Supplementary Information

Photocatalytic C-N coupling toward urea synthesis with Palladium-Supported CeO_2 Catalyst

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Experimental Procedures

Synthesis of CeO_2

CeO_2 nanorods were synthesized via a hydrothermal method[1]. Typically, 0.6513g of $Ce(NO_3)_3 \cdot 6H_2O$ was dissolved in 30 mL of NaOH aqueous solution (6 mol/L) under stirring at room temperature. The mixed solution was magnetically stirred for 1 h at room temperature and then transferred into a100 mL of Teflon-lined stainless steel autoclave. Subsequently, the autoclave was hydrothermally treated at 100 ℃ for 24 h and cooled down to room temperature naturally. The resulting precipitation was collected and washed with DI water and ethanol for several times. Then dried in vacuum at 70 ℃ overnight and the obtained yellow powder was calcined in air at 400 ℃ for 4 h with a ramping rate of 5 ℃/min.

Synthesis of Pd-CeO_2 catalysts

Pd-CeO_2 catalysts were synthesized by the deposition−precipitation method[2]. Ceria nanorods (0.3 g) were dispersed in 80 mL of deionized water and the calculated amount of palladium chloride was dissolved in 20 mL deionized water. Afterwards, a certain amount of $PdCl_2$ aqueous solution was added into the suspension at 50 ℃ under stirring. After stirring for 15 min, the pH value of the mixed solution was adjusted to 10 by the addition of 1 mol/L of Na_2CO_3 aqueous solution. The mixture was stirred at 50 ℃ for additional 3 h and the resulting solid was collected by centrifugation and washing with deionized water for several times and then dried in vacuum at 80 ℃ for 16 h. The acquired solid was heat treated at 200 ℃ for 2 hours in 10% Ar/H_2 (heating rate: 5 ℃/min). The as-prepared Pd-CeO_2 catalysts were labeled as x% Pd-CeO_2 (x =

2, 7, 12, and 16), in which the ‘‘x” represents the nominal Pd loading.

7% Ag-CeO_2, 7% Au-CeO_2 and 7% Pt-CeO_2 nanorods were prepared following the same procedures except the calculated amount of palladium chloride was replaced by 0.03307 g of silver nitrate or 0.04199 g of chlorauric acid trihydrate or 0.05576 g of chloroplatinic acid hexahydrate in the beginning. The actual metal contents in these samples were measured by the inductively coupled plasma-optical emission spectroscopy (ICP-OES).

Determination of Hydrazine

The concentration of hydrazine was detected by the method of Watt and Chrisp[3]. 5.99 g of p-$C_9H_{11}NO$ and 30 mL of hydrochloric acid (HCl) were added to 300 mL of ethanol as the colouring reagent solution of hydrazine. 2 mL of colouring reagent was added to 2 mL of sample solution and then the solution was incubated at dark for 30 min under room temperature. Then the absorbance at 458 nm was obtained by spectrophotometry. The N_2H_4 concentration of the fitting curve and the calibration curve ($y = 0.33694x + 0.01323$, $R^2 = 0.99989$) has a good linear relationship. As shown in the Fig. S11.

Determination of Ammonia

The concentration of ammonia is mainly determined by indophenol blue method[4]. Typically, 0.5 mL of phenol nitroprusside solution and 0.5 mL of alkaline hypochlorite solution are added to 2.0 mL of sample solution containing ammonia. The mixed solution was incubated for 30 min under room temperature and the absorbance at the wavelength λ = 630 nm was obtained by UV-vis spectrophotometry. The calibration curve shows a good linear relation of absorbance with ammonia concentration ($y = 0.01334x + 0.05171$, $R^2 = 0.99917$). As shown in the Fig. S13.

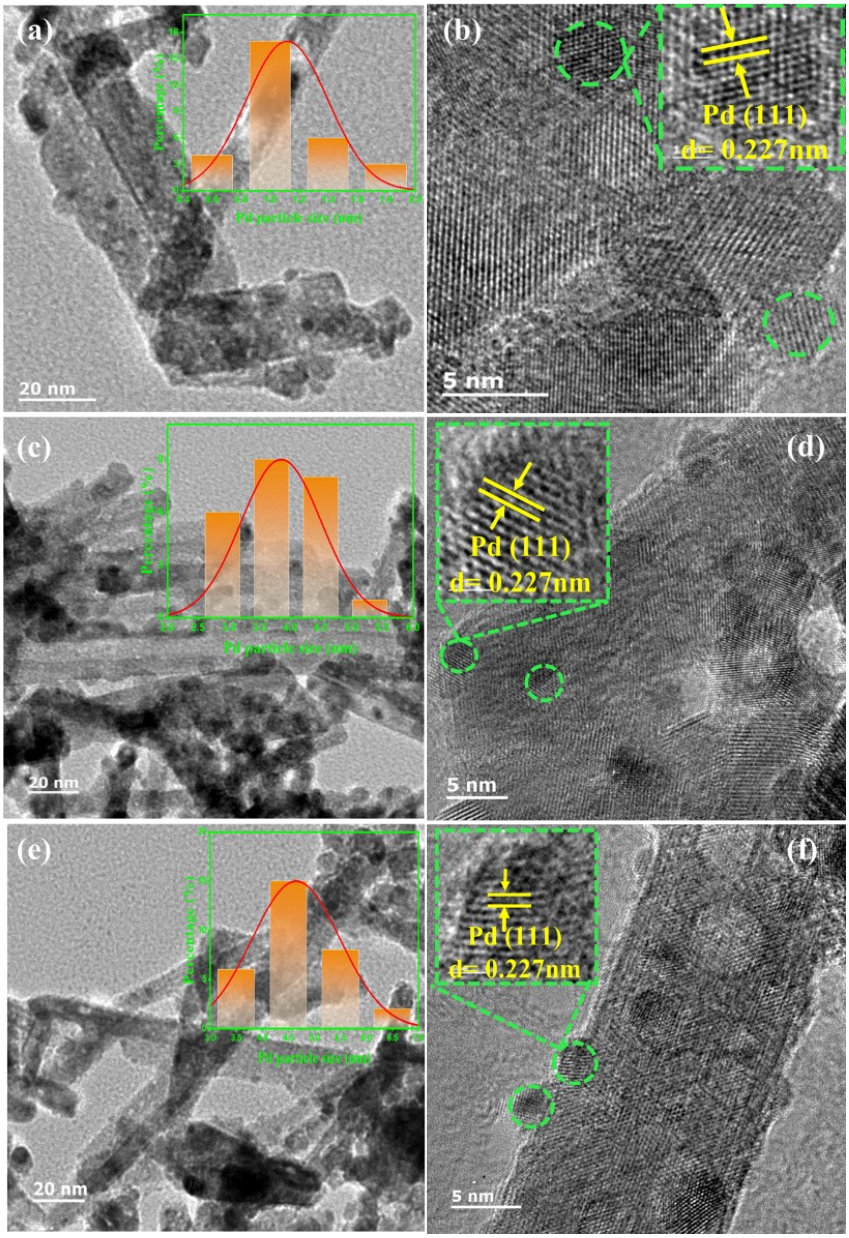
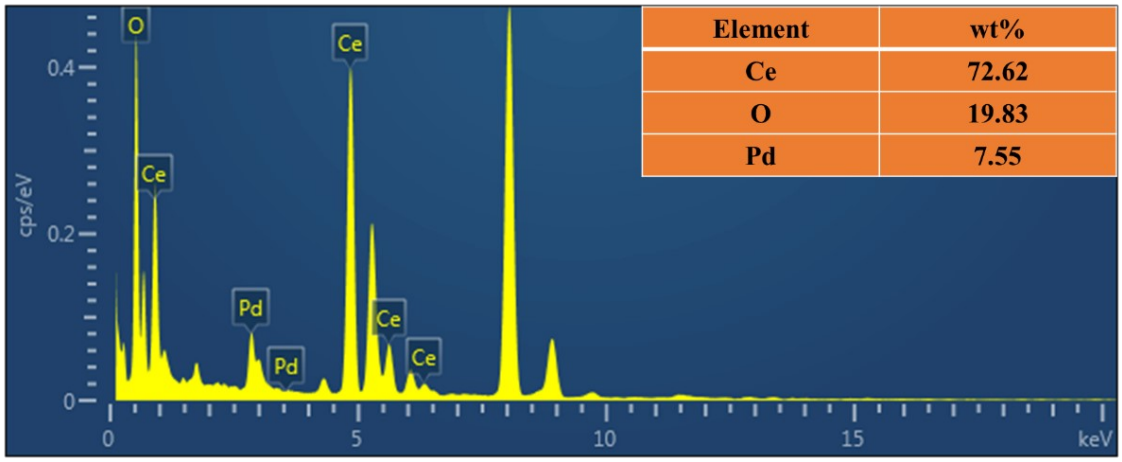


