Supporting information

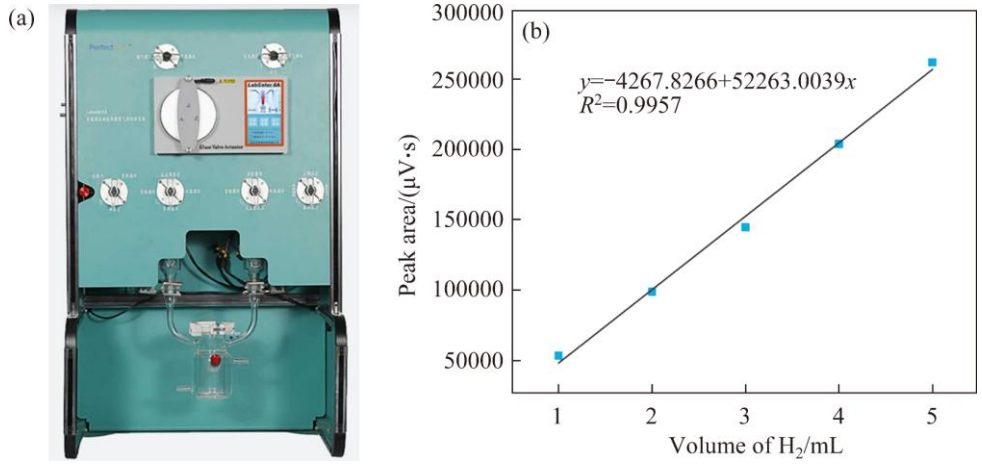

Figure S1 (a) Photocatalytic all-glass closed gas system (Labsolar-6A, PerfectLight); (b) Calibration curve of photocatalytic H_2 evolution

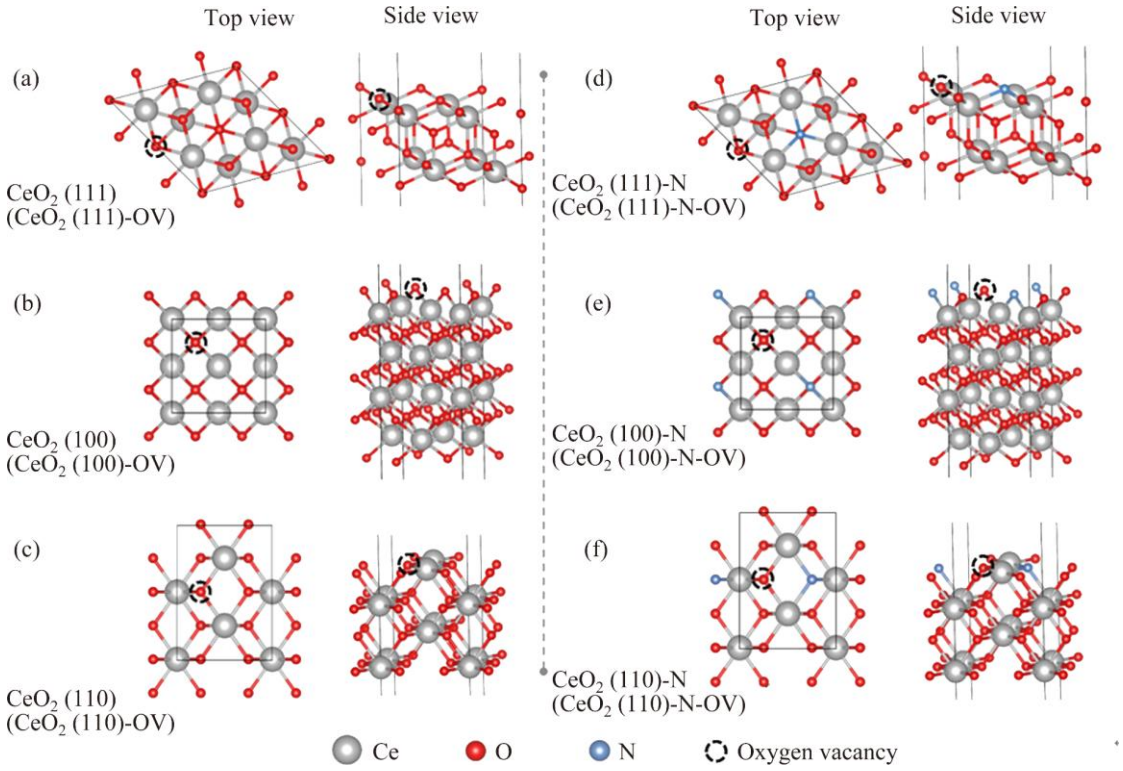

Figure S2 The top and side views of constructed CeO_2 (111), (100), and (110) surfaces

