

Supporting information for
Three-dimensionally ordered macroporous
 $K_{0.5}MnCeO_x/SiO_2$ catalysts: Facile preparation and
fine catalytic performances for soot combustion

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Synthesis of Highly Well-defined PMMA Microspheres

In a typical procedure, 240 mL of deionized water was added into a four-orifice reactor, which was heated by a hot water bath at 80 °C and blown Ar as protection gas. Then, a water-cooling condenser and mechanical stirrer were fixed to the reactor. After that, 120 mL methyl methacrylate monomer was poured into the reactor through the four orifices which were otherwise closed with a stopper. After stirring for 20 min, a solution of potassium persulfate initiator (0.60 g dissolved in 40 mL of deionized water) preheated to 80 °C was added into the reactor. With Ar protection and mechanical stirring, the reaction was allowed to react at 80 °C for 2 h, and then the emulsion was filtered by microfiltration membrane. In order to get PMMA colloidal crystal template, the filtrate was assembled by centrifugation at 3000 rpm for 10 h, the clear liquid was decanted and the solid block was dried at 30 °C for 24 h. Finally, the highly ordered PMMA arrays were obtained.

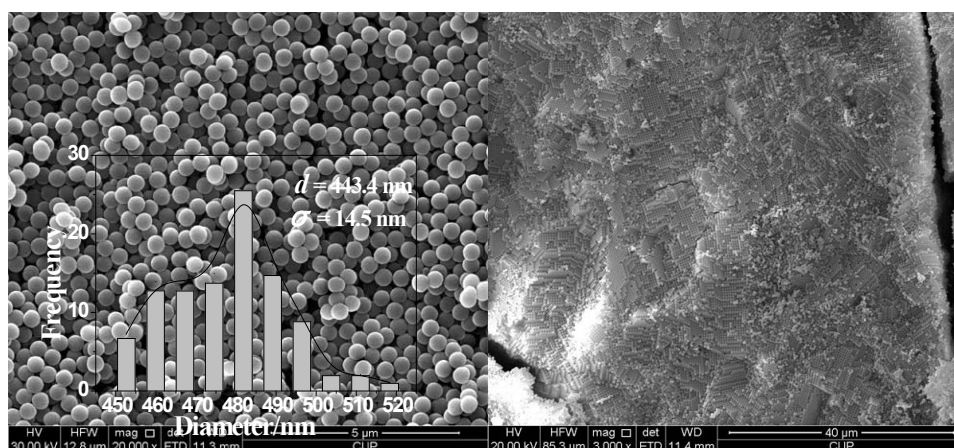


Fig. S1 SEM images of PMMA microspheres (a) and PMMA colloidal crystal templates(b)
(Insert is histograms of PMMA microspheres)

Synthesis of 3DOM SiO₂

In a typical procedure, 4.16 g TEOS was dissolved into the mixture of 2.5 mL water, 5 mL alcohol and 2.5 mL HCl aqueous solution (2mol/L). After that, the hydrolyzation was proceeding in a water bath at 35 °C for 4h. Then, 3 g PMMA arrays were impregnated into the above solution for 2 h. After completely impregnation, the PMMA arrays, which contained the precursor solution, were separated by vacuum filter and dried at 30 °C for 24h. The dried sample was calcined to remove the CCT in a tube furnace with an air flow (80 mL min⁻¹). The temperature-rising rate was 1 °C min⁻¹ from room temperature to 600 °C, and the calcination at 600 °C was kept for 4 h, and 3DOM SiO₂ supports were obtained.

The isothermal reaction for calculation of apparent activation energies

The intrinsic activity of catalyst was based on the TOF value, which was defined as the ratio of the reaction rate to the active site density of catalysts. The reaction rate of soot combustion was determined by an isothermal reaction at different temperature in the kinetic regime; the influences of internal and external mass and heat transfer were all excluded. The total flow rate was 150 mL/min, and the reaction gas composition was the same as for the TPO reaction. The uniform macroporous structure and the small particle diameter (5-20 μm) of catalysts could exclude the intraparticle mass transport limitations. For a total flow rate of 150 mL/min, no external mass transport limitations were detected. The gas analyses were then used to calculate the reaction rate (v) and the specific reaction rate normalized by unit BET surface area (v^*) for soot combustion using the equation.

$$v = -\frac{dn}{mdt} = \frac{CO_2 \times Q_c}{m}; v^* = \frac{v}{S} = \frac{CO_2 \times Q_c}{mS}$$

Where CO_2 is the measured molar fraction of these species in the gas phase, Q_c is the molar flow rate of gases through the reactor (mol), m is the mass of the catalyst (g), and S is the BET surface area of the catalyst (m^2/g).

