Supplementary data

Core-shell structured nanocomposites Ag@CeO$_2$ as catalyst for hydrogenation of 4-nitrophenol and 2-nitroaniline

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1.1. Synthesis of commercial CeO$_2$ supported Ag NPs

0.1 g of commercial CeO$_2$ and 10 mL of 0.005 mM AgNO$_3$ aqueous solution were mixed together. After stirring at room temperature for 2 h, 10 mg of NaBH$_4$ 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 NaBH$_4$ was added to AgNO$_3$ 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 N₂ atmosphere, redox reaction occurs between [Ag(NH₃)₂]OH and Ce(NO₃)₃ in an alkaline condition.

\[
\text{Ag}^+ + 2 \text{NH}_3\cdot\text{H}_2\text{O} = [\text{Ag(NH}_3)_2]^+ + 2 \text{H}_2\text{O} \quad \text{eqn. (S1)}
\]

\[
\text{Ce}^{3+} + 3 \text{OH}^- = \text{Ce(OH)}_3 \quad \text{eqn. (S2)}
\]

\[
\text{Ce(OH)}_3 + [\text{Ag(NH}_3)_2]^+ + \text{OH}^- = \text{Ce(OH)}_4 + \text{Ag} + 2 \text{NH}_3 \quad \text{eqn. (S3)}
\]

\[
\text{Ce(OH)}_4 = \text{CeO}_2 + 2 \text{H}_2\text{O} \quad \text{eqn. (S4)}
\]
Fig. S1. Nitrogen adsorption-desorption isotherms (a) and the pore size distribution (b) of the Ag@CeO$_2$ 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 4-nitrophenolate 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 NaBH$_4$ by Ag@CeO$_2$ NCs at different temperatures (a) and the corresponding Arrhenius plot (b) ($\text{Ag/4-NP} = 0.20$, NaBH$_4$/4-NP = 154).
Fig. S4. Plots of $\ln(C_t/C_0)$ versus time for the catalytic reduction of 2-NA with NaBH$_4$ by Ag@CeO$_2$ NCs at different temperatures (a) and the corresponding Arrhenius plot (b) ($\text{Ag/2-NA} = 0.14$, $\text{NaBH}_4/2\text{-NA} = 316$).
**Fig. S5.** SEM image of the Ag@CeO$_2$ NCs after tenth runs for the catalytic reduction of 4-NP.