Salt-Templated Growth of Monodisperse Hollow Nanostructures

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Electronic Supplementary Information

Materials and methods

Materials: Sodium citrate ($C_6H_5NaO_7$, >98%) and p-Nitrophenol ($C_6H_5NO_3$) were obtained from Energy Chemical (Shanghai). Tetraethyl orthosilicate (TEOS, $C_8H_{20}O_4Si$, 96%) was purchased from TCl (Shanghai) development co., Ltd. Ammonium hydroxide ($NH_3 \cdot H_2O$, 25-28% NH_3 in water) obtained from Mackin Biochemical (Shanghai) co., Ltd. Dopamine hydrochloride ($C_8H_{11}NO_2 \cdot HCl$), sodium borohydride ($NaBH_4$) and silver nitrate ($AgNO_3$, >99%) were purchased from Sigma-Aldrich. Deionized water and ethanol were used throughout the experiment.

Synthesis of silica hollow nanostructures.   In a typical synthesis of hollow silica spheres (inner diameter = 290 nm, thickness = 30 nm), a 48.5 mL of aqueous solution of sodium citrate (0.06 M) and $NH_3 \cdot H_2O$ (6.9%) was quickly added into 1000 mL of ethanol under magnetic stirring.   After the salt was completely precipitated in 2 minutes, 5 mL of TEOS was added.   The reaction mixture was kept standing for at room temperature 5 hours.   The white products were collected by centrifugation, cleaned two times with ethanol and three times with deionized water, and dispersed in 5 mL of ethanol.

Synthesis of hollow polydopamine and N-doped carbon nanostructures. In a typical synthesis of hollow polydopamine nanostructures with the thickness of 33 nm, a 1.5 mL of aqueous solution of sodium citrate (0.06 M) and $NH_3 \cdot H_2O$ (6.9%) was quickly added into 30 mL of ethanol under magnetic stirring.   After the salt was completely precipitated, 0.1 mL of dopamine solution (0.1 g/mL) was added.   The reaction mixture was allowed to stand in oven at 60 °C for 12 hours.   The solution changed from milky white to dark brown.   The products were collected by low-speed centrifugation, washed two times with ethanol and three times with deionized water, and dried under the vacuum.   The same procedure was used to synthesize 60-nm and 89-nm hollow polydopamine spheres except for the use of 0.2 mL and 0.3 mL of dopamine solutions (0.1 g/mL), respectively.   The as-obtained polydopamine powders were converted into N-doped carbon hollow nanostructures through the calcination at 500 °C for 4 hours under nitrogen atmosphere.

Synthesis of Ag@SiO$_2$ yolk-shell nanostructures.   In a typical synthesis of $Ag_{large}@SiO_2$ particles, a 1.5 mL of pre-mixed aqueous solution of sodium citrate (0.06 M), $AgNO_3$ (0.01 M) and $NH_3 \cdot H_2O$ (6.9%) was quickly added into 30 mL of ethanol under magnetic stirring.   After 2 minutes, 250 μL of TEOS was added.   The reaction mixture was allowed to stand at 35 °C for 12 hours.   The as-obtained $Ag_{large}@SiO_2$ yolk-shell particles were collected by centrifugation, washed two times with ethanol and three times with deionized water, and dispersed in water.   The same procedure

was used for the synthesis of $Ag_{samll}@SiO_2$ particles except that the reaction was carried out at 15 °C for 12 hours.

Catalytic reduction of 4-nitrophenol. For the catalytic reduction of 4-nitrophenol, 1 mL of aqueous solutions of 4-nitrophenol (2×10^{-5} M) and 1 mL of freshly prepared aqueous $NaBH_4$ solution (0.1 M) were added into a quartz cuvette under magnetic stirring. After adding the catalysts (0.016 mg of $Ag_{large}@SiO_2$ or 0.002 mg of $Ag_{small}@SiO_2$ particles dispersed in 0.02 mL of water), the bright yellow solution gradually faded as the catalytic reaction proceeded. The UV-vis absorption spectra of the solution were monitored during the reaction. Control experiments were also carried out under similar conditions without $Ag@SiO_2$ catalysts.

Characterizations. Sample morphologies were characterized with a Zeiss scanning electron microscope (SEM) and an FEI Tecnai F20 transmission electron microscope (TEM). The particle size distribution was measured on a MALVERN ZEN3690 system. Fourier transform infrared (FTIR) spectra were obtained with an FTIR spectrometer (Spectrum One, PerkinElmer) using a standard KBr pellet technique. The Brunauer–Emmett–Teller (BET) data were collected from a Micromeritics ASAP 2050 machine from Micromeritics, United States. Powder X-ray diffraction (XRD) patterns of dried samples were recorded on an Empyrean diffractometer with a Cu Kα radiation. The UV-vis spectra were measured using a probe type Ocean Optics QE65 Pro UV-vis spectrophotometer in absorption mode with an integration time of 8 ms.
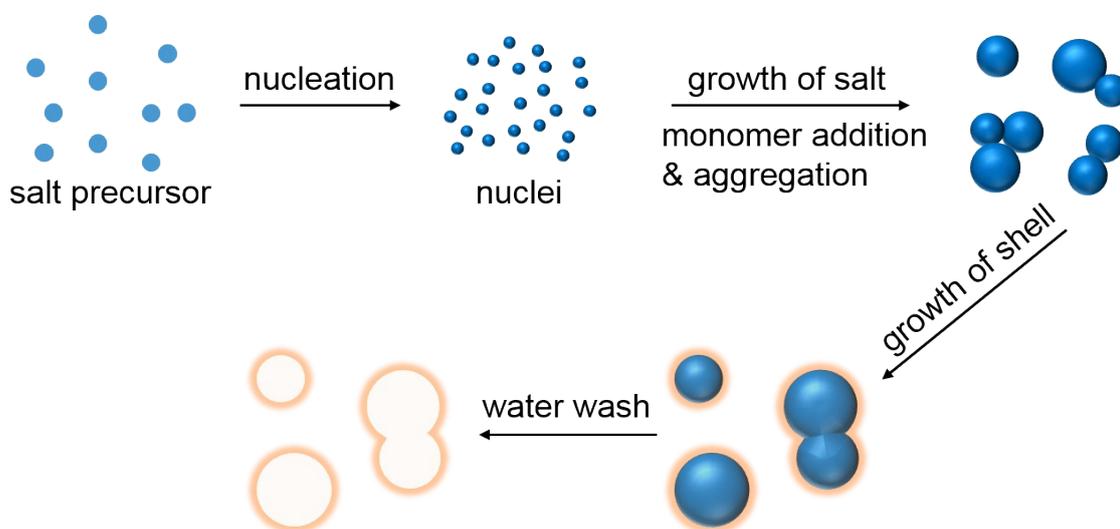
Supplementary Figures