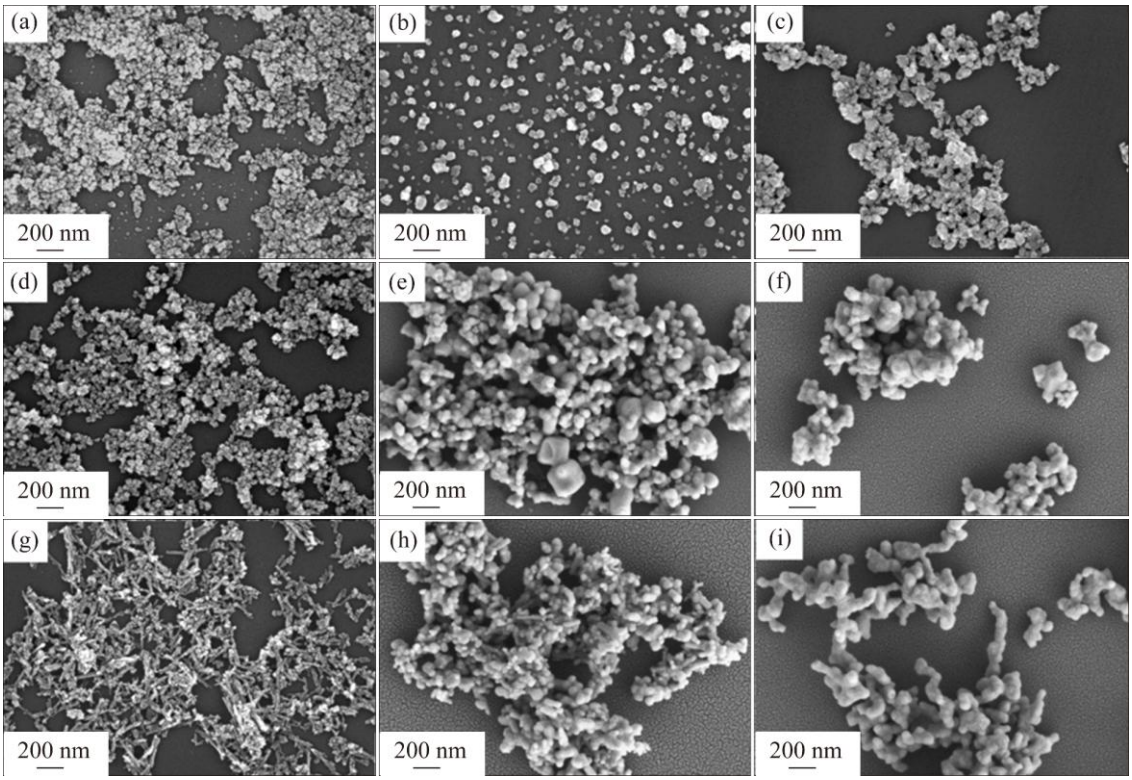

Figure S3 SEM images of P-CeO_2 (a), P-CeO_2-N_2 (b), and P-CeO_2-NH_3 (c), C-CeO_2 (d), C-CeO_2-N_2 (e), and C-CeO_2-NH_3 (f), R-CeO_2 (g), R-CeO_2-N_2 (h), and R-CeO_2-NH_3 (i)

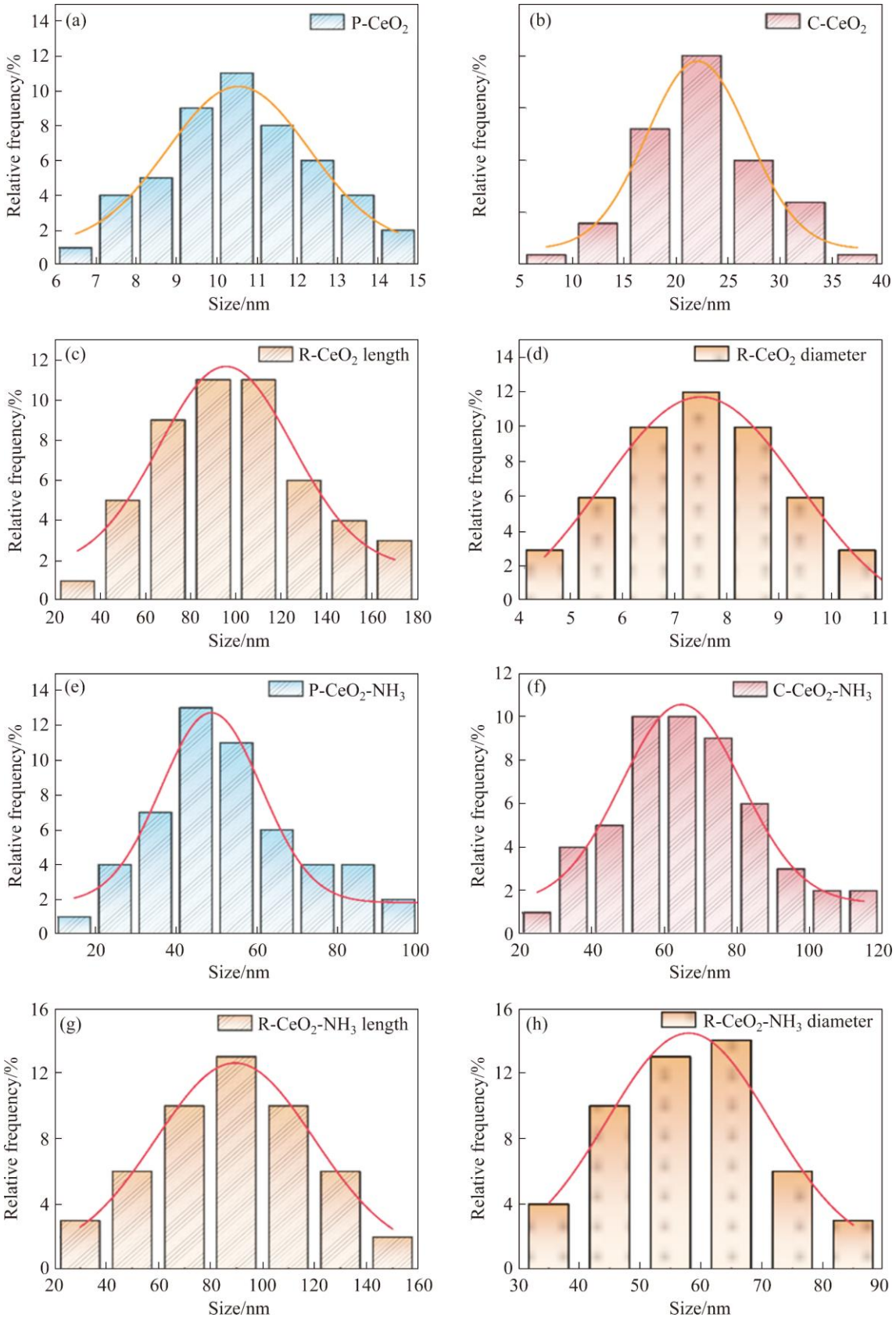

Figure S4 Particle size distribution of P-CeO_2 (a), C-CeO_2 (b), R-CeO_2 (c, d), P-CeO_2-NH_3 (e), C-CeO_2-NH_3 (f), and R-CeO_2-NH_3 (g, h)

