Electronic Supplementary Information

Experimental

1. Synthesis of SiO$_2$@CeO$_2$

SiO$_2$ used here was prepared by a modified Stöber method [29]. Typically, 9 mL ammonia and 25 mL deionized water were added into 60 mL anhydrous ethanol to form a mixture at room temperature. Followed by magnetic stirring for 10 min, 4 mL TEOS was dropped into the mixture above, and the colloid SiO$_2$ can be obtained after stirring for 4 h. The colloid was centrifuged and washed several times with water and ethanol. Finally, SiO$_2$ spheres were dried at 60 °C for 12 h. To coat CeO$_2$ on the SiO$_2$ spheres, 30 mL of Ce(NO$_3$)$_3$·6H$_2$O solution (0.35 mol/L) was added into suspension containing 1.5 g of as-prepared SiO$_2$ spheres and 180 mL of ethanol. After stirring for 0.5 h, the suspension was transferred to Teflon-lined stainless-steel autoclaves and was treated at 140 °C for 12 h in an oven. The obtained precipitates were collected and purified with water and ethanol several times.

2. Synthesis of CeMnO$_x$ hollow nanospheres

To synthsize CeMnO$_x$ composites, Mn element was added into CeO$_2$ by reduction of KMnO$_4$. Specifically, 20 mL KMnO$_4$ solution with different concentrations were added into suspension containing the as-synthesized SiO$_2$@CeO$_2$. After stirring for 12 h at 25 °C, the dark brown precipitates were separated, washed, and dried at 60 °C overnight. To enhance the interaction between Ce and Mn, the precipitates were calcined at 500 °C for 1 h. Finally, SiO$_2$ templates were removed by treating the collected gray powder with 1.0 M NaOH solution three times. The samples treated with KMnO$_4$ solution of different concentrations (0.002, 0.004, 0.008, 0.012, and 0.025 g/L) were denoted as CeMnO$_x$-1, -2, -3, -4, and -5, respectively.

3. Structural and compositional Characterization

X-ray diffraction was performed on a Smartlab type XRD-meter (Japan) utilizing a Cu Kα radiation source. The catalysts were scanned over the range of 2θ from 25 to 65 º. The actual content of Ce and Mn in the catalysts was measured by inductively coupled plasma-atomic emission spectrometry measurements (ICP-AES, Shimadzu ICPE-9800).

The N_2 desorption/adsorption experiment was carried out on ASAP 2020 instrument (Micromeritics Inc.) after degassing at 300 °C for 4 h under vacuum. Scanning electron microscopy (SEM) investigation was obtained by using a Hitachi SU8020 microscope operated at 5.0 kV. Transmission electron microscopy (TEM) images were obtained on a transmission electron microscope (FEI Tecnai G2 F20) with an accelerating voltage of 200 kV.

X-ray photoelectron spectra (XPS) were performed on a Thermo Scientific K-Alpha analyzer using Al Kα X-ray radiation at 1486.6 eV) to obtain the oxidation states of Ce, Mn, and O. The XPS spectra were calibrated based on the binding energy (BE) of C1s core level, 284.6 eV. The ratio of elements with different valence states was computed with the peak area using XPS-PEAK software. Temperature-programmed reduction of H_2 (H_2-TPR) was carried out on an AutoChem II chemisorption analyzer (Micromeritics Inc.) equipped with a thermal conductivity detector (TCD). Before the measurement, 50 mg of catalyst was pre-treated in N_2 (40 mL/min) at 200 ºC for 1 h, and then cooled down to room temperature. The subsequent reducing procedure was carried out in 5 vol. % H_2/Ar at a flow rate of 40 mL/min while the temperature was set from 25 ºC to 800 ºC with a heating rate of 10 ºC /min.

4. Catalytic activity tests

The catalytic performance of CeMnO$_x$ for toluene oxidation was investigated by

loading 50 mg of the composite catalyst into a tubular fixed-bed glass reactor (i.d. 10 mm) at atmospheric pressure. The feed gas composed of 1000 ppm toluene (volume ppm) was generated by passing air through a reactor containing pure toluene in an ice bath at a total flow rate of100 mL·min^{-1}, corresponding to a gas hourly space velocity (GHSV) of about 120,000 h^{-1}. The water resistance test of the catalyst was performed by the introduction of 5 vol.% H_2O vapors through a water vapor generator. Theproducts of the catalytic reaction were analyzed using an online gas chromatography (GC-7820A), coupled with a methane conversion furnace and FID.

