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# Supplementary Information

## Influence of $CeO_2$ Support Morphology on the Structural and $NO_2^-$RR Performance of $CeO_2$@Au Catalyst

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## 1. Detection of the product ammonia

In this study, the concentration of the product ammonia was detected by the indophenol blue method [1], which was carried out as follows: 2.0 mL of diluted electrolyte solution was taken in a colorimetric tube, followed by the addition of 2.0 mL of oxidising agent, 1.0 mL of NaClO, and 0.2 mL of 1 wt.% sodium nitroprusside solution in that order, and the mixture was placed in the dark and left to stand for 1 h. At the end of the standing period, the mixture was analyzed by ultraviolet (UV) test. In this paper, by calibrating the concentration absorbance curves using standard $NH_2SO_4$ solutions of 0 μg $mL^{-1}$, 0.2 μg $mL^{-1}$, 0.5 μg $mL^{-1}$, 1.0 μg $mL^{-1}$, 2.0 μg $mL^{-1}$, and 5.0 μg $mL^{-1}$ as shown in **Fig. S1a-b**, the standard curves we fitted ($A = 0.4567\ C + 0.0237$ with $R^2 = 0.999$) with good linearity. The ammonia yield and Faraday efficiency were calculated as follows:

$$NH_3 \text{ yield rate} = ([NH_3] \times V) / (t \times m) \quad (1)$$

$$FE = (6 \times F \times [NH_3] \times V) / (M \times Q) \times 100\% \quad (2)$$

In this formula, $[NH_3]$ is the concentration of ammonia, V is the volume of the electrolyte, t is the electrolysis time, m is the mass of the catalyst, F is Faraday's constant, M is the relative molecular mass of $NH_3$, and Q is the amount of Coulomb that passes through the electrode during electrolysis.

## 2. Detection of hydrazine

The concentration of the by-product hydrazine ($N_2H_4$) was examined in this study using the Watt-Chrisp method [2]. Take 5.0 mL of electrolyte after electrolysis in the cuvette, add 5.0 mL of freshly prepared colour developer (consisting of a mixture of 5.99 g of

p-dimethylaminobenzaldehyde, 300 mL of ethanol, 30 mL of hydrochloric acid (36%)) to form a mixed solution, and place it in a dark environment to stand for 20 min. At the end of the stationary period, the mixture was analysed by UV detection. In this paper, hydrazine hydrochloride and 0.1 M PBS solution were used as standards and solvents to prepare solutions with $N_2H_4$ concentrations of 0.0 μg mL, 0.2 μg mL, 0.4 μg mL, 0.6 μg mL, 0.8 μg mL, and 1.0 μg mL, respectively, and the absorbance of each solution was measured by using the above mentioned Watt-Chrisp method as shown in **Fig. S1c-d**. As shown, the fitted curves ($A = 1.1194\ C + 0.0716$, $R^2 = 0.999$) were calculated and there was a good linear relationship between $N_2H_4$ concentration and absorbance.