The active site density of catalysts was calculated by isothermal anaerobic titrations. During this process, the soot was regarded as the probe molecule. When the concentration of the produced CO_2 became stable, O_2 was instantaneously removed from the reactant stream. The transient decay in concentration from the steady state was monitored with an online gas chromatograph using an FID detector. Moreover, to avoid the influence of the residual oxygen, the distance between the samples and the detector was as short as possible (about 1 m) and a relatively high feed flow rate (150 mL/min) was used. The number of active redox sites (O^* amount) and the density of active redox sites (O^* density) available to soot under these reaction conditions can be quantified by integrating the diminishing rate of CO_2 formation over time.

$$O^* \text{ amount (mol/g)} = \frac{2P_0V \times A \times 10^{-6}}{RTm}; O^* \text{ density (nm}^{-2}\text{)} = \frac{O^* \text{ amount}}{S \times 10^{18}} \times 6.02 \times 10^{23}$$

Where A is the integrated area of the CO_2 concentration as a function of time (s), V is the volumetric flow rate of gases through the reactor (m^3/s), m is the mass of the catalyst (g), P_0 is the atmospheric pressure (Pa), R is the gas constant, T is the room temperature (K), and S is the BET surface area of the catalyst (m^2/g).

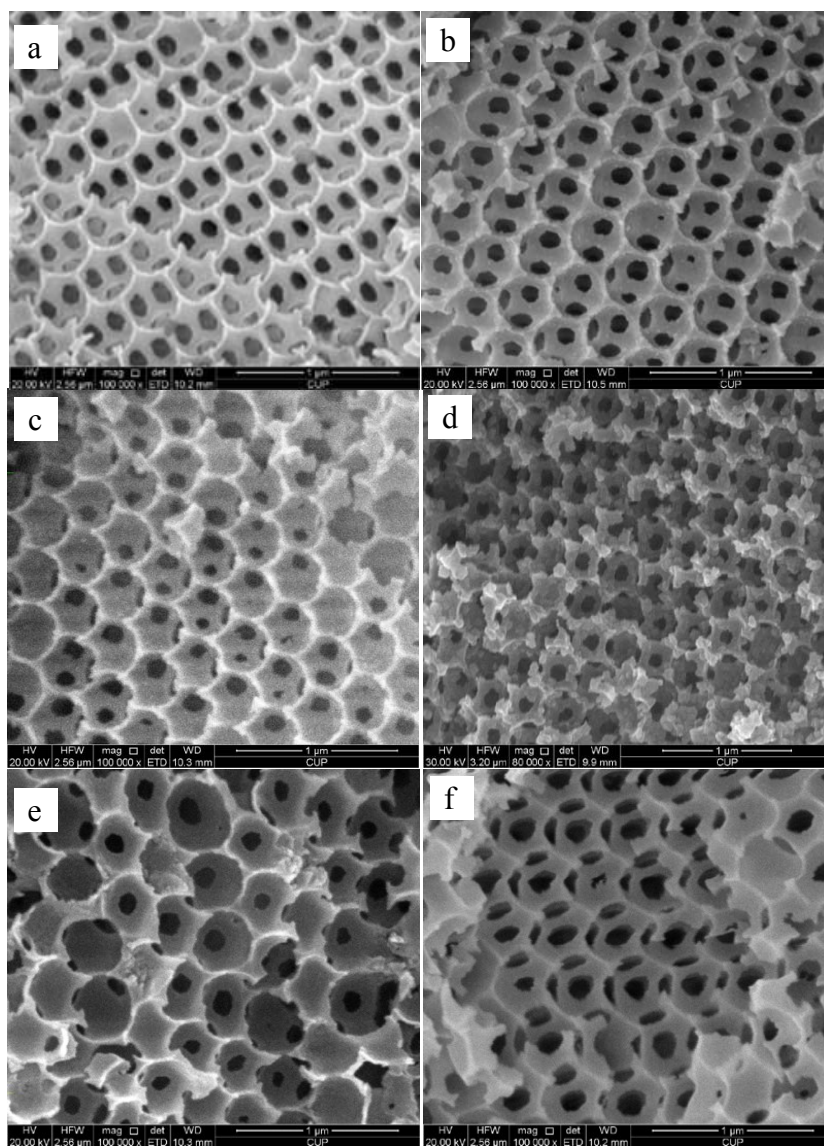


Fig. S2. SEM images of as-prepared 3DOM catalysts (KMnCeO_x/SiO₂-10 (a), KMnCeO_x/SiO₂-30 (b), KMnCeO_x/SiO₂-50 (c), MnO_x/SiO₂-40 (d), CeO_x/SiO₂-40 (e), KNO₃/SiO₂-40 (f))