The removal efficiency (X) of toluene, normalized conversion rate (r) and apparent activation energy (E_a) of this reaction were calculated with the following equations:

$$X(\%) = \frac{C_{in} - C_{out}}{C_{in}} * 100\%$$

$$r(\mu mol \cdot g^{-1}s^{-1}) = \frac{C_{in} * X * V}{m_{cat}}$$

$$lnr = -\frac{E_a}{R} * \frac{1}{T} + lnA'$$

C_{in} and C_{out} represent the toluene concentration in the inlet and outlet gas, respectively; V is the flow rate of feed gas with the unit of mol·s^{-1}; the molar volume of gas used in the equation is 22.4 L·mol^{-1}; m_{cat} is the mass of the catalyst; R was proportional constant; T (K) is reaction temperature; the unit of Ea is kJ·mol^{-1}.
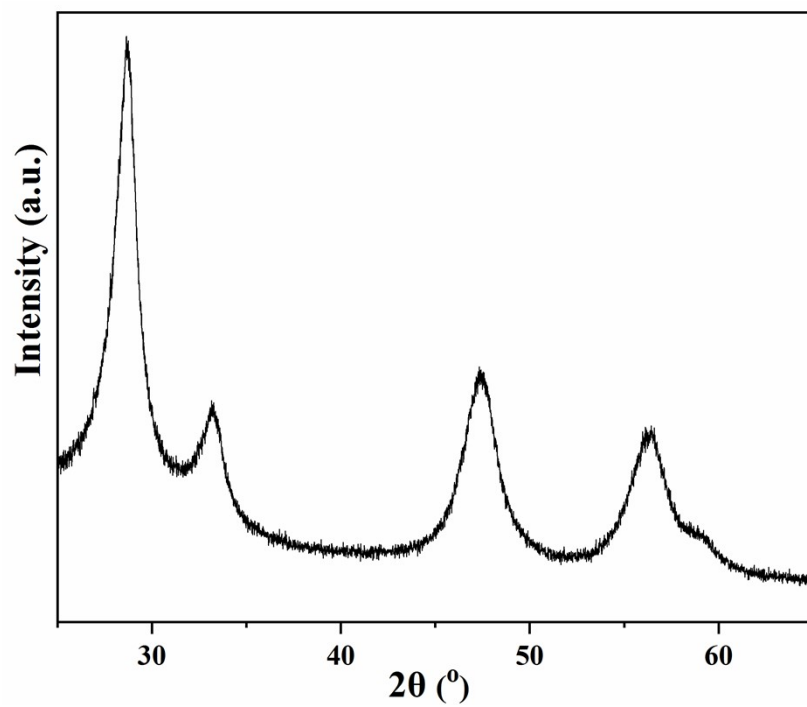
Fig. S1 XRD pattern of SiO_2@CeO_2 obtained by solvothermal method directly.
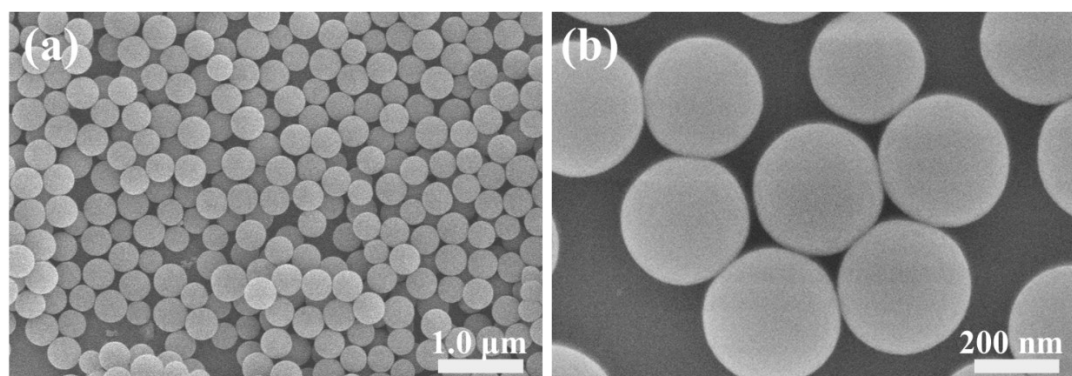

Fig. S2 SEM images of SiO_2 templates with low (a) and high (b) magnification.