Fig. S1 TEM and HRTEM images of the samples. (a-b) 2% Pd-CeO_2, (c-d) 12% Pd-CeO_2 and (e-f) 16% Pd-CeO_2.



Element	wt%
Ce	72.62
O	19.83
Pd	7.55

Fig. S2 The energy dispersive X-ray (EDX) spectroscopy of 7% Pd-CeO_2.

The energy dispersive X-ray (EDX) spectroscopy was used to explore the loading amount of Pd. As shown in Fig. S2, the weight ratio of Pd for 7% Pd-CeO_2 catalyst is 7.55%, which confirmed that palladium has been successfully loaded on the surface of the catalyst. Meanwhile, the weight ratio of Ce and O elements for 7% Pd-CeO_2 catalyst is 72.62% and 19.83%, respectively.

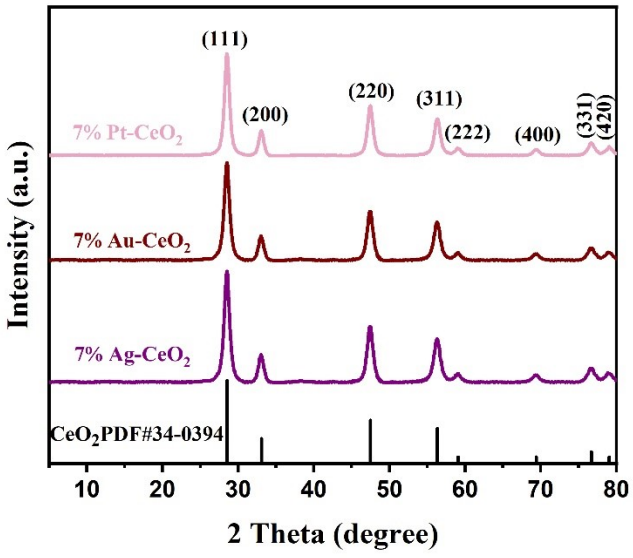


Fig. S3 XRD patterns of 7% Ag-CeO_2, 7% Au-CeO_2 and 7% Pt-CeO_2.

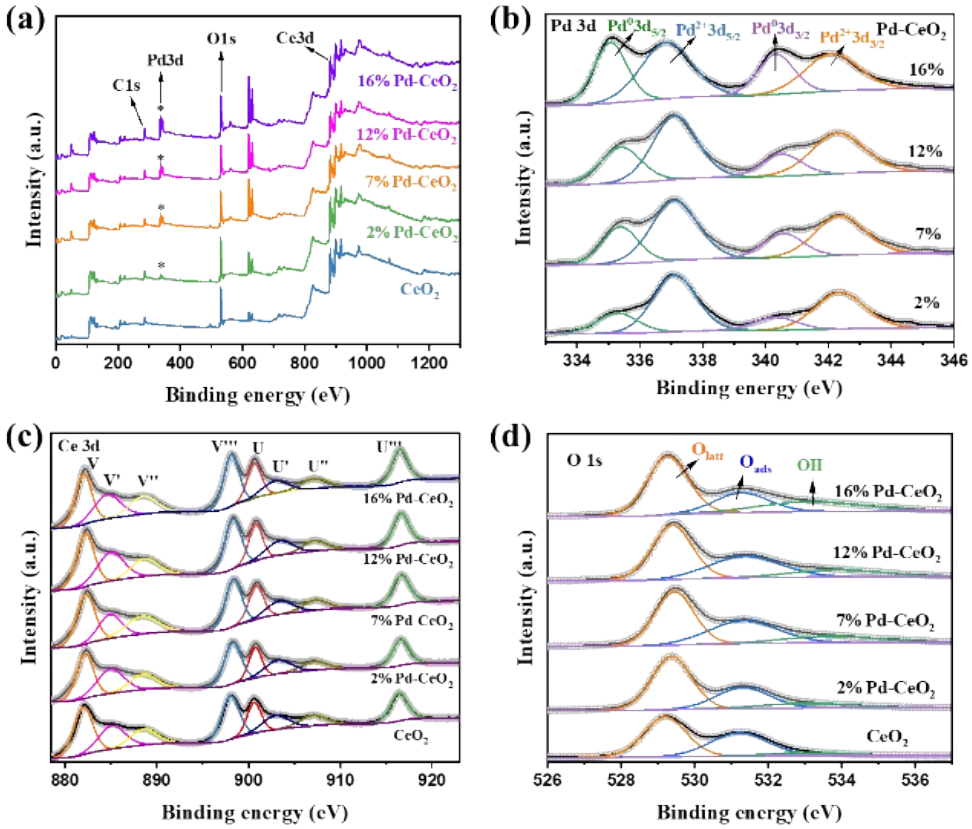


Fig. S4 XPS spectra of the (a) full spectrum, (b) Pd 3d, (c) Ce 3d and (d) O 1s peaks for CeO_2, 2% Pd-CeO_2, 7% Pd-CeO_2, 12% Pd-CeO_2 and 16% Pd-CeO_2.

