

Supporting Information

## **A Versatile Cooperative Template-Directed Coating Method to Construct Uniform Microporous Carbon Shell for Multifunctional Core-shell Nanocomposites**

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### **Experimental Details**

#### **Materials**

Tetraethyl orthosilicate (TEOS, 99 %), resorcinol, formalin solution (37 wt. %), ammonia (28 wt. %), HF (40 wt%),  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$  (99.999 %),  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$  (99.999 %),  $\text{TmCl}_3 \cdot 6\text{H}_2\text{O}$  (99.999 %), NaOH (98 %),  $\text{NH}_4\text{F}$  (98 %), anhydrous  $\text{FeCl}_3$  (99.7 %), trisodium citrate (99.0 %),  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (99.7 %), sodium acetate (99.0 %), ethylene glycol (99.5 %) and ethanol (99.7 %) were purchased from Shanghai Chemical Corp. 1-Octadecene (ODE, 90%), oleic acid (OA, 90%) and polyvinylpyrrolidone (PVP, K-30) were supplied by Alfa Aesar. Polyethylenimine (PEI,  $M_w = 750,000 \text{ g mol}^{-1}$ ) was purchased from Sigma-Aldrich. Cetyltrimethylammonium bromide ( $\text{C}_{16}\text{TMA}^+ \cdot \text{Br}^-$ , 99.0 %) was obtained from Huishi Biochemical Reagent Company of China. All chemicals were used as received without any further purification.

#### **Synthesis of Au Nanoparticles.**

Briefly, 70.8 mL of water was vigorously stirred under reflux and 8.3 mL of  $2.54 \times 10^{-3} \text{ M}$   $\text{HAuCl}_4$  solution was added. The resultant solution was stirred until boiling point was reached again. Then, 4.16 mL of  $10 \text{ mg mL}^{-1}$  sodium citrate solution was added and the system was refluxed for 30 min. Finally, the resultant colloid was

cooled to room temperature. Then, the solution was centrifuged (15,000 rpm; 20 min) and the supernatant was removed. The volume of the concentrated colloid was then adjusted to 2 mL by dilution with water.

### **Synthesis of Au@RF and Au@C nanocomposites.**

For polymer coating, 2 mL of as-obtained gold nanoparticles in water was poured into 5.04 mL of 125 mM aqueous  $C_{16}TMA^+Br^-$  solution and the resulting solution was stirred vigorously for 30 min. The resulting solution was added to a mixture of 0.175 g of resorcinol, 14.1 mL of ethanol and 0.175 mL of ammonia, and the mixture was heated up to 35 °C under stirring. Then, 0.25 mL of formalin solutions was added to the reaction solution. The mixture was cooled to room temperature after 6 h, and then aged at room temperature overnight without stirring. Au@RF was collected by centrifugation, then washed with water and ethanol several times. The obtained Au@RF was heated at 5 °C min<sup>-1</sup> from room temperature to 150 °C and kept at this temperature for 1 h under a nitrogen flow. The temperature was then raised at 5 °C min<sup>-1</sup> to 600 °C or 800 °C and kept at this temperature for 2 h. Au@C was obtained after the product was cooled to room temperature.

### **Preparation of the nitric acid treated Au@C yolk-shell nanocomposites.**

0.05g of as-synthesized Au@C yolk-shell nanocomposites were suspended in 30 mL of concentrated nitric acid. The solution was stirred at 90°C for 10 h. The nitric acid treated Au@C was obtained after the product was cooled to room temperature.

### **Synthesis of Fe<sub>3</sub>O<sub>4</sub> Particles.**

The water dispersible Fe<sub>3</sub>O<sub>4</sub> particles were synthesized according to the method reported by Zhao and his coworkers.<sup>1</sup> Briefly, FeCl<sub>3</sub> (2.6 g, 16 mmol), trisodium citrate (1.0 g, 3.4 mmol), and sodium acetate (4.0 g, 48.8 mmol) were dissolved in ethylene glycol (80 mL) with magnetic stirring. The obtained yellow solution was then transferred and sealed into a Teflon-lined stainless-steel autoclave (200 mL in capacity). The autoclave was heated at 200 °C for 10 h, and then allowed to cool to room temperature. The black products were washed with ethanol and deionized water 3 times, respectively, lastly dried in the air.

