Electronic Supplementary Information (ESI)

Mesoporous $Ce_{1-x}Zr_xO_2$ Solid Solutions Nanofibers as High Efficiency Catalyst for Catalytic Combustion of VOCs

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Preparation of ordered mesoporous $Ce_{0.5}Zr_{0.5}O_2$ solid solution

Ordered mesoporous $Ce_{0.5}Zr_{0.5}O_2$ solid solution was prepared according to Yan's method [1]. Pluronic P123 (0.5 g) was dissolved in 10 mL of ethanol at room temperature. Then, 0.805 g (2.5 mmol) of $ZrOCl_2 \cdot 8H_2O$ and 1.086 g (2.5 mmol) of $Ce(NO_3)_3 \cdot 6H_2O$ was added to the above solution with vigorous stirring. The mixture was covered with a PE film. After being stirred for at least 2 h at room temperature, the homogeneous sol was transferred to an oven and underwent solvent evaporation. After 2 days of aging under the desired temperature and humidity (temperature 40 °C, relative humidity 50%), the gel product was dried in the other oven at 100 °C for 1 day. Calcination was carried out by slowly increasing the temperature from room temperature to 400 °C (1 °C/min ramping rate) and holding at 400 °C for 4 h in air.

Preparation of bulk $Ce_{0.5}Zr_{0.5}O_2$ solid solution

The bulk $Ce_{0.5}Zr_{0.5}O_2$ solid solution was prepared via sol-gel process followed by self-sustaining combustion treatment without the electrospinning procedure. The sol solution was initially prepared by mixing water (12 mL), Pluronic P123 (0.5g, Mav = 5800, $EO_{20}PO_{70}EO_{20}$), PEO (0.3077g, Mn = 1000000), PVP (0.1333g, Mw = 1300000), stoichiometric amount of cerium nitrate, zirconium nitrate, and certain amount of citric acid (CA, the molar ratio of CA : (Ce+Zr) = 2) with magnetic stirring. After being vigorously stirred for 12 h, the water solution was left to evaporate at 80 °C with continuous magnetic stirring, until a sticky gel was obtained. Then the gel was transferred to a ceramic crucible and placed into an oven that was preheated at 300 °C and kept in the oven for 1 h to generate bulk $Ce_{1-x}Zr_xO_2$ solid solutions.

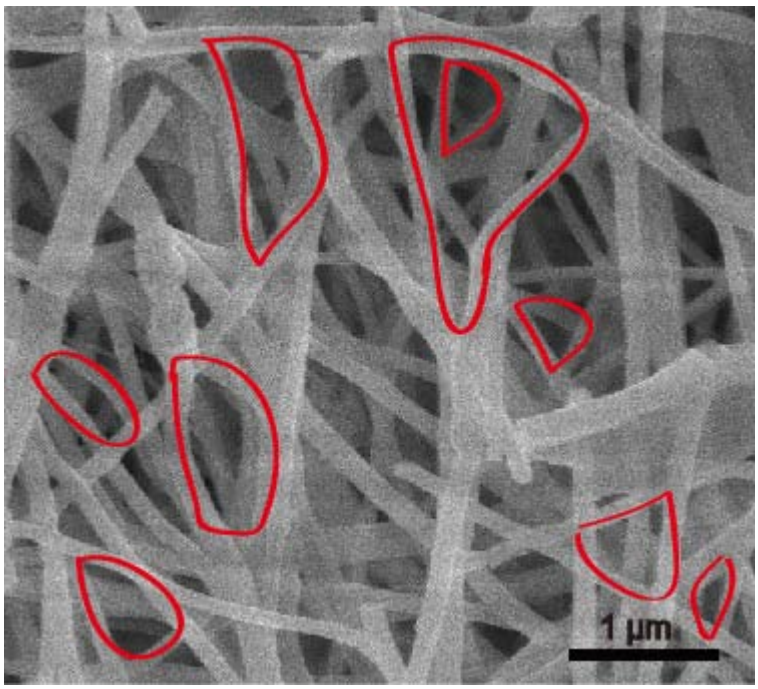

Fig. S1 SEM of $Ce_{0.5}Zr_{0.5}O_2$ nanofibers nonwoven mat with macroporous network prepared at 300 °C (some macropores with different sizes and shapes were marked by red lines)