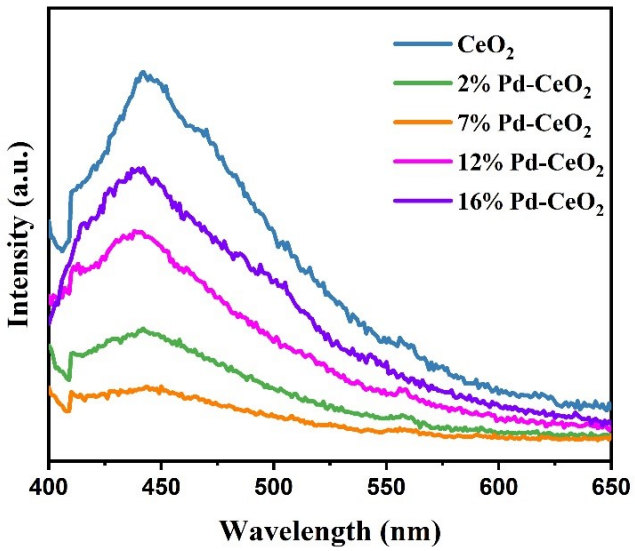


Fig. S5 PL spectra of CeO_2, 2% Pd-CeO_2, 7% Pd-CeO_2, 12% Pd-CeO_2 and 16% Pd-CeO_2.

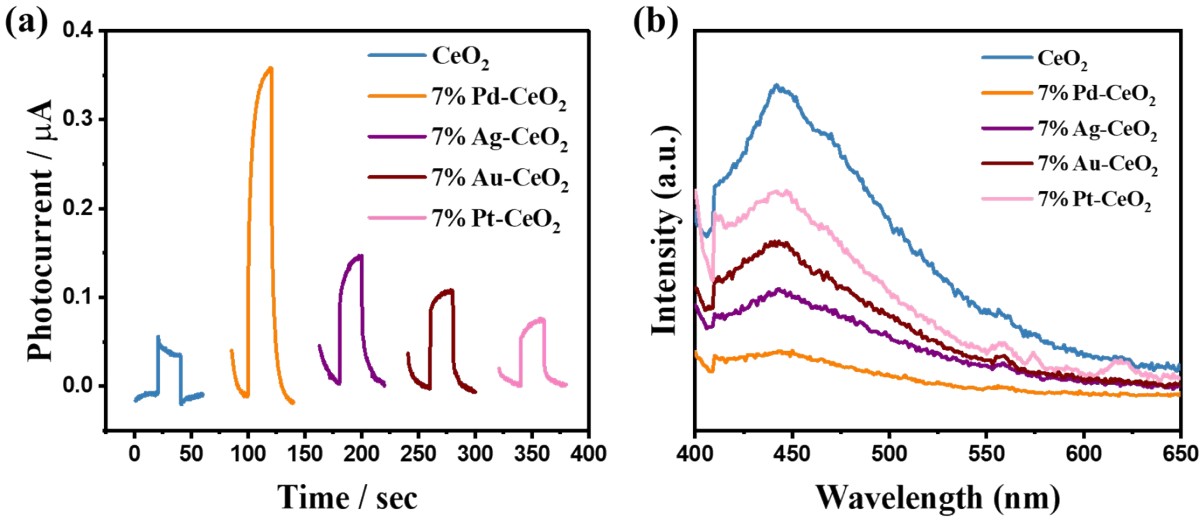


Fig. S6 The electrochemical tests of CeO_2, 7% Pd-CeO_2, 7% Ag-CeO_2, 7% Au-CeO_2 and 7% Pt-CeO_2. (a) Transient photocurrents, (b) PL spectra.

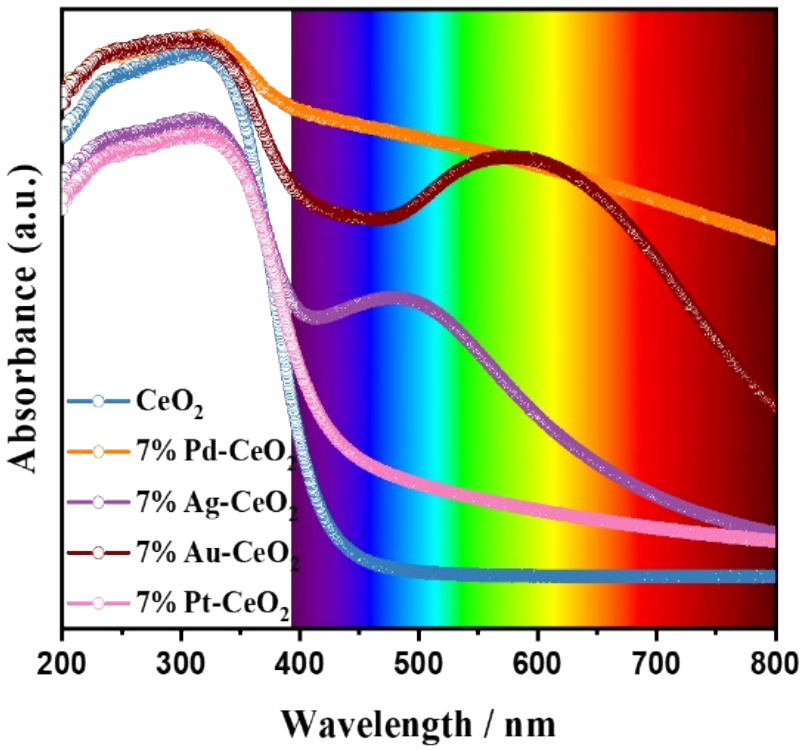


Fig. S7 UV-vis diffuse reflectance spectra of CeO_2, 7% Pd-CeO_2, 7% Ag-CeO_2, 7% Au-CeO_2 and 7% Pt-CeO_2.

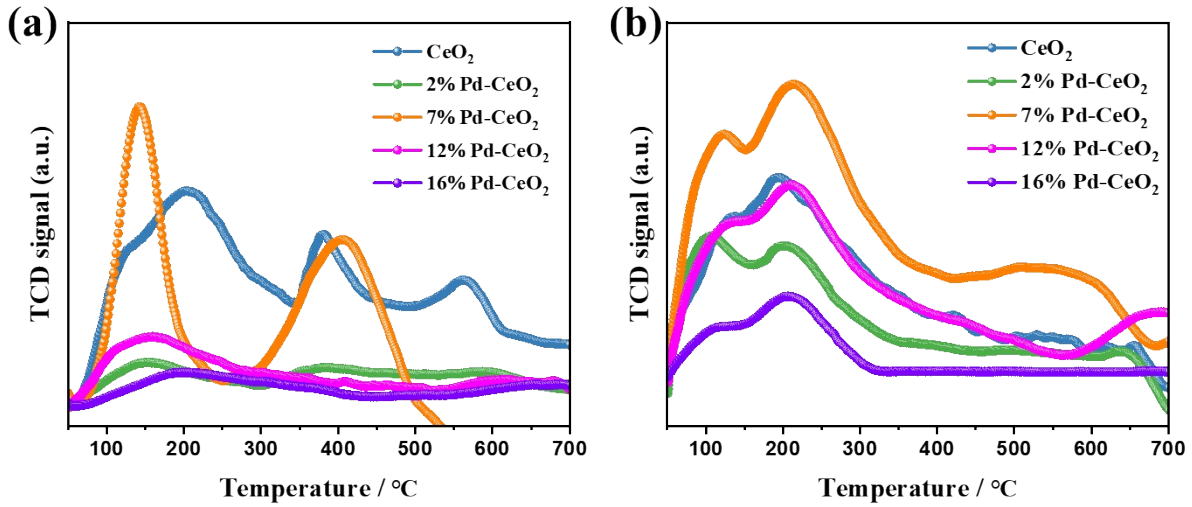


Fig. S8 (a) N_2-TPD spectra and (b) CO_2-TPD spectra of CeO_2, 2% Pd-CeO_2, 7% Pd-CeO_2, 12% Pd-CeO_2 and 16% Pd-CeO_2.

