Electronic supplementary information

Formation of Resorcinol-Formaldehyde Hollow Nanoshells through a Dissolution-Regrowth Process

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EXPERIMENTAL SECTION

Synthesis of RF resin colloids. Typically, monodisperse RF resin colloids were synthesized by using resorcinol and formaldehyde solution as precursors. In the synthesis of the RF resin colloids with low condensation degree, resorcinol (50 mg) and the formaldehyde solution (70 μL) was mixed with 25 mL of deionized water and continuously stirred for 10 min. Subsequently, ammonia aqueous solution (NH_4OH, 160 μL, 2.8 wt%) was added to the reaction solution and stirred at RT for 1 h. After that, RF resin colloids were collected and purified with distilled water by centrifugation.[1] Unless otherwise specified, the stirring rate and centrifugal rate of in the preparation of RF colloids and RF nanoshells are 500 rpm and 6000 rpm, respectively.

Synthesis of hollow RF resin colloids. 2 mL of the RF reaction solution was centrifuged and washed several times to obtain solid RF spheres. Then 1 mL of ethanol was added and dispersed ultrasonically. The uniformly dispersed etching solution was stirred for 10 min to remove the inner part of RF resin colloids. After that, hollow RF resin colloids were collected and purified with deionized water by centrifugation.

Synthesis of mesoporous RF resin colloids. A solution containing absolute ethanol (EtOH, 5 mL) and deionized water (H_2O, 20 mL) was used as a reaction media to prepare RF resin colloids with a high condensation degree, and other preparation conditions and etching parameters were the same as those for preparing hollow RF resin colloids.

Synthesis of yolk-shell RF@RF spheres. Using pure water as a reaction media, a batch of as-prepared RF resin colloids is dispersed in 5 mL of water. Then, 5 mL of RF/H_2O solution, resorcinol (50 mg), and the formaldehyde solution (70 μL) was mixed with 20 mL of deionized water and sonicated continuously for 10 min. Subsequently, ammonia aqueous solution (NH_4OH, 160 μL, 2.8 wt%) was added to the reaction solution and stirred for 1 h at RT. 2 mL of the reaction solution was centrifuged and washed several times to obtain solid RF resin spheres. Then 1 mL of ethanol was added and dispersed ultrasonically. The uniformly dispersed etching solution was stirred for 10 min to remove the inner part of the external RF shell. After that, yolk-shell RF@RF resin colloids were collected and purified with deionized water by centrifugation.

Synthesis of yolk-shell Fe_3O_4@RF spheres. The porous Fe_3O_4 nanoparticles were synthesized through a simple solvothermal route in the presence of PVP. The precipitated black products were collected from the solution with an external magnet and washed with ethanol for a few times. Finally, the prepared Fe_3O_4 nanoparticles were dispersed into 5 mL of deionized water for further use.[2, 3] Then, 1 mL Fe_3O_4/H_2O solution, resorcinol (50 mg), and the formaldehyde solution (70 μL) was mixed with 24 mL of deionized

water and sonicated continuously for 10 min. Subsequently, ammonia aqueous solution (NH_4OH, 160 μL, 2.8 wt%) was added to the reaction solution and sonicated for 1 h at RT. 2 mL of the reaction solution was centrifuged and washed several times to obtain solid spheres. Then 1 mL of ethanol was added and dispersed ultrasonically. The uniformly dispersed etching solution was stirred for 10 min to remove the inner part of the RF shell. After that, yolk-shell Fe_3O_4@RF resin colloids were collected and purified with deionized water by centrifugation.

Synthesis of yolk-shell FeOOH@RF spheres. In a typical synthesis, 1.08 g of $FeCl_3 \cdot 6H_2O$ solid was dissolved in 40 mL of water by vigorous stirring until a homogenous transparent solution was obtained. The solution was sealed a capped glass bottle and maintained at 40 °C in an oven for 6 days. The solid product was collected by centrifugation (11000 rpm, 3 min) and was washed with water several times. Before RF coating, the surface modification of β-FeOOH nanorods by PAA was needed, and then the modified β-FeOOH nanorods were dispersed in water with the concentration of 45 mg/mL. 0.1 mL of PAA-FeOOH/H_2O (45 mg/mL), resorcinol (50 mg), and the formaldehyde solution (70 μL) was mixed with 24.9 mL of deionized water and sonicated continuously for 10 min. Subsequently, ammonia aqueous solution (NH_4OH, 160 μL, 2.8 wt%) was added to the reaction solution and stirred for 1 h at RT. 2 mL of the reaction solution was centrifuged and washed several times to obtain a solid product. Then 1 mL of ethanol was added and dispersed ultrasonically. The uniformly dispersed etching solution was stirred for 10 min to remove the inner part of the external RF shell. After that, yolk-shell FeOOH @RF resin colloids were collected and purified with deionized water by centrifugation.

