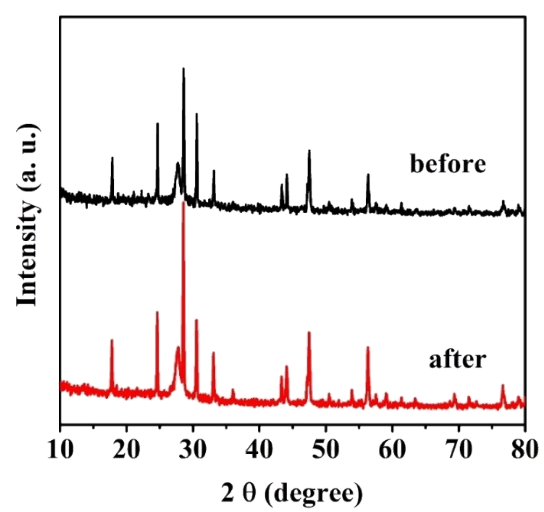


**Fig. S3** SEM image of 2Ce-CN.

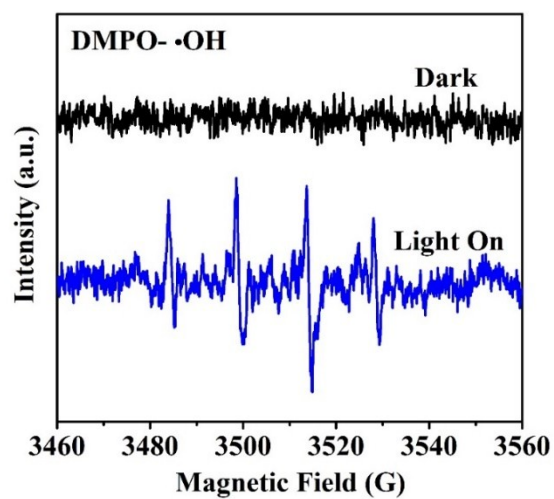




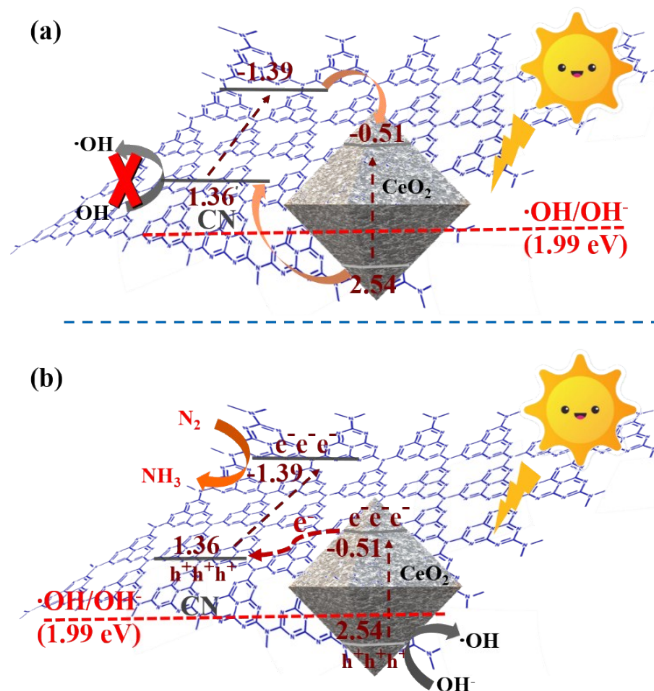
**Fig. S4** FT-IR spectra of 2Ce-CN before and after reaction.



**Fig. S5** XRD patterns of 2Ce-CN before and after being used.



**Fig. S6** The EPR spectra of DMPO-•OH in the presence of CeO<sub>2</sub>-CN.



**Fig. S7** Proposed mechanism for charge transfer path over CeO<sub>2</sub>-CN: traditional model (a) and Z-scheme model (b).

The possible charge transfer process over CeO<sub>2</sub>-CN is proposed in Fig S3. In the hypothetical process shown in Fig. S7a, under light irradiation, the holes on the VB of CeO<sub>2</sub> would transfer to that of CN, while the electrons on the CB of CN would transfer towards that of CeO<sub>2</sub>. However, the oxidation levels of CN (1.36) were lower than the standard redox potential of ·OH/OH<sup>-</sup> (1.99 eV). Therefore, the accumulated holes in the VB of CN cannot react with OH<sup>-</sup> to form ·OH. This is not consistent with the experimental results that ·OH was generated in this photocatalytic process. As shown in Fig. S6, EPR spin-trap tests over CeO<sub>2</sub>-CN with DMPO in water gave rise to the characteristic peaks of the DMPO-hydroxyl radical (·OH) moiety, which suggested that ·OH was generated in the photocatalytic process.

Another mechanism is therefore proposed. In the staggered band heterostructure of CeO<sub>2</sub>-CN shown in Fig. S7b, electrons generated in CeO<sub>2</sub> transferred to the VB of CN as a result of the inner electric field, and subsequently recombined with holes. Thus, nitrogen reduction occurred at the CB of CN, meanwhile, ·OH formed at the VB of CeO<sub>2</sub>. This constituted a Z-scheme heterojunction model.

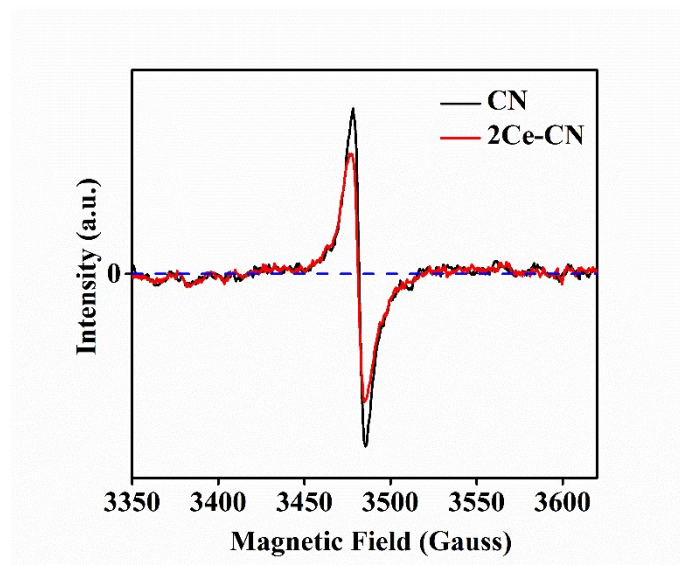


Fig. S8 EPR spectra of CN and 2Ce-CN.