Support information

Monodisperse, Nanoporous Ceria Microspheres Embedded with Pt

Nanoparticles: General Facile Synthesis and Catalytic Application

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General Procedures

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General Procedures

Modification of porous polymer microspheres

To modify the microspheres with quaternary ammonium functional groups on the surface, 2.0 g of Poly (GMA-co-EGDMA) microspheres was dispersed in 50 mL deionized water, and then 9 g of Na_2SO_3 in 10 mL deionized water was added to form a transparent solution. The resulting mixture was stirred in oil bath at 70 °C for 24 hours. The white microspheres were obtained by filtration and washed repeatedly with deionized water and ethanol, after which the microspheres were dried at 60 °C in the oven overnight, denoted as quaternary ammonium group-terminated polymer microspheres.

To obtain the sulfonated microspheres , 2.0 g of Poly (GMA-co-EGDMA) microspheres was dispersed in 25 mL ethanol and 35 mL deionized water. A transparent solution of 5 g of $N(CH_3)_3$ ·HCl and 0.837 g of NaOH dissolved in 15 mL deionized water was then added. The resulting mixture was stirred in oil bath at 50 °C for 24 hours. The white product was filtrated by the sand core funnel, and alternately rinsed with deionized water and ethanol several times. Then the polymer microspheres were dried in an oven at 60 °C overnight, denoted as sulfonated polymer microspheres.

Procedures for the Preparation of Monodisperse Porous Ceria Microspheres

To a suspension of 1 g of those modified polymer microspheres in 3 mL of water, 2 g of $Ce(NO_3)_3 \cdot 6H_2O$ in 2 mL water was added. The mixture was transferred to oven set at 60 °C and then heated for 6 h. The obtained poly (GMA-co-EGDMA)/cerium microspheres was calcined at 600 °C for 12 h.

Procedures for the Preparation of Monodisperse Porous Ceria Microspheres Embedded with Pt Nanoparticles and Other Metal Nanoparticles

40 mL of 0.02 mol/L PtCl₆²⁻ solution was added into the suspension of 5 g of quaternary ammonium group-terminated polymer microspheres dispersed in 200 mL distilled water. After stirring for 6 h at room temperature, the mixture was filtered through sand core funnel and washed repeatedly with water. Then the microspheres were dried in the oven at 60 °C for 6 h. To a suspension of 1 g of those microspheres adsorbed with platinum cations in 3 mL water, 2 g of Ce(NO₃)₃·6H₂O in 2 mL water was added into the mixture, and 1 g of ethylene glycol was added as a reducing agent to obtain Pt nanoparticles. The mixed solution was transferred to oven set at 60 °C and then heat-treated for 6 h. Finally, the obtained poly (GMA-co-EGDMA)/cerium microspheres with platinum cations or nanoparticales was calcined at 600 °C for 12 h. Pd/CeO₂ microspheres were fabricated using similar procedures to that of Pt/CeO₂ microspheres, except that hydrazine hydrate, instead of ethylene glycol, was added after calcination. Au/CeO₂ and Ag/CeO₂ microspheres were synthesized without addition of EG or any other reducing agent, while sulfonated microspheres were used instead of quaternary ammonium group-terminated polymer microspheres for the synthesis of Ag/CeO₂. The same sulfonated microspheres were utilized for preparation of Cu/CeO₂ microspheres, which needed further treated at 330 °C for 12 h in flowing H₂/N₂ (0.5/99.5 v/v) at a heating rate of 10 °C/min.

Procedures for the template-free Synthesis of Pt/CeO₂ Composite

The preparation procedure was similar to that of the Pt/CeO₂ microspheres, except that no polymer microspheres were added as hard template. To 4 mL of 0.02 mol/L PtCl₆²⁻ solution in the crucible, 1 g of Ce(NO₃)₃·6H₂O was added, followed by the addition of 0.5 g of ethylene glycol. The mixture was heated at 60 °C in the drying oven for 6 h and a yellow gel was obtained. The temperature was raised to 110 °C after that. Then the crucible was moved to the muffle furnace and the composite was calcined at 600 °C for 12 h.

Procedures for the Preparation of Bare Pt NPs

The procedure was similar to that of the Pt/CeO₂ composite, except that no cerium precursors were involved. 0.5 g of ethylene glycol was added to 4 mL of 0.02 mol/L $PtCl_6^{2-}$ solution in the crucible, followed by the addition of 55 mg of PVP. The mixture was heated at 60 °C for 6 h and then moved to the muffle furnace for thermal treatment at 600 °C for 12 h.

Procedures for the Preparation of Bare Pt NPs

50 mg of the as-obtained Pt/CeO₂ microspherese calcined at 600 °C were further heat treated at 700 °C and 800 °C respectively for another 2 h in a muffle furnace under air.

