

**Pt/Porous Nanorods of Ceria as Efficient High Temperature Catalysts with
Remarkable Catalytic Stability for Carbon Dioxide Reforming of Methane**

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Synthesis of CeO₂ Cube

1.736 g of Ce(NO₃)₃·6H₂O was dissolved in 10 mL of millipore water (MQ water, 18.2 MΩ·cm), and 19.2 g of NaOH was dissolved in 70 mL of MQ water. Then, the two solutions were mixed under continuous stirring. After 30 min of aging, the solution was transferred into a 100 mL Teflon vessel and sealed tightly in a stainless steel autoclave. The autoclave was transferred into electric oven with a temperature of 180 °C for 24 h. After the autoclave was cooled to room temperature naturally, the resulted slurry was collected by centrifugation, washed with MQ water and ethanol, and then dried at 60 °C overnight. Finally, the ceria cubes were obtained by calcinating the powder at 400 °C for 5 h in air.¹

Synthesis of CeO₂ Nanoparticles

The CeO₂ nanoparticles were prepared by calcinating Ce(NO₃)₃ · 6H₂O precursor at 500 °C for 4 h with a ramping rate of 1 °C/min.

Thermal stability of the CeO₂ nanostructures

The thermal stability of CeO₂ nanoparticles, CeO₂ nonporous nanorods (*NR-Ceria*), CeO₂ porous nanorods (*PN-Ceria*) and CeO₂ cube was evaluated side by side. All ceria nanostructures were calcined at 600 °C and 800 °C for 4 h under ambient conditions, respectively. The heating rate was 1 °C/min. The morphology evolution of nanocerias was displayed in Fig. S2. TEM images were shown in Fig. S2a-c and described the morphology evolution of CeO₂ nanoparticles at various temperatures. The serious sintering of CeO₂ nanoparticles was observed (Fig. S2b-S2c). Raising temperature to 800 °C leads to the significant fusion of small nanoparticles (~ 5 nm) into large particles with irregular shape and a wide size distribution from tens to hundreds of nanometer. The measured surface area of CeO₂ nanoparticles treated at 800 °C was significantly decreased to 8.9 m²/g, compared to 77.4 m²/g for as-synthesized nanoparticles (Fig. S3). The results indicated the low thermal stability of small CeO₂ nanoparticles. With the diameter of ~ 8 nm, both *NR-Ceria* and *PN-Ceria* remain essentially unchanged in terms of diameter and length after calcination at 600 °C (Fig. S2h and S2k). Increasing the calcination temperature of *NR-Ceria* to 800 °C resulted in a massive change of rod-like morphology into spherical particles and shorter rods with large diameter, as evident in Fig. S2i. The surface area of *NR-Ceria* was significantly dropped to 28.9 m²/g after 800 °C calcination, which is only 29.3 % of that of as-synthesized one (98.3 m²/g). In contrast, the configuration of *PN-Ceria* was almost maintained after 800 °C calcination in air for 4 h (Fig. S2l). A closer observation of the calcinated *PN-Ceria* revealed that the length of the nanorods was averagely shorten by ~2 nm, compared to that of as-synthesized structure, indicating the breaking of *PN-Ceria* at high temperatures. The surface area of *PN-Ceria* after 800 °C calcination was 74.7 m²/g,

which was 61 % of as-synthesized one but 2.6 times higher than that of *NR-Ceria* treated at same conditions. It is also important to note that the porous feature of *PN-Ceria* (Fig. S2l) was well preserved, which is apparently contradictory to a general understanding that the nanostructures with small size are fragile at high temperature. The detailed studies are under progress. The plot of surface area versus temperatures for nanocerias presented in Fig. S3 suggests the best thermal robustness of *PN-Ceria*. The thermal stability of CeO_2 cubes and octahedras was not evaluated in details due to their large size and small surface areas. Generally, the nanostructures with a larger crystalline size deliver a better thermal resistance at high temperature. Despite the large size of CeO_2 cubes (39 nm, Fig. S2d), the low thermal stability can be revealed from the large size of the nanostructures annealed for 4 hours at 600 °C (65 nm, Fig. S2e) and 800 °C (129 nm, Fig. S2f). The morphology of CeO_2 cubes was converted into spherical-like, further confirming the low thermal stability of cubes.