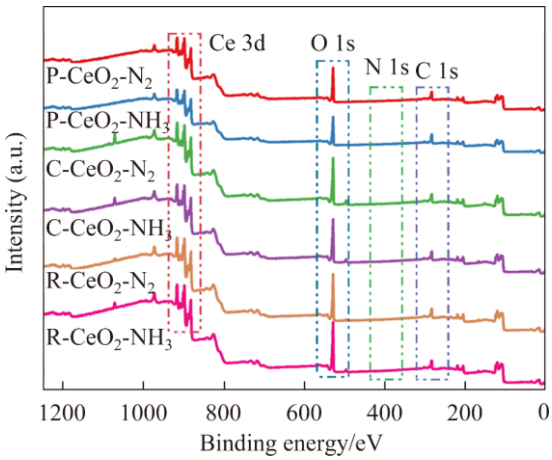

Figure S5 XPS spectra of prepared CeO_2

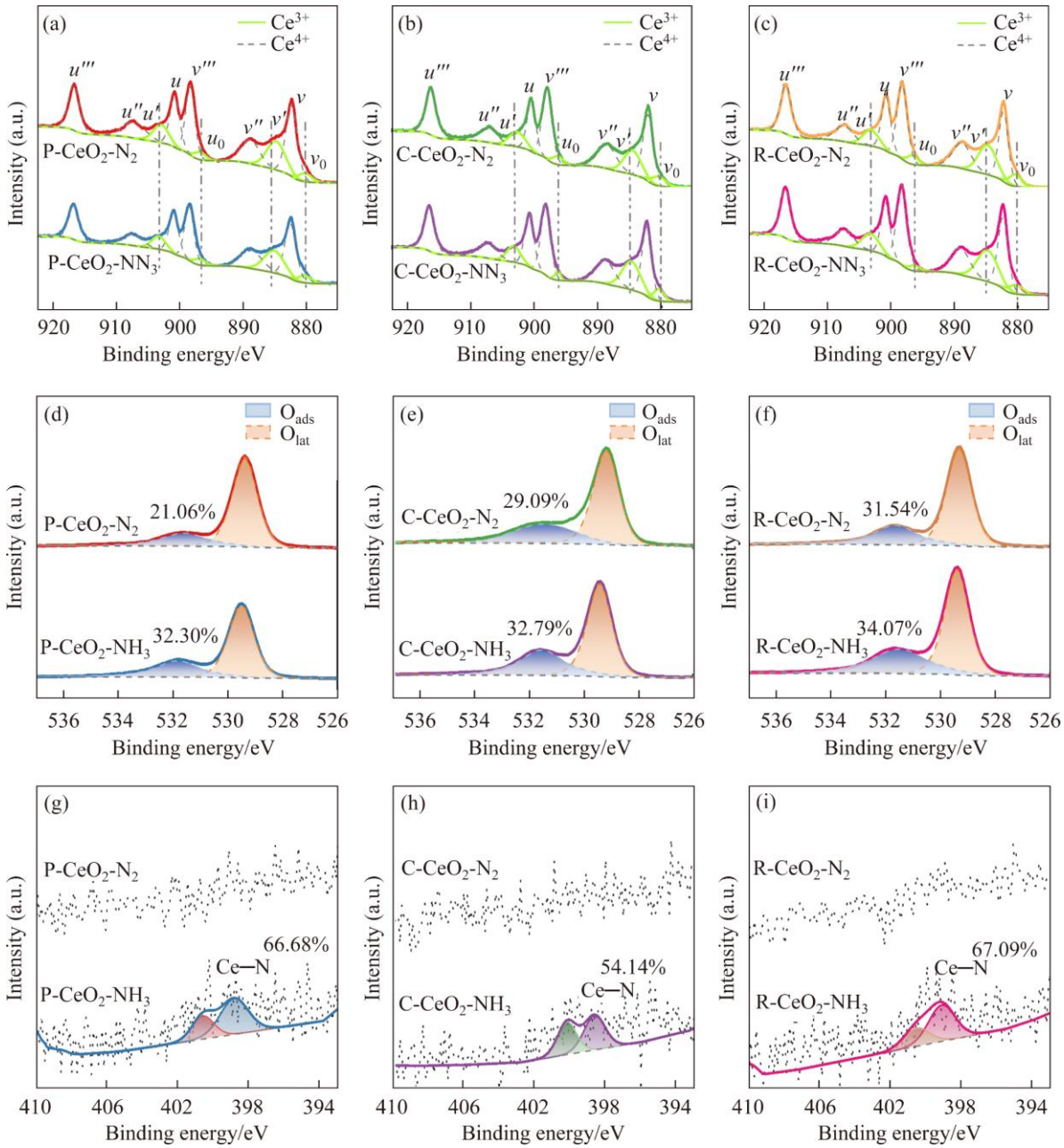

Figure S6 XPS results of the Ce 3d (a–c), O 1s (d–f), and N 1s (g–i) of N-doped CeO_2