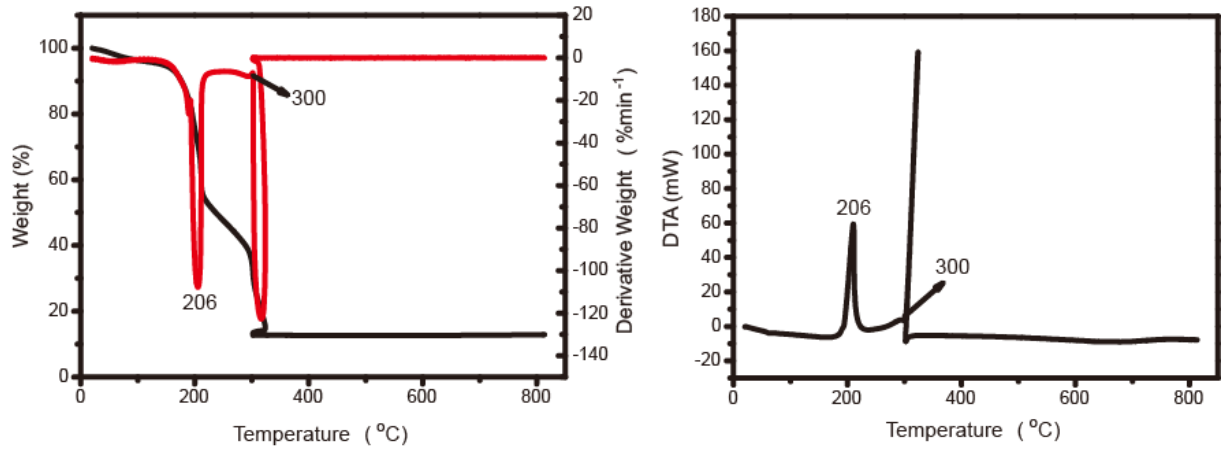

Fig. S2 (Left) TGA-DTG and (Right) DTA profiles of the $Ce_{0.5}Zr_{0.5}O_2$ precursor nanofibers

In order to mimic the calcination conditions, the TG temperature program is designed so that there is a 1 h temperature plateau at 300 °C. The TG plot shows two major weight loss regimes, the first one at around 206 °C, as seen in the DTG plot, can be mainly assigned to the dissociation of PEO in the precursor fibers, resulting in a further 40% weight loss and a strong exothermic peak at 206 °C[2,3]; the second weight loss starting around 290 °C is corresponded to the degradation of PVP[4] and the combustion of nitrate and citric acid, contributing to a very strong exothermic peak at 300 °C (Figure S1) and another 43% weight loss, which are due to the self-sustaining combustion reaction between the metal nitrates and citric acid[5,6]. After the isothermal heating at 300 °C for 1h, the heating step from 300 to 800 °C shows no weight loss, which indicates complete removal of carbonaceous material after heating at 300 °C for 1h.

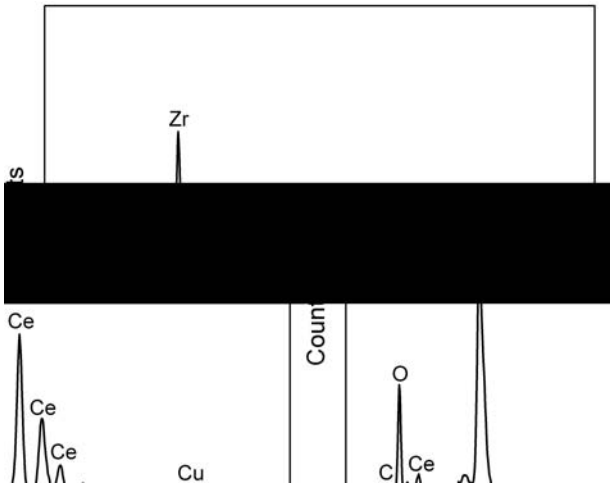

Fig. S3 Energy dispersive X-ray spectroscopy (EDS) of hierarchical porous 3D $Ce_{0.5}Zr_{0.5}O_2$ solid solution. Ce/Zr ratio is measured to be 50.6:49.4. The C and Cu peaks come from the conductive adhesive that was used to fix the sample on the sample support during the SEM observation