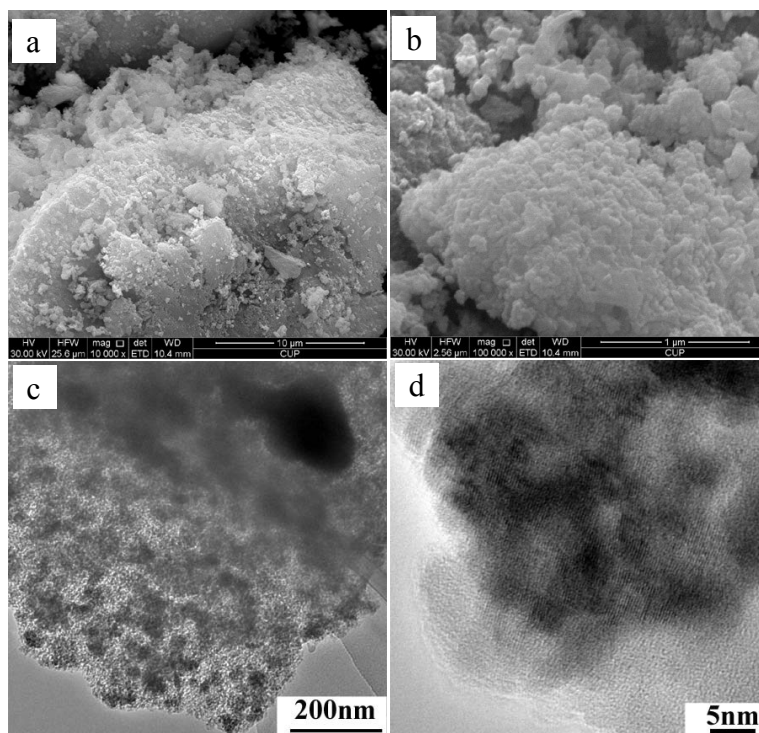


Fig. S3. SEM and TEM images of $K_{0.5}MnCeO_x$ /silica gel-40 catalyst (a,b: SEM images; c,d: TEM iamges)

