Supplementary Information

Facile, general and template-free construction of monodisperse

yolk-shell metal@carbon nanospheres

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Section A. Experimental Sections

Reagents. Pyrrole (Aladdin, purity 99%) and aniline (Guangzhou Chemical Reagent Factory, A.R.) were purified by reduced pressure distillation before use. Triton X-100 (Pharmacia, scientific research level), ammonium peroxydisulfate (APS; Guangzhou Chemical Reagent Factory, A.R.), gold chloride hydrate (Aladdin, 98%), chloroplatinic acid hexahydrate (Macklin, A.R.), L-ascorbic acid (Macklin, A.R.), trisodium citrate (Tianjin Fuchen Chemical Reagent Factory, A.R.), nitrobenzene (Guangzhou Chemical Reagent Factory, A.R.), nitrobenzene (Guangzhou Chemical Reagent Factory, A.R.), and ethanol (Guangzhou Chemical Reagent Factory, A.R.) were used as received.

Synthesis of Au nanoparticle. Briefly, 0.0216 g of HAuCl₄ was added to 237.5 mL of deionized water and then the mixture solution was vigorously stirred under reflux. After that, 0.125 g of sodium citrate dissolved in 12.5 ml of deionized water was added immediately, followed by refluxing for 30 min and cooling down to room temperature. The resulting dispersion was centrifuged (11800 rpm, 30 min) and the supernatant was removed to the designated volume (30-40 ml) by one time.

Synthesis of yolk-shell YS-Au@CNs. The above concentrated Au colloid was used immediately, and 6 ml of Triton X-100 aqueous solution (0.01 g ml⁻¹) and deionized water were added to allow the total volume reaching 60 ml. Subsequently, 0.37 ml (0.09 M) of pyrrole and 0.49 ml (0.09 M) of aniline were added, followed by stirring for 30 min and ultrasonication for another 30 min at room temperature. The mixture was placed at 0 °C for 30 min, and then a precooled aqueous solution of APS (the amount is equal to the total molar of pyrrole and aniline) in 5 ml H₂O was added rapidly and stirred for 30 s vigorously. Then the polymerization was carried out at 0 °C under static condition for 12 h. The product was collected by filtration, washed with water for several times, and then dried, leading to the formation of Au@PACP. YS-Au@CNs were obtained by heating the Au@PACP to designated temperatures (400-950 °C) for 3 hours at a heating rate 2 °C min⁻¹ in a furnace under a N₂ flow. The resulting YS-Au@CNs were denoted as YS-Au@CN-*x*, where the *x* indicates the applied carbonization temperatures. For controlling the diameters of hollow spheres, different amounts of pyrrole and aniline

were used. For instance, 0.07 M aniline and 0.07 M pyrrole (0.38 ml and 0.29 ml, respectively), and 0.05 M aniline and 0.05 M pyrrole (0.27 ml and 0.21 ml, respectively), were used.

Synthesis of CNs-950. 6 ml of Triton X-100 aqueous solution (0.01 g ml⁻¹) and deionized water were added to reach the total volume of 60 ml. Subsequently, 0.37 ml (0.09 M) of pyrrole and 0.49 ml (0.09 M) of aniline were added, followed by stirring for 30 min and ultrasonication for another 30 min at room temperature. The mixture was placed at 0 °C for 30 min, and then a precooled aqueous solution of APS (the amount is equal to the total molar of pyrrole and aniline) in 5 ml H₂O was added rapidly and stirred for 30 s vigorously. Then the polymerization was carried out at 0 °C under static condition for 12 h. The product was collected by filtration, washed with water for several times, and then dried, leading to the formation of PACP. CN-950 were obtained by heating the PACP to 950 °C for 3 h at a heating rate 2 °C min⁻¹ in a furnace under a N₂ flow. "

Synthesis of bimetallic Au/Pt Nanoparticles. First, the Au dispersion was prepared according to the above mentioned strategy by scaling up two times. After cooling down to room temperature, H₂PtCl₆·6H₂O (0.1292 g) was added under continuously stirring in nitrogen atmosphere, and the reaction was heated to 80 °C after dissolution. Then L-ascorbic acid (0.0942 g) was added into the mixture and the reaction was stirred for 0.5 h, followed by cooling down and concentrating to about 30 mL by one-time centrifugation (10000 rpm, 20 min) for the following use.

