Electronic Supplementary Information for

Low Pressure Induced Porous Nanorods of Ceria with High Reducibility and Large Oxygen Storage Capacity: Synthesis and Catalytic Applications

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- Figure S1. TGA of non-porous nanorod precursor, composite of Ce(OH)₃/CeO₂ synthesized in a Pyrex bottle.
- 2. Figure S2. The N₂ adsorption/desorption isotherms of *PN*-Ceria-160 and *PN*-Ceria-R-160 obtained under different pressure conditions.
- 3. Figure S3. XRD spectra of the milky products after mixing Ce(NO₃)₃ and NaOH.
- 4. Figure S4. Characterization of the rod-shaped Ce(OH)₃/CeO₂ precursor obtained under 1.0 atm and the resulting nanoporous CeO₂ rods upon hydrothermal dehydration of the precursor. a, XRD patterns of Ce(OH)₃/CeO₂ precursor and corresponding nanoporous CeO₂ rods. b, TGA of Ce(OH)₃/CeO₂ precursor obtained under 1.0 atm. c, TEM image of the Ce(OH)₃/CeO₂ precursor obtained hydrothermally under 1.0 atm. d, TEM image of the porous nanorods of ceria upon dehydration of the precursor shown in c.
- 5. Figure S5. Plot of the surface area of ceria nanorods vs. weight percentage of

 $Ce(OH)_3$ in the three different $Ce(OH)_3/CeO_2$ precursors prior to their dehydration and subsequent oxidation of the dehydration products.

- 6. Figure S6. Structural characterization of CeO₂ nanocubes, nanooctahedra and nanoparticles: a, TEM image of CeO₂ nanocubes. b, TEM image of CeO₂ nanooctahedra. c, TEM image of CeO₂ nanoparticles. d, XRD spectra of CeO₂ nanocubes, nanooctahedra and nanoparticles.
- Figure S7. XPS analysis of all nanoceria: a, XPS detail spectra of the Ce 3d core level regions for CeO₂ nanocubes and nanooctahedra. b, Survey XPS spectra of all nanoceria.
- Figure S8. XPS analysis. a, Survey XPS spectra of *PN*-CeO₂-160. b, Comparison of *PN*-CeO₂-160 and silicon pellet survey XPS spectra.
- Figure S9. Raman patterns of non-porous CeO₂ nanorods, *PN*-CeO₂-160 and *PN*-CeO₂-R-160: a, Raman patterns of CeO₂ nanorods in the 150-800 cm⁻¹. b, Raman patterns of CeO₂ nanorods in the 450-750 cm⁻¹.
- Figure S10. CO oxidation performance of CeO₂ nanostructures. a, CO oxidation catalyzed by *PN*-CeO₂-160, non-porous CeO₂ nanorods, and CeO₂ nanoparticles. b, The corresponding Arrhenius plot for the three nanoceria catalysts in a.
- 11. Table S1. Summary of previously reported OSC values for CeO₂ and chemical-doped CeO₂ nanostructures.

1. Figure S1 TGA of non-porous nanorod precursor, composite of Ce(OH)₃/CeO₂ synthesized in a Pyrex bottle.



2. Figure S2 The N₂ adsorption/desorption isotherms of *PN*-Ceria-160 and *PN*-Ceria-R-160 obtained under different pressure conditions.



3. Figure S3 XRD spectra of the milky products after mixing Ce(NO₃)₃ and NaOH.



4. Figure S4 Characterization of the rod-shaped Ce(OH)₃/CeO₂ precursor obtained under 1.0 atm and the resulting nanoporous CeO₂ rods upon hydrothermal dehydration of the precursor. **a**, XRD patterns of Ce(OH)₃/CeO₂ precursor and corresponding nanoporous CeO₂ rods. **b**, TGA of Ce(OH)₃/CeO₂ precursor obtained under 1.0 atm. **c**, TEM image of the Ce(OH)₃/CeO₂ precursor obtained hydrothermally under 1.0 atm, respectively. **d**, TEM image of the porous nanorods of ceria upon dehydration of the precursors shown in **c**.



5. Figure S5 Plot of the surface area of ceria nanorods vs. weight percentage of $Ce(OH)_3$ in the three different $Ce(OH)_3/CeO_2$ precursors prior to their dehydration and subsequent oxidation of the dehydration products.



