

Electronic Supplementary Information

One-Pot Synthesis of Core-Shell Au@CeO_{2-δ} Nanoparticles Supported on Three-Dimensionally Ordered Macroporous ZrO₂ with Enhanced Catalytic Activity and Stability for Soot Combustion

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Experimental Section

Synthesis of monodispersed PMMA microsphere and assembly template

Non-crosslinked, monodispersed PMMA microspheres were synthesized using a modified emulsifier-free emulsion polymerization technique with water-oil biphasic double initiators. The deionized water in the forthcoming synthetic steps was distilled and the resistivity of them is exceed $12 \text{ M}\Omega\cdot\text{cm}$. Methyl methacrylate (MMA, 80 ml) as monomer was washed in a separatory funnel three times with 50 ml of NaOH solution (1 mol L^{-1}), and then it was washed three times with 50 ml of water. Finally, the refined monomers were obtained by reduced pressure distillation. The mixture of acetone (100 ml) and water (300 ml) were poured into a four-necked and round-bottomed flask (2000 ml). When the mixture was heated to $70 \text{ }^\circ\text{C}$ by a hot water bath, the refined monomers were also added into it. A Teflon stirring paddle attached to the flask was driven by an electric motor after N_2 was bubbled to deaerate the air for 2h. In a separate polyethylene bottle, 0.31 g of potassium persulfate (KPS, water phase initiator) and 0.18 g of azodiisobutyronitrile (AIBN, oil phase initiator) were added into the water (150 ml). When the solution was heated to $70 \text{ }^\circ\text{C}$, it was added to the flask. Under the constant stirring rate (380 r min^{-1}) and the protection of nitrogen, the mixture was kept at $70 \text{ }^\circ\text{C}$ for 2 h. After the reaction was finished, the reaction system was naturally cooled to room temperature, and the homogenous latex with nearly monodispersed PMMA microspheres were obtained by the filtration with filter paper (pore sizes, $\sim 1\mu\text{m}$). In the present studies, the average diameters of the obtained microspheres were 350 nm which were estimated by using laser particle size analyzer. The latex was centrifuged at 3000 r/min for 10 h to form colloidal crystal templates (CCT). The clear liquid was decanted and the solid block was dried in centrifugal tubes at room temperature. Finally, the highly ordered PMMA template was obtained.

Preparation of 3DOM ZrO_2 support

The 3DOM ZrO_2 solid solution was prepared by colloidal crystal template method using ethylene glycol (EG)-methanol solution of $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ as precursor solution and the preparation process is shown in Figure S1. To obtain 3DOM metal oxides, the solidification of these salts is necessary before the bursts of PMMA template. As using EG-methanol solvent, the heteropolynuclear complex containing zirconium ions came into being at low temperature during the dry process. The solidification of the salt occurred before the decomposition of the template polymer. The stoichiometric amount of $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ was dissolved with 15 ml of EG by stirring in a 100 ml beaker at room temperature for 2 h, and the produced EG solution was poured into a 50 ml volumetric flask. Methanol (6 ml) and EG were added to achieve the solution with desired concentration of methanol (the final concentration of methanol was 12 vol %). Then the inorganic precursors were added to the CCT and permeated the voids between the close-packed spheres, and condensed into a hard inorganic framework upon drying. Excessive liquid was removed from the impregnated microspheres template via a Buchner funnel connected to vacuum. The infiltrated template was allowed to dry in a desiccator using anhydrous calcium chloride at room temperature overnight. Finally, the dried sample was mixed with quartz sand (10-15 mesh) and heated in a quartz tube at the rate of $1 \text{ }^\circ\text{C min}^{-1}$ from room temperature to $650 \text{ }^\circ\text{C}$ in air for 8 h to remove the CCT, and then 3DOM ZrO_2 supports with perfect crystal phases were obtained.

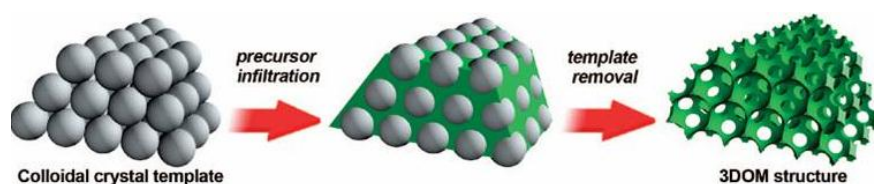


Fig. S1 The schematic diagram for preparing periodic macroporous structures by CCT method.^[1]