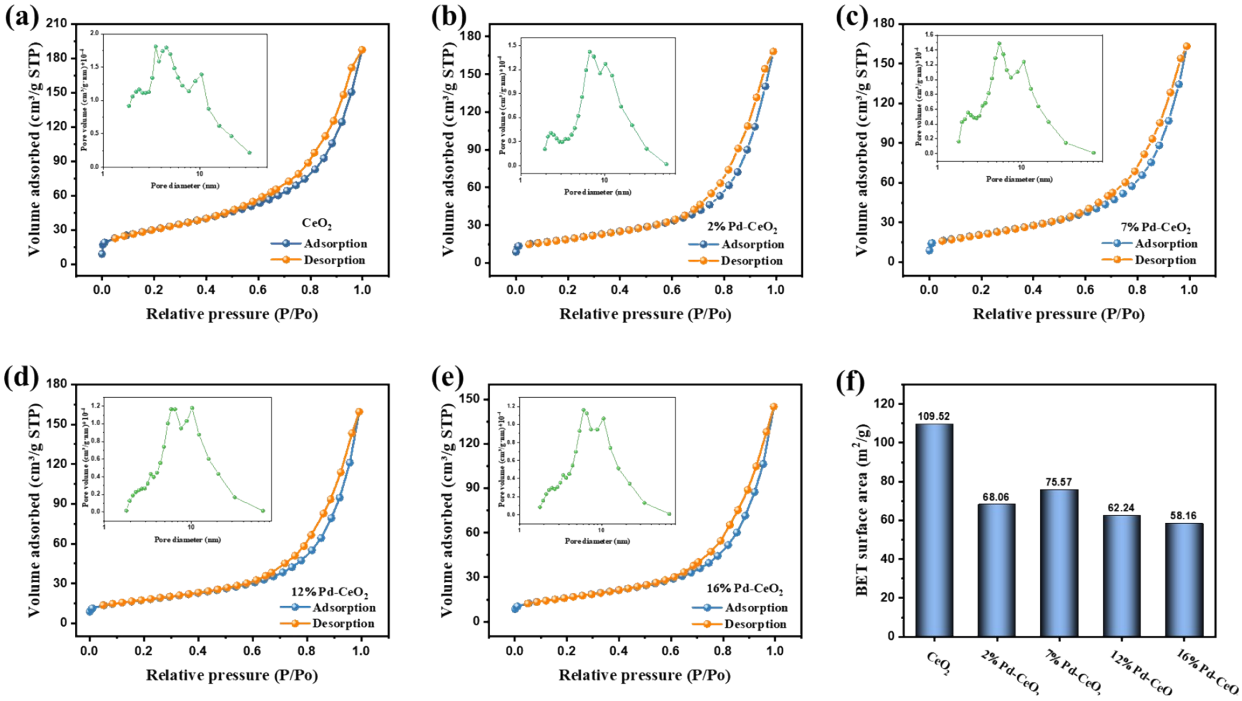


Fig. S9 The N_2 adsorption-desorption isotherms and the corresponding pore size distribution curves (inserts) of (a) CeO_2, (b) 2% Pd-CeO_2, (c) 7% Pd-CeO_2, (d) 12% Pd-CeO_2 and (e) 16% Pd-CeO_2. (f) The specific surface areas of CeO_2, 2% Pd-CeO_2, 7% Pd-CeO_2, 12% Pd-CeO_2 and 16% Pd-CeO_2.

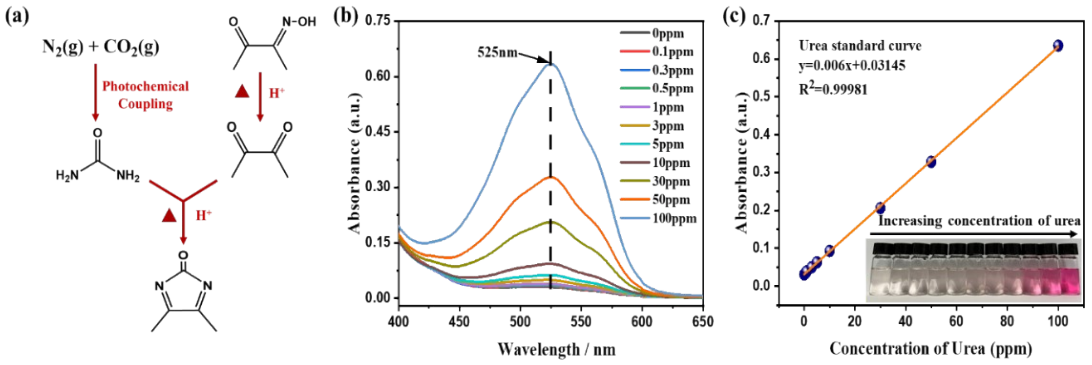


Fig. S10 (a) Reaction mechanism on the diacetyl monoxime method to detect urea. (b) A series of standard solutions with urea concentrations and the absorbance was measured by UV-vis spectrophotometer in the range of 200 to 800 nm. (c) A series of standard solutions with urea concentrations of 0 ppm, 0.1 ppm, 0.3 ppm, 0.5 ppm, 1.0 ppm, 3.0 ppm, 5.0 ppm, 10 ppm, 30 ppm, 50 ppm and 100 ppm respectively and the absorbance at 525 nm was measured by UV-vis spectrophotometer. The calibration curve indicated good linear relation of absorbance with urea concentration (y = 0.006x + 0.03145, R^2 = 0.99981), the inset are the pictures of pink solutions with different urea concentrations.