6. Figure S6 Structural characterization of CeO_2 nanocubes, nanooctahedra and nanoparticles: a, TEM image of CeO_2 nanocubes. b, TEM image of CeO_2 nanooctahedra. c, TEM image of CeO_2 nanoparticles. d, XRD spectra of CeO_2 nanocubes, nanooctahedra and nanoparticles.



7. Figure S7 XPS analysis of all nanoceria: a, XPS detail spectra of the Ce 3d core level regions for CeO₂ nanocubes and nanooctahedra. **b**, Survey XPS spectra of all nanoceria.



As shown in Fig. S7a, the curves of Ce 3d spectra contain eight peaks corresponding to four pairs of spin-orbit doublets. The fitting and labeling of the peaks follow the convention. Letters u and v refer to the $3d_{3/2}$ and $3d_{5/2}$ spin-obit components, respectively. The couples corresponding to one of the two possible electron configurations of the final state of the Ce³⁺ species are labeled as u' and v'. The relative percentage of the cerium species is obtained by the area ratio of Ce⁴⁺ $3d_{5/2}$ (v, v" and v"")/Ce³⁺ $3d_{5/2}$ (v'). The fraction of cerium in the +3 oxidation state can is calculated from the ratio of the sum of areas of the Ce³⁺ species to the sum of areas of the total cerium species.

8. Figure S8 XPS analysis. a, Survey XPS spectra of *PN*-CeO₂-160. **b**, Comparison of *PN*-CeO₂-160 and silicon pellet survey XPS spectra.



9. Figure S9 Raman patterns of non-porous CeO₂ nanorods, *PN*-CeO₂-160 and *PN*-CeO₂-R-160: **a**, Raman patterns of CeO₂ nanorods in the 150-800 cm⁻¹. **b**, Raman patterns of CeO₂ nanorods in the 450-750 cm⁻¹. The signal of non-porous CeO₂ nanorods was enlarged twice due to its weak intensity.



10. Figure S10 CO oxidation performance of CeO_2 nanostructures. a, CO oxidation catalyzed by *PN*-CeO₂-160, non-porous CeO₂ nanorods, and CeO₂ nanoparticles. b, The corresponding Arrhenius plot for the three nanoceria catalysts in **a**.



11. Table S1 Summary of previously reported OSC values for CeO₂ and chemical-doped CeO₂ nanostructures.

| doped CeO ₂ nanostructures. | | | |
|---|-------------------------|------------------------------|-----------|
| Sample | BET (m ² /g) | OSC (µmol O ₂ /g) | Reference |
| CeO ₂ nanoplates | 32 | 230.5 | 1 |
| CeO ₂ nanocrystals | 61 | 357 | 2 |
| CeO ₂ particles | 12 | 183 | 3 |
| CeO ₂ nanorods | 60.8 | 277 | 4 |
| CeO ₂ particles | 93 | 258 | 5 |
| CeO ₂ -ZrO ₂ particles | 135 | 934 | 5 |
| La-Ce _{0.2} Zr _{0.8} O ₂ particles | 144 | 363 | 6 |
| Ni-Ce _{0.67} Zr _{0.33} O ₂ particles | 152 | 730 | 7 |

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D. Wang, Y. Kang, V. Doan-Nguyen, J. Chen, R. Küngas, N. L. Wieder, K. Bakhmutsky, R. J. Gorte and C. B. Murray, *Angew. Chem. Int. Ed.*, 2011, 50, 4378-4381.

- J. Zhang, H. Kumagai, K. Yamamura, S. Ohara, S. Takami, A. Morikawa, H. Shinjoh, K. Kaneko, T. Adschiri and A. Suda, *Nano Lett.*, 2011, 11, 361-364.
- A. Gayen, K. R. Priolkar, P. R. Sarode, V. Jayaram, M. S. Hegde, G. N. Subbanna and S. Emura, *Chem. Mater.*, 2004, 16, 2317-2328.
- H.-X. Mai, L.-D. Sun, Y.-W. Zhang, R. Si, W. Feng, H.-P. Zhang, H.-C. Liu and C.-H. Yan, J. Phys. Chem. B, 2005, 109, 24380-24385.
- S. Letichevsky, C. A. Tellez, R. R. de Avillez, M. I. P. da Silva, M. A. Fraga and L. G. Appel, *Appl. Catal. B*, 2005, 58, 203-210.
- Q. Wang, G. Li, B. Zhao, M. Shen and R. Zhou, *Appl. Catal. B*, 2010, **101**, 150-159.
- 7. G. Li, Q. Wang, B. Zhao and R. Zhou, Appl. Catal. B, 2011, 105, 151-162.