Supporting Information

Central-radial bi-porous nanocatalysts with accessible high units loading and robust magnetic recyclability for 4-nitrophenol reduction

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Experimental section

Materials

Cetyltrimethylammonium bromide (CTAB), triethanolamine (TEA), sodium salicylate (NaSal), tetraethyl orthosilicate (TEOS), ferric acetylacetonate ($Fe(acac)_3$), triethylene glycol (TEG), polyvinyl pyrrolidone (PVP, Mw~40000) and sodium borohydride ($NaBH_4$) were purchased from Sigma-Aldrich. Chloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$) and poly(ethyleneimine) (PEI, Mw~1800) were purchased from Aladdin. Potassium carbonate (K_2CO_3), hydroxylamine hydrochloride ($NH_2OH \cdot HCl$), hydrochloric acid (HCl), ethanol, methanol, sodium hydroxide (NaOH), ammonia aqueous solution (25%-28%) and 4-nitrophenol (4-NP) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ultrapure water was produced by a Millipore Milli-Q system.

Synthesis of dentritic silica spheres (dSi)

Briefly, the TEA (68 mg) was added into 25 mL of H_2O which was magnetically stirred at 80 ºC for 30 min. The solution was added with 380 mg of CTAB and 193 mg of NaSal and stirred for 1 h. The mixture was injected with 4 mL of TEOS and stirred for another 2 h at 80 ºC. The dSi spheres were collected by centrifugation and washed with ethanol for several times. The extraction of residue organic templates was performed by dispersing the precipitates in HCl/methanol mixture and shaking at 60 ºC for 6 h and repeated for 2-3 times. The final product was washed with ethanol and dispersed in 50 mL of ethanol.

Synthesis of dSi/IO

In a typical synthesis process, a wet precipitate of dSi spheres from the above ethanol dispersion (7.5 mL), 360 mg of $Fe(acac)_3$ and 40 mg of PEI (Mw~1800) was added with 30 mL of TEG in a two-neck flask and ultrasonicated for homogenization. The flask was filled with argon on a Schlenk line and then maintained at 210 °C for 2 h with vigorous stirring, which was further heated to 285 °C and stirred for another 1 h. After cooled to room temperature, the reaction mixture was added with 15 mL of acetone and the product was obtained by magnetic separation and washed with ethanol for several times.

Synthesis of dSi/IO/Au-s

The $HAuCl_4$ solution (0.2 mL, 50 mM) was mixed with 1 mL of water, and the above solution was added with 0.1 mL of K_2CO_3 solution (0.2 M) under stirring, until the colour changed from yellow to colourless. Then the solution was added into 4 mL of water containing 2.5 mg of dSi/IO in an ice bath and stirred for 10 min. The freshly prepared $NaBH_4$ solution (40 μL, 0.1 M) was swiftly injected into the above mixture which was stirred for 2 min. The dSi/IO/Au-s was collected by a magnet, washed with water, and re-dispersed in 1 mL of water.

Synthesis of dSi/IO/Au

For the AuNPs growth, the $HAuCl_4$ solution (50 μL, 50 mM) was first added into 3 mL of water, followed by the addition of 37.5 μL of K_2CO_3 solution (0.2 M) and stirred until the solution became colourless. The as prepared dSi/IO/Au-s dispersion (0.5 mL) and 25 mg of PVP (Mw~40000) dissolved in 0.5 mL of water were added into the above solution and stirring for 10 min. Then the $NH_2OH\cdot HCl$ solution (0.5 mL, 25 mM) was slowly injected into the above mixture. After reacted for 1 h, the dSi/IO/Au composites were collected by a magnet and washed with water.