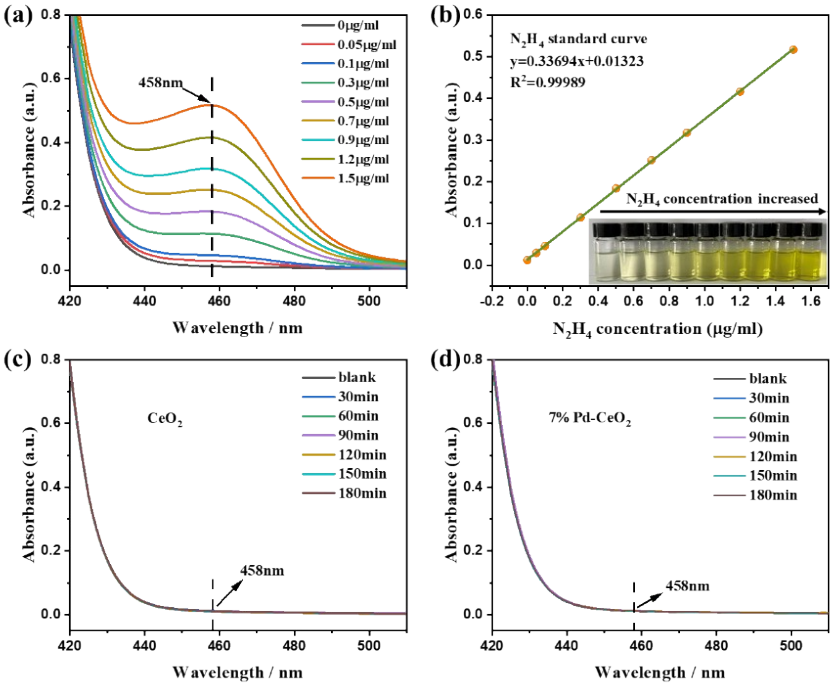


Fig. S11 Calibration curve for quantification of N_2H_4 by the method of Watt and Chrisp.

(a) A series of standard solutions were prepared with the concentrations of 0, 0.05, 0.1, 0.3, 0.5, 0.7, 0.9, 1.2 and 1.5 μg ml^{-1} respectively and absorbance at 458 nm were obtained after addition of color regent for 20 min. (b) The fitting curve shown good linear relation of absorbance with N_2H_4 concentration (y = 0.33694x + 0.01323, R^2 = 0.99989) of independent calibration curves and the inset were the pictures of yellow solutions with different N_2H_4 concentrations. (c-d) The absorbance of CeO_2 and 7% Pd-CeO_2 at 458 nm in different time periods was measured by UV-vis spectrophotometer.

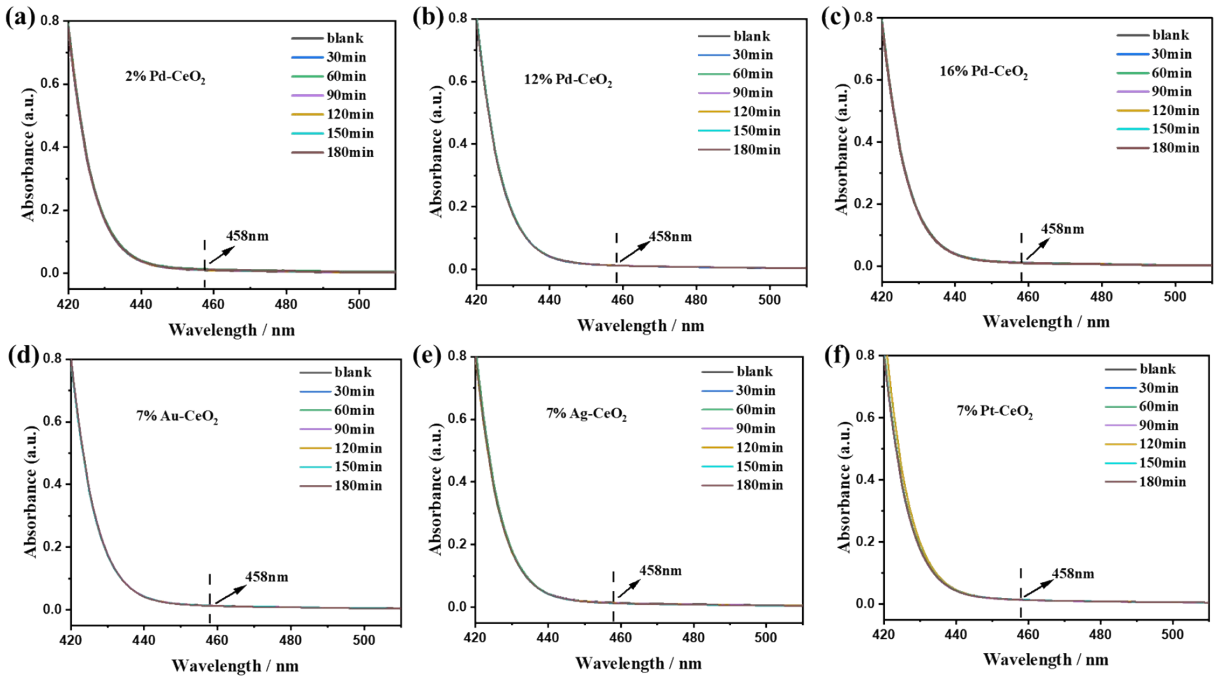


Fig. S12 The absorbance of a series of samples at 458 nm in different time periods was measured by UV-vis spectrophotometer. (a) 2% Pd-CeO_2, (b) 12% Pd-CeO_2, (c) 16% Pd-CeO_2, (d) 7% Au-CeO_2, (e) 7% Ag-CeO_2, (f) 7% Pt-CeO_2.

The experimental results indicated that barely any N_2H_4 was generated during the photocatalytic urea synthesis.

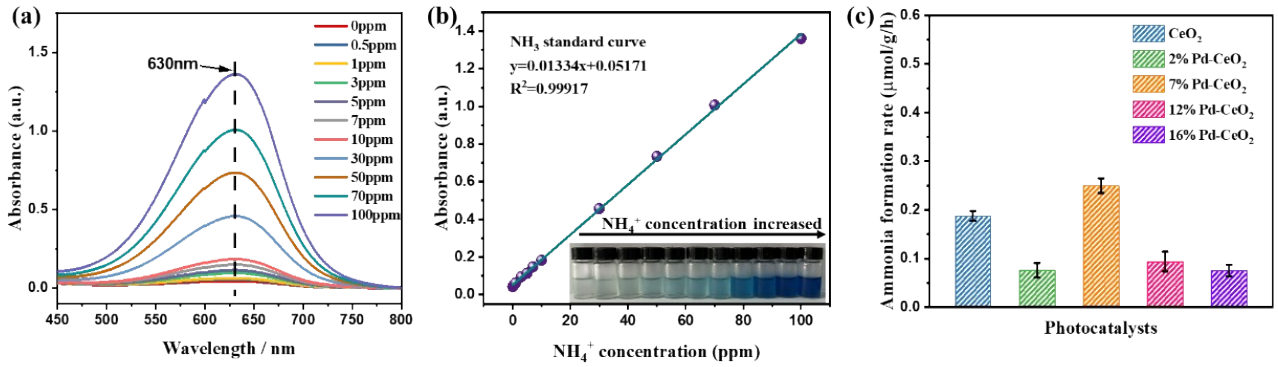


Fig. S13 The quantification of ammonia concentration by the indophenols blue method. (a) A series of standard solutions with ammonia concentrations of 0 ppm, 0.5 ppm, 1 ppm, 3 ppm, 5 ppm, 7 ppm, 10 ppm, 30 ppm, 50 ppm, 70 ppm and 100 ppm respectively and the absorbance at 630 nm was measured by UV-vis spectrophotometer. (b) The calibration curve for quantification of ammonia has good linear relation of absorbance with ammonia concentration ($y = 0.01334x + 0.05171$, $R^2 = 0.99917$). (c) The ammonia formation rates of CeO_2, 2% Pd-CeO_2, 7% Pd-CeO_2, 12% Pd-CeO_2 and 16% Pd-CeO_2.