### **Synthesis of Fe<sub>3</sub>O<sub>4</sub>@RF and Fe<sub>3</sub>O<sub>4</sub>@C nanocomposites.**

For polymer coating, 0.08 g of as-obtained Fe<sub>3</sub>O<sub>4</sub> particles was homogeneously dispersed in deionized water (30.4 mL) by ultrasonication, followed by the addition of 0.92 g of C<sub>16</sub>TMA<sup>+</sup>Br<sup>-</sup>, 0.175 g of resorcinol, 14.1 mL of ethanol and 0.175 mL of ammonia, and stirring at 35 °C for 30 min to form a uniform dispersion. Then, 0.25 mL of formalin solutions was added to the dispersion under stirring. The mixture was cooled to room temperature after 6 h, and then aged at room temperature overnight without stirring. Fe<sub>3</sub>O<sub>4</sub>@RF was collected by centrifugation, then washed with water and ethanol several times. The obtained Fe<sub>3</sub>O<sub>4</sub>@RF was heated at 5 °C min<sup>-1</sup> from room temperature to 150 °C and kept at this temperature for 1 h under a nitrogen flow. The temperature was then raised at 5 °C min<sup>-1</sup> to 600 °C or 800 °C and kept at this

temperature for 2 h. Fe<sub>3</sub>O<sub>4</sub>@C was obtained after the product was cooled to room temperature.

### **Preparation of Mesoporous Silica Nanoparticles (MSNs).**

Briefly, 6.4 mL of water, 0.9 g of ethanol, 1.04 g of a 25 wt % CTAC solution, and 0.02 g of DEA were mixed and stirred in a water bath at 40 °C for 30min. Then 0.73ml of TEOS (3.25 mmol) was added into the mixture dropwise within 2 min under stirring. The solution turned white gradually. A further 2 h of stirring was necessary. The mixture was cooled to room temperature and then aged overnight without stirring. The products were washed with ethanol and deionized water 3 times, respectively, lastly dried in the air.

### **Synthesis of MSN@RF and MSN@C nanocomposites.**

For polymer coating, 0.08 g of as-obtained MSNs was homogeneously dispersed in deionized water (7.04 mL) by ultrasonication, followed by the addition of 0.23 g of CTAB, 0.035 g of resorcinol, 2.82 mL of ethanol and 0.01 mL of ammonia, and stirring at 35 °C for 30 min to form a uniform dispersion. Then, 0.05 mL of formalin solutions was added to the dispersion under stirring. The mixture was cooled to room temperature after 6 h, and then aged at room temperature overnight without stirring. MSN@RF was collected by centrifugation, and then washed with water and ethanol several times. The obtained MSN@RF was heated at 5 °C min<sup>-1</sup> from room temperature to 150 °C and kept at this temperature for 1 h under a nitrogen flow. The

temperature was then raised at  $5\text{ }^{\circ}\text{C min}^{-1}$  to  $600\text{ }^{\circ}\text{C}$  or  $800\text{ }^{\circ}\text{C}$  and kept at this temperature for 2 h. MSN@C was obtained after the product was cooled to room temperature.

### **Synthesis of hexagonal phase NaYF<sub>4</sub> nanocrystals**

The OA coated NaYF<sub>4</sub> nanocrystals were synthesized according to the method reported by Qin and his coworkers.<sup>2</sup>

### **Synthesis of NaYF<sub>4</sub>@RF and NaYF<sub>4</sub>@C nanocomposites.**

For polymer coating, 0.02 g of as-obtained NaYF<sub>4</sub> particles dispersed in chloroform (1 mL) by ultrasonication was poured into 7.04 mL of 90 mM C<sub>16</sub>TMA<sup>+</sup>Br<sup>-</sup> solution and the resulting solution was stirred vigorously for 30 min. The formation of an oil-in-water microemulsion resulted in a turbid solution. Then, the mixture was heated up to  $60\text{ }^{\circ}\text{C}$  and aged at that temperature for 10 min under stirring to evaporate the chloroform. The resulting solution was added to a mixture of 0.175 g of resorcinol, 14.1 mL of ethanol and 0.175 mL of ammonia, and the mixture was cooled down to  $35\text{ }^{\circ}\text{C}$  under stirring. Then, 0.25 mL of formalin solution was added to the reaction solution. The mixture was cooled to room temperature after 6 h, and then aged at room temperature overnight without stirring. NaYF<sub>4</sub>@RF was collected by centrifugation, then washed with water and ethanol several times. The obtained NaYF<sub>4</sub>@RF was heated at  $5\text{ }^{\circ}\text{C min}^{-1}$  from room temperature to  $150\text{ }^{\circ}\text{C}$  and kept at this temperature for 1 h under a nitrogen flow. The temperature was then raised at

5 °C min<sup>-1</sup> to 600 °C or 800 °C and kept at this temperature for 2 h. NaYF<sub>4</sub>@C was obtained after the product was cooled to room temperature.