Synthesis of dSi/IO/Au/mSi

The mesoporous silica coating was performed as following: the obtained dSi/IO/Au composites were dispersed in 30 mL of CTAB water solution (3 mM) and added with 300 μL of NaOH solution (0.1 M). The TEOS (30 μL) was subsequently injected and the mixture was stirred at room temperature for at least 24 h. The as prepared dSi/IO/Au/mSi composites were magnetically separated and washed with methanol thoroughly for removing the residue surfactants in the mesopores.

Catalytic reduction of 4-NP

In a typical reaction process, the 4-NP aqueous solution (3 mL, 2 mM) was added into 6 mL of freshly prepared $NaBH_4$ solution (0.1 M) and magnetically stirred at room temperature. Subsequently, the dSi/IO/Au/mSi aqueous dispersion (20 μL, 2 mg/mL) was introduced. At the time intervals of 1.5 min, a fraction of the reaction solution was taken out for the UV-Vis absorption measurement. To evaluate the recyclability of the nanocatalyst, the amounts of 4-NP, $NaBH_4$ and dSi/IO/Au/mSi were increased by 20 times the original value. The catalyst was harvested by a magnet after each reaction and was used in the next catalytic reaction.

Characterizations

The transmission electron microscopy (TEM), energy disperse spectrum (EDS) and EDS elemental mapping were performed on FEI F30 electron microscope operated at 200 kV. The scanning electron microscopy (SEM) was carried out using FEI NanoSEM450 electron microscope. The X-ray diffraction (XRD) pattern was acquired by Bruker D8 ADVANCE diffractometer with Cu-Kα radiation ($\lambda = 1.54$ Å). The room temperature magnetic hysteresis curve was measured by a superconducting quantum interference device magnetometer (MPMS-7, Quantum Design). The nitrogen sorption isotherm was recorded with an Autosorb-IQ surface area and pore size analyser (Quantachrome Instruments). The hydrodynamic diameter and Zeta potential were acquired with a Malvern Zetasizer NanoZS Instrument. The UV-Vis absorption spectra were recorded by a Perkin-Elmer Lambda 750 spectrometer.