Fig. S1 Schematic illustration of conventional NaCl-templated routes to polydisperse hollow nanostructures. Due to the poor colloidal stability of NaCl particles, both monomer addition and aggregation modes occur during the growth of salt, leading to polydisperse template.
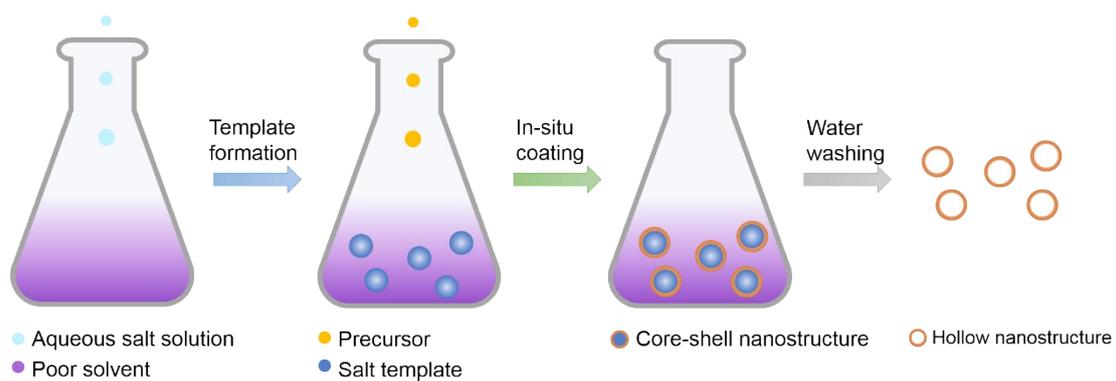
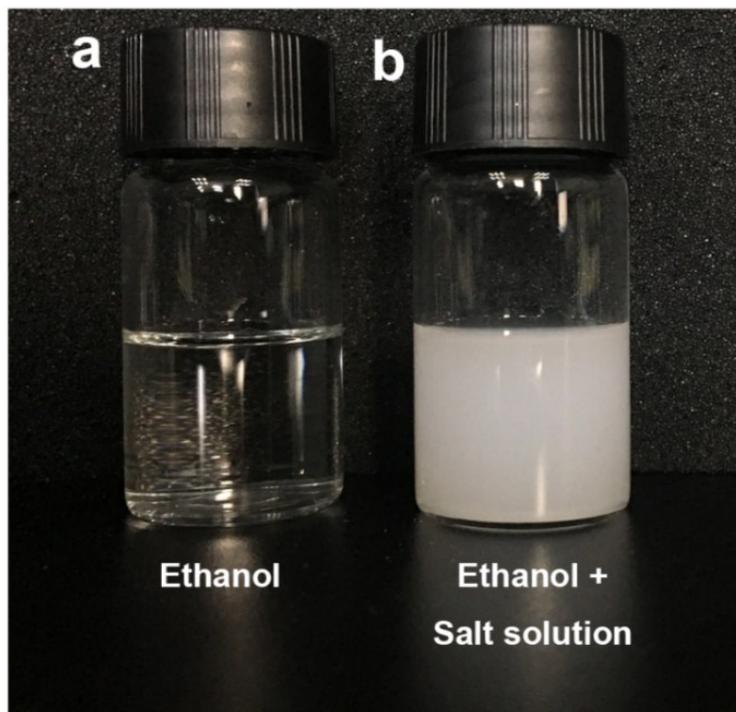**Fig. S2** Schematic illustration of the general one-pot salt-templated route to hollow nanostructures.