Synthesis of yolk-shell Ag@RF spheres. In a standard synthesis, an aqueous solution containing 50 mg of resorcinol, 70 uL of formaldehyde, and 1 mL of 0.01 M $AgNO_3$ were mixed with 24 mL of water in a glass vial under vigorous magnetic stirring. The solution was then heated to boiling. After 160 μL of 2.8 wt%, NH_4OH was injected, the solution was refluxed for 5 min, and then the glass vial containing the reaction solution was transferred to cold water. 2 mL of the reaction solution was centrifuged and washed several times to obtain solid products.[4] Then 1 mL of ethanol was added and dispersed ultrasonically. The uniformly dispersed etching solution was stirred for 10 min to remove the inner part of the external RF shell. After that, yolk-shell Ag@RF resin colloids were collected and purified with deionized water by centrifugation.

Synthesis of Au seeds (5 nm): 1mL of $HAuCl_4$ solution (5 mM) and 1mL of sodium citrate tribasic dihydrate (TSC) solution (5 mM) were added to 18 mL of Mili-Q water under magnetic stirring. After dispersion, 0.6 mL of fresh $NaBH_4$ solution (0.1 M) was added to the above mixed solution under stirring, and subsequent stirring was continued at RT for 4 h. After the reaction was completed, the obtained Au seeds solution was sealed in a refrigerator and protected from light.

Synthesis of Au NPs (40 nm): 2.5 mL of 5 wt% PVP (M_W, 10000) solution, 1.25 mL of L-ascorbic acid (AA) solution (0.1 M), 1 mL of KI solution (0.2 M) and 300 μL of $HAuCl_4$ solution (0.25 M) were added to 10 mL of Mili-Q water in turn under magnetic stirring. After dispersing evenly, 250 μL of as-prepared Au seeds (5 nm) solution was added to the above mixed solution, and subsequent stirring was continued at RT for 15 min. After the reaction was completed, the obtained Au NPs (40 nm) solution was sealed in a refrigerator and protected from light.

Synthesis of Au@RF yolk-shell NPs:: 5 mL of as-prepared Au NPs (40 nm) solution, resorcinol (50 mg), and the formaldehyde solution (70 μL) was mixed with 20 mL of deionized water and sonicated continuously for 10 min. Subsequently, ammonia aqueous solution (NH_4OH, 160 μL, 2.8 wt%) was added to the reaction

solution and stirred for 2 h at RT. 2 mL of the Au@RF NPs reaction solution was centrifuged and washed several times to obtain solid Au@RF NPs. Then 1 mL of ethanol was added and dispersed ultrasonically. The uniformly dispersed etching solution was stirred for 10 min to remove the inner part of Au@RF core-shell resin colloids. After that, hollow Au@RF NPs resin colloids were collected and purified with distilled water by centrifugation. At last, the Au@RF yolk-shell NPs were dispersed in 40 mL of deionized water.

Synthesis of Ag@RF yolk-shell NPs with the seeded growth method: 0.5 mL of $AgNO_3$ solution (50 mM), 20 μL of TSC solution (0.1 M) and 20 μL of citric acid (CA) solution (0.1 M) were added to 5 mL of deionized water in sequence, and the above mixture solution was used as the stock solution. 2 mL of Au@RF yolk-shell NPs solutions, 110 μL of PVP (M_W, 55000) solution (10 mM) and 20 μL of AA solution (0.1 M) are mixed and dispersed evenly by magnetic stirring. The stock solution at an injection rate of 0.01ml/min was added to Au@RF yolk-shell NPs mixed solutions. The progress of the reaction was monitored by online UV-VIS spectroscopy, and the reaction was stopped after the spectrum shifted significantly. The above reaction solution was washed and centrifuged multiple times to obtain the final product.

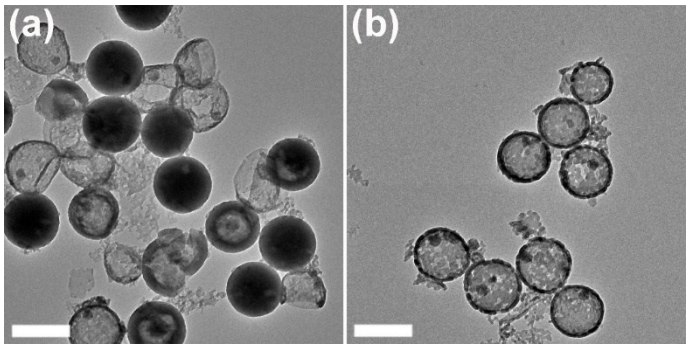

Figure S1. TEM images of RF resin colloids first prepared with pure water as the reaction media at RT for 1 h, and then etched with 1 mL of ethanol at RT for (a) 1 min and (b) 2.5 min. Scale bars = 500 nm.

