

Electronic Supplementary Information

Experimental

1. Chemicals

Hexamethylenetetramine (HMT), tetraethyl orthosilicate (TEOS), and cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) were purchased from Sigma-Aldrich. Absolute ethanol (EtOH) and aqueous ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28%) were purchased from Tianjin Guangfu Chemical Co. Ltd. All chemicals were of analytical grade and used as received without further purification. Deionized water was used throughout the experiments.

2. Preparation of catalysts

2.1 Preparation of SiO_2 spheres with different particle sizes.

SiO_2 spheres were prepared according to the classical Stöber sol-gel method [1]. Different amounts of TEOS (2~10 ml) were added into the mixture solution (62 ml EtOH and 25 ml H_2O) containing $\text{NH}_3 \cdot \text{H}_2\text{O}$ (1~3 ml) with magnetic stirring. Then the mixture was continued to stir for 1~4 h. the obtained products were centrifuged from the solution, and washed with water and ethanol several times, and then were dried in an oven for 12 h at 80 °C.

2.2 Preparation of $\text{SiO}_2 @ \text{CeO}_2$ core-shell spheres with different particle sizes

$\text{SiO}_2 @ \text{CeO}_2$ were prepared by in-situ precipitation of CeO_2 in the presence of SiO_2 under alkaline condition according to our previous work [2]. Typically, SiO_2 spheres (200 mg) were dispersed in the mixed solution of water (40 mL) and ethanol (40 mL) ultrasonically. Then, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (100 mg) dissolving in water (40 mL) and HMT (600 mg) dissolving in water (40 mL) were added in turn. The mixture was kept under reflux at 80 °C for 2 h. $\text{SiO}_2 @ \text{CeO}_2$ were centrifuged from the solution, and washed with water and ethanol several times, and then were dried in an oven for 12 h at 80 °C. Finally, the obtained products were dried in an oven at 80 °C and calcined under air at 500 °C for 5 h.

2.3 Preparation of $\text{SiO}_2 @ \text{CeO}_2 @ \text{SiO}_2$ composites

$\text{SiO}_2 @ \text{CeO}_2 @ \text{SiO}_2$ composites were prepared through a versatile Stöber sol-gel method as follows [1]. $\text{SiO}_2 @ \text{CeO}_2$ composites (150 mg) were dispersed in the mixture solution of ethanol (280 mL), deionized water (70 mL) and concentrated ammonia solution (5.0 mL, 28 wt%). Then, TEOS (3.0 mL) was added dropwise under vigorous stirring in 10 min, and the mixture was allowed to proceed for 10 h at room temperature under continuous mechanical stirring. The resultant $\text{SiO}_2 @ \text{CeO}_2 @ \text{SiO}_2$ composites were centrifuged from the solution, and followed by washing with deionized water and ethanol for 3 times, respectively. Finally, the obtained products were dried in an oven at 80 °C and calcined under air at 500 °C for 5 h.

2.4 Preparation of mh- CeO_2

The target mh-CeO₂ was achieved by using KOH solution (1 M) to remove the SiO₂ template (both SiO₂@CeO₂ and SiO₂@CeO₂@SiO₂) at 80 °C for 4 h, then the hollow spheres were obtained by centrifuging and washing with deionized water and ethanol for 3 times. Finally, the obtained products were dried in an oven at 80 °C.

3. Characterizations of prepared materials and catalysts

These micro-materials were characterized by inductively coupled plasma (ICP), powder X-ray diffraction (XRD), transmission electron microscopy (TEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), X-ray photoelectron spectroscopy (XPS), and fourier transform-infrared (FT-IR). XRD measurements were performed on a Rigaku D/max-2400 diffractometer using Cu-K α radiation as the X-ray source in the 2 θ range of 5–80°. The size and morphology of the magnetic microparticles were observed by a Tecnai G2 F30 transmission electron microscope and samples were obtained by placing a drop of a colloidal solution onto a copper grid and evaporating the solvent in air at room temperature. Ce content of the catalyst was measured by ICP on IRIS Advantage analyzer. Magnetic measurements of the prepared catalysts were investigated with a Quantum Design VSM at room temperature in an applied magnetic field sweeping from -8 to 8 kOe. XPS was recorded on a PHI-5702 instrument and the C1s line at 284.8 eV was used as the binding energy reference. GC-MS (Agilent 5977E) was employed to monitor the catalytic activity.

4. Typical procedure for one-pot synthesis of imines from benzyl alcohols and anilines

Typical procedure for one-pot synthesis of imines from benzyl alcohols and anilines were according to our previous work [3]. Typically, benzyl alcohols (1 mmol) and benzyl anilines (2 mmol) was added to a mesitylene solvent (1.5 mL) containing mh-CeO₂ (20 mg) as catalyst. The resultant mixture was stirred under 800 rpm at 60 °C for 12 h. The product was analyzed qualitatively using gas chromatography-mass spectrometry (GC-MS).

After each cycle of the reaction, the catalyst was centrifuged from the solution and successively washed with ethanol and water for several times, then dried in an oven at 80 °C and calcined under air at 500 °C for 5 h. The resultant catalyst could be used for the next cycle experiment.