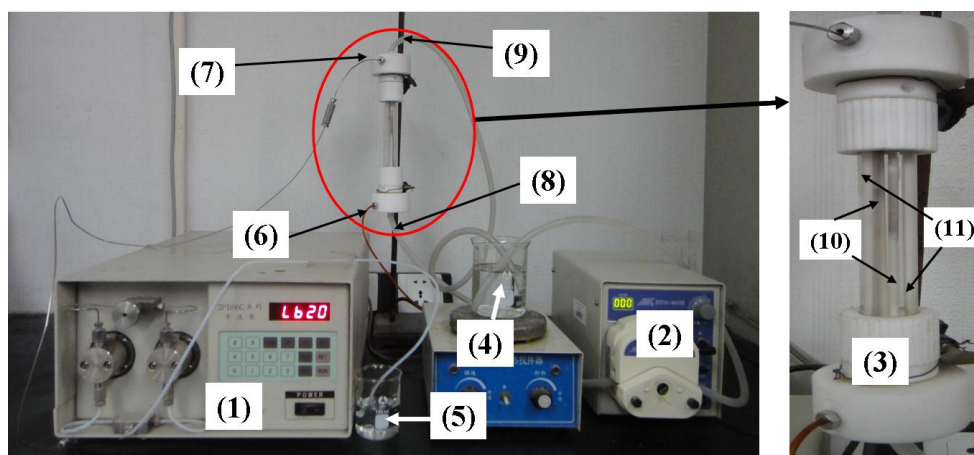


Fig. S2 The digital photos of GBMR device. The right photo is the ceramic membrane reactor composed of four ceramic membrane tubes, which is the core of the device of GBMR method.^[2]

- (1) The constant flow pump (HLB-2020, Satellite Manufactory of Beijing, P.R. China).
- (2) The peristaltic pump (BT00-600M, Baoding Lange Co., Ltd, P.R. China).
- (3) The ceramic membrane reactor consisted of four ceramic membrane tubes (Φ 3 mm \times 160 mm, Hyflux Group of Companies, Singapore), which is the core of the device of GBMR method.
- (4) Beaker I filled with mixture solution (HAuCl_4 , $\text{Ce}(\text{NO}_3)_3$, 3DOM ZrO_2 and PVP).
- (5) Beaker II filled with reductant solution (NaBH_4) or precipitation agent ($\text{NH}_3 \cdot \text{H}_2\text{O}$).
- (6) The inlet of hydrogen.
- (7) The inlet of reductant solution (NaBH_4) or precipitation agent ($\text{NH}_3 \cdot \text{H}_2\text{O}$).
- (8) The inlet of mixture solution.
- (9) The outlet of mixture solution and hydrogen.
- (10) Two ceramic membrane tubes used for the dispersion of reductant solution (NaBH_4).
- (11) Two ceramic membrane tubes used for the dispersion of hydrogen bubbling.