The percentage of Ce^{3+} and O_{ads} can be calculated by the following formula [1]:

$$C_{Ce^{3+}} = \frac{\text{Peak area}(v_0, u_0, v', u')}{\text{Total peak area}} \times 100\%$$

$$C_{O_{ads}} = \frac{\text{Peak area}(O_{ads})}{\text{Total peak area}} \times 100\%$$

$$C_{(Ce\text{-}N)} = \frac{\text{Peak area}(Ce\text{-}N)}{\text{Total peak area}} \times 100\%$$

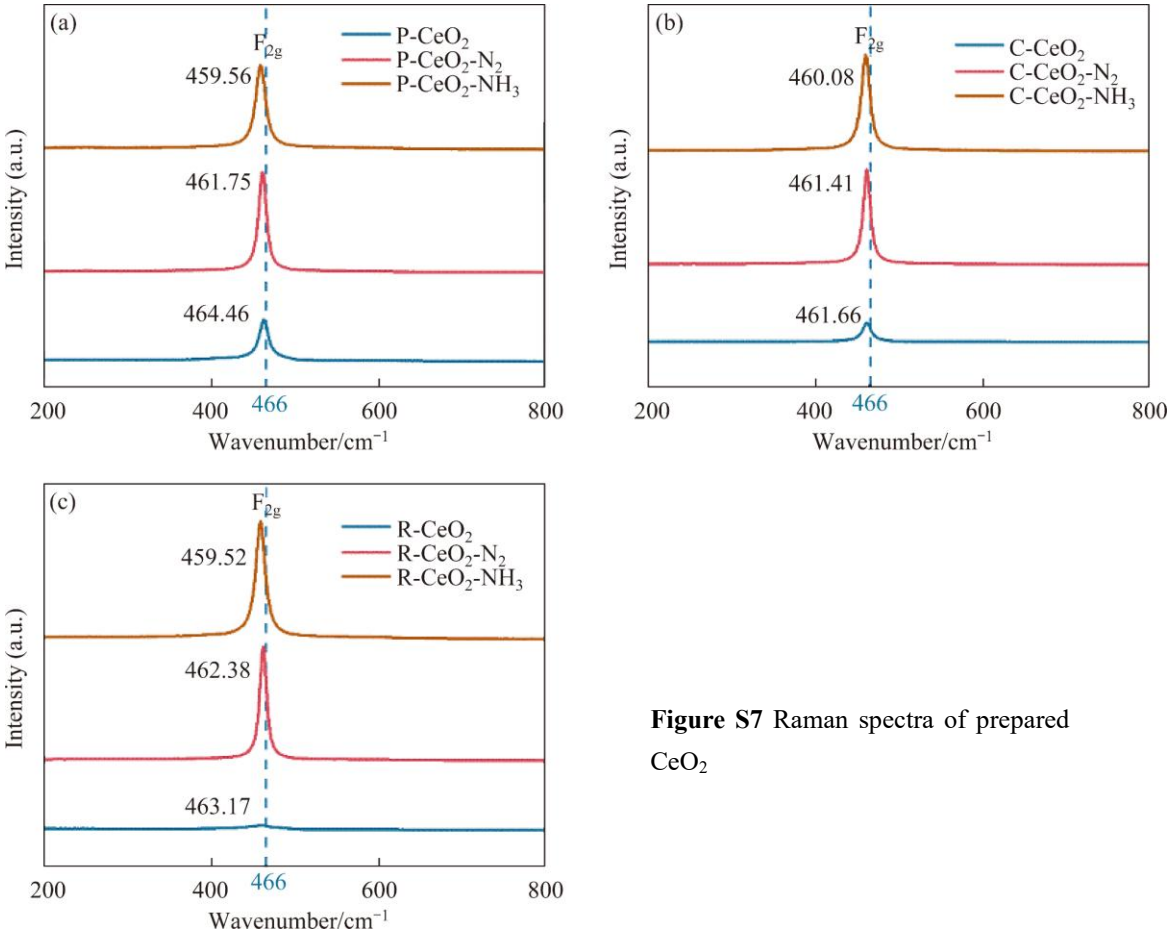

Figure S7 Raman spectra of prepared CeO_2

Due to the low concentration of the organic solution and weak adsorption, the photocatalytic kinetics followed the Langmuir-Hinshelwood model (L-H model) is [2]:

$$\ln\frac{c_0}{c} = kt$$

where k is the apparent rate constant, and t is the photocatalytic reaction time.