Fig. S3 Digital photos of 10-mL ethanol solutions (a) without and (b) with the addition of an aqueous solution of sodium citrate and ammonium hydroxide (0.5 mL).
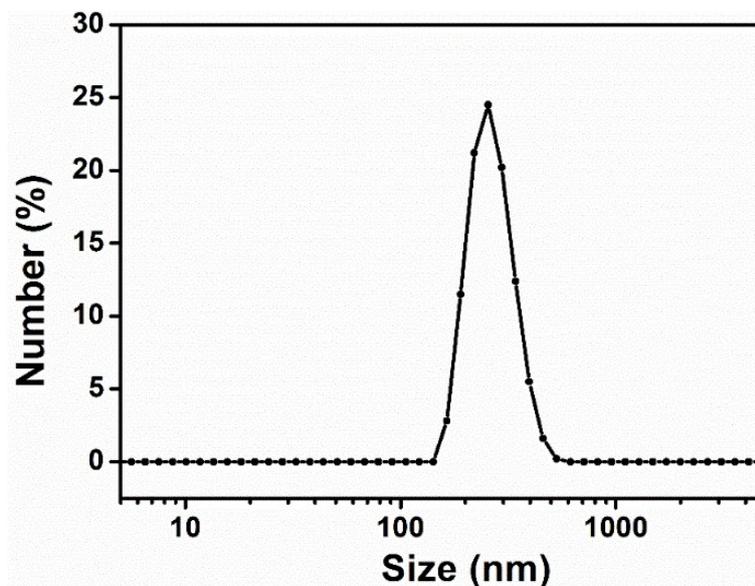
Fig. S4 DLS curve of salt templates used for growing the sample shown in **Fig. 1b** of the main text. A single narrow peak was observed, suggesting the good monodispersity of the salt templates.
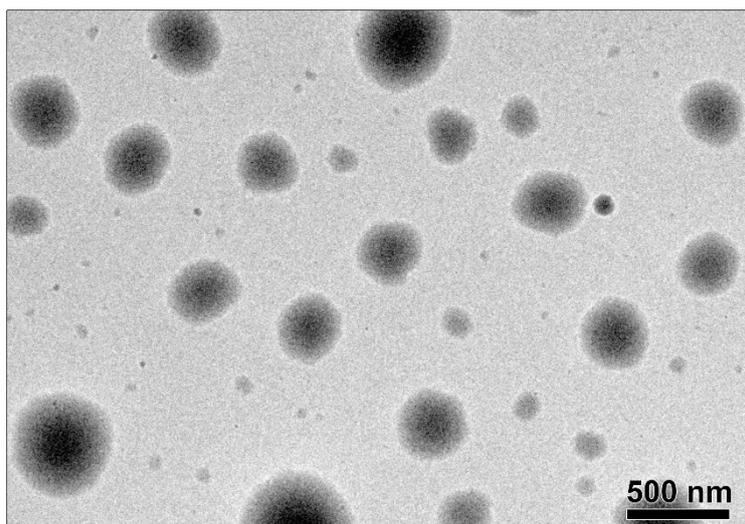
Fig. S5 TEM image of salt templates after drying their colloidal dispersion on the TEM grid, revealing their vulnerability to the aggregation and structural damage during the collecting and drying process.
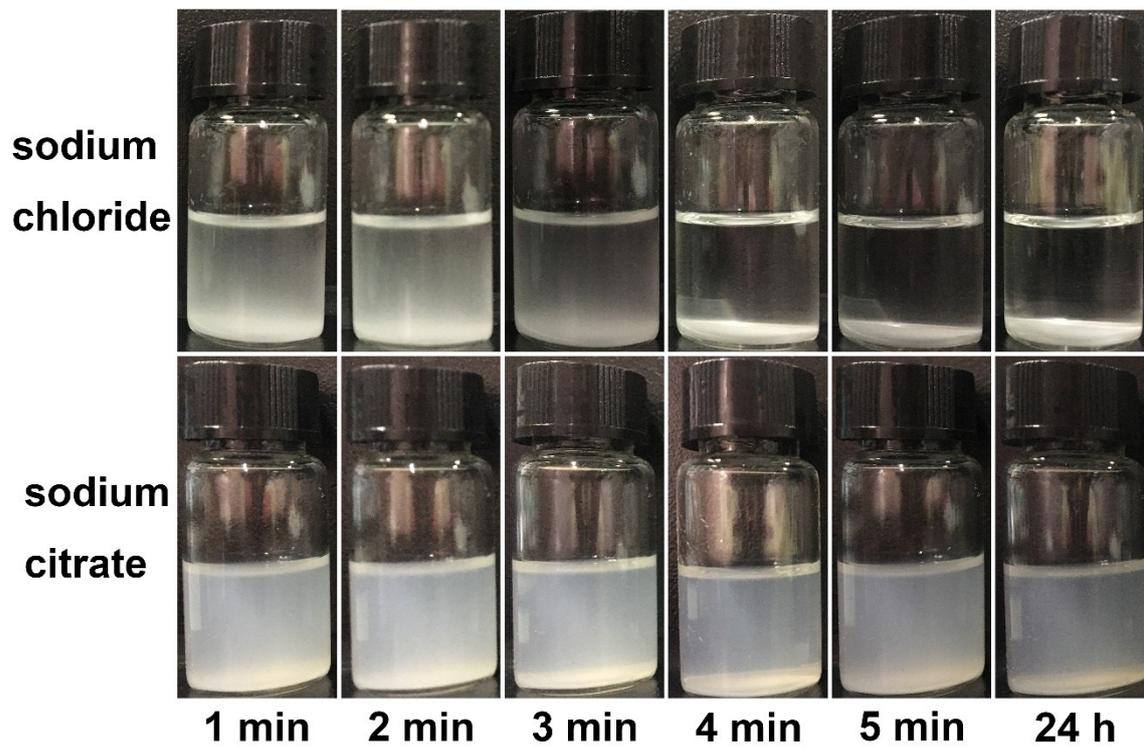
Fig. S6 Digital photos showing the comparison of colloidal stability of NaCl and sodium citrate particles in the water-ethanol solution.
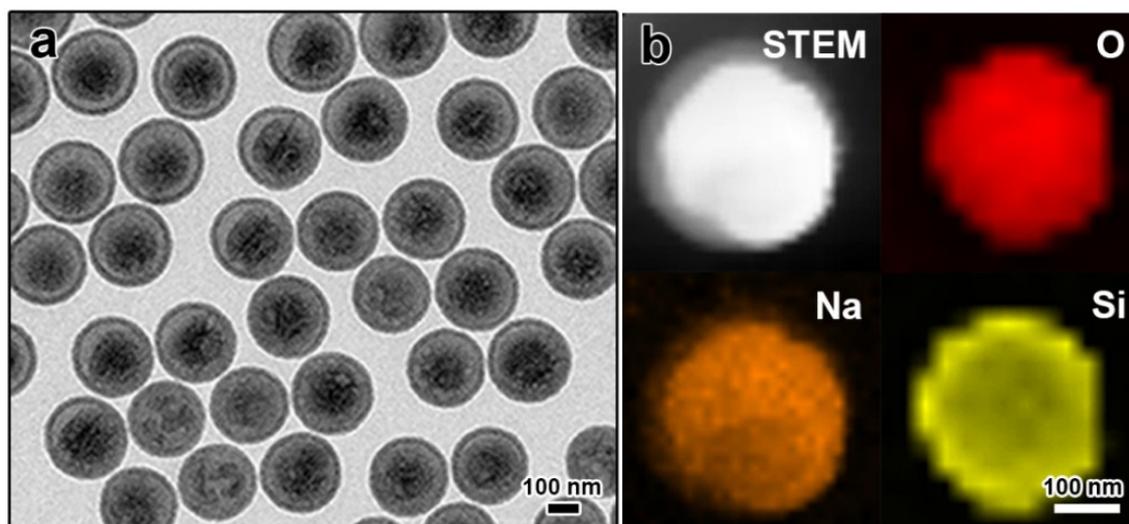
Fig. S7 (a) TEM image of a typical salt@SiO$_2$ sample prepared in ethanol before removing the salt templates by water washing.　(b) Elemental mapping of a salt@SiO$_2$ particle before water washing.
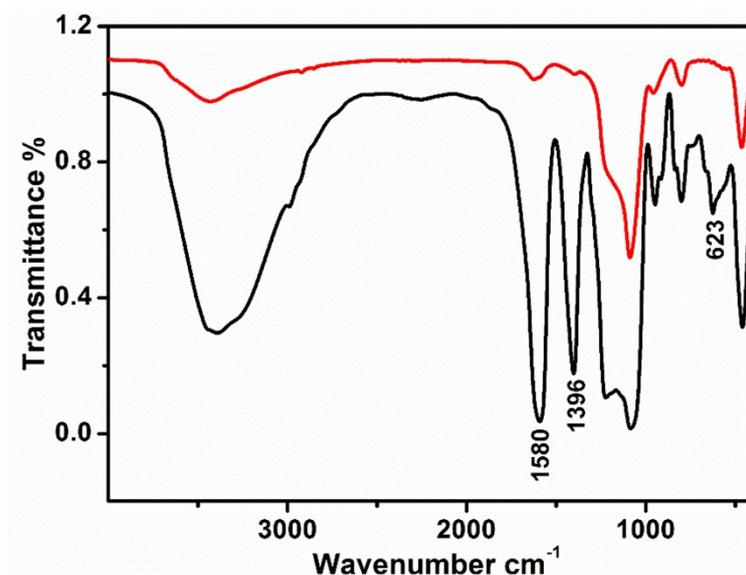
Fig. S8 FTIR spectrum of the salt@SiO$_2$ sample before (black line) and after (red line) washing by water.　The peaks at 623, 1396 and 1580 cm^{-1} correspond to citrate.
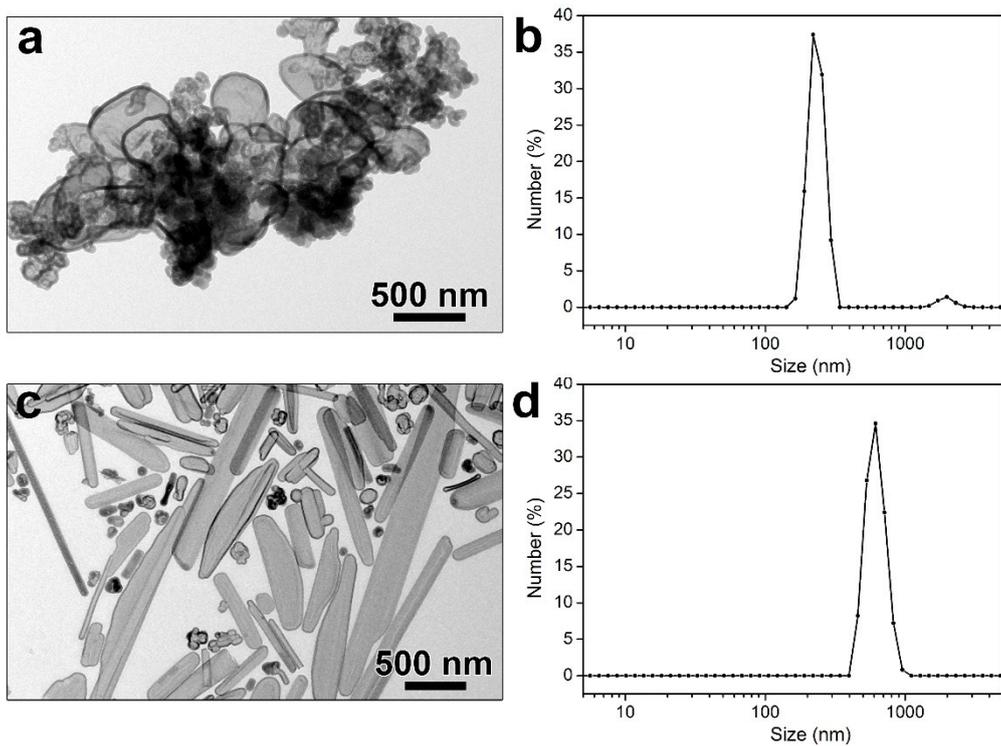
Fig. S9 TEM images of hollow silica particles obtained by using (a) Na_2SO_4 and (c) $NaNO_3$ as the templates.   DLS curves of the salt templates of (b) Na_2SO_4 and (d) $NaNO_3$, confirming their polydisperse nature.
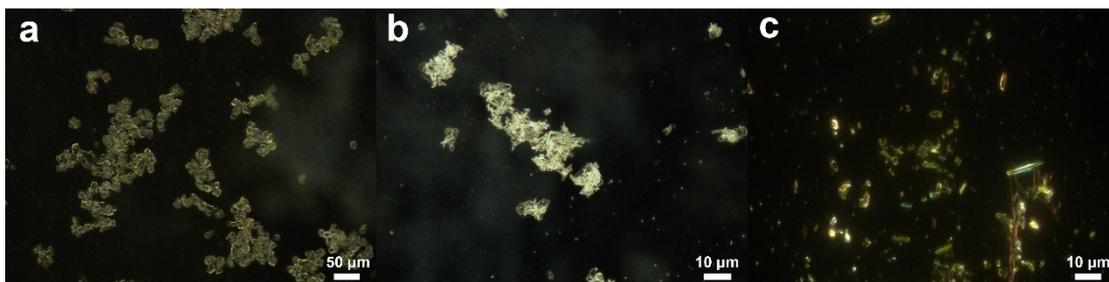
Fig. S10 Optical microscopy images of precipitated slat crystals by putting slat solution into ethanol. (a) NaCl, (b) Na_2SO_4 and (c) $NaNO_3$.
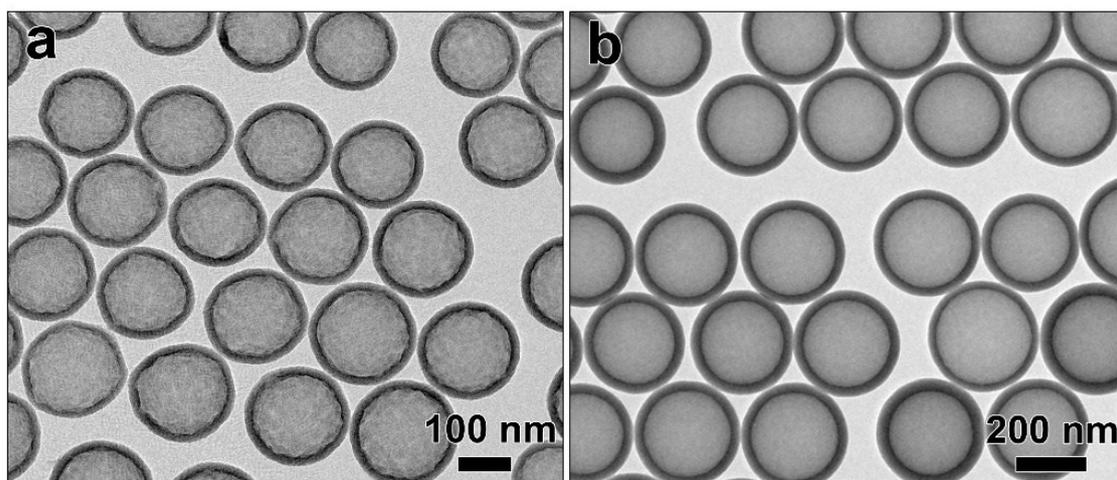
Fig. S11 (a) TEM image of hollow SiO$_2$ particles grown in 2-propanol. Growth conditions: 1.5 mL of aqueous solution of sodium citrate (0.06 mol/L) and ammonium hydroxide (6.9%), 30 mL of 2-propanol, 0.15 mL of TEOS, reaction time = 5 h. (b) TEM image of hollow SiO$_2$ particles grown in 1-propanol. Growth conditions: 1.5 mL of aqueous solution of sodium citrate (0.06 mol/L) and ammonium hydroxide (6.9%), 30 mL of 1-propanol, 0.15 mL of TEOS, reaction time = 5 h.
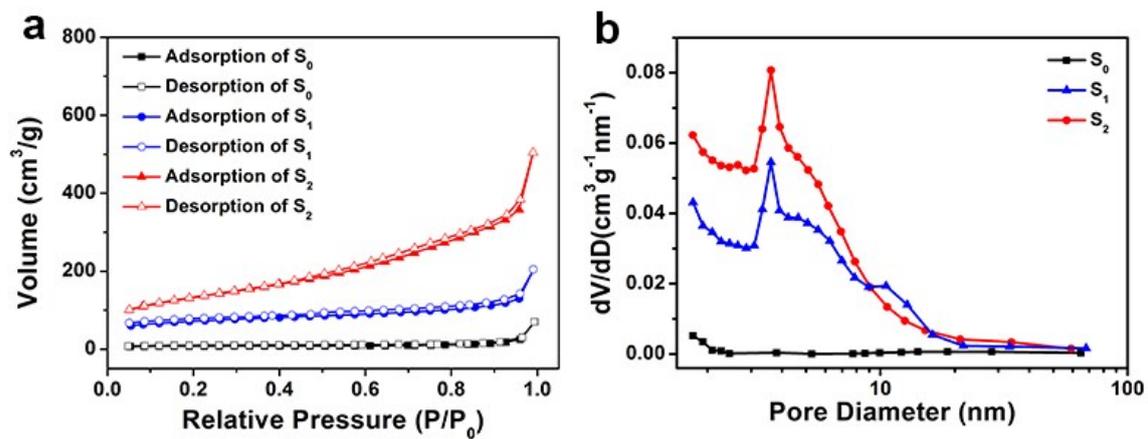
Fig. S12 (a) N_2 adsorption–desorption isotherms and (b) the corresponding pore size distributions of samples S_0, S_1 and S_2 with different porosities.
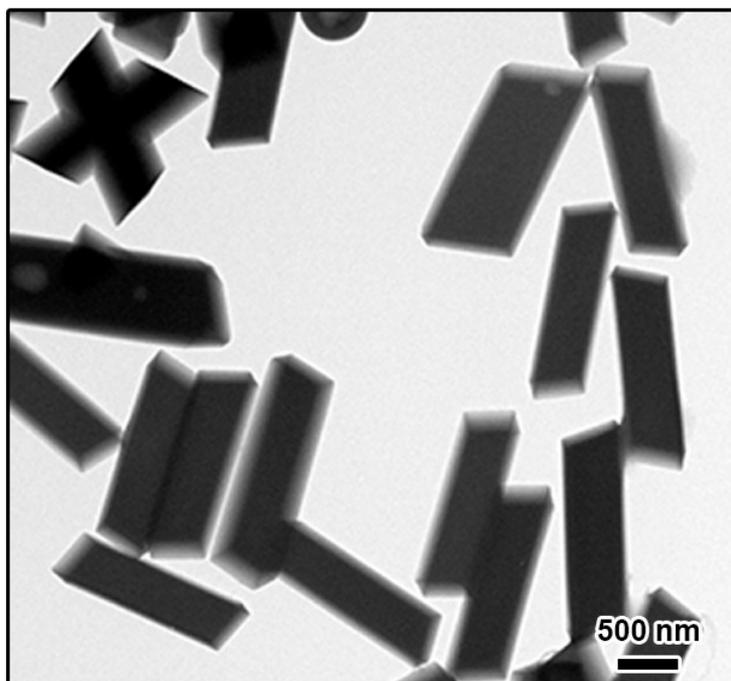
Fig. S13 TEM image of cuboidal salt templates. Growth conditions: 1.5 mL of aqueous solution with sodium citrate (0.12 mol/L) and ammonium hydroxide (6.9%), 30 mL of ethanol, 0.15 mL of TEOS, reaction time = 5 h. The agitation was provided by ultrasonication for 2 minutes. The formation of cuboids could be attributed to the crystallization of salt templates at higher supersaturation degrees. The use of ultrasonication was also important to provide the necessary energy for the rearrangement of ions into highly ordered crystal structures. Spheres instead of cuboids were formed in the control experiments either by lowering the degree of supersaturation or by replacing ultrasonication with magnetic stirring (**Fig. S15**). X-ray diffraction (XRD) results confirmed the better crystallinity of cuboidal templates than that of their spherical counterparts (**Fig. S16-17**).
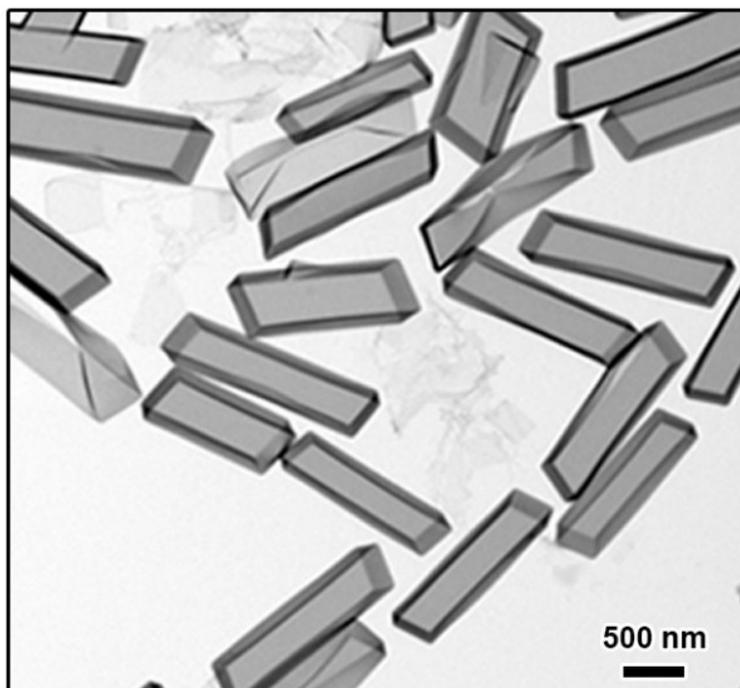
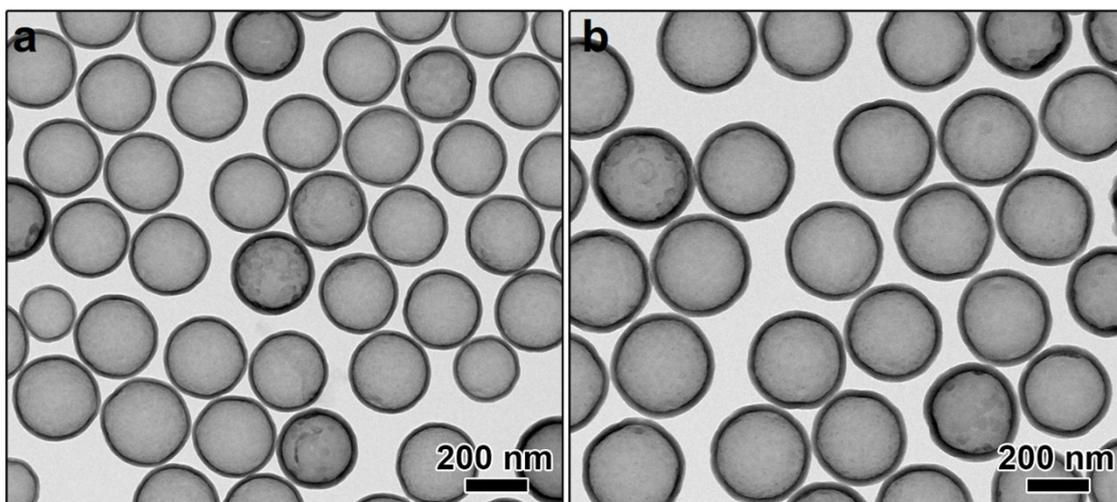**Fig. S14** TEM image of hollow SiO$_2$ cuboids.