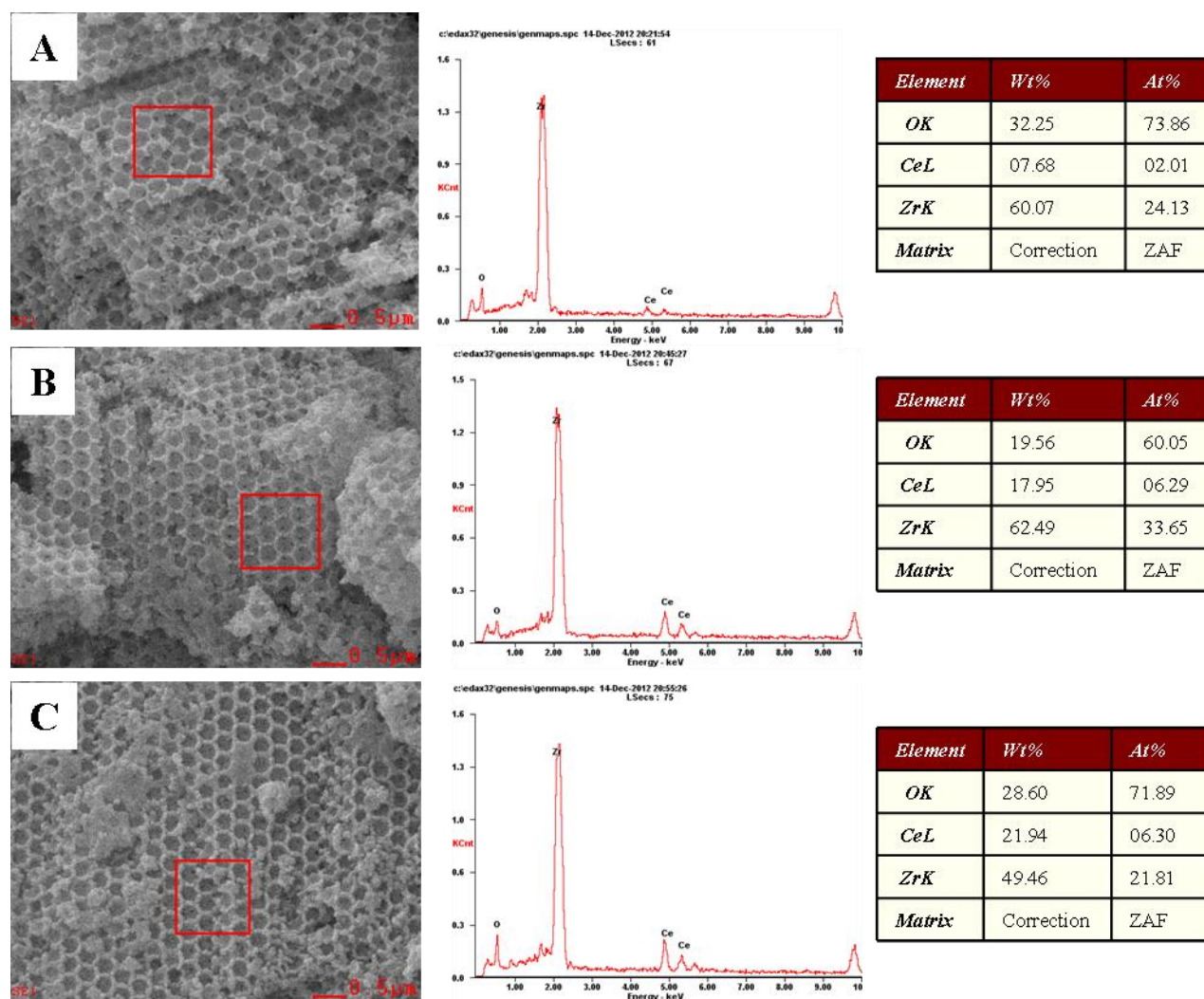


Fig. S3 SEM images, SEM-EDX spectra and the surface molar ratios of CeO_2 to ZrO_2 determined by EDX spectra over 3DOM $\text{Au@CeO}_{2-\delta}/\text{ZrO}_2$ catalysts prepared by GBMR/P method. A. $\text{Au@CeO}_{2-\delta}/\text{ZrO}_2$ -2; B. $\text{Au@CeO}_{2-\delta}/\text{ZrO}_2$ -5; C. $\text{Au@CeO}_{2-\delta}/\text{ZrO}_2$ -10

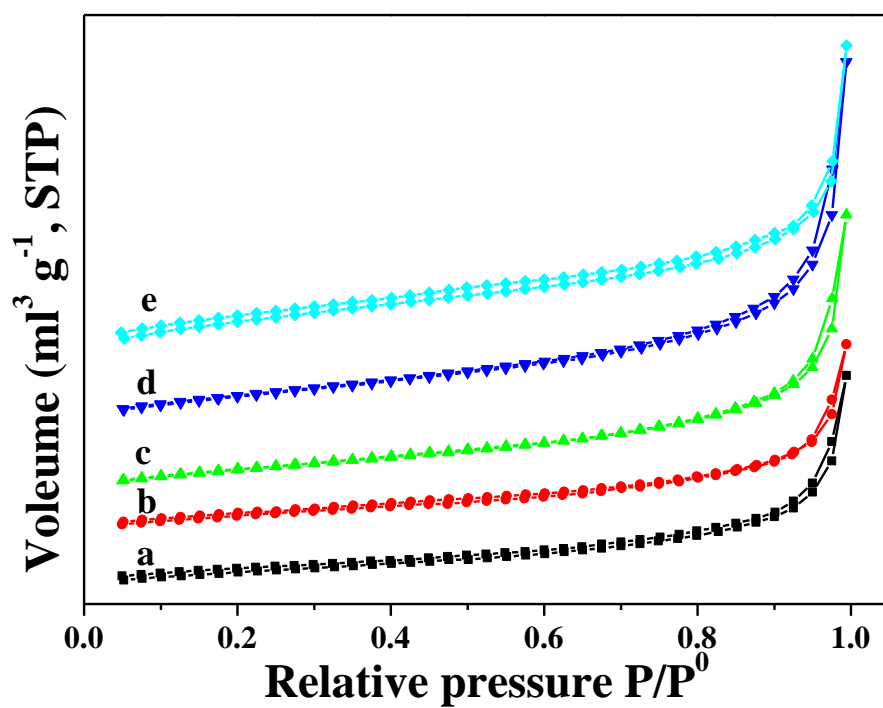


Fig. S4 Nitrogen adsorption-desorption isotherms of 3DOM ZrO₂, Au/ZrO₂ and Au@CeO_{2.8}/ZrO₂ catalysts. a. ZrO₂; b. Au/ZrO₂; c. Au@CeO_{2.8}/ZrO₂-2; d. Au@CeO_{2.8}/ZrO₂-10