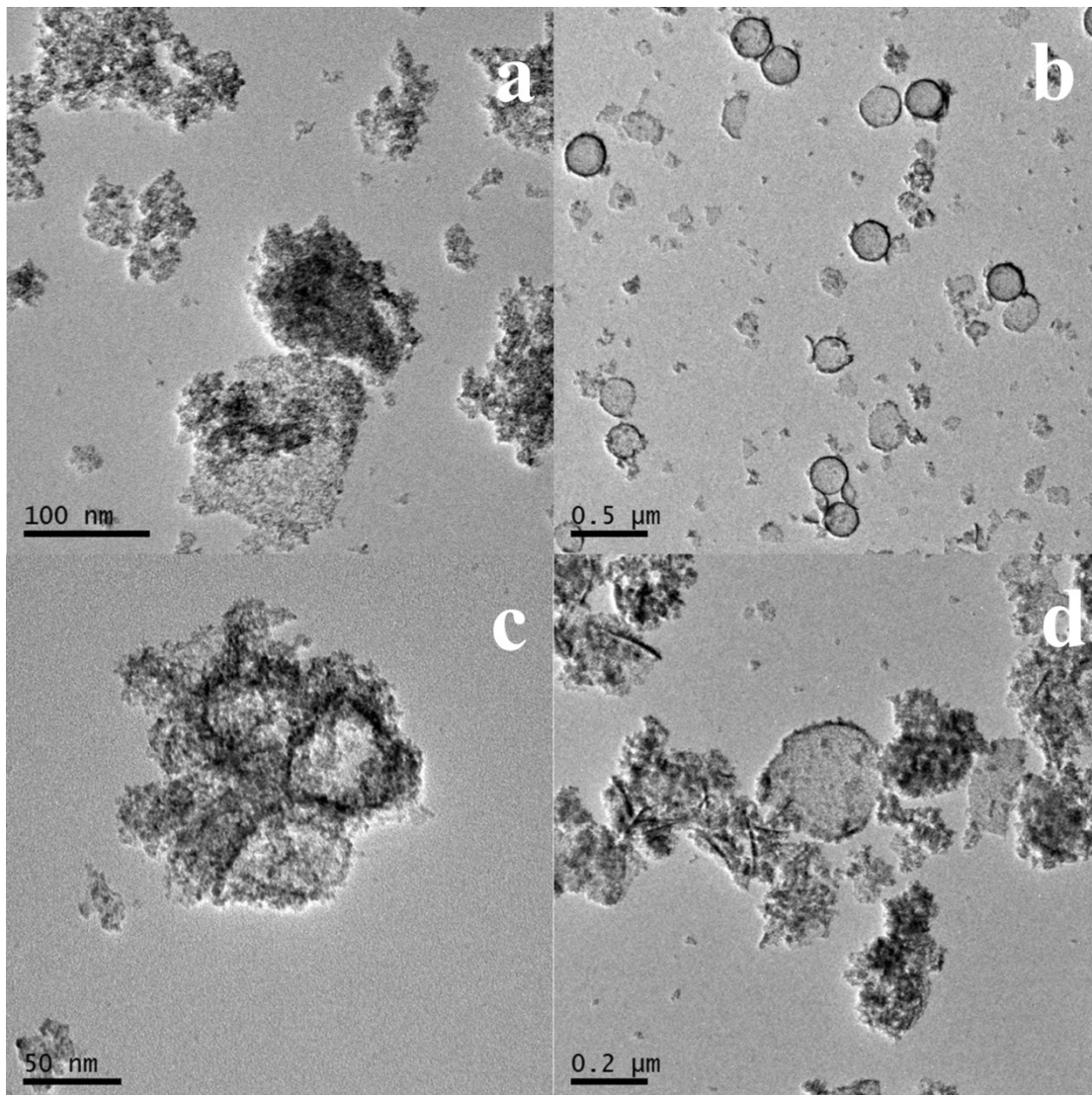


Fig. S1 TEM images of SiO₂@CeO₂ after calcination and etching with different SiO₂ particle sizes (a) SiO₂ 70nm, (b) SiO₂ 150nm, (c) SiO₂ 240nm and (d) SiO₂ 360nm.