The by-product ammonia was detected by indophenol blue method. The results showed that only a small amount of ammonia was produced in the photocatalytic reaction.

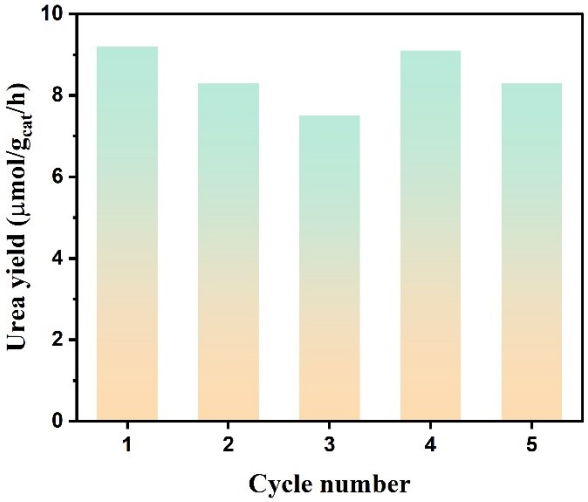


Fig. S14 Photocatalytic cycling tests for 7% Pd-CeO_2 with CO_2+N_2 as feeding gases.

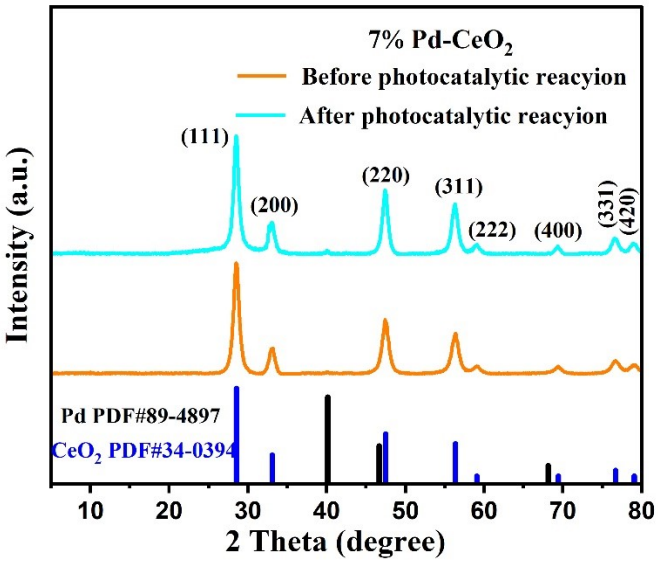


Fig. S15 XRD pattern of 7% Pd-CeO_2 before and after cycle experiments of photocatalytic reaction.

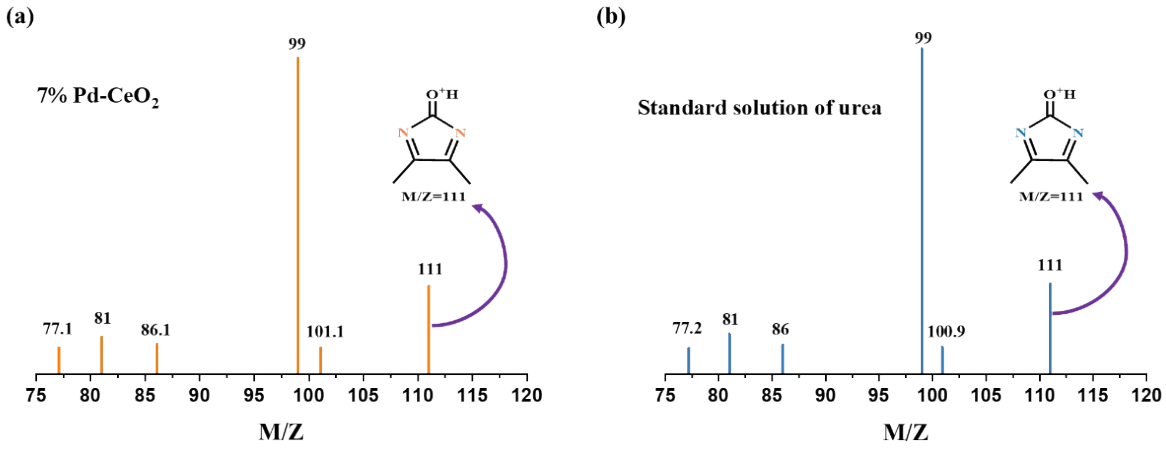


Fig. S16 (a) The mass spectrum of 7% Pd-CeO_2. (b) The mass spectrum of urea standard solution with 10 ppm.

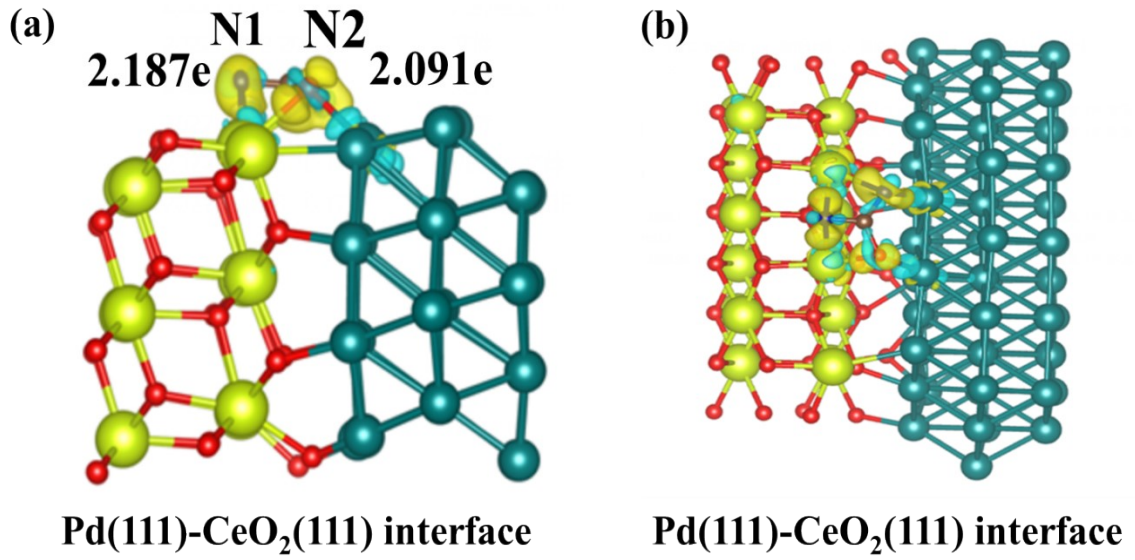


Fig. S17 The differential charge density of *NCON at Pd (111)-CeO_2 (111) interface. (a) Side view, (b) Top view. (The blue color represents electron consumption and the yellow color represents electron accumulation).

