Three dimensionally ordered macroporous $Ce_{1-x}Zr_xO_2$ solid solutions for diesel soot combustion

Electronic Supplementary Information

Preparation of 3DOM $Ce_{1-x}Zr_xO_2$ solid solutions:

The first step in the preparation of 3DOM $Ce_{1-x}Zr_xO_2$ solid solutions was to synthesize a well-ordered colloidal template using monodisperse polymethyl methacrylate (PMMA) spheres and polystyrene (PS) spheres. PMMA spheres (444 nm) were prepared using a modified emulsifier-free emulsion polymerization method [S1] which the methyl methacrylate (MMA) were polymerized at 70 ºC with AIBN and KSP as initiator. PS spheres (454 nm) were supplied by Professor Shengli Chen in Chinese University of Petroleum. Either PMMA or PS colloidal crystal template was prepared by centrifugation (3000 rpm, 10h) of the colloidal suspension in a 50 ml centrifugation tube. The templates were dried at room temperature and annealed at 110 °C for 10 min before being soaked in the liquid precursor. The second step is to prepare the liquid precursor. The stoichiometric amount of cerium nitrate and zirconium oxide chloride were dissolved in an ethylene glycol (EG)-methanol (20~40 vol%) mixed solvent by stirring at room temperature, and the produced solution was poured into a volumetric flask. The mixed solvent was added in amounts necessary to achieve the desired concentration (2M). Then, the dried PS or PMMA colloidal crystal was soaked in the produced solution for some hours. Excess solution was removed by filtration. The obtained composite of PMMA (PS)/inorganic precursor was dried in air at room temperature overnight. Then the dried sample was calcined in a tube furnace with an air flow (80 ml/min). The temperature-rising rate was 1 °C/min from room temperature to 650 °C, and the calcination at 650 °C was kept for 5 h. Finally, the 3DOM $Ce_{1-x}Zr_xO_2$ solid solutions were obtained. (Figure S1)

Synthesis of disordered macroporous $Ce_{1-x}Zr_xO_2$ solid solutions:

The EG-methanol solution of cerium nitrate and zirconium oxide chloride, which was produced during the process of preparation of 3DOM samples, was heated in a muffle oven at the rate of 1 °C/min from room temperature to 650 °C and held for 5 h. Then we obtained some samples with a lot of disordered macropores. (Fig. S2)

Characterization:

Images of SEM were obtained with Hitachi S-4800 using an accelerating voltage of 5.0 kV. TEM images were taken on the Hitachi H-800 transmission electron microscope using an accelerating voltage of 200 kV. XRD spectra were recorded on a Shimadzu XRD 6000 diffractometer using Cu Kα radiation (λ=1.5046 Å). The Raman spectra were recorded using a LabRam-HR800UV Raman spectrometer (Jobin Yvon) with a He-Gd laser (325 nm). Nitrogen adsorption measurements were performed on a Micromeritics ASAP 2010 adsorption analyzer. Specific surface areas were calculated by the Brunaure-Emmert-Teller (BET) method. Intrusion/extrusion mercury measurements were performed using a Micromeritics AutoPore IV 9500.

Catalytic activity measurement:

The catalytic activities of 3DOM $Ce_{1-x}Zr_xO_2$ solid solutions and disordered macroporous materials of $Ce_{1-x}Zr_xO_2$ for soot combustion were tested with a temperature-programmed oxidation (TPO) reaction on a fixed-bed tubular quartz system. The reaction temperature varied during each TPO run from 200 to 600 °C at a 2 °C /min rate. The soot was Printex-U (diameter, 25 nm, purchased from Degussa). The mixture of the catalyst and soot (catalyst to soot, 10:1, mass ratio) were mixed, soaked in 3 ml ethanol, ultrasonicated for 3 min, and at last dried at 100 °C for 2 h. The dried mixture of soot and catalyst were placed in the tubular quartz reactor. Reactant gases containing 10% O_2 and 2000 ppm NO balanced with He were passed through a mixture of the catalyst and soot at a flow rate of 100 ml/min. The outlet gas compositions were analyzed on-line using gas chromatograph (GC, Sp-3420, Beijing, China) equipped with a FID detector. The catalytic performance for catalysts was evaluated by the values of T_{10}, T_{50}, and T_{90}, which were defined as 10%, 50%, and 90% of the soot, respectively, were oxidized at the temperature T during the TPO procedure.

