Supplementary data

Core-shell structured nanocomposites Ag@CeO₂ as catalyst for hydrogenation of 4-nitrophenol and 2-nitroaniline

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1.1. Synthesis of commercial CeO₂ supported Ag NPs

0.1 g of commercial CeO₂ and 10 mL of 0.005 mM AgNO₃ aqueous solution were mixed together. After stirring at room temperature for 2 h, 10 mg of NaBH₄ was added into this aqueous solution. The product was purified by centrifugation and dried at 313 K in vacuum overnight.

1.2. Synthesis of free Ag NPs

With constant vigorous stirring, a certain amount NaBH₄ was added to AgNO₃ aqueous solution (10 mL, 0.15 M). The obtained product was further washed with anhydrous ethanol and water three times. It was obtained by drying in vacuum oven at 313 K overnight.

Under N_2 atmosphere, redox reaction occurs between $[Ag(NH_3)_2]OH$ and $Ce(NO_3)_3$ in an alkaline condition.

$$Ag^+ + 2 NH_3 \cdot H_2O = [Ag(NH_3)_2]^+ + 2 H_2O$$
 eqn. (S1)

$$Ce^{3+} + 3 OH^{-} = Ce(OH)_{3}$$
 eqn. (S2)

$$Ce(OH)_3 + [Ag(NH_3)_2]^+ + OH^- = Ce(OH)_4 + Ag + 2 NH_3$$
 eqn. (S3)

$$Ce(OH)_4 = CeO_2 + 2 H_2O \qquad eqn. (S4)$$



Fig. S1. Nitrogen adsorption-desorption isotherms (a) and the pore size distribution (b)

of the Ag@CeO₂ NCs.



Fig. S2. UV-vis absorption spectra of 4-Nitrophenolate ion (black line), 4-AP (red line), and 4-NP (blue line).

Initially, the 4-NP solution, which have a light yellow color, rapidly turned bright yellow upon the addition of NaBH₄ solution because of the formation of 4nitrophenolate ions in the alkaline conditions.²⁵⁻²⁸ The corresponding absorption peak shifted from 317 nm (assigned to 4-NP) to 400 nm (assigned to 4-nitrophenolate ion), and the absorption peak at 298 nm is 4-AP which is colourless after the complete reduction.



Fig. S3. Plots of $ln(C_t/C_0)$ versus time for the catalytic reduction of 4-NP with NaBH₄ by Ag@CeO₂ NCs at different temperatures (a) and the corresponding Arrhenius plot (b) (Ag/4-NP = 0.20, NaBH₄/4-NP = 154).



Fig. S4. Plots of $\ln(C_t/C_0)$ versus time for the catalytic reduction of 2-NA with NaBH₄ by Ag@CeO₂ NCs at different temperatures (a) and the corresponding Arrhenius plot (b) (Ag/2-NA = 0.14, NaBH₄/2-NA = 316).



Fig. S5. SEM image of the $Ag@CeO_2$ NCs after tenth runs for the catalytic reduction of 4-NP.