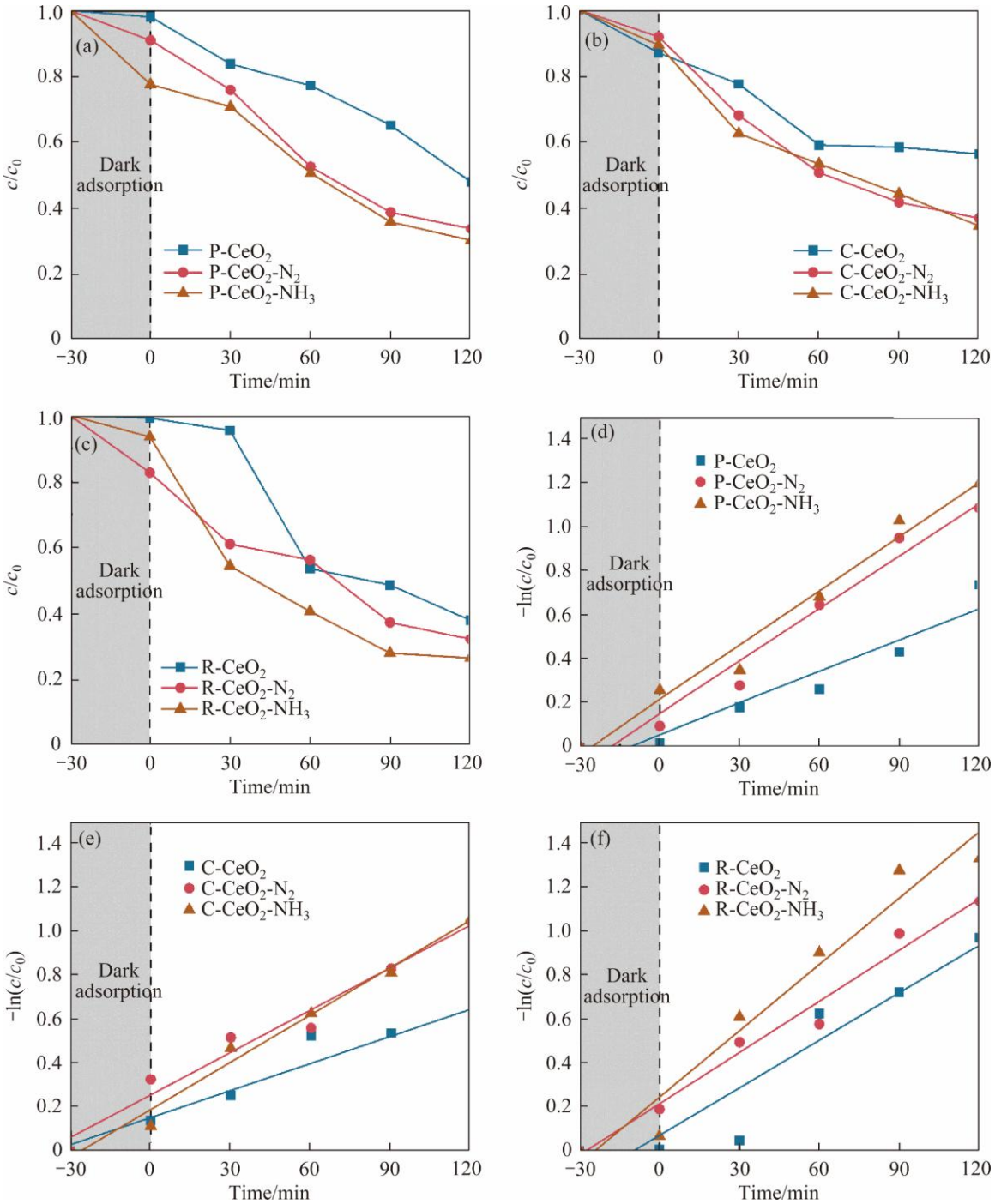

Figure S8 The photodegradation efficiency (c/c_0) and the fitted kinetics curves of TC by prepared CeO_2

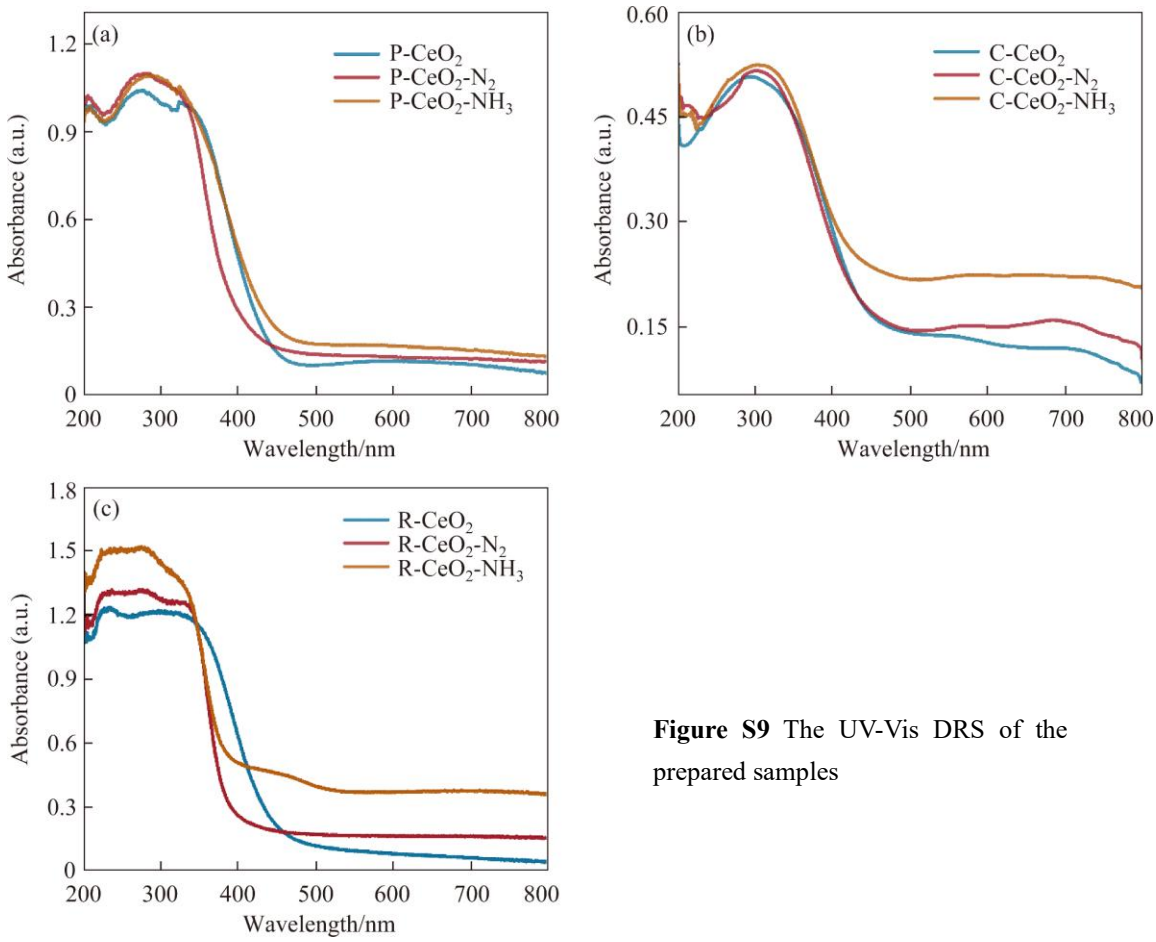

Figure S9 The UV-Vis DRS of the prepared samples

The band gap is calculated by Tauc's formula [3]:

$(\alpha hv)^n = A(hv - E_g)$

where α, h, v, A and E_g represent the absorption coefficient, Planck's constant, photon frequency, proportionality constant, and band gap of a semiconductor, respectively, and the value of n for CeO_2 with a direct band gap is 2 [4].