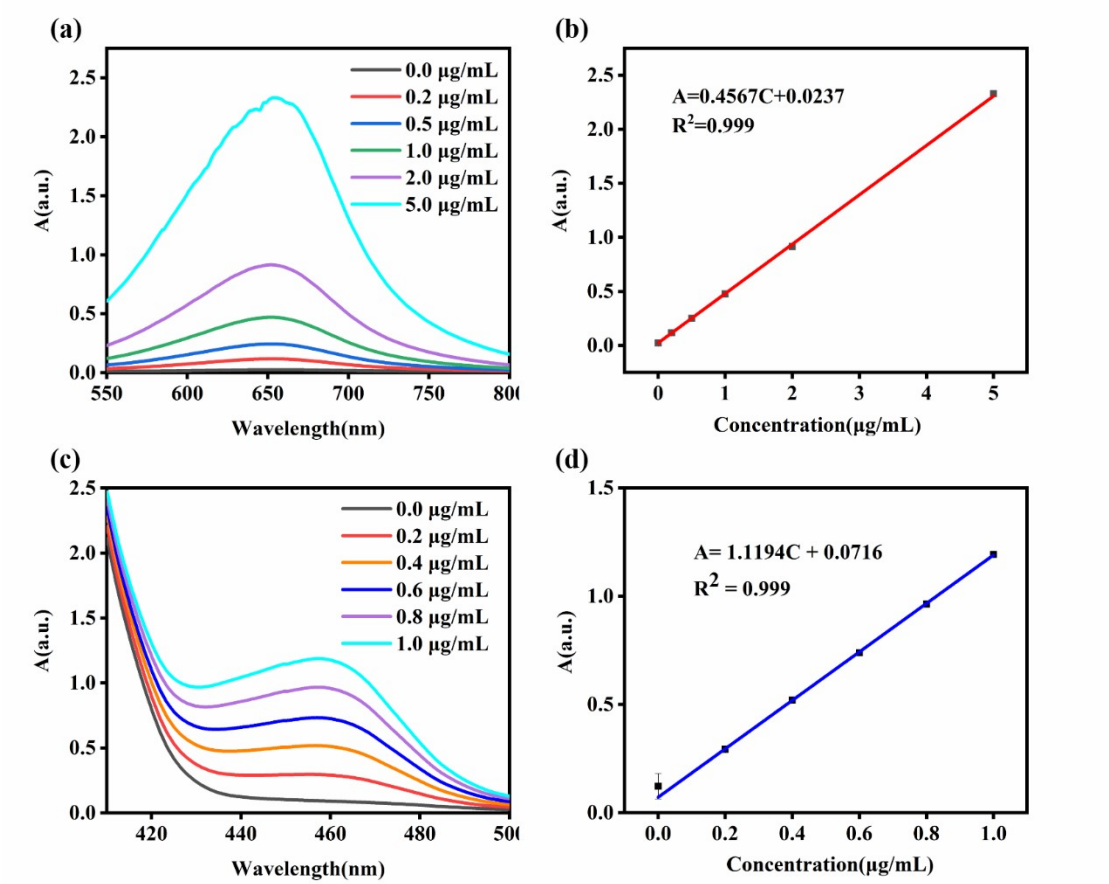


**Figure S1**. (a) UV absorption spectra at different $NH_3$ concentrations and (b) Ammonia nitrogen standard curve; (c) UV-Vis absorption spectra of different concentrations of $N_2H_4$and (d) Standard curve of $N_2H_4$.