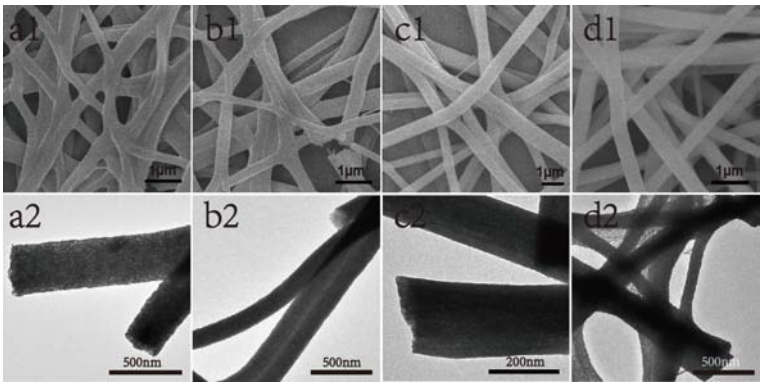

Fig. S4 (a1) SEM image of 10%Y_2O_3 modified $Ce_{0.5}Zr_{0.5}O_2$ nanofibers; (b1) SEM image of 10% La_2O_3 modified $Ce_{0.5}Zr_{0.5}O_2$ nanofibers; (c1) SEM image of 10% NiO modified $Ce_{0.5}Zr_{0.5}O_2$ nanofibers; (d1) SEM image of 10% MnO_2 modified $Ce_{0.5}Zr_{0.5}O_2$ nanofibers; (a2) TEM image of 10%Y_2O_3 modified $Ce_{0.5}Zr_{0.5}O_2$ nanofibers; (b2) TEM image of 10% La_2O_3 modified $Ce_{0.5}Zr_{0.5}O_2$ nanofibers; (c2) TEM image of 10% NiO modified $Ce_{0.5}Zr_{0.5}O_2$ nanofibers; (d2) TEM image of 10% MnO_2 modified $Ce_{0.5}Zr_{0.5}O_2$ nanofibers.

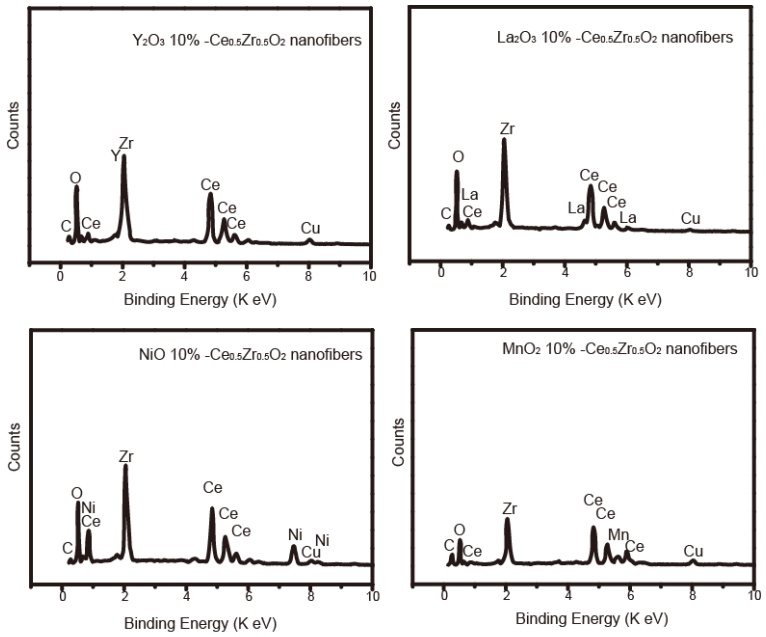

Fig. S5 Energy dispersive X-ray (EDX) spectra of 10%Y_2O_3 modified $Ce_{0.5}Zr_{0.5}O_2$, 10% La_2O_3 modified $Ce_{0.5}Zr_{0.5}O_2$, 10% NiO modified $Ce_{0.5}Zr_{0.5}O_2$, 10% MnO_2 modified $Ce_{0.5}Zr_{0.5}O_2$ nanofibers prepared at 300 ^oC