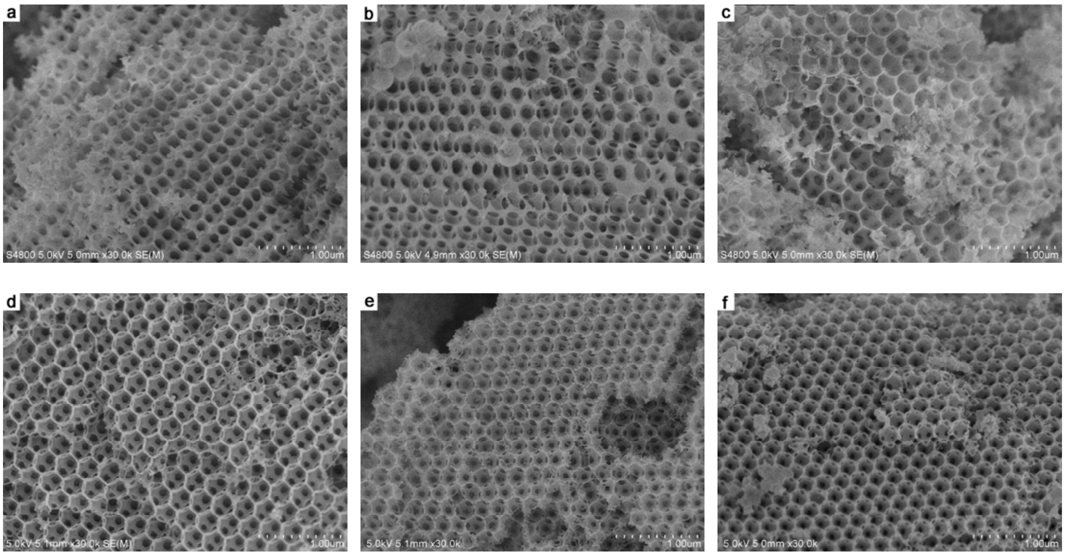

Fig. S1 SEM images of 3DOM $Ce_{1-x}Zr_xO_2$ solid solutions obtained by calcination at 650 °C of PMMA (diameter, 444 nm, a-e) and PS (diameter, 454 nm, f) colloidal crystal infiltrated by EG-methanol solution(20~40 vol%) of ceria nitrate and zirconium oxide chloride (total metal concentration was 2M). The temperature-rising rate was 1 °C/min from room temperature to 650 °C, and the calcination at the temperature of 650 °C was kept for 5 h.

a. $Ce_{0.95}Zr_{0.05}O_2$; b. $Ce_{0.8}Zr_{0.2}O_2$; c. $Ce_{0.6}Zr_{0.4}O_2$; d. $Ce_{0.5}Zr_{0.5}O_2$; e. $Ce_{0.2}Zr_{0.8}O_2$; f. $Ce_{0.5}Zr_{0.5}O_2$.

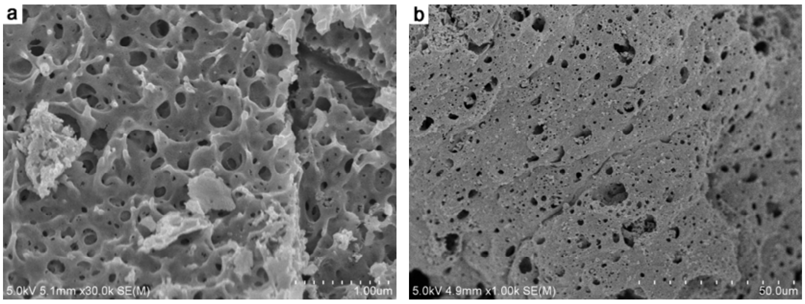

Fig. S2 SEM image of disordered macroporous $Ce_{1-x}Zr_xO_2$ (a, x=0.3; b, x=0.2) obtained by calcination (650 °C) of EG-methanol solution of mixed ceria nitrate and zirconium oxide chloride (total metal concentration was 2M) in a muffle oven. The temperature-rising rate was 1 °C /min from room temperature to 650 °C, and the calcination at 650 °C temperature was kept for 5 h.