Then, the valence band (E_{vb}) can be calculated by formula:

$E_{vb} = E_{cb} + E_g$

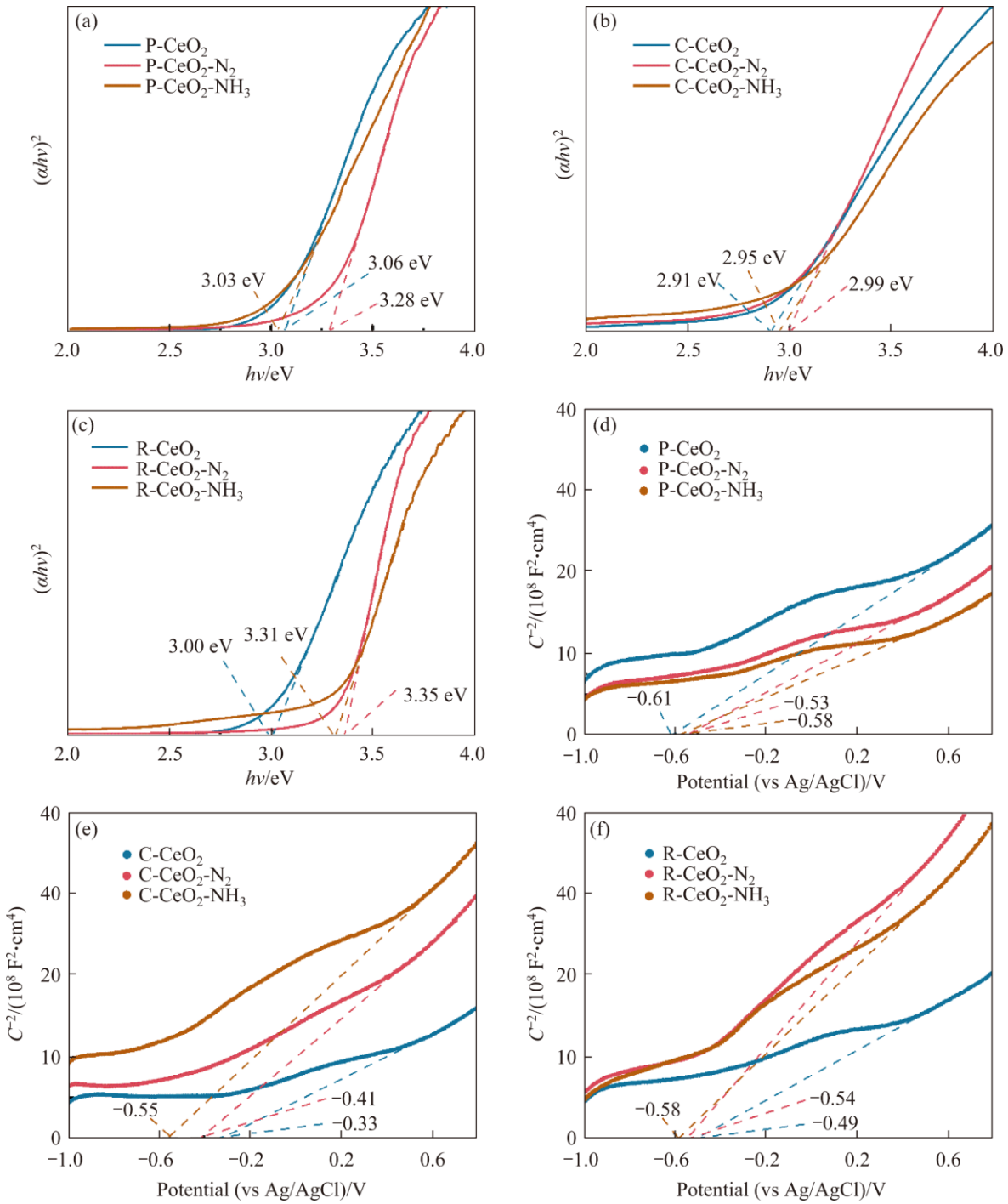

Figure S10 The Kubelka-Munk plots (a–c) and Mott-Schottky plots (d–f) of the prepared samples (*C* is the electric capacity)

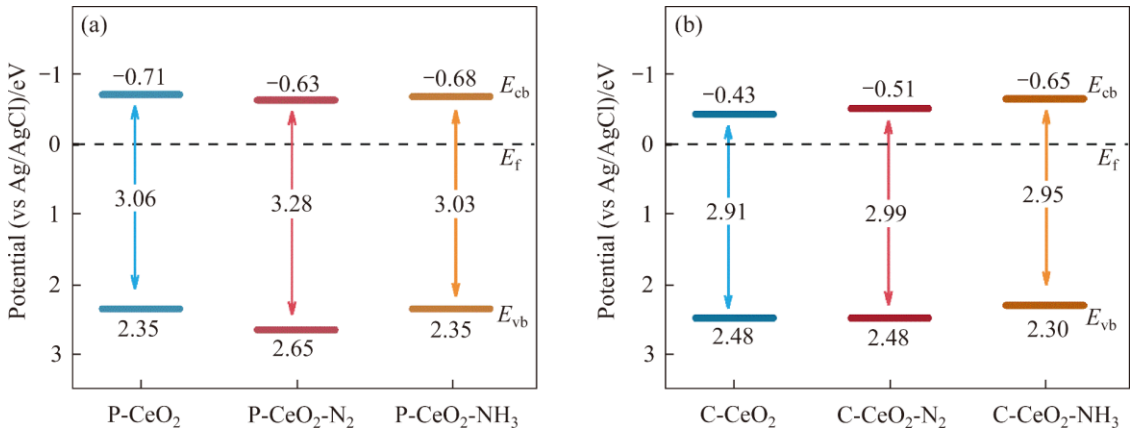

Figure S11 The potential diagrams of band structures of P-CeO_2 (a) and C-CeO_2 (b) systems