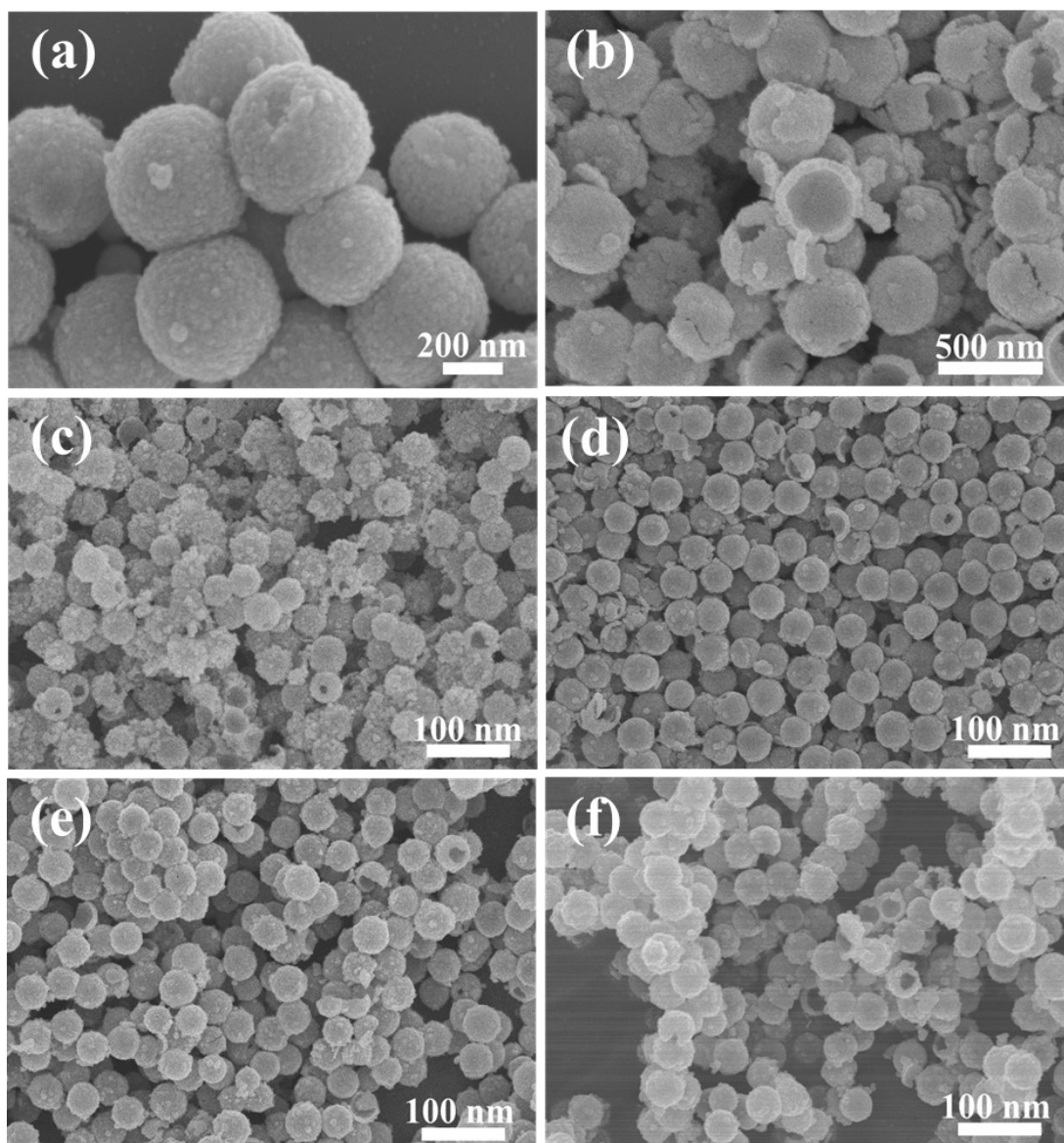Fig. S3 SEM images of SiO$_2$@CeO$_2$ before NaOH treatment (a), and the as-prepared CeO$_2$ (b),

CeMnO$_x$-1 (c), CeMnO$_x$-2 (d), CeMnO$_x$-4 (e), and CeMnO$_x$-5 (f) hollow sphered catalysts.