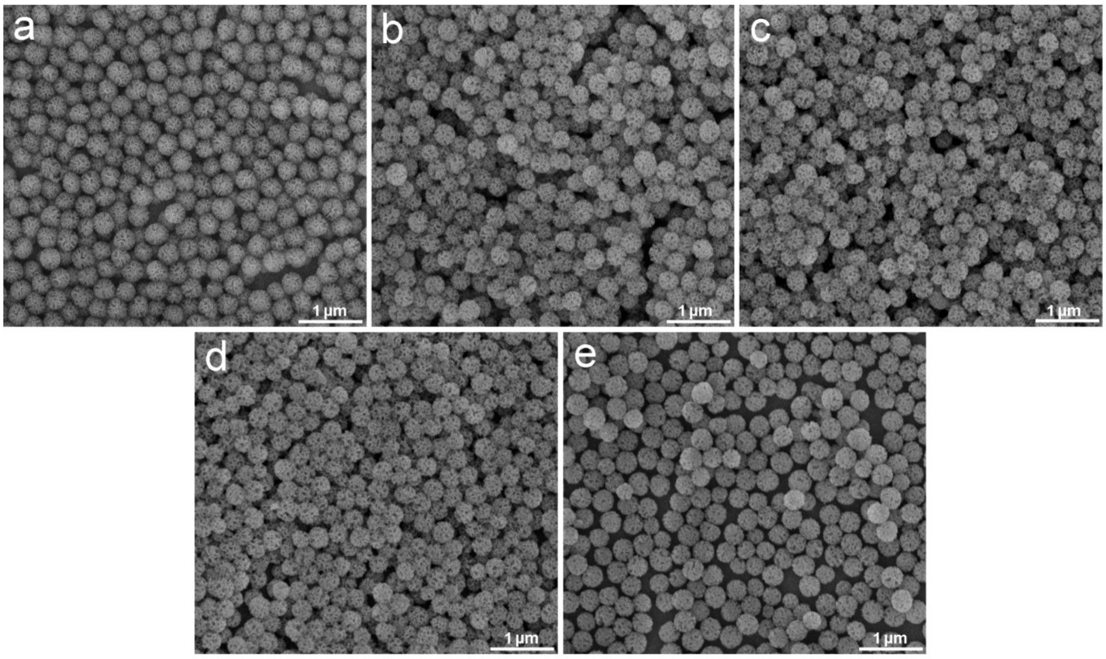

Fig. S1 SEM images of dSi (a), dSi/IO (b), dSi/IO/Au-s (c), dSi/IO/Au (d) and dSi/IO/Au/mSi (e) nanospheres, respectively.

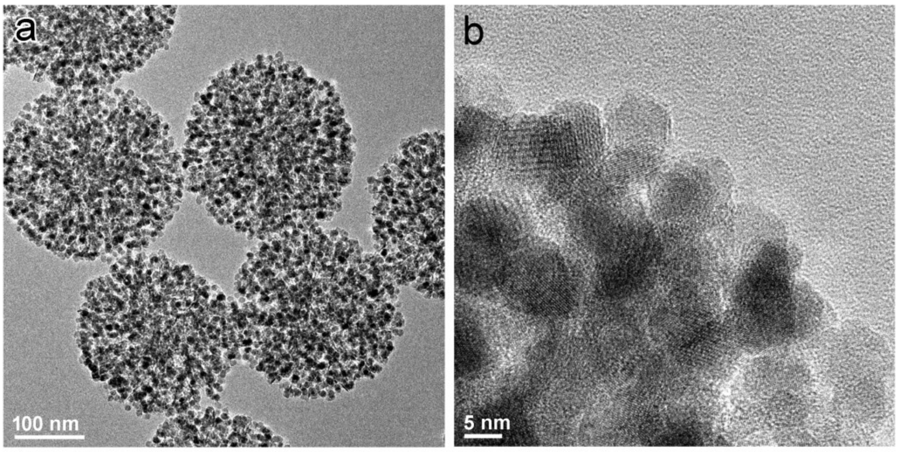

Fig. S2 TEM image of TEG stabilized dSi/IO (dSi/IO-TEG) nanospheres (a) and enlarged TEM image of a single sphere (b).

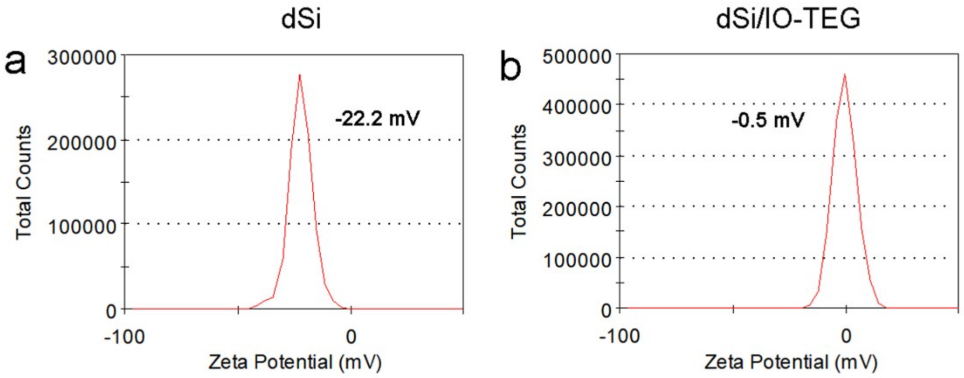

Fig. S3 Zeta potential distribution of aqueous dispersions of dSi templates (a) and TEG stabilized dSi/IO (dSi/IO-TEG) nanospheres (b).