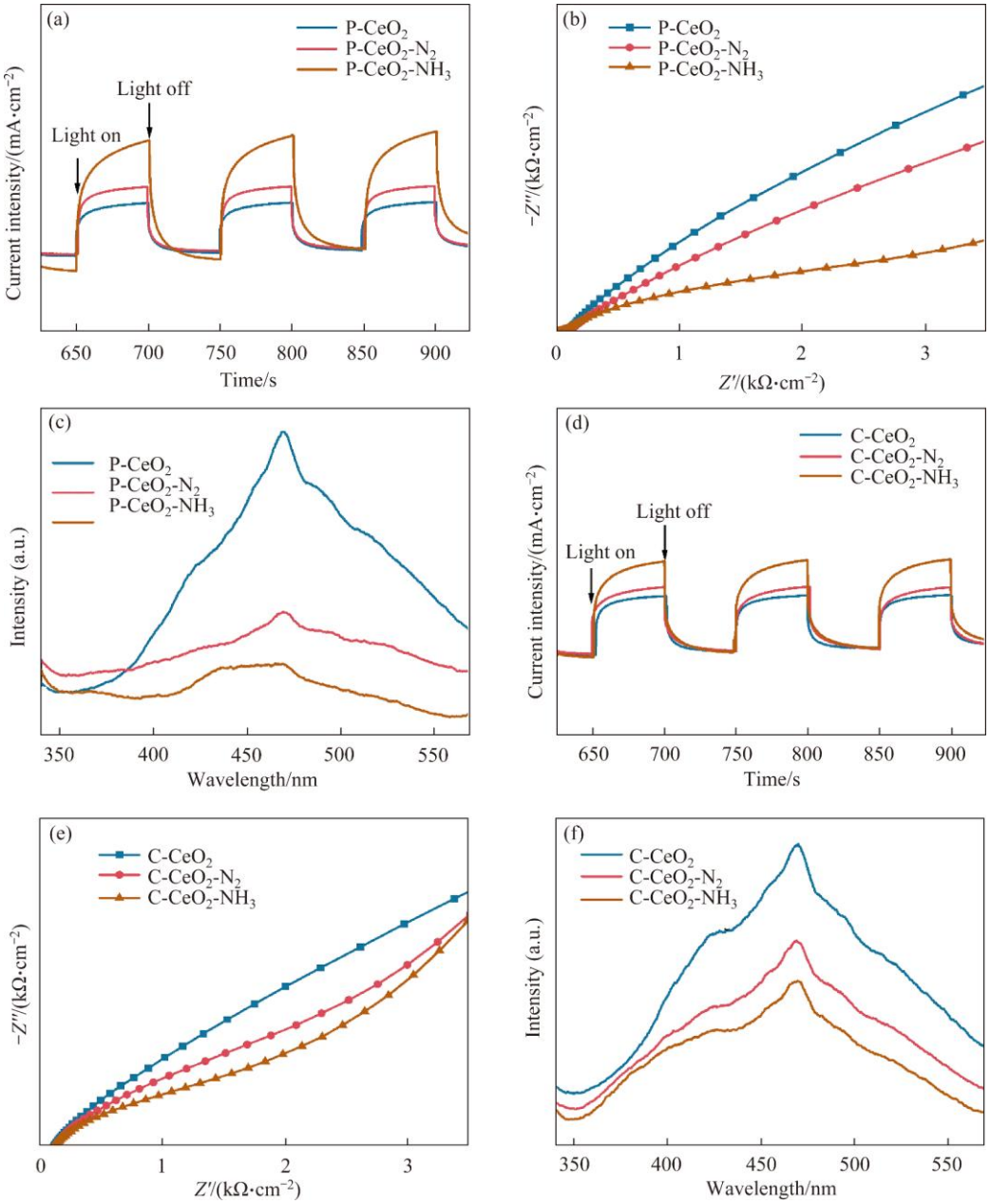

Figure S12 The photocurrent curves (a and d), impedance spectra (b and e), and PL spectra (c and f) of samples