Synthesis of bimetallic Au/Ag Nanoparticles. First, the Au dispersion was prepared according to the above mentioned strategy. After cooling down to room temperature, hydroquinone (0.0104 g) was added under continuously stirring in dark place for 5 minutes. Then 1 mL silver nitrate solution (0.0108 gml⁻¹) was added into the mixture and the reaction was stirred for 0.5 h, followed by concentrating to about 30 mL by one-time centrifugation (8000 rpm, 30 min) for the following use.

Synthesis of YS-Au/Pt@CNs. The synthesis step is the same to that of YS-Au/Pt@CNs, except that 0.0084 g polyvinylpyrrolidone (PVP) was added to the mixture of Au/Pt nanoparticle with designated volum (*i.e.*, 54 ml) and stirred for 12 h before adding monomers and Triton X-100 for polymerization.

Synthesis of bimetallic YS-Au/Ag@CNs. The synthesis step is the same to that of YS-Au@CNs, except that the carbonization conditions are different. The YS-Au/Ag@CNs were obtained by heating the Au/Ag@PACP to 500 °C for 3 hours at a heating rate 5 °C min⁻¹ in a furnace under a N₂ flow.

Control experiments.

a. For centrifugation effect of Au nanoparticles on the formation of yolk-shell structure, 250 ml of Au dispersion after reduction was purified by 3 times' centrifugation (11800 rpm, 30 min), and the other conditions were kept the same. Specifically, after first centrifugation, the colloid was concentrated to about 30-40 ml by removing the supernatant, followed by adjusting to 100 ml by adding water for second round centrifugation. The colloid was concentrated to about 25 ml after second centrifugation, followed by adjusting to 50 ml by adding water for third round centrifugation. The colloid was concentrated to about 30-40 ml after second centrifugation. The supernatated to about 30-40 ml after the third centrifugation.

b. For the aggregation effect caused by keeping the Au nanoparticles for a certain time prior to polymerization, preparation conditions were the same except that before polymerization, the concentrated Au nanoparticles was kept for 5 days.

c. For the polymerization temperature effect on the formation of yolk-shell structure, preparation conditions were all same except that the polymerization was carried out at 30 °C.

Material characterizations. The nanostructures of the samples were investigated by a Hitachi S-4800 scanning electron microscope (SEM), and FEI Tecnai G2 Spirit transmission electron microscope (TEM). About 100 nanoparticles in a SEM image were picked at random, and then a statistical analysis of particle size distribution was carried

out. N2 adsorption measurement was carried out using a Micromeritics ASAP 2020 The BET surface area (SBET) was determined by analyzer at 77 K. Brunauer-Emmett-Teller (BET) theory. The total pore volume (Vt) was estimated from the amount adsorbed at a relative pressure P/P_0 of ca. 0.99. The pore size distribution was analyzed by original density functional theory (DFT) combined with non-negative regularization and medium smoothing. Dynamic light scattering (DLS) measurements were carried out at 25 °C on a Brookheaven Zeta PALS Instrument with a 532 nm laser at a scattering angle of 90 °. The Au content in the yolk-shell nanocomposite was monitored using a thermogravimetric analysis (Netzsch Company, TG-209 F3) under oxygen flow with a heating rate of 10 °C min⁻¹. Raman spectrum was conducted on a Renishaw inVia Laser Micro-Raman Spectrometer. X-Ray diffraction (XRD) patterns were recorded on a D-MAX 2200 VPC diffractometer using Cu Ka radiation (40 kV, 26 mA). X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250 Spectrometer. Binding energies were calibrated by using containment carbon ($C_{1s} = 284.8$ eV). UV-vis spectra were recorded by using a Shimadzu UV-3150 UV-vis-NIR Spectrophotometer.