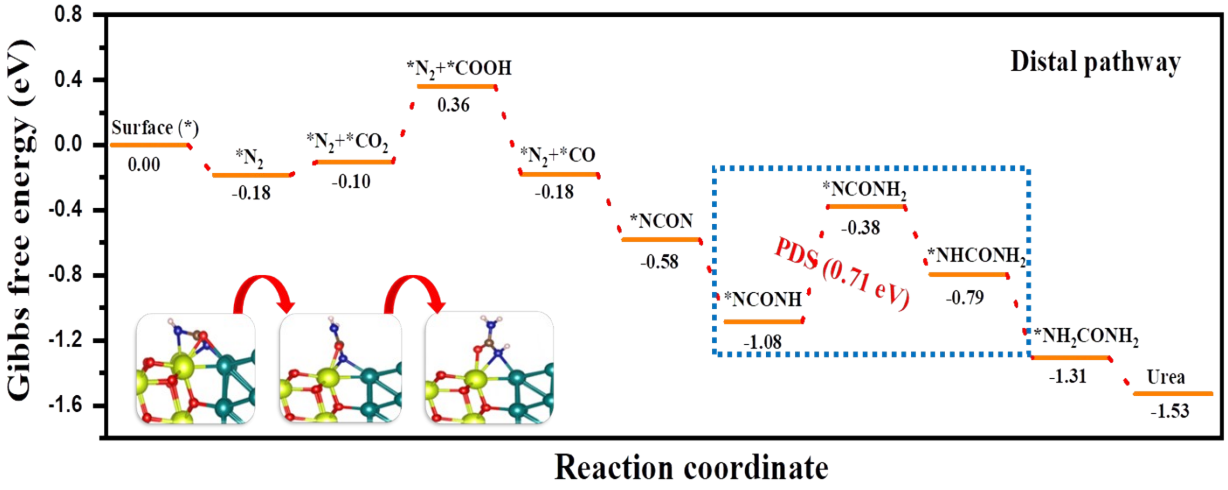


Fig. S18 The free energy diagram of urea production via distal pathway. The insets are the reaction processes of *$NHCONH_2$ key intermediate. The yellow, red, pink, blue and green balls represent Ce, O, H, N and Pd atoms, respectively.

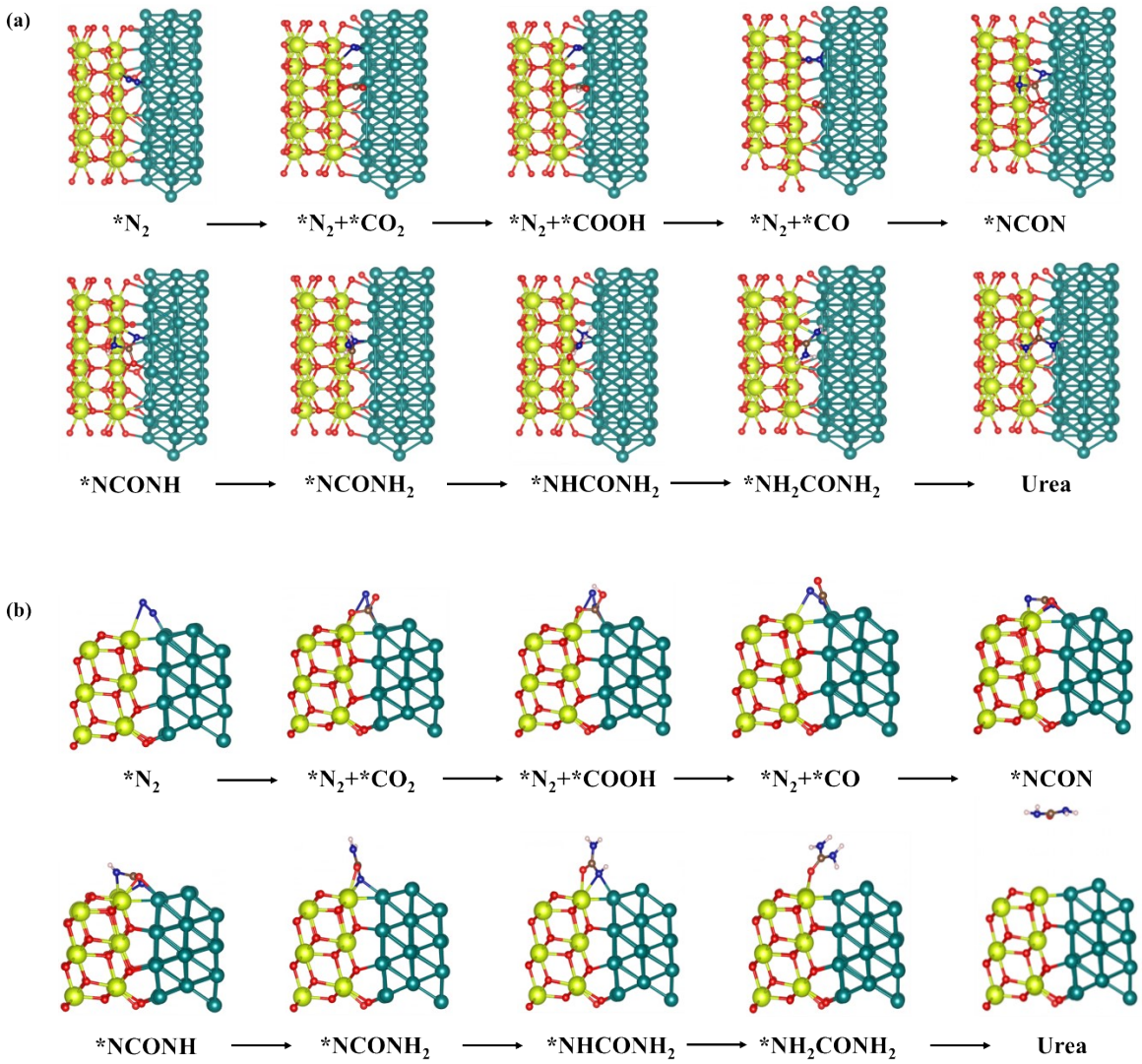


Fig. S19 The structural diagram of urea production process through distal pathway. (a) Top view. (b) Side view. The meanings of the colored balls: Ce (yellow), O (red), H (pink), N (blue) and Pd (green).