Fig. S15 TEM images of hollow SiO$_2$ particles obtained with different conditions: a) 0.06 mol/L of sodium citrate with ultrasonication; b) 0.12 mol/L of sodium citrate without ultrasonication.   Other conditions were kept the same as the sample shown in **Fig. S13**.
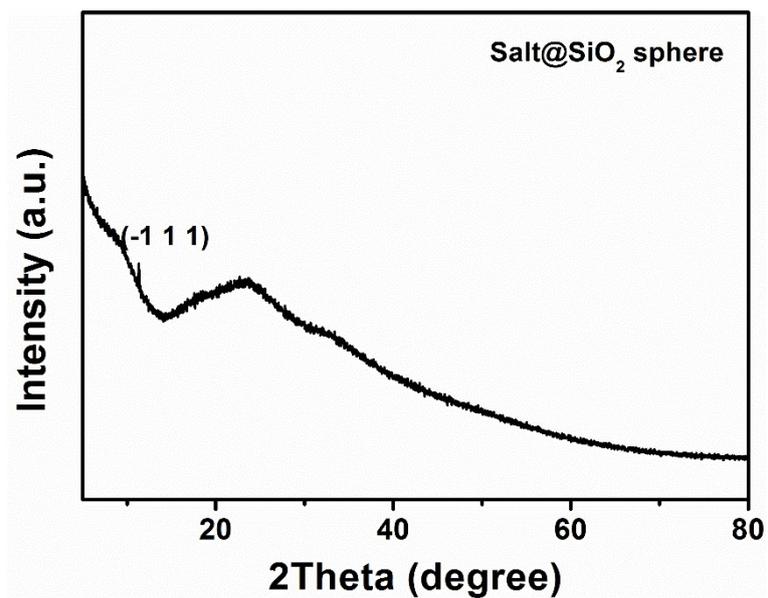
Fig. S16 XRD pattern of salt@SiO$_2$ spheres shown in **Fig. S7a**.
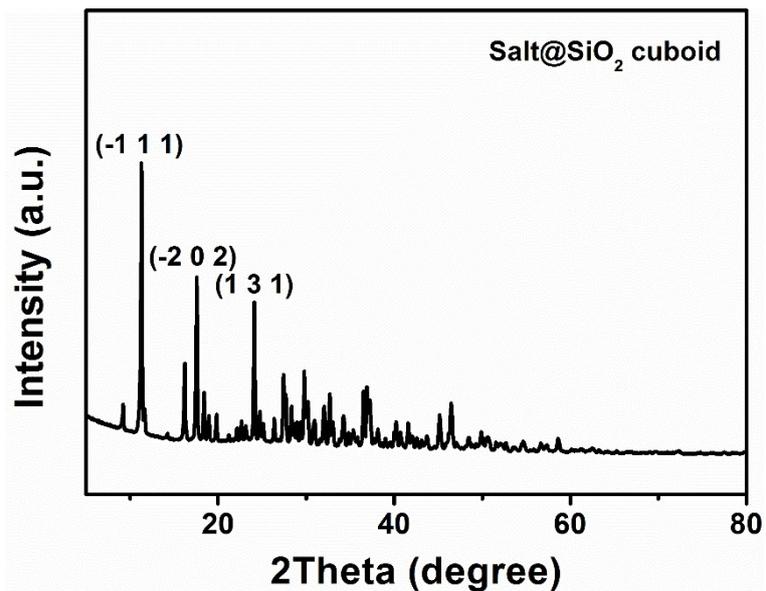
Fig. S17 XRD pattern of salt@SiO$_2$ cuboids shown in **Fig. S13**.　The XRD peaks can be indexed to trisodium citrate dihydrate (JCPDS: 016-1170).
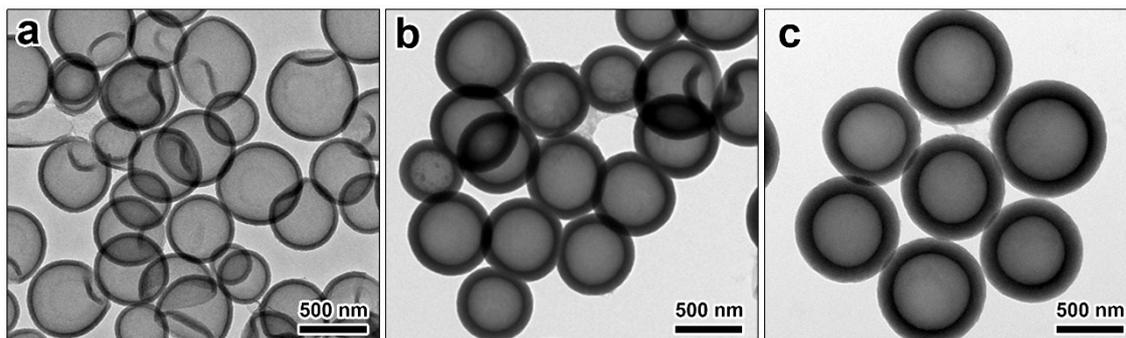
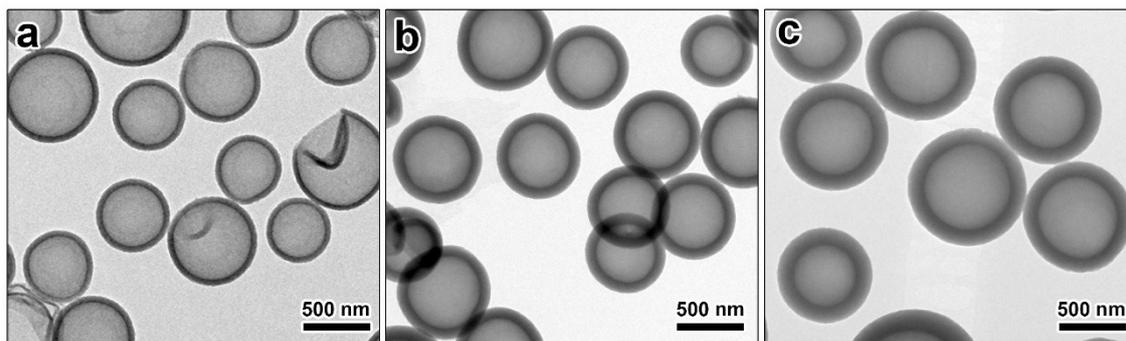**Fig. S18** TEM images of hollow polydopamine nanostructures with different thicknesses.