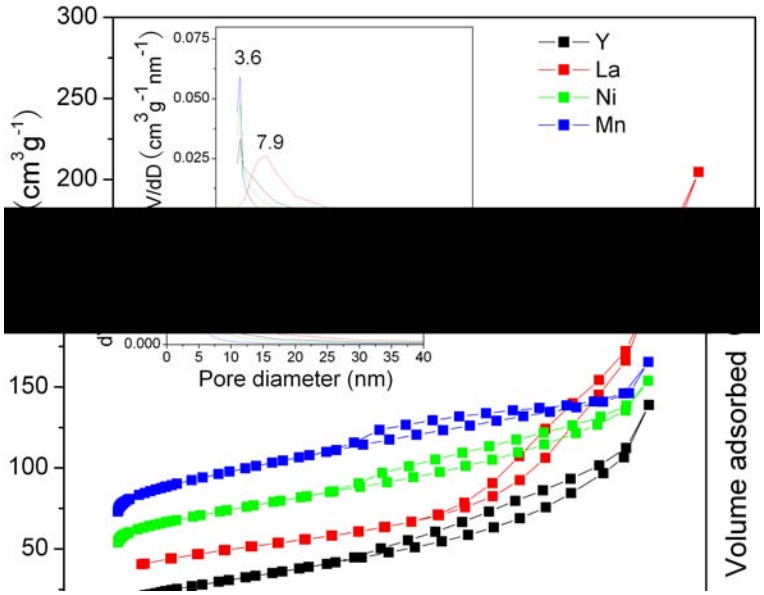

Fig. S6 N_2 adsorption-desorption isotherms of Y, La, Ni and Mn modified $Ce_{1-x}Zr_xO_2$ nanofibers synthesized at 300 ^oC (Inset: corresponding pore size distribution curves deduced from the desorption branches).

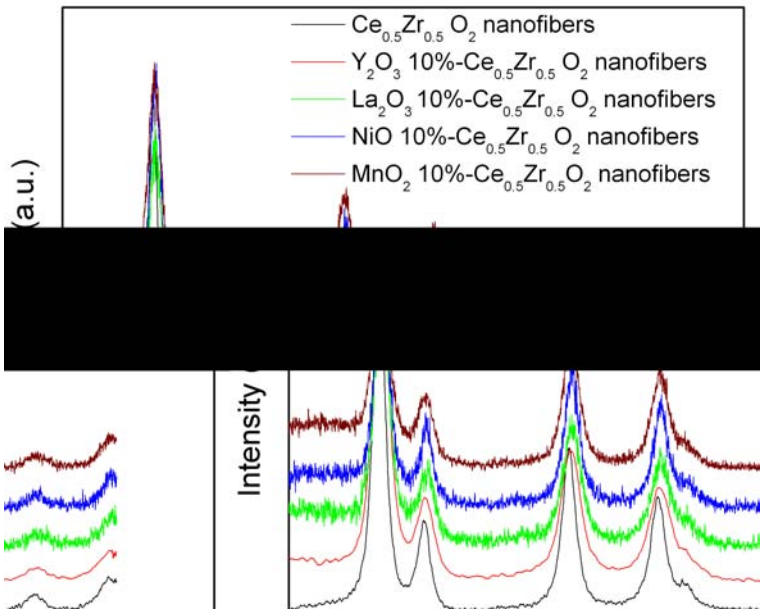

Fig. S7 X-ray diffraction patterns of $Ce_{0.5}Zr_{0.5}O_2$, 10%Y_2O_3 modified $Ce_{0.5}Zr_{0.5}O_2$, 10% La_2O_3 modified $Ce_{0.5}Zr_{0.5}O_2$, 10% NiO modified $Ce_{0.5}Zr_{0.5}O_2$, 10% MnO_2 modified $Ce_{0.5}Zr_{0.5}O_2$ nanofibers prepared at 300 ^oC