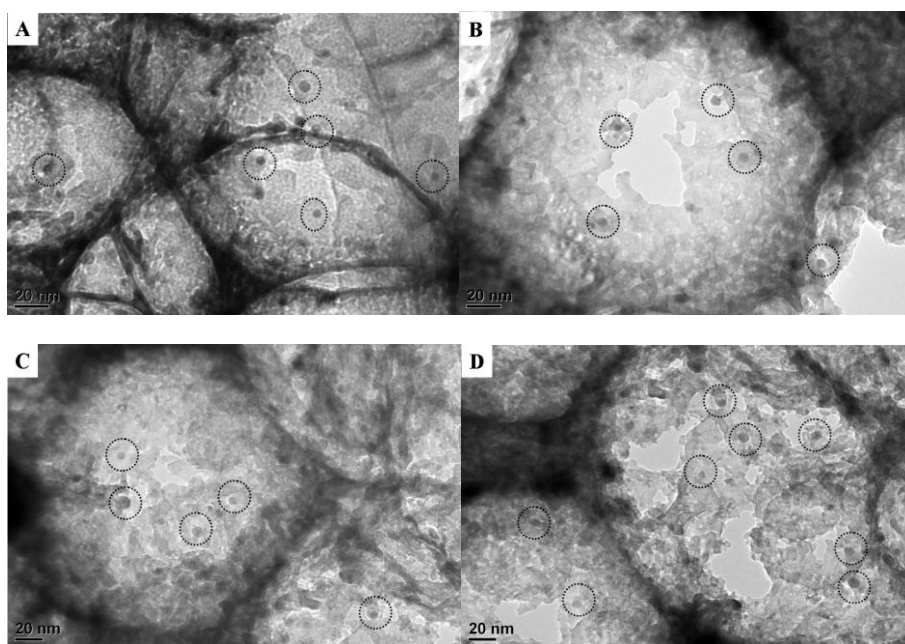


Fig. S5 TEM images of 3DOM Au@CeO_{2.8}/ZrO₂ catalysts. The black rings in (B, D, F) images show the Au@CeO_{2.8} core-shell structured NPs. A. Au/ZrO₂; B. Au@CeO_{2.8}/ZrO₂-2; C. Au@CeO_{2.8}/ZrO₂-5; D. Au@CeO_{2.8}/ZrO₂-10

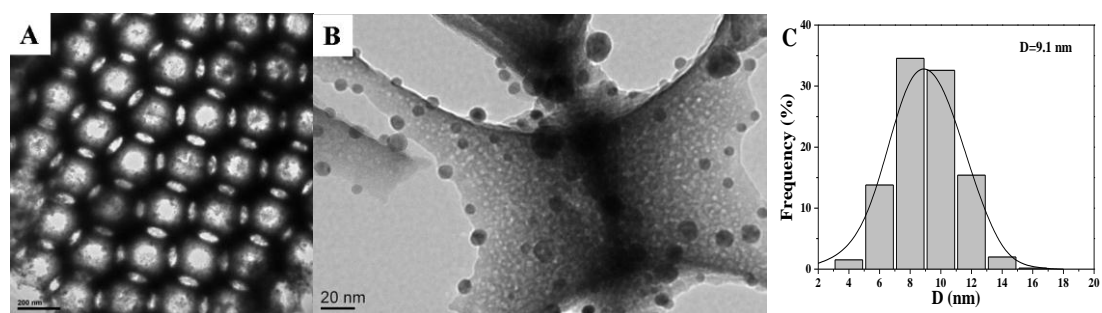


Fig. S6 TEM (A-B) images and the size distribution of supported Au nanoparticles (C) of 3DOM Au/ZrO₂ catalyst obtained by calcination at 500 °C for 2 h.

References

- [1] A. Stein, F. Li and N. R. Denny, *Chem. Mater.* 2008, **20**, 649.
- [2] Y. Wei, J. Liu, Z. Zhao, A. Duan, G. Jiang, C. Xu, J. Gao, H. He and X. Wang, *Energy Environ. Sci.* 2011, **4**, 2959.