Redox Properties of *PN-CeO₂* and *NR-CeO₂*

The reduction characteristics of the freshly prepared catalysts were studied in the temperature range from room temperature to 900 °C. As shown in Fig. S6, H_2 -TPR profiles of *PN-Ceria* and *NR-Ceria* exhibit two distinct temperature windows, below and above 510 °C. Their peak temperatures and intensities are strongly depended on their morphology. The temperature windows below 510 °C are assigned to removal of surface active oxygen (e.g. oxygen vacancies, surface lattice oxygen) and the removal of the surface hydroxyl groups.^{2,3} The significantly strong intensity of the peaks below 510 °C for *PN-Ceria* was caused by the high Ce^{3+} concentration. The H_2 -TPR profile for *PN-Ceria* demonstrates that high concentration of oxygen vacancies is formed, compared to the H_2 -TPR profile of *NR-Ceria*. The conclusion is consistent with the experimental results of XPS and our previous reported CO-TPR profiles.⁴ The temperature windows above 510 °C represent the reduction of bulk oxygen from ceria. Compared to the second reduction window of *NR-Ceria* at 850 °C corresponded to the lattice oxygen, the large shift of the second reduction window of *PN-Ceria* to a much lower temperature of 585 °C indicates that the rapider migration of lattice oxygen from the bulk towards surface for *PN-Ceria*. It might be attributed to the short migration pathway of bulk oxygen induced by the porous feature of *PN-Ceria*. Since the CRM reaction takes place up to 800 °C in the presence of H_2 and CO, the stronger and broader reduction peaks from room temperature to 800 °C for *PN-Ceria* indicate the amount of oxygen provided to CRM by *PN-Ceria* is much larger than that by *NR-Ceria*.

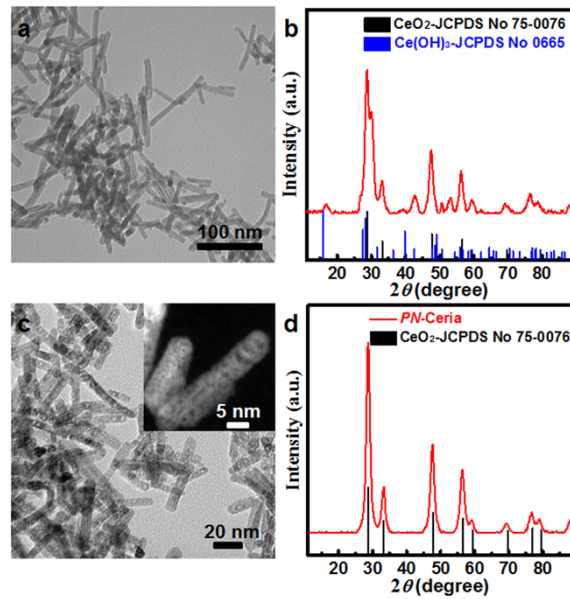


Fig. S1. (a) TEM image of PN-Ceria precursor. (b) XRD spectrum of PN-Ceria precursor. (c) TEM image of PN-Ceria, inset is the dark field TEM of PN-Ceria. (d) XRD spectrum of PN-Ceria.

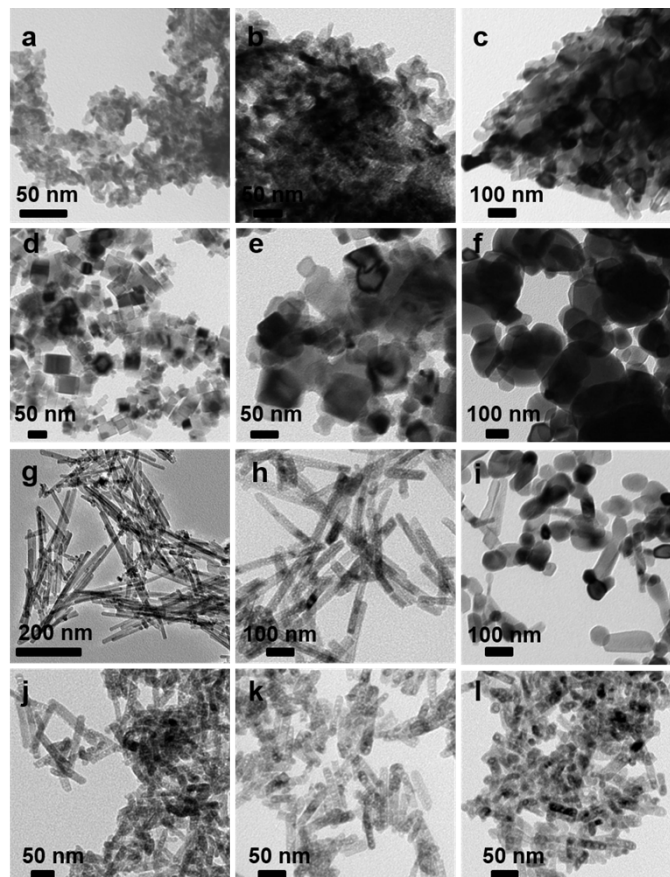


Fig. S2. TEM characterization of CeO_2 nanoparticles, *NR*-Ceria and *PN*-Ceria calcined at 600 °C and 800 °C. (a) As-synthesized CeO_2 nanoparticles, (b) CeO_2 nanoparticles-600 °C, (c)

CeO₂ nanoparticles-800 °C, (d) As-synthesized CeO₂ cubes, (e) CeO₂ cubes -600 °C, (f) CeO₂ cubes-800 °C, (g) As-synthesized NR-Ceria, (h) NR-Ceria-600 °C, (i) NR-Ceria-800 °C, (g) As-synthesized PN-Ceria, (k) PN-Ceria-600 °C, (l) PN-Ceria-800 °C.