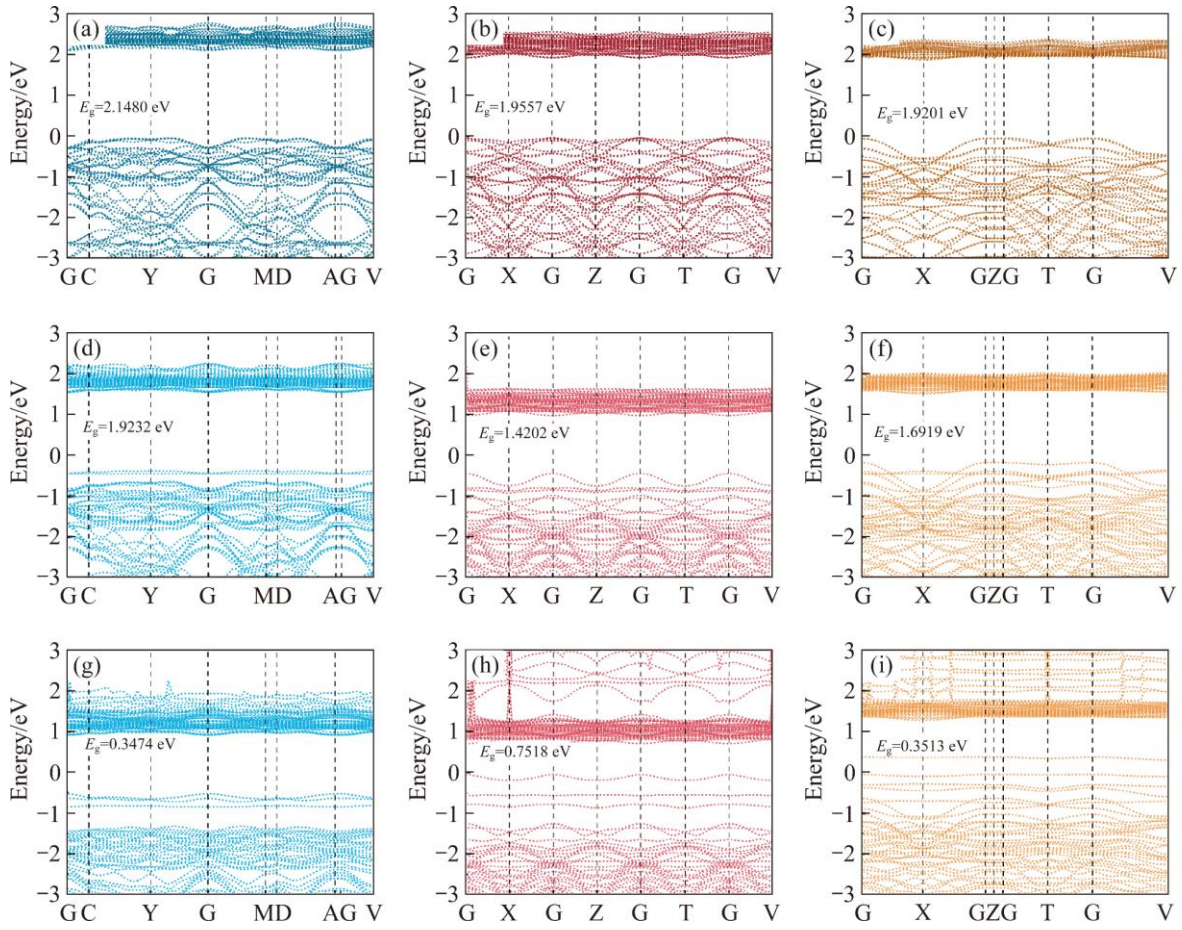

Figure S13 Band structures of CeO_2 (111) (a), CeO_2 (100) (b), CeO_2 (110) (c), CeO_2 (111)-N (d), CeO_2 (100)-N (e), CeO_2 (110)-N (f), CeO_2 (111)-N-OV (g), CeO_2 (100)-N-OV (h), CeO_2 (110)-N-OV (i)

Table S1 The calculated Ce^{3+}, O_{ads} and Ce-N contents of XPS results

Sample	c_{Ce3+}/%	c_{Oads}/%	c_{Ce-N}/%
P-CeO_2-N_2	23.48	21.06	—
P-CeO_2-NH_3	24.35	32.30	66.68
C-CeO_2-N_2	22.30	29.09	—
C-CeO_2-NH_3	23.33	32.79	54.14
R-CeO_2-N_2	24.30	31.54	—
R-CeO_2-NH_3	25.08	34.07	67.09

Table S2 The DFT calculated energy of surface models and formation energy of the doped system

Sample	E_{surf-N}/eV	E_{surf}/eV	E_O/eV	E_N/eV	E_{form}/eV
CeO_2 (111)	−189.8195	−191.7122			3.2857
CeO_2 (100)	−188.4499	−190.2218	−1.6278	−3.0208	3.1649
CeO_2 (110)	−189.0781	−190.8074			3.1223

Table S3 The DFT calculated energy of surface models and formation energy of oxygen vacancy

Sample	E_{surf}/eV	$E_{surf\text{-}OV}$/eV	$\frac{1}{2}E_{O_2}$/eV	E_{OV}/eV
CeO_2 (111)	−191.7122	−184.8496	−4.8893	1.9733
CeO_2 (111)-N	−189.8195	−183.3776		1.5526
CeO_2 (100)	−190.2218	−183.4457		1.8868
CeO_2 (100)-N	−188.4499	−182.0358		1.5248
CeO_2 (110)	−190.8074	−183.8746		2.0435
CeO_2 (110)-N	−189.0781	−182.7026		1.4862

References

[1] WANG Fan, LI Jun-qi, CHEN Chao-yi, et al. Enhancement effects of surface and bulk oxygen vacancies on the photocatalytic properties of ceria [J]. Molecular Catalysis, 2023, 549: 113507. DOI: 10.1016/j.mcat.2023.113507.

[2] LIU Bao-shun, ZHAO Xiu-jian, TERASHIMA C, et al. Thermodynamic and kinetic analysis of heterogeneous photocatalysis for semiconductor systems [J]. Physical Chemistry Chemical Physics, 2014, 16(19): 8751−8760. DOI: 10.1039/c3cp55317e.

[3] ABOU EL-ENEIN S A, ALI A M, ABDEL-MONEM Y K, et al. Novel lanthanide(III) 4-methylbenzoylhydrazide complexes as precursors for lanthanide oxide nanophotocatalysts [J]. RSC Advances, 2019, 9(72): 42010−42019. DOI: 10.1039/c9ra08080e.

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