Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Urea-assisted template method to synthesize mesoporous N-doped CeO_2 sorbents for CO_2 capture

Yangang Wang,[a] Chaochuang Yin,[a] Hengfei Qin,[b] Yunzhu Wang,[a] Yaguang Li,[a] Xi Li,[b] Yuanhui Zuo,[a] Shifei Kang,*[a] Li-Feng Cui*[a]

Experimental Section

Synthesis of mesoporous N-doped CeO_2: Mesoporous N-doped CeO_2 (M-NCeO_2) material was synthesized as follows. Typically, 10 g of urea and 1.0 g of cerium nitrate hexahydrate ($Ce(NO_3)_3{\bullet}6H_2O$) were dissolved in distilled water, after stirring for several minutes, the mixture was put into oven and dried for a night to evaporate water at 60 °C. Finally, the powders were collected and placed into an alumina crucible with a cover to heat at 550 °C for 2 h in the muffle furnace under air atmosphere with a rate of 15 °C/min.

Synthesis of ordered mesoporous CeO_2: The ordered mesoporous CeO_2 was synthesized as the reported procedure.[1] In a typical synthesis process, 12 mmol of $Ce(NO_3)_3{\bullet}6H_2O$ was dissolved into 15 ml of acetone. After the solution became clear, 2 g of SBA-15 hard template was added and the mixture was stirred for 2 h in a beaker, then the mixture was transferred to a clean flat Petri dish and the solvent was evaporated. In order to obtain higher loadings, the above dried hybrid powder was calcined at 200 °C for 6h to decompose the metal precursors, and then the impregnation step was repeated, but the amount of precursor was reduced to 2/3 compared to the first step. The resulting products were calcined in the muffle furnace at 500 °C for 4h with a heating ramp of 2K/min to decompose the inorganic precursor. Finally, the silica template was removed using a 2M NaOH aqueous solution and this etching process was repeated for three times. The resulting material is denoted as OM-CeO_2.

Structural Characterization: Wide-angle X-ray diffraction patterns were collected in θ-2θ mode using Bruker D8 Advance diffractometer (Cu Kα1 radiation, λ=1.5406 Å), operated at 40 kV and 40 mA (scanning step: 0.02 °/s). Transmission electron microscope (TEM) images were taken using a JEOL JEM-2010 electron microscope with an acceleration voltage of 200 kV. The Brumauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. The pore size distributions were derived from the desorption branches of the isotherms using the Barrett-Joyner-Halanda (BJH) method. Before carrying out the measurement, each sample was degassed at 200 °C for more than 2 h. Fourier-transform infrared (FT-IR) spectra (800-4000 cm^{-1} with a resolution of 0.4 cm^{-1}) of the samples (1 wt% sample + 99 wt% KBr) were obtained on a Bruker Vertex 70 spectrometer. X-ray photoelectron spectroscopy (XPS) measurement was carried out on a RBO upgraded PHI-5000C ESCA system (Pekin Elmer) using monochromated Al Kα X-rays (hν = 1486.6 eV) as a radiation at 250 W. All binding energies were calibrated by using the contaminant carbon (C_{1S}= 284.6 eV) as a reference.

CO_2 capture behaviors test: The CO_2 capture behaviors of the CeO_2 materials were measured by a STA 8000 thermal gravimetric analyzer (TGA) under ambient pressure as follows: 10-20 mg of the sample was loaded into an alumina pan, heated to 250 °C and held at this temperature in flowing Ar (25 mL/min) for 120 min to remove physisorbed moisture and other gas, the temperature was then decreased (10 °C/min) and equilibrated at 30 °C. Adsorption was started by switching the gas to pure CO_2 (25 mL/min), and the temperature was maintained at 30 °C for 20 min. Desorption of CO_2 was performed by heating the sample to 250 °C with a ramp of 10 °C /min, keeping for 120 min and then decreasing to 30 °C under Ar atmosphere. The cycles of adsorption and desorption were repeated in order to test the ability of the sorbents to retain their CO_2 sorption capacity. In the case of adsorption–desorption cycles, after adsorption was saturated, the samples were heated at 250 °C in Ar atmosphere and the CO_2 was desorbed, then cooled down to 30 °C, and allowed to adsorb CO_2 again for 20 min. This process was repeated for fifteen runs to evaluate any changes in CO_2 uptake.

