# **Electronic Supporting Information**

# Three-dimensionally ordered macroporous Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>-supported gold nanoparticles: synthesis with controllable size and super catalytic performance for soot oxidation

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### **Experimental Section**

#### Synthesis of monodispersed PMMA microsphere and assembly of template

Non-crosslinked, monodispersed PMMA microspheres were synthesized using a modified emulsifier-free emulsion polymerization technique with water-oil biphase double initiators. All water in the forthcoming synthetic steps was distilled and deionized to a resistivity of at least 12 M $\Omega$ ·cm. Methyl methacrylate (MMA, 80 ml) was washed in a separatory funnel three times with 50 ml of 1 M NaOH, then washed three times with 50 ml of water. And it was refined by reduced pressure distillation. A four-necked, 2000 ml round-bottomed flask was filled with the mixture of acetone (100 ml) and water (300 ml) and heated to 70 °C by a hot water bath, following the addition of the refined monomers. An electric motor was attached to the flask and to drive a Teflon stirring paddle and N<sub>2</sub> was bubbled to deaerate the air for 2 h. In a separate 160 ml polyethylene bottle, 0.31 g of 2, 2'-azobis (2-methylpropionamide) dihydrochloride (AIBA, water phase initiator) and 0.18 g of azodiisobutyronitrile (AIBN, oil phase initiator) were added into 150 ml of water, and then the solution was heated to 70 °C and added to mixture solutions. Under constant stirring (380 r/min) and with N<sub>2</sub> bubbling, the mixture was kept at 70 °C for 2 h. After the reaction was finished, the colloid sol was naturally cooled to room temperature, and obtained the homogenous latex with nearly monodispersed PMMA microspheres through filter paper with pores size of 1µm. 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 templates were obtained.

#### Preparation of 3DOM Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> support

The 3DOM  $Ce_{0.8}Zr_{0.2}O_2$  oxide was prepared by colloidal crystal template method using ethylene glycol (EG)-methanol solution of various metal nitrates (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, ZrOCl<sub>2</sub>·8H<sub>2</sub>O) as precursor solution in Figure S1. To obtain 3DOM metal oxides, the solidification of these salts is necessary before the bursts of template polymethyl methacrylate. As using EG-methanol solvent, the heteropolynuclear complex containing cerium and zirconium ions using EG-methanol solution as solvent came into being at low temperature during the dry process, indicating that the solidification of the two salts occurred before the decomposition of the template polymer. The stoichiometric amounts of mixed metal nitrates were 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 infiltered 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 °C/min from room temperature to 550 °C in air for 5 h to remove the CCT, and then 3DOM  $Ce_{0.8}Zr_{0.2}O_2$  support possessing perfect crystal phases was obtained.



**Fig. S1:** The schematic diagram for preparing periodic macroporous structures by colloidal crystal template method <sup>[1]</sup>.



**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.

- (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 ( $\Phi$  3 mm  $\times$  160 mm,
- Hyflux Group of Companies, Singapore), which is the core of the device of GBMR method.
- (4) Beaker 1 filled with mixture solution (HAuCl<sub>4</sub>, 3DOM Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> support and PVP).
- (5) Beaker 2 filled with reductant solution (NaBH<sub>4</sub>).
- (6) The inlet of hydrogen.
- (7) The inlet of reductant solution (NaBH<sub>4</sub>).
- (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<sub>4</sub>).
- (11) Two ceramic membrane tubes used for the dispersion of hydrogen bubbling.