Fig. S19 TEM images of hollow N-doped carbon nanostructures obtained through the treatment at 500 °C in N_2 for 4 hours.
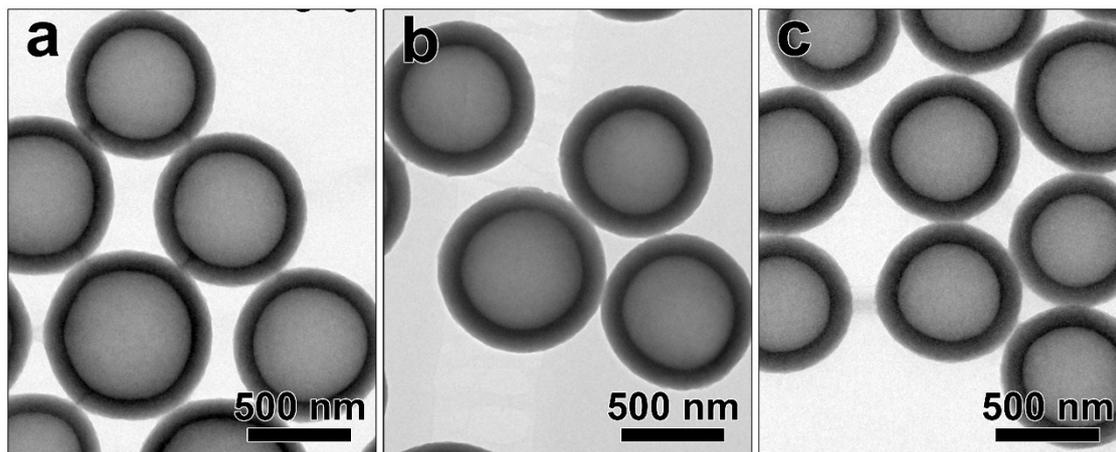
Fig. S20 TEM images of N-doped carbon nanostructures obtained through the treatment at 700 °C, 800 °C and 900 °C in N_2 for 4 hours, respectively.
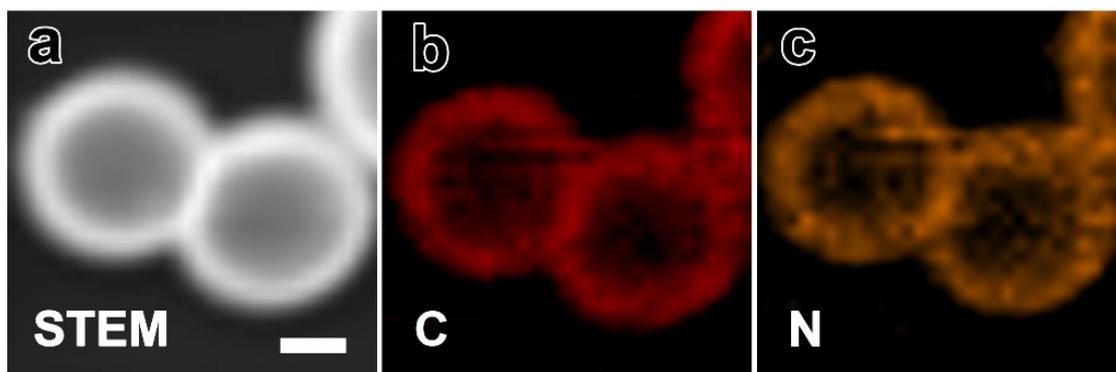
Fig. S21 Elemental mapping of hollow nitrogen-doped carbon shells obtained through the treatment of hollow dopamine particles at 500 °C in N_2 for 4 hours. The scale bar is 200 nm.
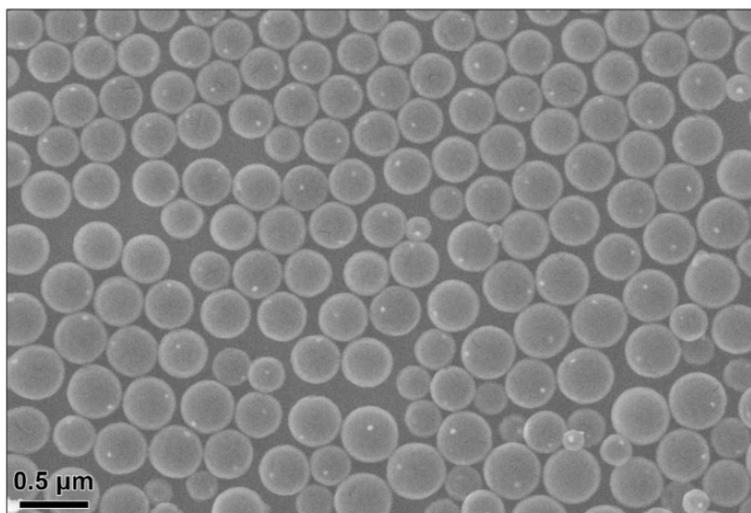
Fig. S22 SEM image of the $Ag_{large}@SiO_2$ sample shown in Fig. 3b of the main text. The image was recorded in the backscattered image (BSD) mode at an acceleration voltage at 15 kV.