### **Synthesis of PEI-coated SiO<sub>2</sub> spheres**

Briefly, 0.08 g of SiO<sub>2</sub> spheres obtained from stöber method was homogeneously dispersed in deionized water (20 mL) by ultrasonication, followed by the addition of 0.1 g of PEI, and stirring at 35 °C for 30 min to form a uniform dispersion. The resultant dispersion was stirred for 24 h to allow complete adsorption of the polymer on the SiO<sub>2</sub> spheres surface. After this time, the solution was centrifuged (10,000 rpm; 10 min) to remove the unadsorbed polymers. The PEI-coated products were redispersed in 7.04 mL of water.

### **Synthesis of PEI-coated SiO<sub>2</sub>@RF and SiO<sub>2</sub>@C nanocomposites.**

For polymer coating, 7.04 mL of as-obtained SiO<sub>2</sub> spheres in water was poured into a mixture of 0.23 g of C<sub>16</sub>TMABr, 0.035 g of resorcinol, 2.82 mL of ethanol and 0.01 mL of ammonia, and the mixture was heated up to 35 °C under stirring to form a clear homogeneous dispersion. Then, 0.05 mL of formalin solutions was added to the dispersion. The mixture was cooled to room temperature after 6 h, and then aged at room temperature overnight without stirring. PEI-coated SiO<sub>2</sub>@RF was collected by centrifugation, then washed with water and ethanol several times. The obtained PEI-coated SiO<sub>2</sub>@RF was heated at 5 °C min<sup>-1</sup> from room temperature to 150 °C and kept at this temperature for 1 h under a nitrogen flow. The temperature was then

raised at  $5\text{ }^{\circ}\text{C min}^{-1}$  to  $600\text{ }^{\circ}\text{C}$  or  $800\text{ }^{\circ}\text{C}$  and kept at this temperature for 2 h.  $\text{SiO}_2@\text{C}$  was obtained after the product was cooled to room temperature.

### **Synthesis of Au@SiO<sub>2</sub> nanocomposites.**

Briefly, 212.5 mL of water was vigorously stirred under reflux and 25 mL of  $2.54 \times 10^{-3}$  M  $\text{HAuCl}_4$  solution was added. The resultant solution was stirred until boiling point was reached again. Then, 12.5 mL of  $10\text{ mg mL}^{-1}$  sodium citrate solution was added and the system was refluxed for 30 min. Finally, the resultant colloid was cooled to room temperature. Next, a solution of  $0.325\text{ mL}$  of  $12.8\text{ mg mL}^{-1}$  polyvinylpyrrolidone (pvp), which was freshly prepared by dissolution in water with ultrasonication (30 min), was added to a previously prepared, cold, colloidal gold solution (240 mL). The resultant mixture was stirred for 24 h to allow complete adsorption of the polymer on the gold surface. After this time, the solution was centrifuged (15,000 rpm; 20 min) and the supernatant was removed. The volume of the concentrated colloid was then adjusted to 6 mL by dilution with water. The colloid was vigorously stirred for 5 min, followed by addition of 18.90 mL of ethanol premixed with 0.84 mL of ammonia. Immediately afterwards, a solution of tetraethylorthosilicate (1.19 mL) in ethanol (12.80 mL) was added. The reaction mixture was then stirred for an additional 12 h at room temperature. The resultant colloid was centrifuged (10,000 rpm; 30 min), with ethanol and deionized water 3 times, respectively, and lastly dried in the air.