The typical preparative procedures were described as follows: The mixture solution (HAuCl<sub>4</sub>, 3DOM Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> support and PVP) was driven by a peristaltic pump (Baoding Lange Co., Ltd) and the rotate speed at 200 rpm (~360 ml min<sup>-1</sup>) to form a tubal cycling flow. A reductant solution (NaBH<sub>4</sub>) (1 ml min<sup>-1</sup>, 50 ml) was injected to the membrane reactor with two ceramic membrane tubes ( $\Phi$  3 mm  $\times$  160 mm, Hyflux Group of Companies, Singapore) by a constant flow pump (HLB-2020, Satellite Manufactory of Beijing). Meantime, the hydrogen gas was also injected by the two other membrane tubes. The metal precursor solution flowed in the glass tube reactor and outside the ceramic tubes. The NaBH<sub>4</sub> solution was infiltrated through the abundant holes (d=40 nm) on the wall of the ceramic tubes into the glass tube reactor, where the reduction of metal ions occurred immediately when the two solutions met. The hydrogen bubbling-assisted stirring operation (40 ml min<sup>-1</sup>) was developed to vigorously stir the solution and to make the reaction homogenous. The synthesis process was stopped after complete consumption of the NaBH<sub>4</sub> solution. The reaction system was further vigorously bubbled with hydrogen gas for 1 h, and then kept static for 1 h. Then, the product was filtered and washed with distilled water at 60  $^{\circ}$ C until the Cl<sup>-</sup> was completely removed according to a test with AgNO<sub>3</sub>. The final products were dried in an oven at 200 °C for 1 h and the desired 3DOM Au<sub>n</sub>/Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalysts were obtained.

## **Results Section.**



Fig. S3: SEM image of the three-dimensional ordered PMMA colloidal crystal template.



**Fig. S4:** XRD patterns (Left) of  $Ce_{0.8}Zr_{0.2}O_2$  support with different thermal treatments at 550 °C (a) and 1000 °C (b). Detail of the normalized XRD patterns (Right) of 3DOM  $Ce_{0.8}Zr_{0.2}O_2$  oxide after different thermal treatments shows the fitting of the mains reflections in the region 26~32 °. The presence of a single symmetric reflection (b) suggests the existence of a single phase  $Ce_{0.8}Zr_{0.2}O_2$  oxide.



Fig. S5: TEM, HRTEM images and size distribution of Au nanoparticles of 3DOM  $Au_{0.005}/Ce_{0.8}Zr_{0.2}O_2$  (A-B),  $Au_{0.01}/Ce_{0.8}Zr_{0.2}O_2$  (C-D) and  $Au_{0.06}/Ce_{0.8}Zr_{0.2}O_2$  (E-F) catalysts.



Fig. S6: The FT-IR spectra of 3DOM  $Au_n/Ce_{0.8}Zr_{0.2}O_2$  catalysts with different Au loading amounts.



**Fig. S7:** TEM images and size distribution of Au nanoparticles of 3DOM  $Au_{0.04}/Ce_{0.8}Zr_{0.2}O_2(2.6)$  catalyst used one cycle.



**Fig. S8.** The CO<sub>2</sub> concentration profiles for soot oxidation over the particles  $Ce_{0.8}Zr_{0.2}O_2$  and 3DOM  $Au_n/Ce_{0.8}Zr_{0.2}O_2$  catalysts with different Au contents (A) and particle sizes (B).



**Fig. S9:** The CO<sub>2</sub> concentration profiles of stability test of 3DOM  $Au_{0.04}/Ce_{0.8}Zr_{0.2}O_2$  (2.6) catalyst for soot combustion under the condition of loose contact between catalyst and soot.



**Fig. S10:** TEM (A), HRTEM images (B) and size distribution (C) of Au nanoparticles of 3DOM  $Au_{0.04}/Ce_{0.8}Zr_{0.2}O_2$  catalyst prepared by GBMR method under the condition without hydrogen (0 ml min<sup>-1</sup>).



**Fig. S11:** TEM (A), HRTEM images (B) and size distribution (C) of Au nanoparticles of 3DOM  $Au_{0.04}/Ce_{0.8}Zr_{0.2}O_2$  catalyst prepared by GBMR method under the condition of the flow rate of the reductant solution (5 ml min<sup>-1</sup>).



**Fig. S12:** TEM (A) images and size distribution (B) of Au nanoparticles of 3DOM  $Au_{0.04}/Ce_{0.8}Zr_{0.2}O_2$  catalyst prepared by the conventional chemical reduction method.

<sup>[1]</sup> A. Stein, F. Li and N. R. Denny, Chem. Mater. 2008, 20, 649.