Adsorption properties of ethanethiol. Adsorption of ethanethiol on YS-Au@CN-950 were obtained by measuring their concentrations at various times by gas chromatography-mass spectrometer (GC-MS, 6890-5975 B) equipped with a HP-5-MS capillary column (30 m*0.32 mm i.d.*0.25 µm film thickness) from Agilent (Palo Alto, CA, USA). Specifically, 20 mg of YS-Au@CN-950 or CN-950 was added into a conical flask, and then 50 ml of ethanethiol solution in n-hexane (1000 ppm) was added quickly. After that, the suspension was shaken with a rate of 170 rpm at 25 °C. At intervals, about 0.1 mL of supernate was taken out for the GC-MS measurement. The carrier was helium, and its flow rate was 1.2 ml min⁻¹. The concentration was calculated using the standard curve produced with the gradient dilution method. The adsorption amount is calculated according to the equation $C = (c_0V_0-c_1V_1)/m$, where c_0 , V_0 , c_1 , V_1 and m represent the initial concentration, initial volume, concentration, volume after adsorption and the mass of adsorbent (e.g., YS-Au@CN-950 and CN-950).

Catalytic reduction of nitrobenzene and 4-nitrophenol. The catalytic reduction of nitrobenzene and 4-nitrophenol was studied with a UV-Vis-NIR spectrophotometer. YS-Au@CN-950 (1 mg ml⁻¹) was homogeneously dispersed in H₂O by ultrasonication. Then 0.3 ml of the above suspension was added to a mixture containing sodium borohydride solution (2 mL, 10 mM) and 4-nitrophenol (1 ml, 0.11 mM) solution, or a mixture containing sodium borohydride solution (1 ml, 10 mM) and nitrobenzene solution (2 ml, 0.11 mM). After that, the reaction progress was monitored by measuring UV-vis absorption spectra of the mixture.

Section B. Supplementary Figures



Figure S1. Large-scale SEM images of (a) yolk-shell Au@PACP and (b) YS-Au@CN-950. Note that SEM images were sputter-coated with Au prior to the observations.



Figure S2. High resolution TEM image of the Au nanoparticle yolk and porous carbon shell in YS-Au@CN-950.



Figure S3. SEM and TEM images of YS-Au@CNs obtained at different carbonization temperatures: (a, b) YS-Au@CN-400, (c, d) YS-Au@CN-600, and (e, f), YS-Au@CN-800. Note that SEM images were sputter-coated with Au prior to the observations.



Figure S4. XPS spectra of YS-Au@CN-8000 and YS-Au@CN-950.



Figure S5. Raman spectra of YS-Au@CN-800 and YS-Au@CN-950.



Figure S6. XRD patterns of YS-Au@CN-800, YS-Au@CN-600 and YS-Au@CN-400.



Figure S7. Thermogravimetric analysis curves of YS-Au@CN-400, YS-Au@CN-600, YS-Au@CN-800, and YS-Au@CN-950.



Figure S8. Dynamic light scattering (DLS) curve of Au nanoparticles in Triton X-100 aqueous solution.



Figure S9. SEM image of Au@PACP composite prepared under the sample conditions, except that the Au colloid after centrifugation was left for 5 days prior to polymerization. Note that photos were taken directly without Au sputtering, so as to well identify the aggregated Au in our sample.



Figure S10. SEM images of Au@PACP composite with different magnifications prepared under the sample conditions, except that the polymerization temperature was 30 °C. Note that photos were taken directly without Au sputtering, so as to well identify the aggregated Au in our sample.



Figure S11. (a) SEM and (b) TEM images of yolk-shell Au@crosslinked polystyrene, and (c) SEM and (d) TEM images of yolk-shell Au@carbon that carbonized at 950 °C. Yolk-shell Au@crosslinked polystyrene was prepared by a procedure of selective etching of core-shell-shell nanostructures.^[1] Briefly, spherical Au nanopartilces were coated with SiO₂ interlayer template and then polystyrene-based polymers, followed by crosslinking to form shell carbon precursor, and the subsequent selective removal of the silica interlayer to yield yolk-shell Au@crosslinked polystyrene. The carbonization process is the same to that of YS-Au@CN-950.



YS-Au@CN-800 obtained by using pyrrole and aniline monomer concentrations of (a) 0.05M, (b) 0.07M, and (c) 0.09M.



Figure S13. The out and inner diameters of Au@PACP and YS-Au@CNs.



Figure S14. (a) N₂ adsorption-desorption isotherms of YS-Au@CN-800, YS-Au@CN-600 and Au@CN-400; YS-Au@CN-800 and YS-Au@CN-600 were offset vertically by 50 and 30 cm³ g⁻¹ STP, respectively. (b) DFT pore size distributions of YS-Au@CN-800, YS-Au@CN-800 and YS-Au@CN-400.