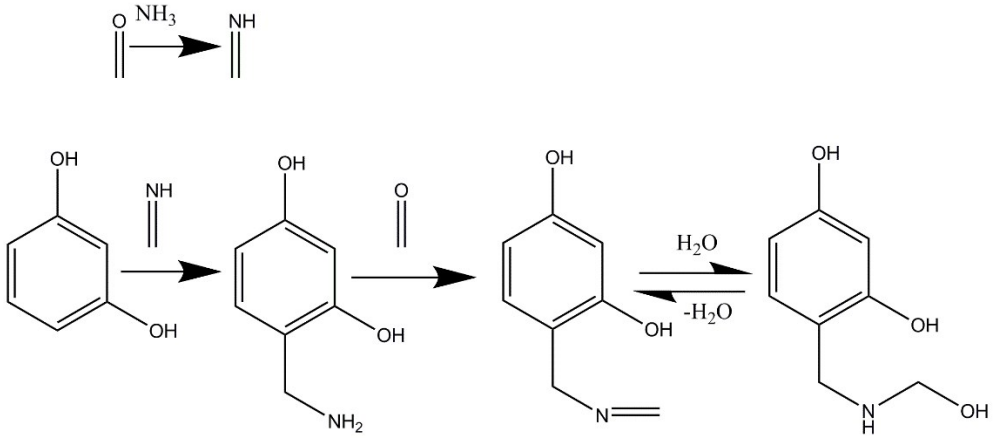

Figure S2. The proposed formation mechanism of monomer structure in ethanol etching

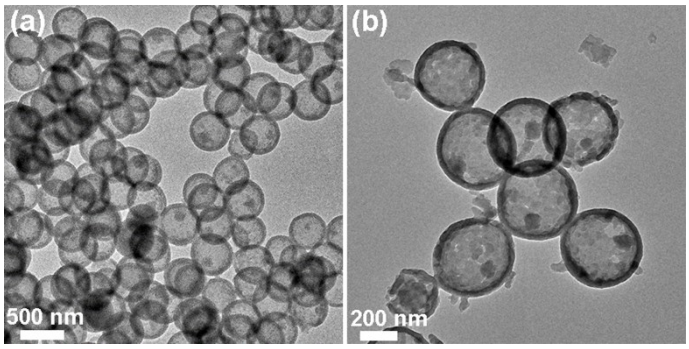

Figure S3. (a) TEM images of hollow RF nanoshells with enlarging the RF etching process by 25 times. (b) TEM images of hollow RF nanostructures heated in water at 100 °C for 3 h and then etched by DMF for 4.5 days.

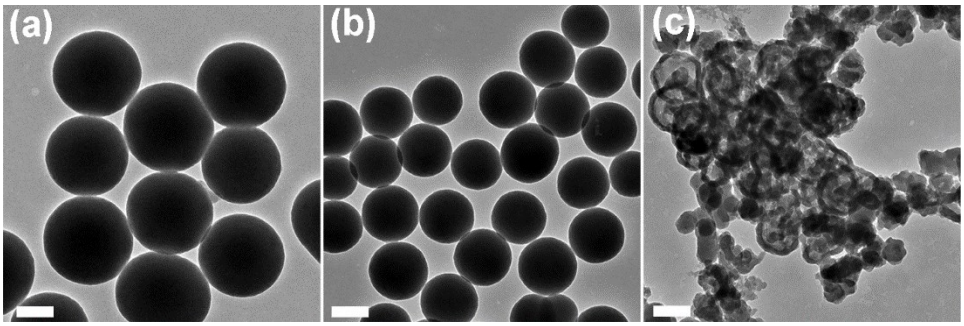

Figure S4. (a) TEM images of RF colloids first prepared at 50 °C, and then etched with 1 mL of ethanol at RT for 10 min. (b) TEM images of RF colloids first prepared with 420 µL of NH_4OH, and then etched with 1 mL of ethanol at RT for 10 min. (c) TEM images of RF colloids first prepared at 17.5 µL of formaldehyde solution, and then etched with 1 mL of ethanol at RT for 10 min. Scale bars = 200 nm