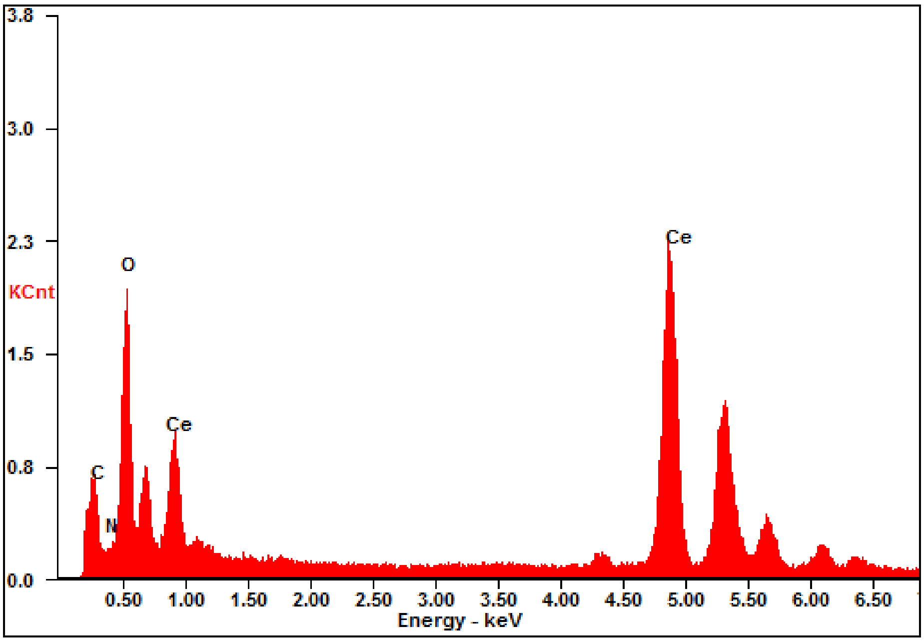

Fig S1. EDX spectrum of the M-NCeO_2 sample.