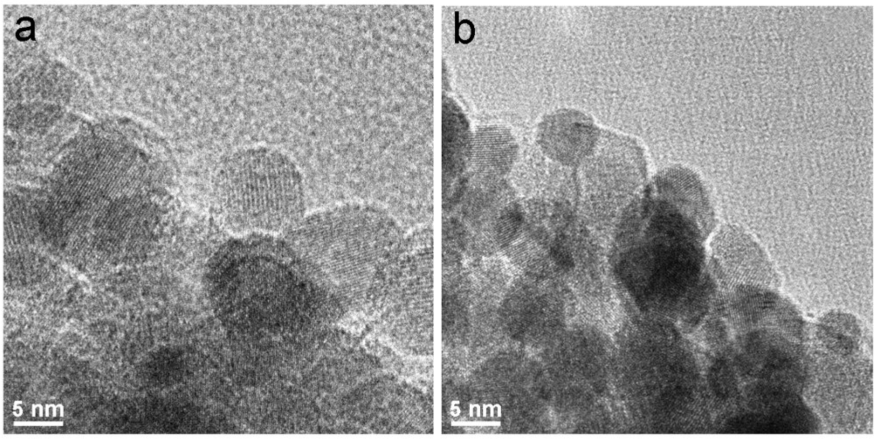

Fig. S4 Enlarged TEM images of dSi/IO nanosphere (a) and dSi/IO/Au nanosphere (b).

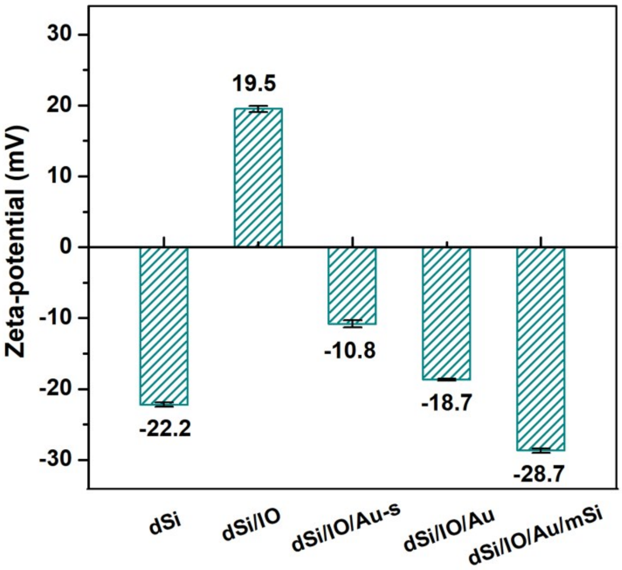

Fig. S5 Zeta potentials of aqueous dispersions of dSi, dSi/IO, dSi/IO/Au-s, dSi/IO/Au and dSi/IO/Au/mSi nanospheres, respectively.

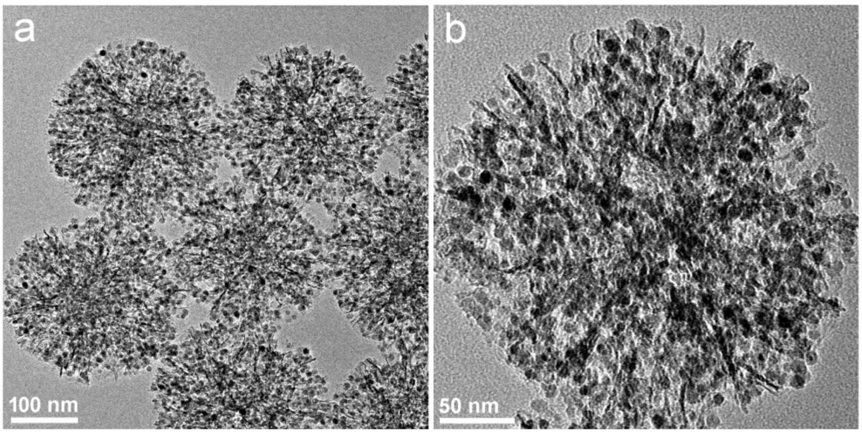

Fig. S6 TEM image of dSi/IO nanospheres with decreased IOs loading density (a) and enlarged TEM image of a single sphere (b).