Fig. S23 XRD pattern of the $Ag_{large}@SiO_2$ sample shown in **Fig. 3b** of the main text. The XRD peaks can be indexed to silver (JCPDS: 087-0717).
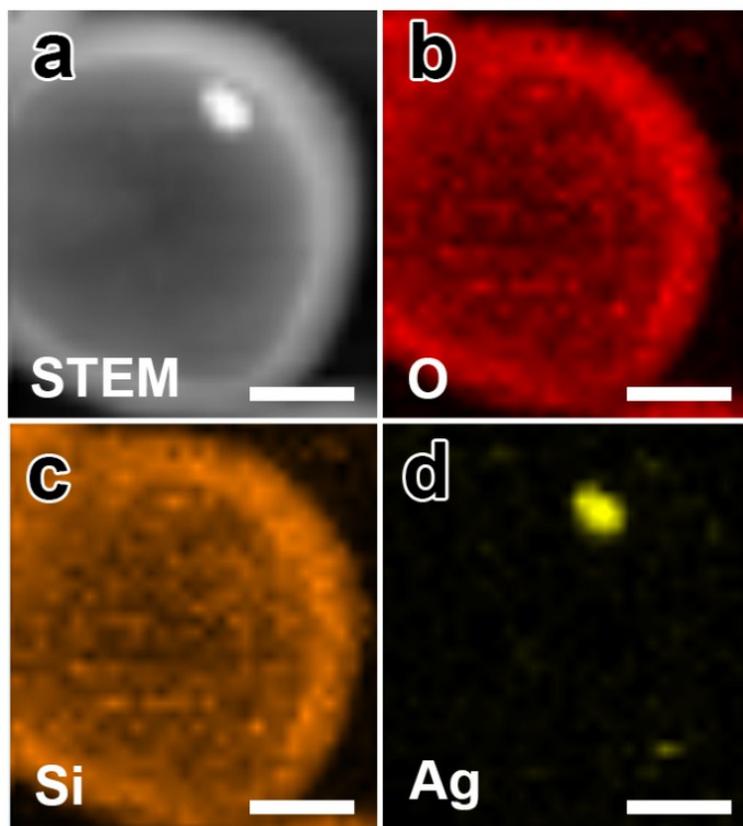
Fig. S24 Elemental mapping of the $Ag_{large}@SiO_2$ sample shown in **Fig. 3b** of the main text. The scale bars are 100 nm for all images.
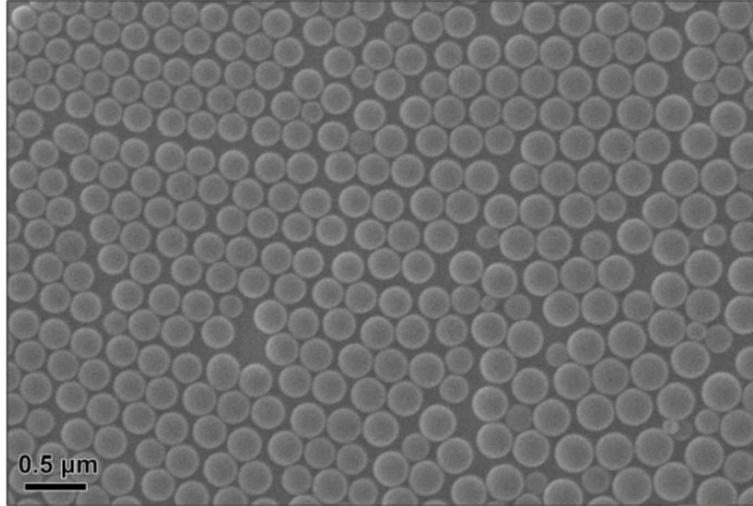
Fig. S25 SEM image of the Ag$_{small}$@SiO$_2$ sample shown in **Fig. 3d** of the main text.

