Supplementary Information

Pd nanoparticles partially embedded in the inner wall of nitrogen-doped carbon hollow spheres as nanoreactors for catalytic reduction of 4-nitrophenol

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Experimental section

1. Synthesis

1.1 Synthesis of Pd nanoparticles

Pd nanoparticles were synthesized according to a reported method.[1] In a typical synthesis, PVP and citric acid (275 mg) were dissolved in distilled water (8.0 mL) in a three-necked flask refluxed at 90 °C under stirring. Sodium tetrachloropalladate (II) (7.3 mM) was dissolved in distilled water (3.0 mL), and this aqueous solution was then rapidly added into the flask. The reaction mixture was heated at 90 °C for 26 h.

1.2 Synthesis and surface functionalization of silica nanospheres (silica-NH_2)

The silica nanospheres were prepared using a modified Stöber method.[2] In a typical synthesis, 6 mL of TEOS were rapidly added into a mixture of ethanol (74 mL), distilled water (10 mL), and ammonium aqueous solution (25-28%, 3.15 mL). Then, the mixture was stirred for 12 h at room temperature. The white silica nanospheres were recovered and purified by three centrifugation and re-dispersion cycles with

distilled water. It was dried at 100 °C for 6 h.

For preparing the $–NH_2$ terminated silica nanospheres, 0.5 g of the silica nanospheres was added into a mixture of isopropanol (90 mL) and APTS (0.75 mL) and stirred at 80 °C for 2 h to functionalize the silica surface with amino groups. After washing with isopropanol twice via centrifugation and decantation, $–NH_2$ terminated silica nanospheres were obtained. The weight of silica-NH_2 nanospheres is around 0.46 g. The resulting $–NH_2$ terminated silica nanospheres were then dispersed in distilled water (10 mL).

1.3 Synthesis of Pd/silica-NH_2 composite nanospheres

Pd nanoparticles were adsorbed onto the $–NH_2$ functionalized silica nanospheres by adding the above $–NH_2$ terminated silica nanospheres (4.8 mL) into the solution containing Pd nanoparticles (55 mL) that was further diluted in 125 mL distilled water under sonication. After the solution was equilibrated for 10 min, the colloidal solution was centrifuged and the precipitate was washed with distilled water once and dispersed in distilled water (125 mL). This gave a colloidal solution of Pd/silica-NH_2 composite nanospheres. The weight of Pd/silica-NH_2 composite nanospheres is around 0.23 g in the colloidal solution.

1.4 Synthesis of Pd/silica-NH_2@polydopamine composite nanospheres and Pd@NC nanoreactors

Dopamine (500 mg) was added into the solution containing Pd/SiO_2-NH_2 composite nanospheres. Then, the pH of the solution was adjusted to around 9. After 12 h of stirring, the Pd/silica-NH_2@polydopamine composite nanospheres were collected by centrifugation, washed with ethanol and dried at 100 °C. The weight of obtained Pd/silica-NH_2@polydopamine composite nanospheres is around 0.34 g. Then, the synthesized nanospheres were calcined in N_2 atmosphere at 600 °C for 1 h with a heating rate of 2 °C/min. Washing twice with 0.5 mol/L NaOH solution (V_{EtOH}/V_{H2O}=1:1) at 100 °C results in the formation of Pd@NC nanoreactors. After the sample was cooled to ambient temperature, the solid product was collected, washed with distilled water and ethanol, and dried at 100 °C for 12 h. The weight of

Pd@NC is around 0.032 g.

2. Materials characterization

The microscopic features of the samples were characterized by TEM (JEOL, JEM-2010F) operating at 200 kV and SEM (Hitachi, S-4800). XRD pattern was collected on a Rigaku D/Max-2550PC X-ray diffractometer with CuKa radiation. The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectrometer with Al Ka (1486.6 eV) as the X-ray source. The Pd content in the reaction solution was quantitatively analyzed by inductively coupled plasma mass spectrometry (Prodigy ICP-OES).

3. General procedures for catalytic reduction of 4-nitrophenol and its derivatives

The catalytic reduction reaction was carried out in a standard quartz cell with a 1 cm path length at room temperature. The procedure entailed mixing $NaBH_4$ solution (1 mL, 0.05 mol/L) with 4-nitrophenol solution (2 mL, 5×10^{-5} mol/L) in the quartz cell. After that Pd@NC nanoreactors suspension (0.5 mL, 50 mg/L) was added to the solution and the absorption spectra were recorded immediately in the range of 200-550 nm by Techcom UV-1102 spectrophotometer at room temperature. The intensity of the absorption peak at 400 nm in UV-vis spectroscopy was used to monitor the process of the conversion of 4-nitrophenol to 4-aminophenol. After each cycle of reaction, another 4-nitrophenol (45 μL, 2.28×10^{-3} mol/L) and $NaBH_4$ (45 μL, 1.1 mol/L) were added to the reaction solution to study the catalytic stability of the Pd@NC nanoreactors. In a control experiment, the catalytic activity of a commercial 5 wt% Pd/C catalyst (0.5 mL, 20 mg/L, Sinopharm Chemical Reagent Com., Ltd) was tested following the procedure described above. The procedure for catalytic reduction of 2-amino-4-nitrophenol (NPNP) and 2-chloro-4-nitrophenol (ClPNP) is similar to that of 4-nitrophenol.