Catalytic Study

For catalytic reduction of 4-NP, aqueous solution of 4-NP (5 mM, 5 mL) was mixed with fresh aqueous solution of NaBH₄ (0.4 M, 25 mL) in a three-necked round-bottom flask, and then 2 mL aqueous dispersion of Pt/CeO₂ microspheres (2.0 mg) was rapidly added with mechanical stirring. The UV-visible absorption spectra of the reaction mixture were recorded at room temperature to monitor the reaction progress. Catalytic activities of the catalysts were estimated by pseudo-first-order rate constants of plot of $\ln[C(t)/C(0)]$ against the reaction time.

Recyclability Test

In the recyclability test, 2.0 mg of the Pt/CeO₂ microspheres (Pt/CeO₂ composite) was dispersed in fresh aqueous solution of NaBH₄ (0.4 M, 25 mL), and then aqueous solution of 4-NP (5 mM, 5 mL) was added into the solution with mechanical stirring. The UV-visible absorption value for the peak at 400 nm was measured over the whole reaction every 3 minutes. After the reaction completed, the microspheres were collected through centrifugation at 2000 rpm for 2 min and washed with water and alcohol. The catalysts were dried and reused directly without further treatment for another 4 cycles. Activities were evaluated by reaction time.

Recovery ratio Study

Recovery ratio of Pt/CeO_2 microspheres and Pt/CeO_2 composite were compared in the reduction of 4-NP. 118.8 mg of Pt/CeO_2 microspheres was dispersed in fresh aqueous solution of NaBH₄ (0.4 M, 25 mL) with mechanical stirring, followed by the addition of aqueous solution of 4-NP (5 mM, 5 mL). After centrifugation at 2000 rpm at room temperature for 2 min, the microspheres were collected and recovery ratio was calculated. 118.4 mg of Pt/CeO_2 composite was used in the recovery ratio study and the procedures were similar to that of Pt/CeO_2 microspheres shown above. The recovery ratio was calculated based on the amount of fresh Pt/CeO_2 microspheres and Pt/CeO_2 composite before the first catalytic cycle.



Figure S1. SEM images of polymer microsphere template.



Figure S2. (a) Nitrogen adsorption/desorption isotherms of polymer microsphere template; and (b) the corresponding BJH pore size distributions (inset, textural properties).



Figure S3. FT-IR spectra of (a) porous poly (GMA-co-EGDMA) microspheres. (b) microspheres with quaternary ammonium groups, and (c) sulfonated microspheres.



Figure S4. SEM image of microspheres after sol-gel process before calcination.



Figure S5. The particle size distribution of polymer microspheres (blue line), quaternary ammonium groupterminated microspheres (denoted as Quarternized Microspheres in the figure, red line), and Pt/CeO₂ microspheres (black line).



Figure S6. Enlarged HRTEM image of Pt/CeO₂ microspheres.



Figure S7. XRD patterns of (a) CeO₂ microspheres, (b) Pt/CeO₂ microspheres, and (c) Pt/CeO₂ composite. The arrow indicating diffraction peak from embedded metal NPs.



Figure S8. (a) Nitrogen adsorption/desorption isotherms of Pt/CeO₂ microspheres; and (b) the corresponding BJH pore size distributions (inset, textural properties).



Figure S9. SEM images of Pt/CeO₂ composite.



Figure S10. Time-dependent absorption spectra of the reaction solution in the presence of (a) CeO_2 microspheres and (b) bare Pt NPs.



Figure S11. Plot of $\ln[C(t)/C(0)]$ against the reaction time for the catalytic reduction of 4-NP with Pt/CeO₂ composite.



Figure S12. Recyclability of Pt/CeO₂ microspheres (5 cycles) in the model reaction.



Figure S13. Temperature stability of Pt/CeO₂ microspheres under 600 °C, 700 °C and 800 °C.

Functionalization of Polymer Microspheres:



Scheme S14. Synthetic scheme for the preparation of sulfonated microspheres and the adsorbance of metal cations.



Figure S15. SEM and TEM images of the as-prepared ceria microspheres loaded with different metal nanoparticles: (a, b) SEM images of Pd/CeO₂ microspheres; (c) TEM images of Pd/CeO₂ microspheres; (d, e) SEM images of Au/CeO₂ microspheres; (f) TEM image of Au/CeO₂ microspheres; (g, h, i) SEM images of Cu/CeO₂ microspheres; and (j, k, l) SEM images of Ag/CeO₂ microspheres.



Figure S16. (a) STEM-DF images of a detailed view on an individual Au/CeO₂ microsphere and the corresponding elemental mappings of (b) Au, (c) O, and (d) Ce.



Figure S17. (a) STEM-DF images of a detailed view on an individual Pd/CeO₂ microsphere and the corresponding elemental mappings of (b) Pd, (c) O, and (d) Ce.

Table S1

Table S1 Metal loadings of metal NPs/CeO ₂ microspheres	
Samples	Metal loading
Au/CeO ₂ microspheres	4.1 wt%
Pd/CeO ₂ microspheres	4.1 wt%
Ag/CeO ₂ microspheres	1.2 wt%
Cu/CeO ₂ microspheres	1.2 wt%

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