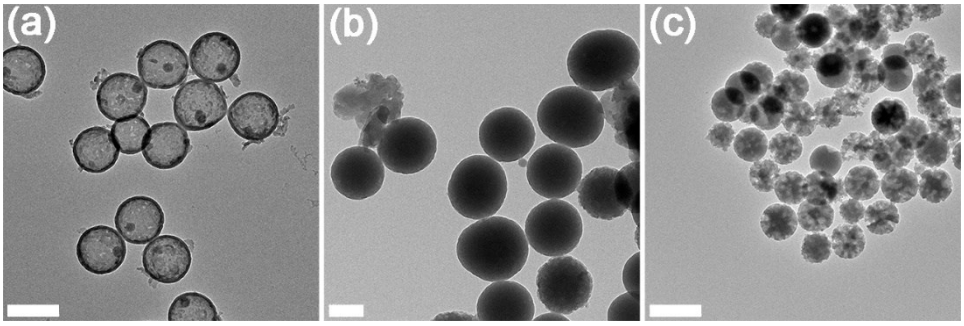

Figure S5. (a) TEM images of RF colloids first prepared with different volume ratios of ethanol/water: volume ratio of ethanol/water = (a) 0 mL: 25 mL at RT for 1 h, and then etched with 1 mL of ethanol at RT for 10 min. TEM images of RF colloids prepared with a volume ratio of ethanol/water: 5 mL: 20 mL at RT for 1 h, and then etched with 2 mL of ethanol and water mixture with a different volume ratio of ethanol/water: volume ratio of ethanol/water = (b) 1:4, (c) 1:1 at RT for 10 min. Scale bars =500 nm.

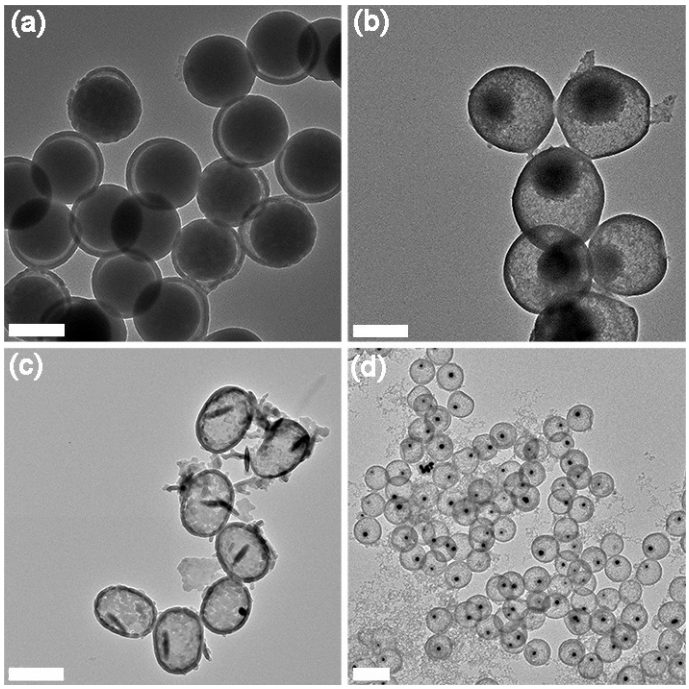

Figure S6. TEM images of yolk-shell structures with a large field of view produced by reacting with core-shell (a) RF@RF spheres, (b) Fe_3O_4@RF spheres, (c) FeOOH@RF spheres, (d) Ag@RF spheres with 1 mL of ethanol etching at RT for 10 min. Scale bars = 500 nm.

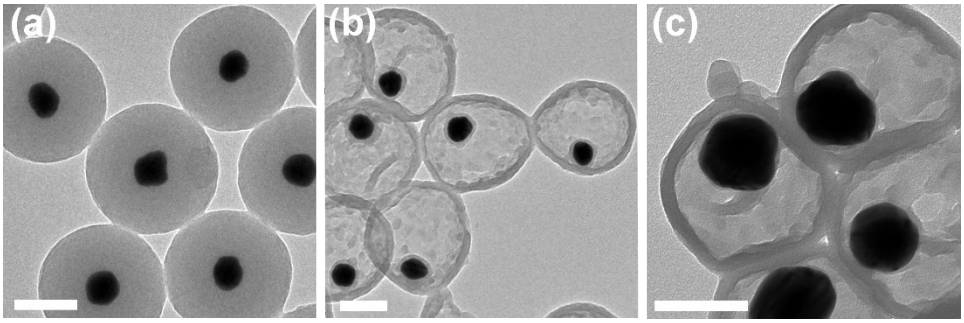

Figure S7. TEM images of (a) Au@RF core-shell NPs, (b) Au@RF yolk-shell NPs obtained by ethanol etching, (c) Ag@RF yolk-shell NPs obtained via seeded growth method. Scale bars =100 nm.

References:

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