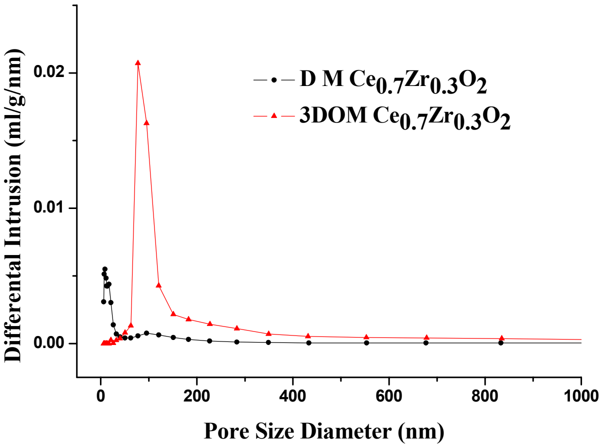

Fig. S3 Macroscopic pore sizes distribution of 3DOM and D M $Ce_{0.7}Zr_{0.3}O_2$ obtained through mercury intrusion porosimetry：

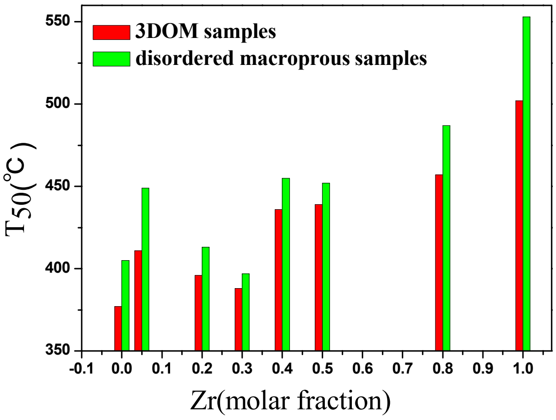

Fig. S4 T_{50} of $Ce_{1-x}Zr_xO_2$ oxides with different macroporous structures for diesel soot combustion versus Zr molar fraction

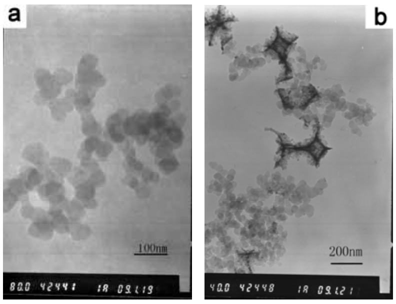

Fig. S5 TEM images of (a) soot (Printex U, purchased from Degussa) and (b) the mixture of 3DOM samples after being soaked in 3 ml ethanol, ultrasonicated, and then dried at 110 °C. The aim is to demonstrate that soot was embedded into the inner pores of 3DOM samples with the help of ultrasonic.

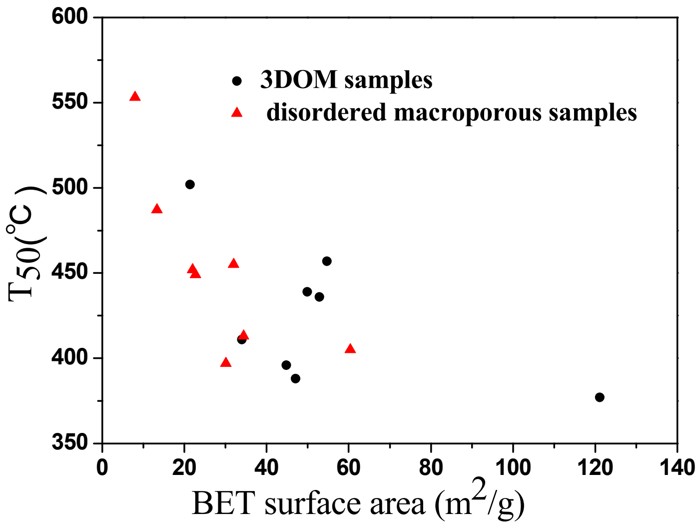

Fig. S6 T$_{50}$ parameter versus BET surface area of all 3DOM and D M Ce$_{1-x}$Zr$_x$O$_2$ oxides