### **Catalytic reductions of nitrobenzene and 4-nitrophenol by nitric acid treated Au@C yolk-shell nanocomposites.**

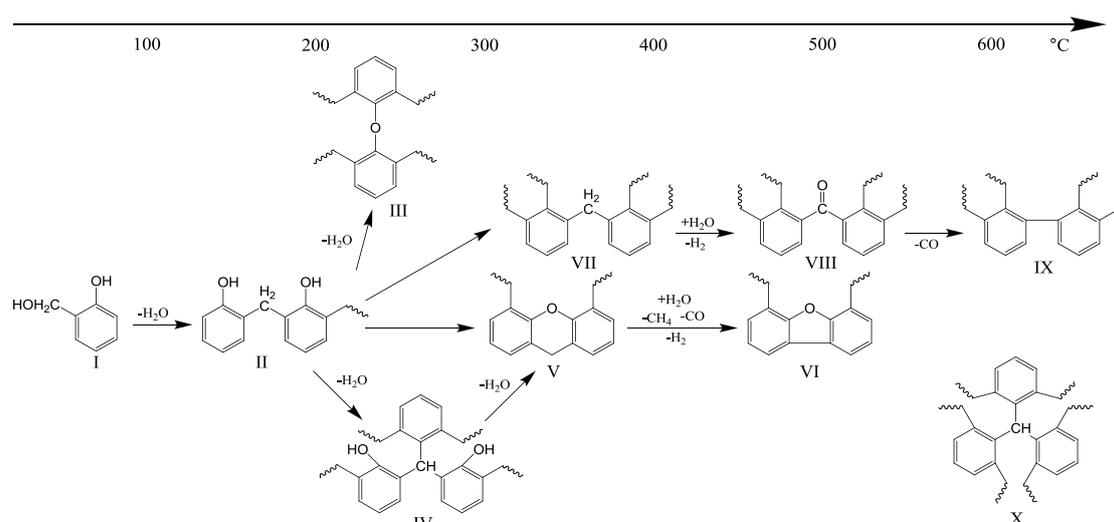
Sodium borohydride solution (0.3 mL, 0.1mM) was added to a 4-nitrophenol or nitrobenzene solution (2.7 mL, 0.11 mM) contained in a glass vessel. The solution was purged with N<sub>2</sub> to remove oxygen from the system. Thereafter, 1 mg of the nitric acid treated yolk-shell Au@C particles was added. Immediately after addition of composite particles, UV/Vis spectra of the sample were taken in the range of 250-550 nm for 4-nitrophenol and 200-400 nm for nitrobenzene.

### **Catalytic reductions of nitrobenzene and 4-nitrophenol by Au nanoparticles.**

Sodium borohydride solution (0.3 mL, 0.1mM) was added to a 4-nitrophenol or nitrobenzene solution (2.7 mL, 0.11 mM) contained in a glass vessel. The solution was purged with N<sub>2</sub> to remove oxygen from the system. Thereafter, 0.1 ml of the Au nanoparticles was added. Immediately after addition of composite particles, UV/Vis spectra of the sample were taken in the range of 250-550 nm for 4-nitrophenol and 200-400 nm for nitrobenzene.

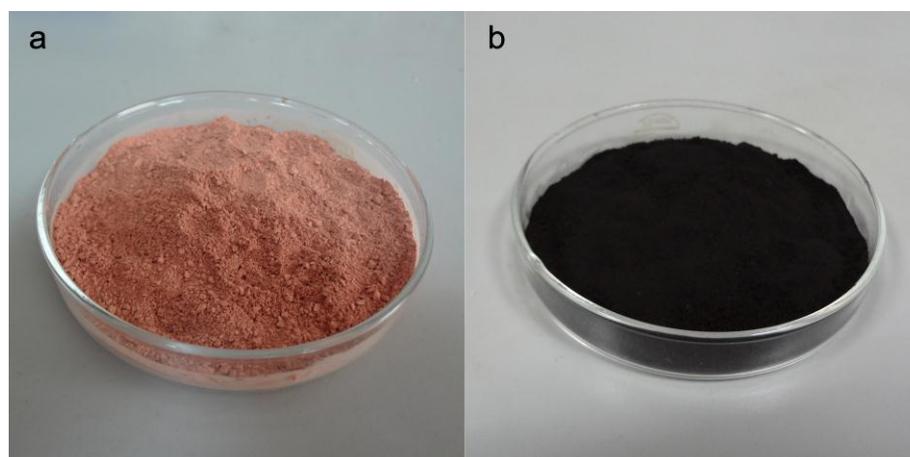
### **References**

1. J. Liu, Z. Sun, Y. Deng, Y. Zou, C. Li, X. Guo, L. Xiong, Y. Gao, F. Li and D. Zhao, *Angewandte Chemie International Edition*, 2009, **48**, 5875-5879.
2. F. Shi, J. Wang, D. Zhang, G. Qin and W. Qin, *Journal of Materials Chemistry*, **21**, 13413-13421.
3. E. Fitzer and W. Schäfer, *Carbon*, 1970, **8**, 353-364.