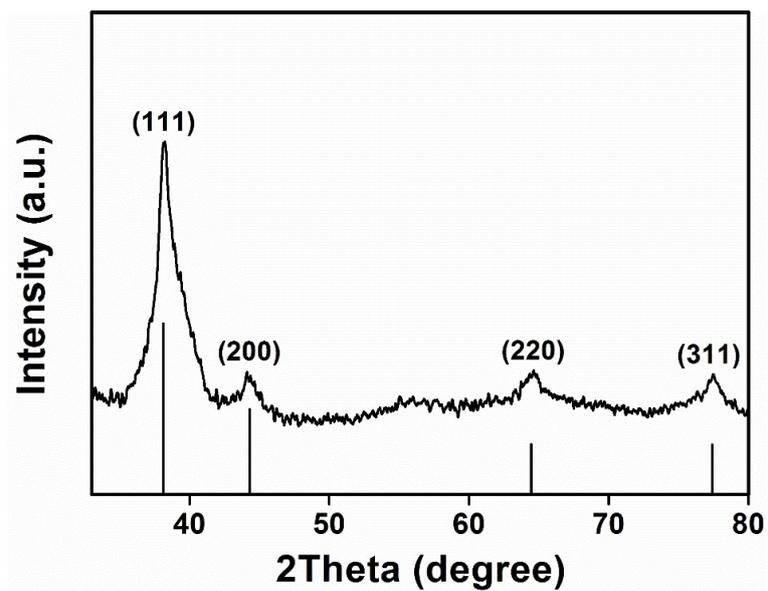**Fig. S26** Cycling stability of catalytic performance for Ag@SiO$_2$ samples. The reaction time of each cycle is (a) 15 minutes for Ag$_{small}$@SiO$_2$, and (b) 25 minutes for Ag$_{large}$@SiO$_2$. After each cycle, the catalyst was collected by centrifugation. Then, 4-nitrophenol and NaBH$_4$ solution were added into the catalyst to trigger the next run of the reaction.