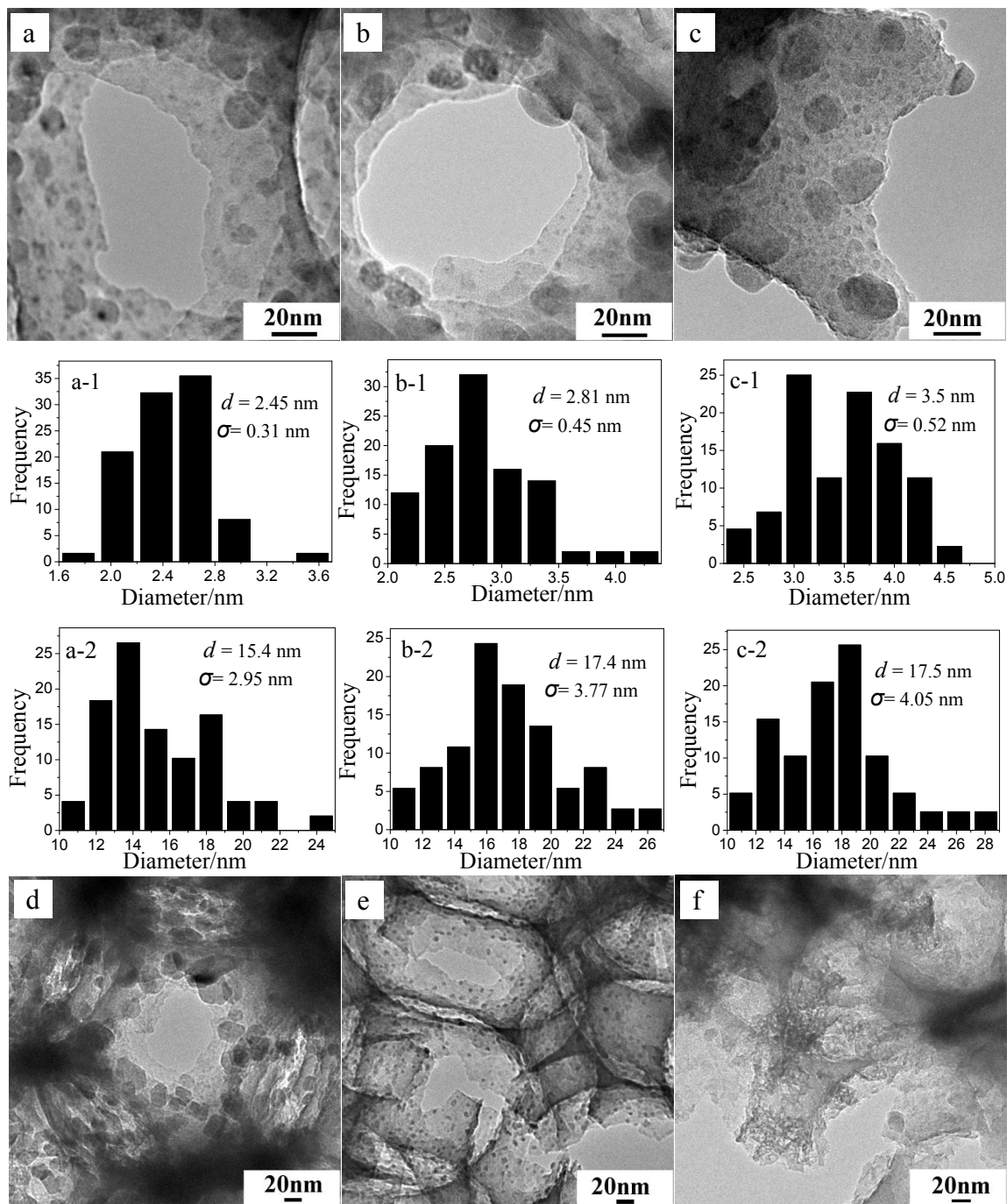


Fig. S4. TEM images of 3DOM $\text{KMnCeO}_x/\text{SiO}_2$ catalysts and size distribution of KMnCeO_x nanoparticles ($\text{KMnCeO}_x/\text{SiO}_2$ -20(a), $\text{KMnCeO}_x/\text{SiO}_2$ -40(b), $\text{KMnCeO}_x/\text{SiO}_2$ -60(c), size distribution of small NPs (a-1, b-1, c-1), size distribution of large NPs (a-2, b-2, c-2), $\text{KMnO}_x/\text{SiO}_2$ -40(d), $\text{KCeO}_x/\text{SiO}_2$ -40(e), $\text{MnCeO}_x/\text{SiO}_2$ -40(f)

