Supporting Information

## A cationic surfactant assisted selective etching strategy to hollow mesoporous silica spheres

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## **Experimental section**

**Chemicals.** Tetraethyl orthosilicate (TEOS) was purchased from Alfa Aesar. Polyvinylpyrrolidone (PVP10) was purchased from Alfa Aesar from Aldrich. Ammonia solution (25-28%), cetyltrimethyl ammonium bromide (CTAB), ethanol, isopropanol, ferric chloride (FeCl<sub>3</sub>·6H<sub>2</sub>O), sodium phosphate monobasic anhydrous (NaH<sub>2</sub>PO<sub>4</sub>), hydrogen tetrachloroaurate (III) trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O), sodium citrate tribasic dehydrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·3H<sub>2</sub>O), and sodium carbonate were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). All the reagents were used without further purification. Deionized water was used in all experiments.

**Synthesis of** *s***SiO**<sub>2</sub> **with particle sizes of 470 nm and 130 nm.** *s*SiO<sub>2</sub> with particle sizes of 470 nm were synthesized as follows. 4.2 mL of TEOS were rapidly added into a mixture of ethanol (45 mL), deionized water (1.85 mL), and ammonium aqueous solution (25-28%, 49 mL). The mixture was then

stirred at room temperature for 6 h, resulting in the formation of a white silica colloidal suspension. *s*SiO<sub>2</sub> with particle sizes of 130 nm were synthesized as follows. 3 mL of TEOS were rapidly added into a mixture of ethanol (37 mL), deionized water (5 mL), and ammonium aqueous solution (25-28%, 1.6 mL). The mixture was then stirred at room temperature for 0.5 h, resulting in the formation of a white silica colloidal suspension. The silica particles were centrifugally separated from the suspension and washed with deionized water and ethanol.

Synthesis of ellipsoid-shaped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> ( $\alpha$ HMSS volk-shell structures. Ellipsoid-shaped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was synthesized by aging a solution containing 1.08 g of FeCl<sub>3</sub>·6H<sub>2</sub>O, and 14 mg of NaH<sub>2</sub>PO<sub>4</sub> dissolved in 200 mL deionized water at 100 °C for 24 h. For SiO<sub>2</sub> coating, 50 mg of as-prepared ellipsoid-shaped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was first dispersed in a mixture of isopropanol (100 mL), H<sub>2</sub>O (20 mL), and ammonium (3 mL). Then 0.3 ml of TEOS was added under vigorous stirring every 4 h up to a total TEOS volume of 0.6 ml. The resultants were collected by centrifuging and then cleaned three times with water and ethoanol. For CTAB/SiO<sub>2</sub> coating, 50 mg of prepared  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>( $\partial_s$ SiO<sub>2</sub> core-shell particles dispersed in 10 mL of deionized water by ultrasonication for 15 min. The suspension was then added into a solution containing CTAB (75 mg), deionized water (15 mL), ethanol (15 mL), and ammonium solution (0.275 mL). After the reaction with stirring for 6 h, the products were collected by centrifugation, washed and redispersed in 10 mL of deionized water. For synthesis of ellipsoid-shaped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@HMSS-W, briefly, 50 mg of prepared α-Fe<sub>2</sub>O<sub>3</sub>@sSiO<sub>2</sub> core-shell particles were treated in a mixture of H<sub>2</sub>O (20 mL), CTAB (12.5 mg), and Na<sub>2</sub>CO<sub>3</sub> (212 mg) at 35 °C for 24 h. For synthesis of ellipsoid-shaped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@HMSS-O, briefly, 212 mg of Na<sub>2</sub>CO<sub>3</sub> were added into the well-sonicated water suspension of the above Fe<sub>2</sub>O<sub>3</sub>@sSiO<sub>2</sub>@CTAB/SiO<sub>2</sub>, and then the mixture was treated at 50 °C for 10 h. The as-obtianed  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@HMSS-W and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@HMSS-O were collected by centrifugation and extensively washed with deionized water and ethanol.

Synthesis of Au@HMSS yolk-shell structures. Monodisperse gold nanoparticles were synthesized as

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follows. 18.0 mg of HAuCl<sub>4</sub>·3H<sub>2</sub>O was dissolved in 30mL water and heated to boil under vigorous stirring. 1.0 mL (3.0wt%) of sodium citrate aqueous solution was injected quickly into above mixture and then refluxed for 30 min. After the solution was cooled down to room temperature, an aqueous solution of PVP10 (12.8 g/L, 0.235 mL) was added to the colloidal gold solution to modify the surface of gold nanoparticles to facilitate silica coating. The solution was stirred for 24 h at room temperature. The PVP-modified gold nanoparticles were collected by centrifugation and re-dispersed in 2.0 mL water. In a typical silica coating process, gold nanoparticles covered by PVP (1.0 mL) was added into a mixture of isopropanol (46 mL), H<sub>2</sub>O (6.6 mL), and ammonium (1.28 mL). Then 0.4 ml of TEOS was added under vigorous stirring stirred for another 6 h. The resultants were collected by centrifuging and then cleaned three times with water and ethoanol. For CTAB/SiO<sub>2</sub> coating, 50 mg of prepared Au@sSiO<sub>2</sub> core-shell particles dispersed in 10 mL of deionized water by ultrasonication for 15 min. The suspension was then added into a solution containing CTAB (75 mg), deionized water (15 mL), ethanol (15 mL), and ammonium solution (0.275 mL). After the reaction with stirring for 6 h, the products were collected by centrifugation, washed and redispersed in 10 mL of deionized water. For synthesis of Au@HMSS-W, briefly, 50 mg of Au@sSiO<sub>2</sub> core-shell particles were treated in a mixture of H<sub>2</sub>O (20 mL), CTAB (12.5 mg), and Na<sub>2</sub>CO<sub>3</sub> (212 mg) at 35°C for 24 h. For synthesis of Au@HMSS-O, briefly, 212 mg of Na<sub>2</sub>CO<sub>3</sub> were added into the well-sonicated water suspension of the above Au@sSiO2@CTAB/SiO2, and then the mixture was treated at 50 °C for 10 h. The as-obtianed Au@HMSS-W and Au@HMSS-O were collected by centrifugation and extensively washed with deionized water and ethanol.



Fig. S1 Low-magnification (a) and high-magnification (b) SEM images of HMSS-W.



Fig. S2 The histogram of size distribution estimated from the SEM image: (a) diameter of  $nSiO_2$ , (b) out diameter of HMSS-W, (c) inner diameter of HMSS-W.

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Fig. S3 TEM image (a) and the corresponding pore size distribution (b) of HMSS-W obtained by using the CTAC; TEM image (c) and the corresponding pore size distribution (d) of HMSS-W obtained by using the  $C_{12}TAB$ .



**Fig. S4** Low-magnification (a) and high-magnification (b) TEM images of HMSS-W obtained by using the *s*SiO<sub>2</sub> with particle sizes of 470 nm.

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**Fig. S5** Low-magnification (a) and high-magnification (b) TEM images of the product obtained by using the 10 mg/mL CTAB in the synthetic procedure of HMSS-W.



Fig. S6 Low-magnification (a) and high-magnification (b) SEM images of HMSS-O.



Fig. S7 TEM images: (a) Au@SiO<sub>2</sub>, (b)Au@HMSS-W, (c) Au@SiO<sub>2</sub>@CTAB/SiO<sub>2</sub>, and (d) Au@HMSS-O.