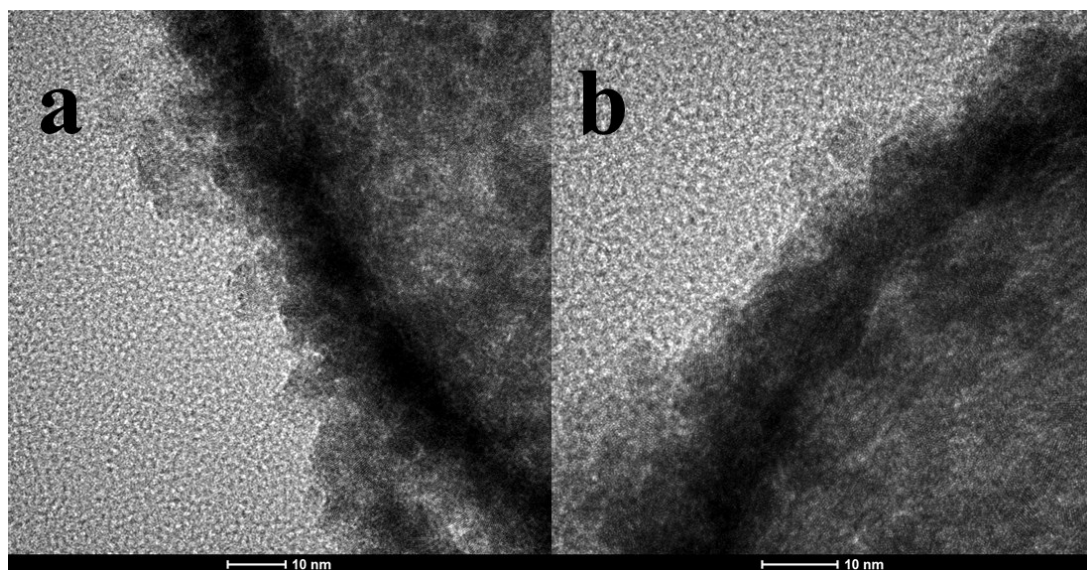


Fig. S2 HRTEM images of mh-CeO₂.

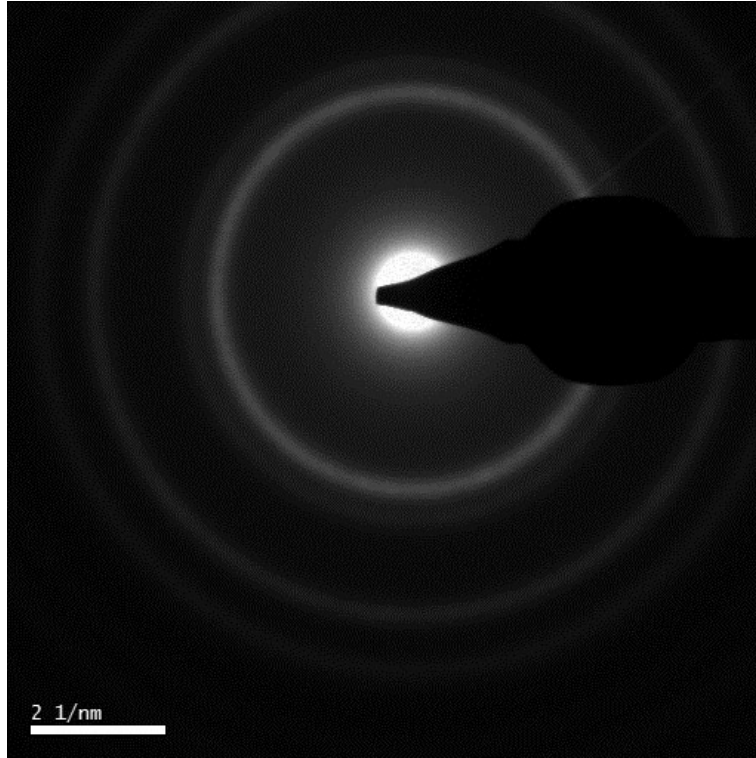


Fig. S3 Selected area electron diffraction (SAED) pattern for mh-CeO₂.

Table S1 One-pot synthesis of N-Benzylideneaniline from aniline and benzyl alcohol using mh-CeO₂ as catalyst under different stirring speed ^a.

Entry	Stirring speed [rpm]	Conv. of BA [%] ^b	Select. of NBA [%] ^b	TOF _{NBA} [mmol·h ⁻¹ ·g ⁻¹] ^c
1	200	23	97	0.93
2	400	55	98	2.25
3	600	87	97	3.52
4	800	99	98	4.04
5	1000	99	98	4.04
6	1200	96	98	3.92

^a Reaction conditions: mh-CeO₂ 20 mg, benzyl alcohol (1.0 mmol), aniline (2.0 mmol), mesitylene (1.5 mL), 60 °C, 12 h, air as oxidant.

^b Determined by GC-MS.

^c TOF_{NBA}: turnover frequency, i.e., moles of desired product (NBA) formed per catalyst (mh-CeO₂) amount per hour.

References

- [1] W. Stöber, A. Fink, E. Bohn, Controlled growth of monodisperse silica spheres in the micron size range, *J. Colloid Interface Sci.*, 1968, **26**, 62-69.
- [2] B. Yuan, Y. Long, L. Wu, K. Liang, H. Wen, S. Luo, H. Huo, H. Yang, J. Ma, TiO₂@h-CeO₂: a composite yolk-shell microsphere with enhanced photodegradation activity, *Catal. Sci. Technol.*, 2016, **6**, 6396-6405.
- [3] Y. Long, Z. Gao, J. Qin, P. Wang, W. Wu, L. Zhang, Z. Dong, J. Ma, CeO₂ immobilized on magnetic core-shell microparticles for one-pot synthesis of imines from benzyl alcohols and anilines: Support effects for activity and stability, *J. Colloid Interface Sci.*, 2019, **538**, 709-719.