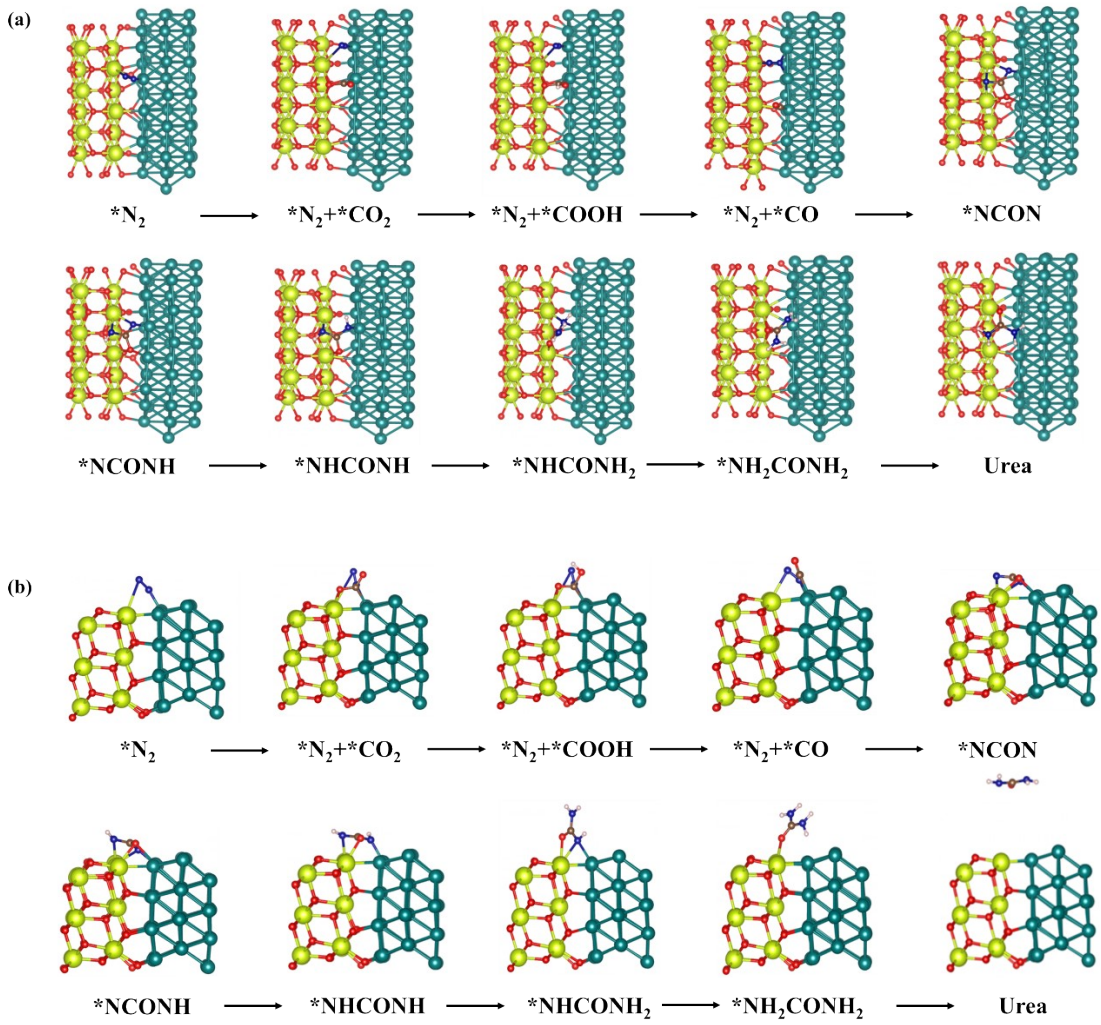


Fig. S20 The structural diagram of urea production process through alternating pathway. (a) Top view. (b) Side view. The meanings of the colored balls: Ce (yellow), O (red), H (pink), N (blue) and Pd (green).

Table S1 The loading content of metals in the m-CeO_2 NRs samples.

Sample	2% Pd-CeO_2	7% Pd-CeO_2	12% Pd-CeO_2	16% Pd-CeO_2	7% Au-CeO_2	7% Ag-CeO_2	7% Pt-CeO_2
Metal content (wt.%)	2.2	6.6	11.7	15.6	6.7	6.8	6.7

Table S2 Specific surface area and pore size of the samples.

Samples	**BET surface area (m^2/g)**	**Pore size (nm)**	**Pore volume (cm^3/g)**
CeO_2	109.52	8.36	0.20
2%Pd-CeO_2	68.06	11.91	0.18
7%Pd-CeO_2	75.57	10.59	0.17
12%Pd-CeO_2	62.24	12.57	0.15
16%Pd-CeO_2	58.16	12.19	0.14

Table S3 The binding energy of Pd 3d from XPS spectrum over 2% Pd-CeO_2, 7% Pd-CeO_2, 12% Pd-CeO_2 and 16% Pd-CeO_2.

Binding Energy (eV)				
Samples	**Pd 3d**			
	Pd^0 $3d_{5/2}$	**Pd^{2+} $3d_{5/2}$**	**Pd^0 $3d_{3/2}$**	**Pd^{2+} $3d_{3/2}$**
2%Pd-CeO_2	335.2	337.1	340.3	342.3
7%Pd-CeO_2	335.4	337.1	340.6	342.4
12%Pd-CeO_2	335.4	337.1	340.5	342.3
16%Pd-CeO_2	335.1	336.8	340.3	342.1

Table S4 The binding energy of Ce 3d from XPS spectrum over CeO_2, 2% Pd-CeO_2, 7% Pd-CeO_2, 12% Pd-CeO_2 and 16% Pd-CeO_2.

Binding Energy (eV)								
Samples	**Ce $3d_{5/2}$ (eV)**				**Ce $3d_{3/2}$ (eV)**			
	V	**V'**	**V''**	**V'''**	**U**	**U'**	**U''**	**U'''**
CeO_2	882.1	885.2	888.6	898.1	900.7	903.0	907.1	916.5
2%Pd-CeO_2	882.2	885.0	888.6	898.3	900.8	903.2	907.2	916.6
7%Pd-CeO_2	882.3	884.9	888.4	898.4	900.9	903.5	907.3	916.7
12%Pd-CeO_2	882.3	885.0	888.7	898.3	900.8	903.5	907.2	916.7
16%Pd-CeO_2	882.0	884.7	888.5	898.2	900.6	903.0	907.2	916.5

Table S5 The binding energy of O 1s from XPS spectrum over CeO_2, 2% Pd-CeO_2, 7% Pd-CeO_2, 12% Pd-CeO_2 and 16% Pd-CeO_2.

Binding Energy (eV)			
Samples	**O 1s**		
	O_{latt}	**O_{ads}**	**OH^-**
CeO_2	529.2	531.2	533.0
2%Pd-CeO_2	529.3	531.3	533.1
7%Pd-CeO_2	529.4	531.3	533.6
12%Pd-CeO_2	529.4	531.3	533.8
16%Pd-CeO_2	529.3	531.2	533.1

References

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2. K. Ma, W. Liao, W. Shi, F. Xu, Y. Zhou, C. Tang, J. Lu, W. Shen and Z. Zhang, *Journal of Catalysis*, 2022, **407**, 104-114.
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4. W. Zhang, D. Han, M. Dai, Y. Fan, G. Pan, W. Liang, Q. Zheng, D. Qin, D. Han, Y. He and L. Niu, *ACS Sustainable Chemistry & Engineering*, 2021, **9**, 15331-15343.