Table S1 The BET surface area and total pore volume of dSi, dSi/IO, dSi/IO/Au and dSi/IO/Au/mSi nanospheres, respectively.

Sample	dSi	dSi/IO	dSi/IO/Au	dSi/IO/Au/mSi
BET surface area (m^2 g^{-1})	531	215	120	182
Total pore volume (cm^3 g^{-1})	2.20	0.83	0.50	0.28

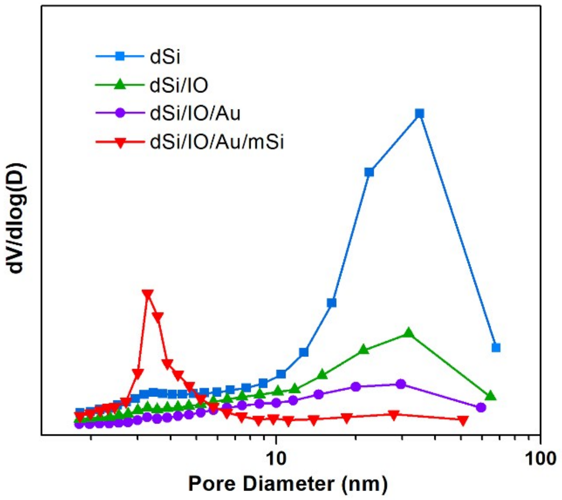

Fig. S7 The BJH pore-diameter distribution of dSi, dSi/IO, dSi/IO/Au and dSi/IO/Au/mSi nanospheres, respectively.

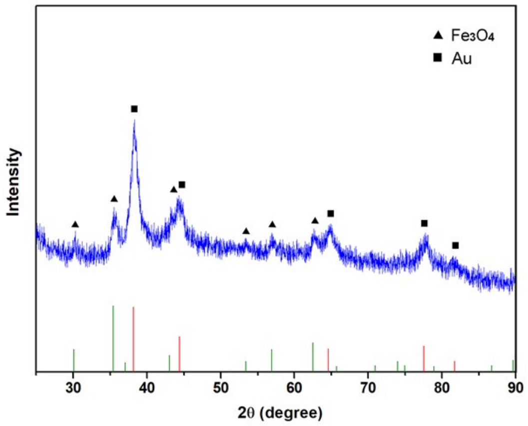

Fig. S8 The XRD pattern of the dSi/IO/Au/mSi nanocatalyst after 5 circles of catalytic reduction of 4-NP by $NaBH_4$. Vertical lines stand for diffractions according to JCPDS#19-0629 (green) and JCPDS#04-0784 (red).

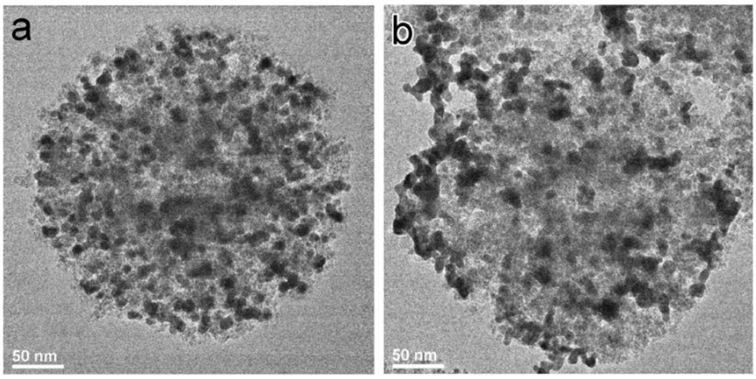

Fig. S9 TEM images of dSi/IO/Au/mSi (a) and dSi/IO/Au (b) nanospheres after 5 circles of catalytic reduction of 4-NP by $NaBH_4$, respectively.