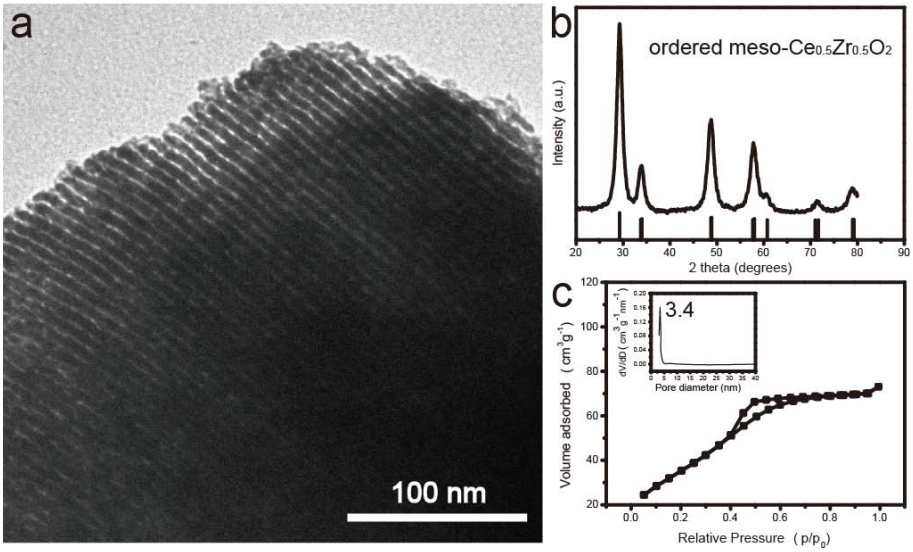

Fig. S8 (a) TEM image of ordered meso- $Ce_{0.5}Zr_{0.5}O_2$; (b) X-ray diffraction patterns of ordered meso-$Ce_{0.5}Zr_{0.5}O_2$; (c) N_2 adsorption-desorption isotherms of ordered meso- $Ce_{0.5}Zr_{0.5}O_2$ synthesized at 400 ^oC (Inset: corresponding pore size distribution curve deduced from the desorption branche)

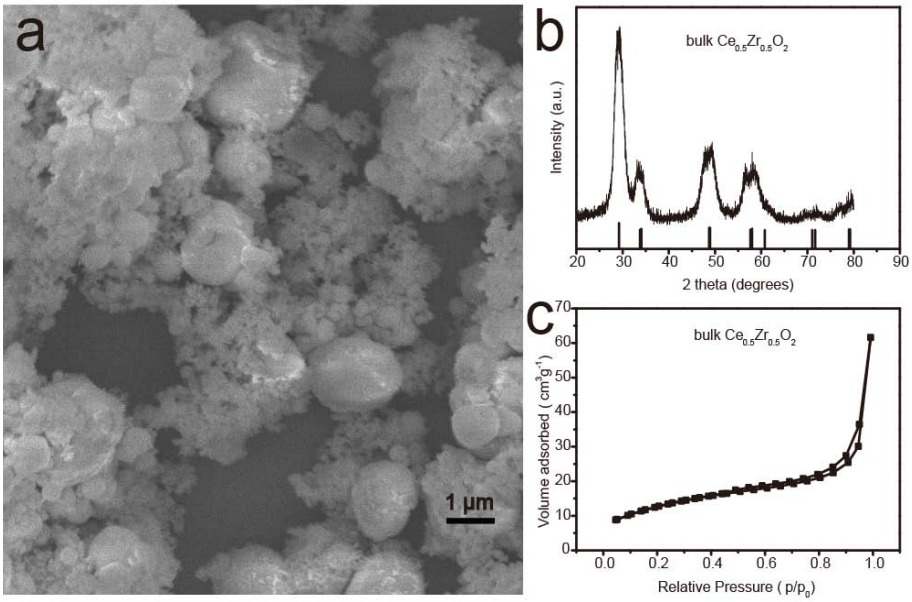

Fig. S9 (a) SEM image, (b) X-ray diffraction patterns, and (c) N_2 adsorption-desorption isotherms of bulk $Ce_{0.5}Zr_{0.5}O_2$ synthesized at 300 ^oC

Reference:

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