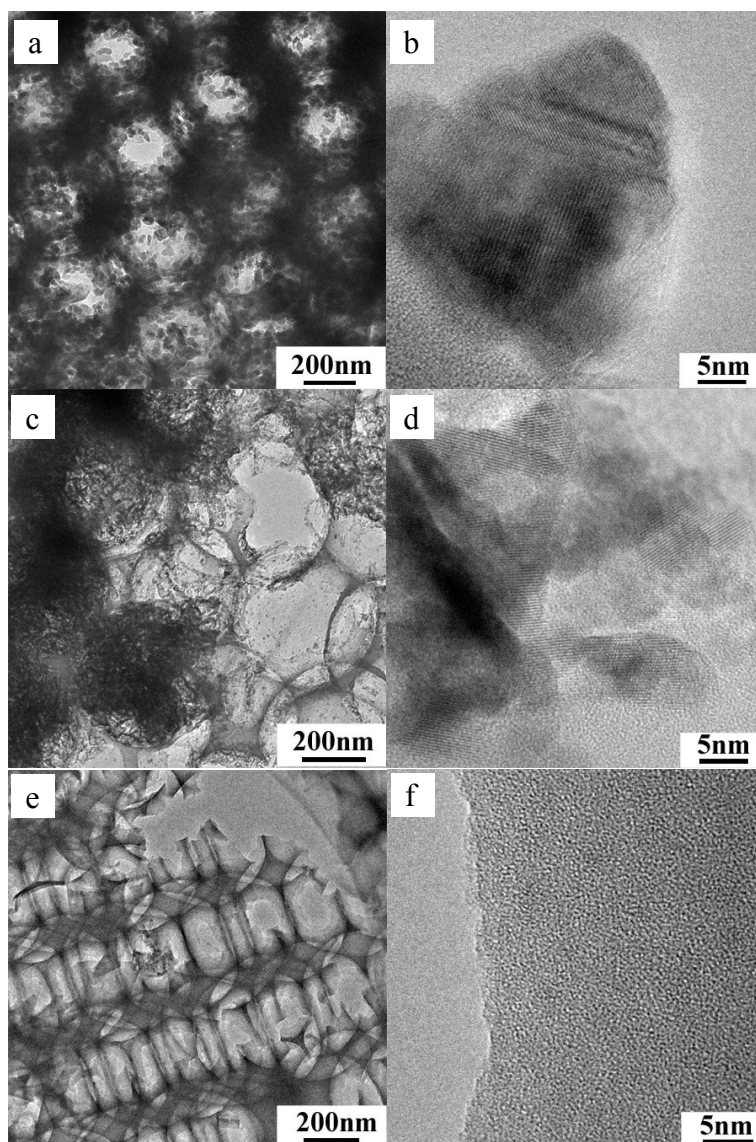


Fig. S5. TEM and HRTEM images of as-prepared catalysts (MnO_x/SiO₂-40 (a,b), CeO_x/SiO₂-40 (c,d), KNO₃/SiO₂-40 (e,f))

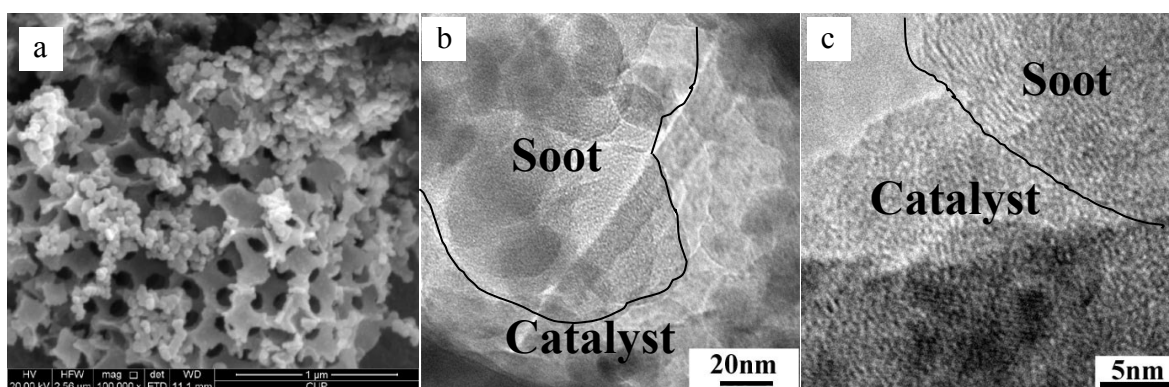


Fig. S6. SEM(a), TEM(b) and HRTEM(c) images of 3DOM $K_{0.5}MnCeO_x/SiO_2-40$ and soot complex. TEM image are obtained under the reaction conditions: 10% O_2 , 2000ppm NO, Ar balance gas, total gas flow: 50mL/min, reaction temperature 270 °C.

Steps for hydrothermal treatment of catalyst

The hydrothermal treatment of catalyst was carried out on a fixed-bed tubular quartz reactor. In a typical process, 100 mg $K_{0.5}MnCeO_x/SiO_2-40$ catalyst was placed in the fixed-bed tubular quartz reactor ($\Phi=8$ mm), and then the mixture gases containing 10% O_2 and 10% water vapor balanced with Ar are introduced into the quartz reactor by a flow rate of 50 mL min^{-1} . After that, the temperature was ramped at 5 $^{\circ}C\ min^{-1}$ from room temperature to 600 $^{\circ}C$, and was kept at 600 $^{\circ}C$ for 4 h. Finally, the hydrothermal treated catalyst was obtained after it cold to room temperature.

Table S1 XRF results of $K_{0.5}MnCeO_x/SiO_2-40$ for contents of K, Mn, Ce and Si

Catalysts	K/wt%	Mn/wt%	Ce/wt%	Si/wt%
Fresh catalyst	3.40	9.41	21.16	26.52
Catalyst with hydrothermal treatment	3.53	9.33	21.30	26.42
Used catalyst with hydrothermal treatment	3.39	9.25	21.30	26.45

Table S2 Catalytic activities of $K_{0.5}MnCeO_x/SiO_2-40$ under different treatment conditions

Catalysts	$T_{10}/^{\circ}C$	$T_{50}/^{\circ}C$	$T_{90}/^{\circ}C$	$S_{CO_2}^{m}/\%$	ΔT_{10}	ΔT_{50}	ΔT_{90}
Pure soot	482	564	609	71.6	--	--	--
$K_{0.5}MnCeO_x/SiO_2-40$	273	315	348	97.1	209	249	261
$K_{0.5}MnCeO_x/SiO_2-40$ with hydrothermal treatment	339	427	470	90.2	143	137	139