Supplementary Tables

Table S1：Comparison of catalytic activity.

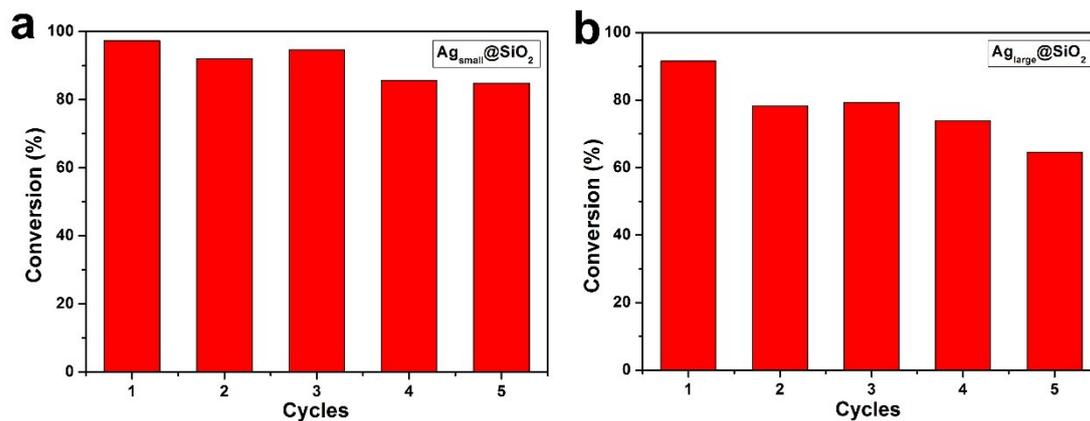| Catalyst	Metal amount (mg)	Rate constant k (min^{-1})	Rate constant per unit mass k_{nor} (min^{-1}mg^{-1})	Reference
Ag$_{small}$@SiO$_2$	$1.1*10^{-4}$	$2.3*10^{-1}$	$2.1*10^3$	This work
Ag$_{large}$@SiO$_2$	$1.0*10^{-3}$	$1.1*10^{-1}$	$1.1*10^2$	This work
AuPt@BGNs/Fe$_3$O$_4$	$9.2*10^{-3}$	8.6	$9.4*10^2$	1
Au NPs/chitosan	$1.6*10^{-1}$	3.4	$1.6*10$	2
Pd@Ru NSs	$1.6*10^{-3}$	$2.2*10^{-1}$	$1.4*10^2$	3
Au@SiO$_2$	$3.2*10^{-1}$	$8.4*10^{-1}$	2.7	4
2% Au@2% Ag/ZIF-8	$1.4*10^{-1}$	$3.0*10^{-1}$	2.2	5
Fe$_3$O$_4$@SiO$_2$-Au@mSiO$_2$ microspheres	$2.1*10^{-2}$	$2.0*10^{-1}$	9.5	6
Ru NFs with *fcc* crystal structure	$2.2*10^{-2}$	$2.2*10^{-2}$	1.0	7
Ru NWs with *hcp* crystal structure	$2.2*10^{-2}$	$5.0*10^{-3}$	$2.3*10^{-1}$	7

Notes and References

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7) Ye, H.; Wang, Q.; Catalano, M.; Lu, N.; Vermeylen, J.; Kim, M. J.; Liu, Y.; Sun, Y.; Xia, X., *Nano Lett.* **2016**, *16*, 2812.

Table S2：Comparison of different methods for the fabrication of hollow SiO$_2$ spheres.

Categories \ Methods		Hard-templating method[8]	Self-templating method[9]	Salt-templated method*
Efficiency	Steps	3	3	1
	Time	1 days	1 day	5 hours
Toxicity	Toxic raw materials	Raw materials for Polystyrene, Ammonia	PVP, NaOH, Ammonia,	Ammonia
Cost#	Energy cost	450 °C for 1 h	100 °C for 3 h	No heat treatment
	Materials cost	~$1800 /g	~$40 /g	~$2 /g
Scalability	Instruments	beaker/flask, stirring plate, oven, centrifuge	beaker/flask, sitrring plate, heating mantle, centrifuge,	beaker/flask, centrifuge,
	Mass of products	~0.015 g	~0.025 g	1.4 g

Notes and References

8) Lu, Y.; McLellan, J.; Xia, Y., *Langmuir* **2004**, *20*, 3464.

9) Zhang, Q.; Zhang, T.; Ge, J.; Yin, Y., *Nano Lett.* **2008**, *8*, 2867.

*This work.

Estimated based on materials consumed without the inclusion of energy cost (see details below)

Estimation of Materials Cost

Price of the Materials:

500 mL of TEOS ($5), 100 g of PVP ($10), 500 mL of ammonia ($2), 500 g of NaOH ($7), 500 mL of ethanol ($1.5), 500 mL of 2-propanol ($13) and 500 g of sodium citrate ($5) from Sinopharm Chemical Reagent Co., Ltd.

0.1 g of Polystyrene beads ($200) from Nano-Micro Tech. Ltd.

1. Hard-templating method

In one batch synthesis, 0.013 g of Polystyrene beads, 20 mL of 2-propanol, 0.5 mL of ammonia, 54 μL of TEOS were used for preparing 14.7 mg of hollow silica spheres. (0.013*200/0.1+20*13/500+0.5*2/500+0.054*5/500)/0.0147 = 1804.

The materials cost by hard-templating method is about $1804 per gram products.

2. Self-templating method

In one batch synthesis, 1 mL of TEOS, 1 mL of ammonia, 20 mL of 2-propanol, 5 g of PVP and 0.1 g of NaOH were used for preparing 25 mg of hollow silica.

(1*5/500+1*2/500+20*13/500+5*10/100+0.1*5/500)/0.025 = 41.4

The materials cost by self-templated method is about $41.4 per gram products.

3. Salt-templated method

In one batch synthesis, 5 mL of TEOS, 1 L of ethanol, 12 mL of ammonia and 0.88 g of sodium citrate were used for preparing 1.4 g of hollow silica for one time.

(5*5/500+1000*1.5/500+12*2/500+0.88*5/500)/1.4 = 2.2

The cost of per gram hollow silica by salt-templated method is about $2.2.

In practice, the ethanol and sodium citrate could be reused, which would further reduce the materials cost.