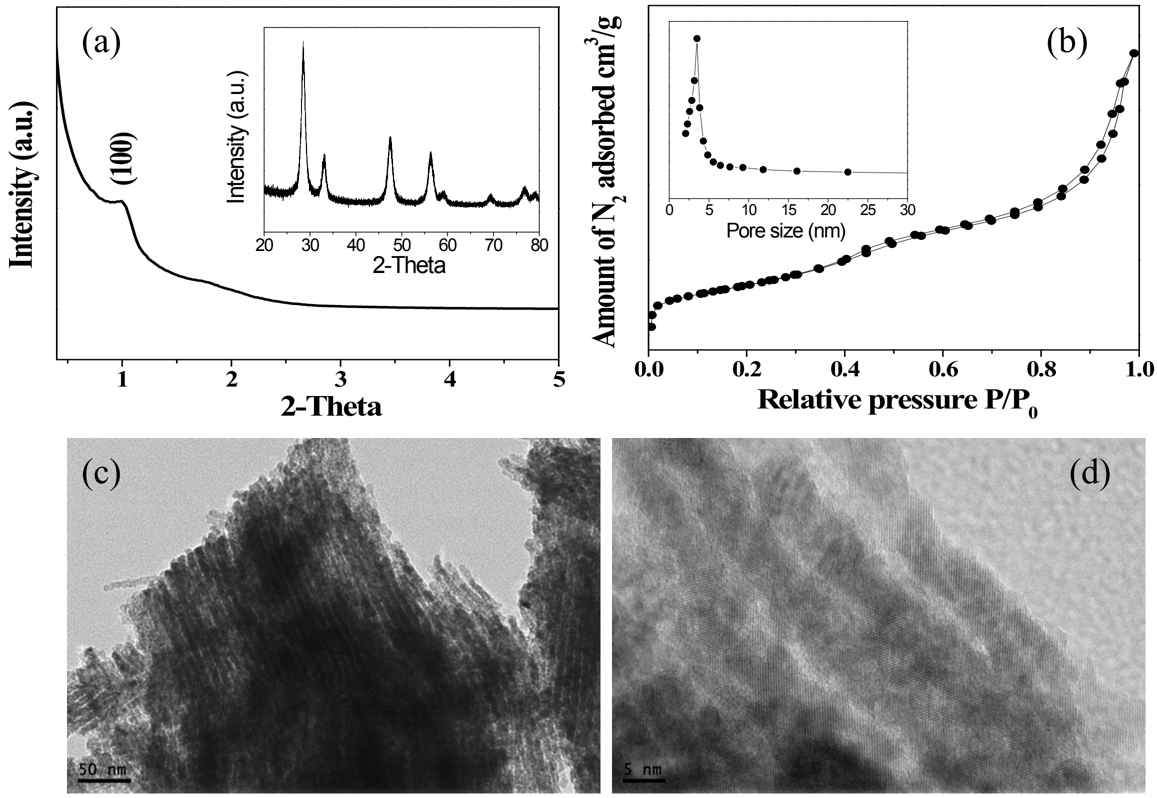

Fig S2. (a) XRD patterns, (b) N_2 adsorption–desorption isotherm and corresponding pore size distribution curve (inset), and (c, d) TEM images of the OM-CeO_2.

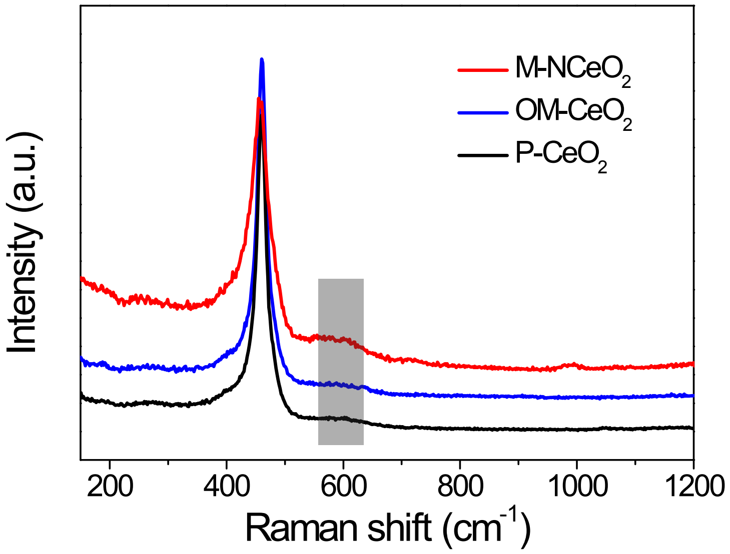

Fig S3. Raman spectra of the M-$NCeO_2$, P-CeO_2, and OM-CeO_2.

Table S1. Textural properties and summary of the XPS data for M-NCeO$_2$, P-CeO$_2$, and OM-CeO$_2$.

Sample	Surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)	$Ce^{3+}/(Ce^{3+}+Ce^{4+})$ % (XPS analysis)
P-CeO$_2$	51.2	8.46	0.470	21.2
M-NCeO$_2$	124.8	3.40	0.523	28.9
OM-CeO$_2$	126.4	3.35	0.305	21.6

Reference

1. Y. G. Wang, F. Wang, Y. T. Chen, D. F. Zhang, B. Li, S. F. Kang, X. Li and L. F. Cui, *Appl. Catal., B*, 2014, 147, 602-609.