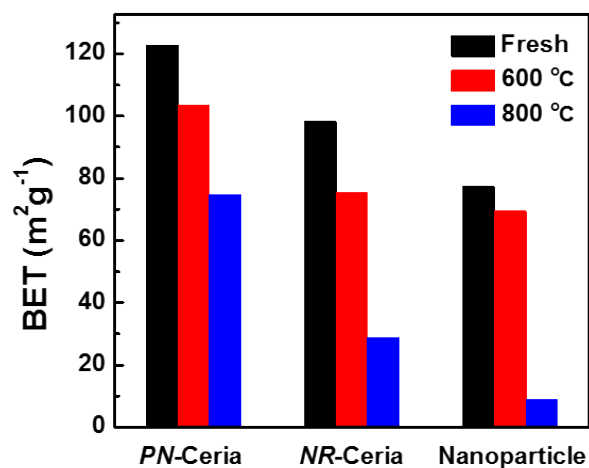


Fig. S3. The evolution of the surface areas of various CeO₂ supports treated at different calcination temperatures under ambient conditions.

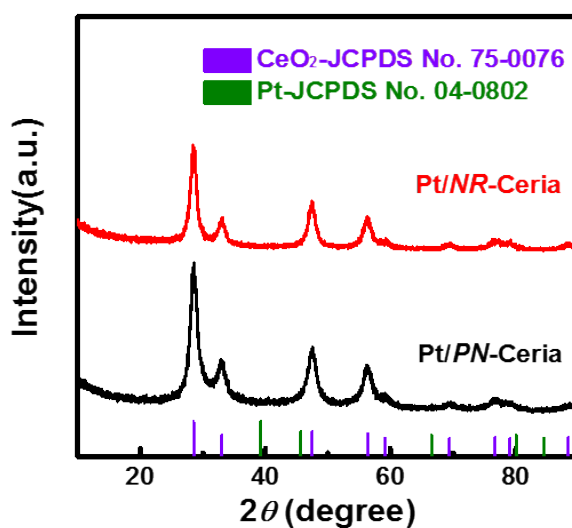


Fig. S4. XRD patterns of the reduced Pt/PN-Ceria and Pt/NR-Ceria catalysts.

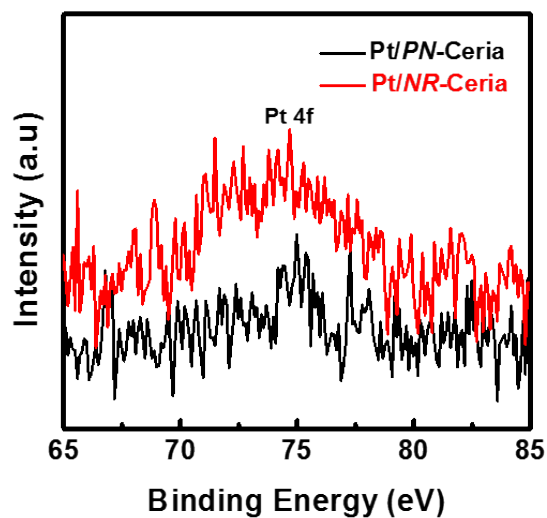


Fig. S5. XPS spectra of the Pt 4f for Pt/PN-Ceria and Pt/NR-Ceria catalysts.

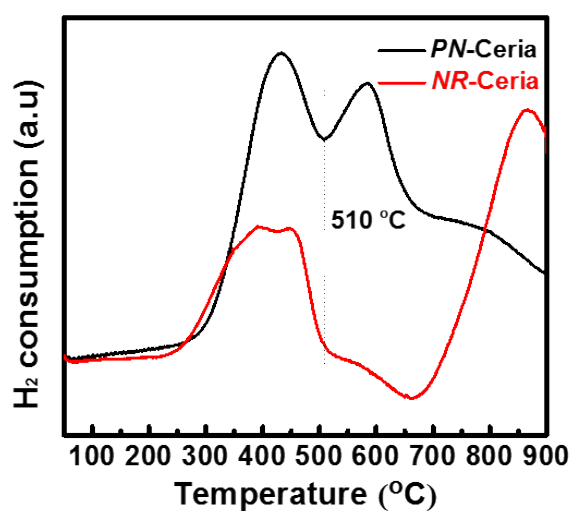


Fig. S6. H₂-TPR profiles of PN-Ceria and NR-Ceria.

References

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