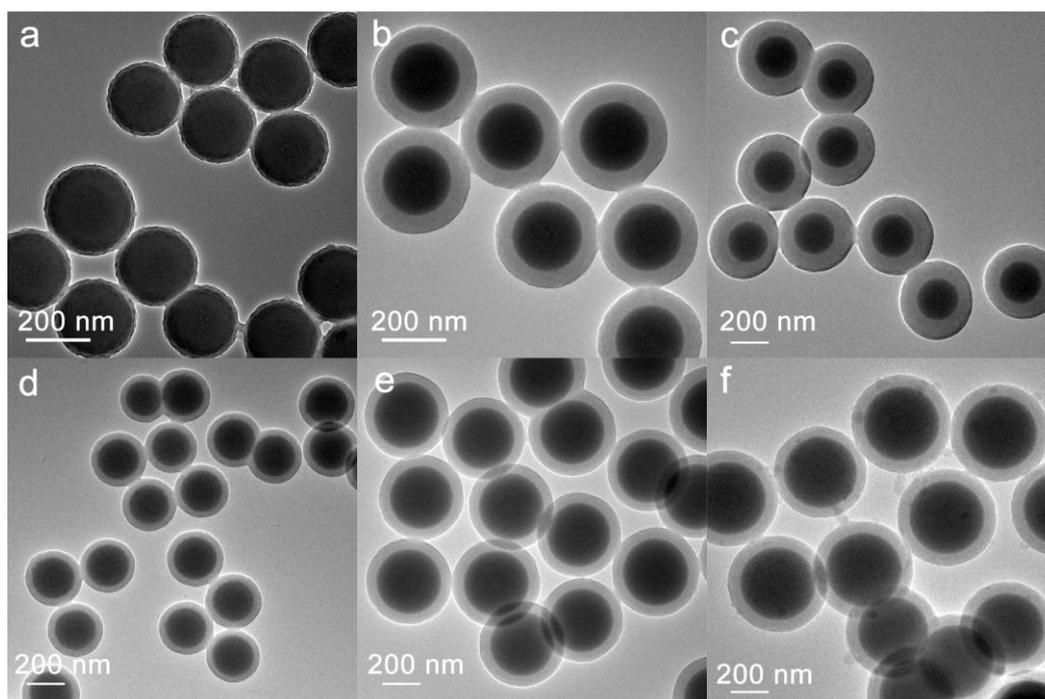


**Figure S1.** Pyrolysis chemistry of phenol-formaldehyde polymer.

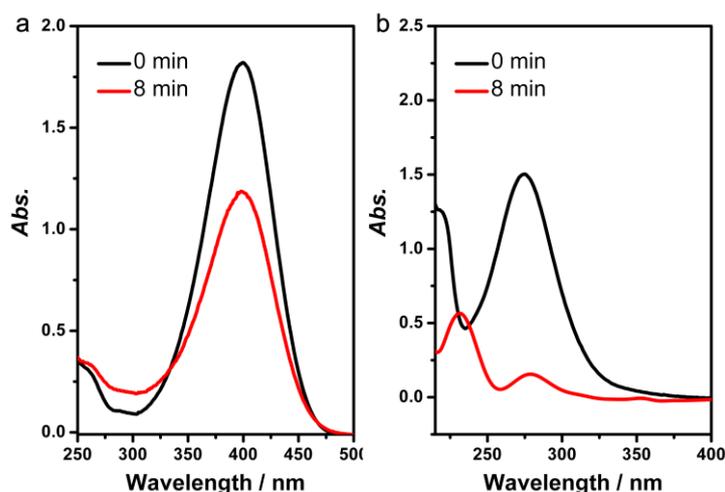
Figure S1 illustrates the pyrolysis mechanism of the phenol-formaldehyde polymer.<sup>3</sup> During the hardening, methylene bridges are formed by condensation and release of water (I and II). The first step of the pyrolysis is assumed to be the formation of ether bonds by a reaction of 2 phenolic groups (III) and again a release of water. In addition to this reaction, a condensation of a phenolic group with a methylene bridge takes place to yield a diphenyl methane structure (IV). The cyclic ether diphenyl pyrene (V), identified above 400 °C, can be explained by a chemical condensation of 2 phenolic groups accompanied by cyclization. Glasslike carbon is formed by deep pyrolysis of highly crosslinked phenol-formaldehyde polymer.