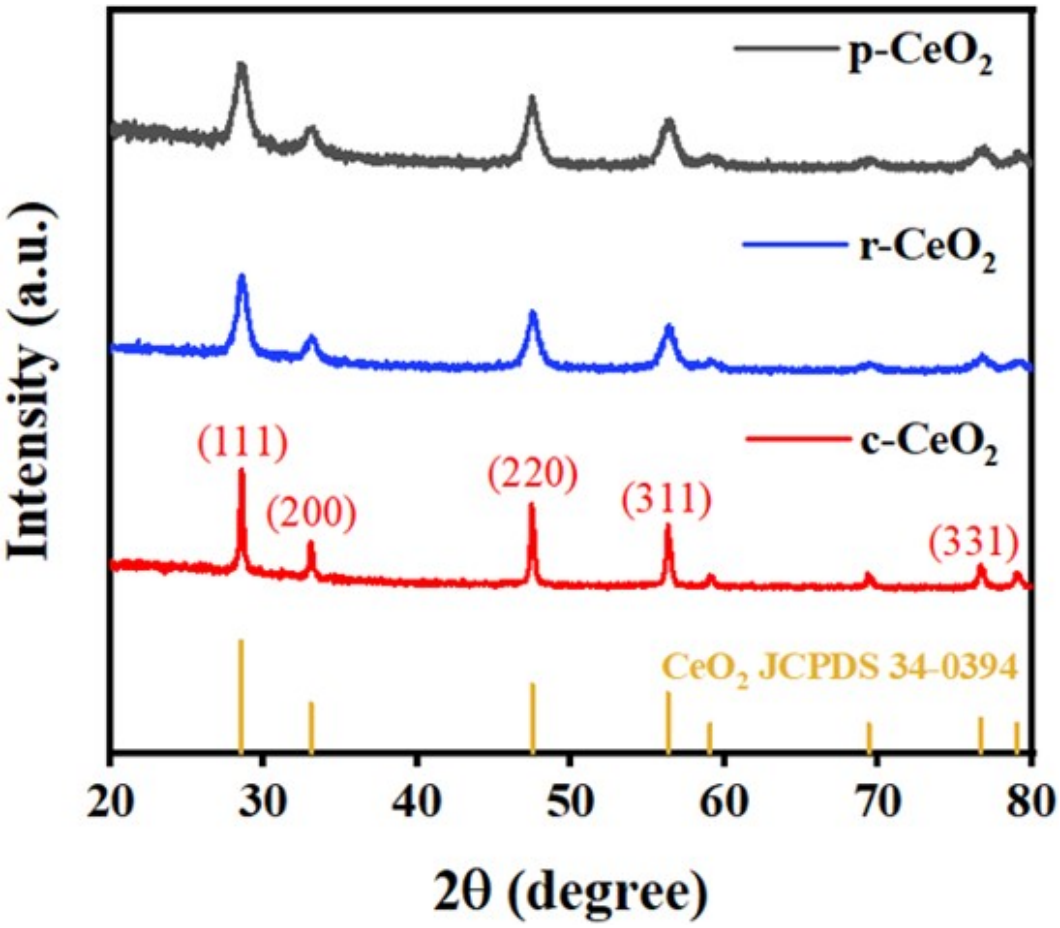


**Figure S2**. XRD plots of c-$CeO_2$, r-$CeO_2$ and p-$CeO_2$.

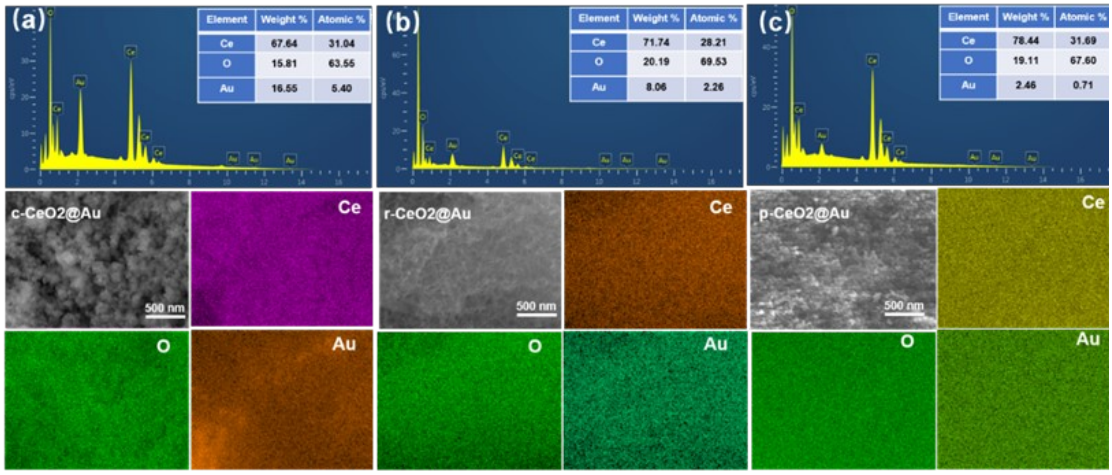


**Figure S3**. EDS plots of (a) c- CeO2@Au, (b) r-CeO2@Au and (c) p-CeO2@Au.

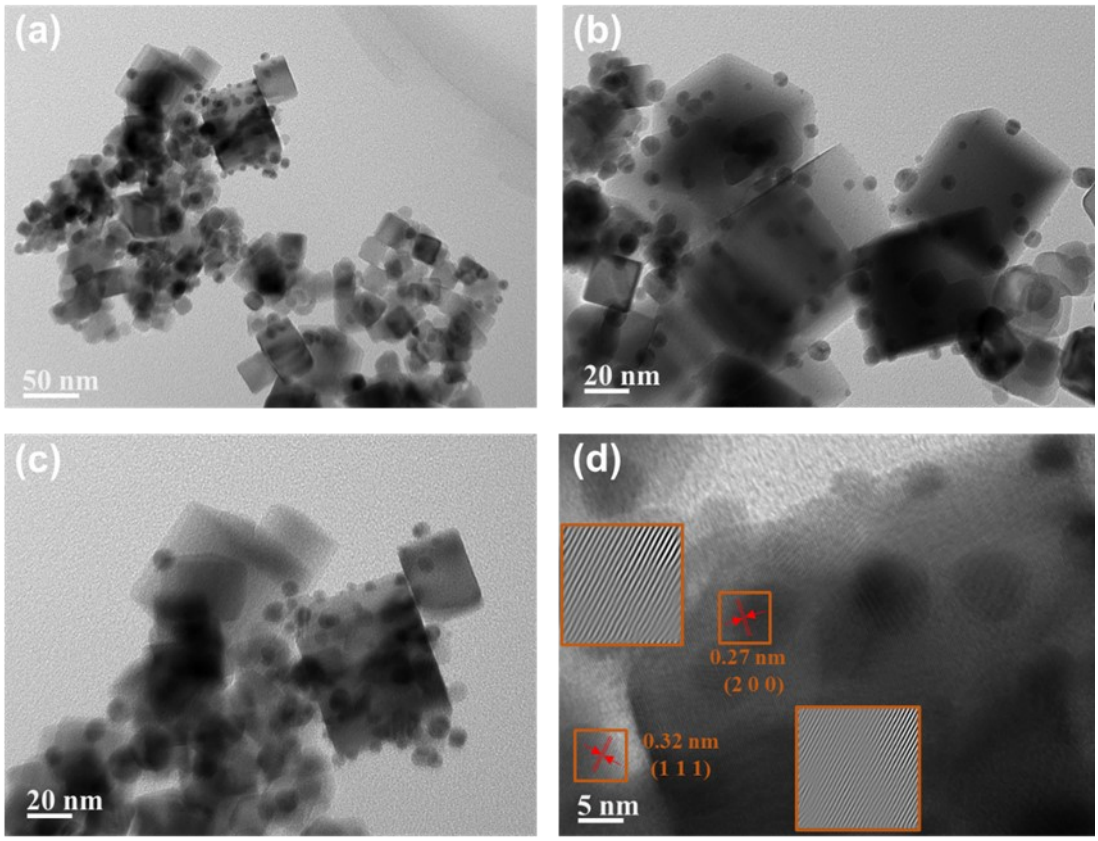


**Figure S4.** (a-c) TEM maps of c-$CeO_2$@Au; (d) HR-TEM analysis of c-$CeO_2$@Au.

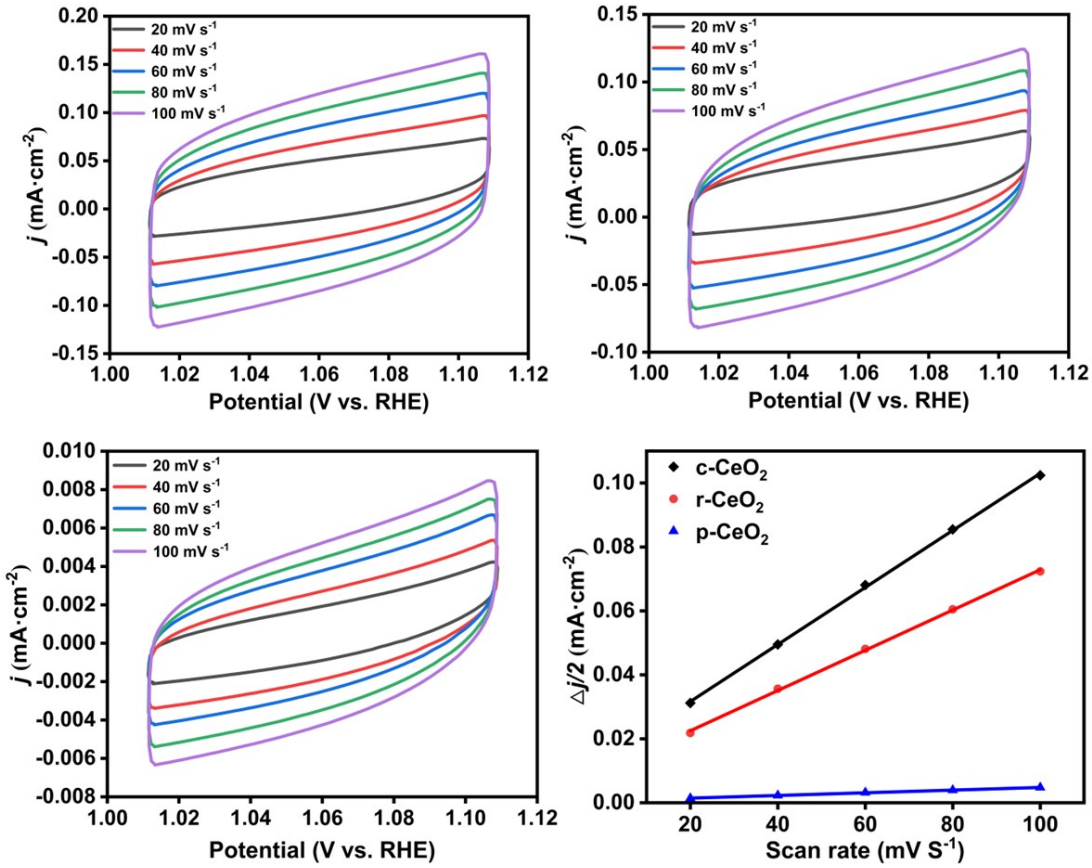


**Figure S5.** CV curves of (a) c-$CeO_2$, (b) r-$CeO_2$ and (c) p-$CeO_2$ at different scanning rates; (d) plots of current density versus scanning rate.

**Table S1**. ICP testing of c-$CeO_2$@Au, r-$CeO_2$@Au and p-$CeO_2$@Au.

| Materials | Elements | content（%） |
|---|---|---|
| c- $CeO_2$@Au | Au | 38.88 % |
| r-$CeO_2$@Au | Au | 35.99 % |
| p-$CeO_2$@Au | Au | 19.88 % |

## References

[1] D Zhu, L Zhang, RE Ruther, RJ Hamers, Photo-illuminated diamond as a solid-state source of solvated electrons in water for nitrogen reduction, *Nature materials.*, 2013, **12**, 836-841.

[2] Watt G W, Chrisp J D, Spectrophotometric method for determination of hydrazine, *Analytical Chemistry.*, 1952, **24**, 2006-2008.