Figure S15. (a) SEM and (b) TEM images of Au/Ag@PACP; (d) SEM and (e) TEM images of Au/Pt@PACP; particle size distribution histograms from analysis of SEM images for (c) Au/Ag@PACP and (f) Au/Pt@PACP.



Figure S16. SEM images of PACP polymer obtained with adding various PVP amounts: (a) 0.0084 g, (b) 0.0420 g and (c) 0.0840 g.



Figure S17. (a) SEM and (b) TEM images of YS-Au/Ag@CN-500; (d) SEM and (e) TEM images of YS-Au/Pt@CN-950; particle size distribution histograms from analysis of SEM images for (c) YS-Au/Ag@CN-500 and (f) YS-Au/Pt@CN-950.



Figure S18. N_2 adsorption-desorption isotherms of YS-Au/Pt@CN-950 (red) and YS-Au/Ag@CN-500 (black).



Figure S19. XRD patterns of YS-Au/Pt@CN-950 and YS-Au/Ag@CN-500.



Figure S20. N₂ adsorption-desorption isotherm of CN-950.



Figure S21. Plots of $\ln(C_t/C_0)$ versus time for the catalytic reduction of (a) nitrobenzene and (b) 4-nitrophenol for YS-Au@CN-950, YS-Au@CN-800 and YS-Au@CN-400.

Section C. Supplementary Tables

Table S1. Parameters determined by Raman spectra of YS-Au@CN-800 and YS-Au@CN-950.

Sampla	Peak center (cm ⁻¹)			_	Peak area (%)			I (nm)
Sample	D	А	G		D	А	G	$-L_a(IIII)$
YS-Au@CN-800	1343	1527	1590		72.3	12.6	15.1	0.91
YS-Au@CN-950	1333	1528	1587		69.6	9.92	20.4	1.28

Table S2. BET surface areas of reported yolk-shell nanomaterials with different yolk and shell species.

Sample	SBET	Ref.
YS-Au@CN-950	1145	This work
Yolk-shell CuO@carbon	86	[2]
Yolk-shell carbon@TiO ₂	234	[3]
Yolk-shell silicon@mesoporous carbon	582	[4]
Yolk-shell ZnO@carbon microspheres	98	[5]
Yolk-shell Fe ₃ O ₄ @carbon	139	[6]
Yolk-shell Au@mHCS	202	[7]
Yolk-shell CaCO ₃ @carbon	381	[8]
Yolk-shell Au@polyethyleneimine-derived carbon	148	[9]
Yolk-shell Ag@C@SnO2@TiO2	116	[10]
Yolk-shell Co/N-PCMs	374	[11]

Table S3. Pore structure parameters of Au@PACP and YS-Au@CNs.

Sample	S _{BET} (m ² g ⁻¹)	S _{Langmuir} (m ² g ⁻¹)	$\frac{S_{mic}}{(m^2 g^{-1})}$	V _{mic} (cm ³ g ⁻¹)	V _{total} (cm ³ g ⁻¹)
Au@PACP	43	64	-	-	0.13
YS-Au@CN-400	320	431	203	0.09	0.25
YS-Au@CN-600	401	538	301	0.14	0.36
YS-Au@CN-800	521	696	424	0.20	0.50
YS-Au@CN-950	1145	1534	891	0.42	0.77
YS-Au@CN -0.07M-800	477	637	373	0.17	0.42
YS-Au@CN -0.05M-800	504	674	396	0.19	0.50
YS-Au/Pt@CN-950	844	1058	637	0.27	0.81

Samula —	Rate constant (min ⁻¹)			
Sample	Nitrobenzene	4-Nitrophenol		
YS-Au@CN-400	7.20×10 ⁻³	5.16×10 ⁻³		
YS-Au@CN-800	2.34×10 ⁻²	1.98×10 ⁻²		
YS-Au@CN-950	5.82×10 ⁻²	4.08×10 ⁻²		

Table S4. Rate constants of catalytic reduction of nitrobenzene and 4-nitrophenol using YS-Au@CNs.

Section D. Supplementary References

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