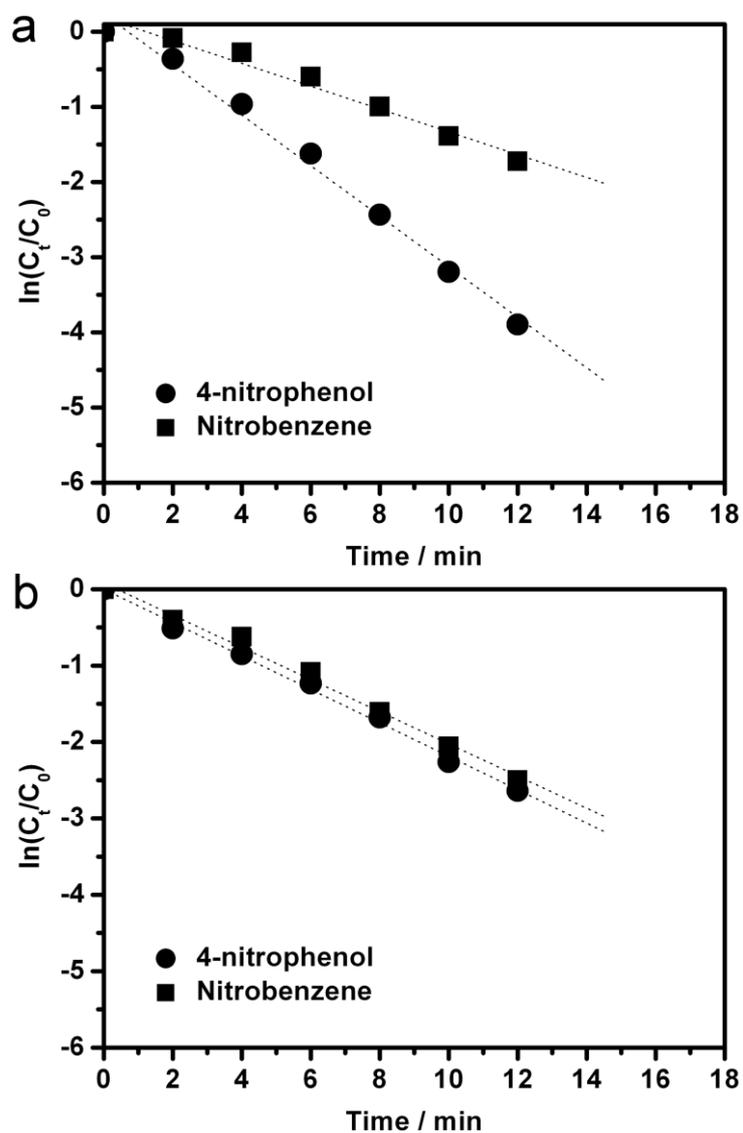
**Figure S2.** Photo of powder of SiO<sub>2</sub>@RFs and SiO<sub>2</sub>@Cs. Both SiO<sub>2</sub>@RF and SiO<sub>2</sub>@C nanocomposites were synthesized in one pot and placed in 8 cm dishes.



**Figure S3.** Characterization results of the series of SiO<sub>2</sub>@RF composites with tunable sizes. TEM images (a-c) show SiO<sub>2</sub>@RFs with identical core sizes of ca. 210 nm but varied shell thicknesses: a) 10 nm, b) 50 and c) 100 nm. TEM images (d-f) of SiO<sub>2</sub>@RFs with average diameters of d) 290 nm, e) 450 nm, and f) 530 nm; with average core sizes of 230 nm, 335 nm, and 430 nm.



**Figure S4.** UV-vis absorption spectra of (a) 4-nitrophenol and (b) nitrobenzene reduced by sodium borohydride using Au@C yolk-shell particles as catalyst.



**Figure S5.** Kinetic analysis of the catalytic reductions. Plot of  $\ln(C_t/C_0)$  versus time for nitrobenzene and 4-nitrophenol using a) nitric acid treated Au@Cs and b) Au nanoparticles as catalysts.