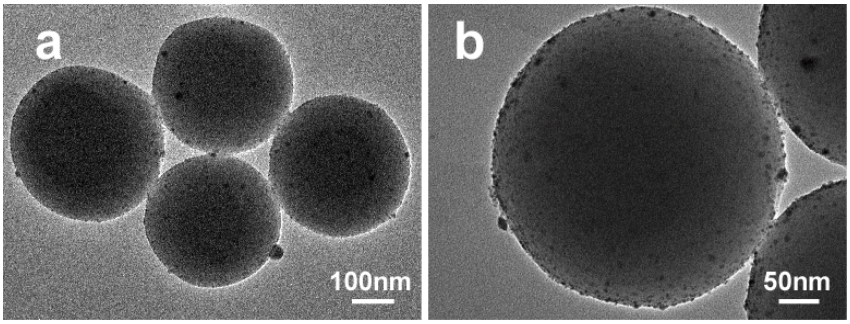

Fig. S1 (a) TEM and (b) high-magnification TEM images of Pd/silica-NH_2 composite spheres.

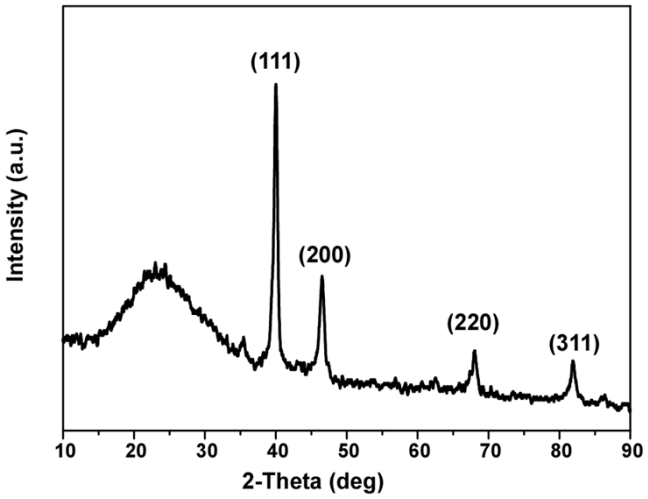

Fig. S2 XRD pattern of Pd@NC nanoreactors.

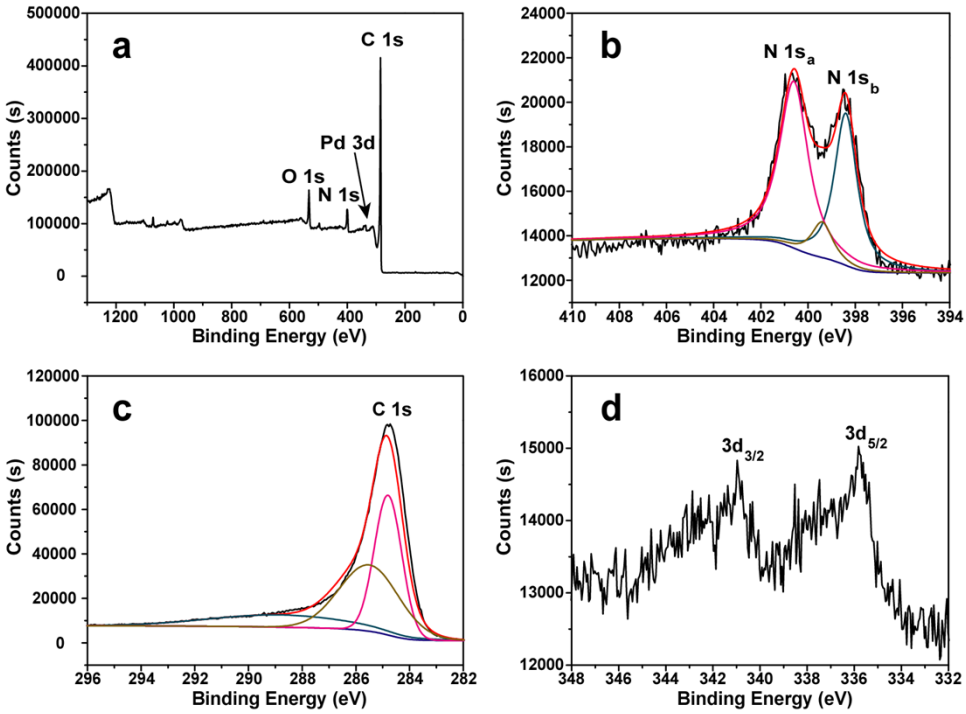

Fig. S3 XPS spectra of Pd@NC nanoreactors: (a) survey spectrum, (b) N1s spectrum, (c) C1s spectrum and (d) Pd3d spectrum.

Reference

1. Y. Wang, A. V. Biradar, C. T. Duncan and T. Asefa, ***J. Mater. Chem.***, 2010, **20**, 7834-7841.
2. S.-W. Bian, Y.-P. Zhao and C.-Y. Xian, ***Mater. Lett.***, 2013, **111**, 75-77.