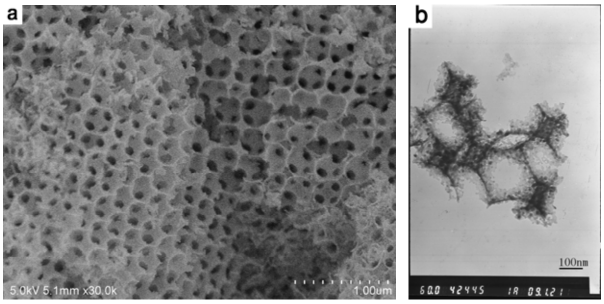

Fig. S7 SEM (a) and TEM (b) images of 3DOM Ce$_{0.7}$Zr$_{0.3}$O$_2$ after soot combustion reaction.

Table S1 The crystalline sizes, surface areas, and porosity data of $Ce_{1-x}Zr_xO_2$ oxides with different macroporous structures

Catalyst	crystalline size/nm[a]	BET surface area /m^2/g		Porosity/%	
	3DOM	3DOM	D M	3DOM	D M
CeO_2	7.3	121.1	60.4	87.6	--
$Ce_{0.95}Zr_{0.05}O_2$	13.6	34.0	22.7	87.3	--
$Ce_{0.8}Zr_{0.2}O_2$	8.3	44.8	34.4	90.7	--
$Ce_{0.7}Zr_{0.3}O_2$	8.2	47.1	30.1	90.3	74.5
$Ce_{0.6}Zr_{0.4}O_2$	5.9	52.9	32.0	88.9	69.8
$Ce_{0.5}Zr_{0.5}O_2$	6.7	49.9	22.0	89.4	62.1
$Ce_{0.2}Zr_{0.8}O_2$	12.9	54.7	13.3	89.3	--
ZrO_2	21.0	21.4	8.0	90.7	--

a. Crystallite sizes were calculated from the width of the (111) line (JCPSD: 43-1002) using the Scherreer equation.

Table S2 The combustion temperatures of soot over $Ce_{1-x}Zr_xO_2$ solid solutions with different morphologies and pore structures

Catalyst	T_{10}/°C		T_{50}/°C		T_{90}/°C	
	3DOM	D M	3DOM	D M	3DOM	D M
CeO_2	236	338	377	405	400	436
$Ce_{0.95}Zr_{0.05}O_2$	345	364	411	449	432	471
$Ce_{0.8}Zr_{0.2}O_2$	348	372	396	413	424	473
$Ce_{0.7}Zr_{0.3}O_2$	345	349	388	397	415	421
$Ce_{0.6}Zr_{0.4}O_2$	365	358	436	455	464	472
$Ce_{0.5}Zr_{0.5}O_2$	382	366	439	452	482	469
$Ce_{0.2}Zr_{0.8}O_2$	350	377	457	487	475	497
ZrO_2	265	317	502	553	520	576

From Table S2, we can see that either 3DOM or DM samples, CeO_2 and $Ce_{0.7}Zr_{0.3}O_2$ show the best performance for soot oxidation. The pure CeO_2 gave the highest activity for soot oxidation mainly due to its best redox property. For the sample of $Ce_{0.7}Zr_{0.3}O_2$, the same activity trend has been reported previously either loose or tight contact between soot and catalysts (J. Catal., 2008, 259, 123; Catal. Today, 2006, 114, 40), also has been reported for the selectively catalytic reduction of NO_x by hydrocarbons (Appl. Catal. B, 2007, 74, 278). The explanations of these results were that cerium-rich samples have greater availability of surface Ce^{4+} sites and have a better ability to donate oxygen for soot oxidation. Additionally, in our study the high activity of $Ce_{0.7}Zr_{0.3}O_2$ might be due to the fact of the coexistence of tetragonal phase and cubic phase based on the XRD and Raman characterization results.

References:

S1. B. T. Holland, C. F. Blanford, T. Do, A. Stein. *Chem. Mater.* 11 (1999) 795.