

Supporting Information

Sol-gel Coating of Inorganic Nanostructures with Resorcinol-Formaldehyde Resin

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Experimental Section

Chemicals Tetraethylorthosilicate (TEOS), zirconium(IV) butoxide (TBOZ), poly (vinyl pyrrolidone) (PVP, Mw~55,000), ammonium hydroxide (NH₃.H₂O, 28% by weight in water), hydroxypropyl cellulose (HPC, Mw=80,000), anhydrous iron (III) chloride (FeCl₃, 97%), iron (III) perchlorate hexahydrate (Fe(ClO₄)₃·6H₂O), sodium dihydrogen phosphate anhydrous (NaH₂PO₄, 99%), diethylene glycol (DEG, 99%), resorcinol, and cetyltrimethylammonium bromide (CTAB, 98%), poly (allylamine), poly (acrylic acid) (Mw=1,800) were purchased from Sigma-Aldrich. Ethanol and formaldehyde (37% solution) were obtained from Fisher. Tetrabutyl orthotitanate (TBOT, 99%) was purchased from Fluka. Absolute ethyl alcohol (200 proof) was purchased from Gold Shield Chemical. All chemicals were used as received without further purification.

Coating SiO₂ colloids with RF shells. SiO₂ spheres with diameters around 360 nm were prepared through a modified Stöber method,¹ by rapidly adding TEOS (4.5 mL) into a mixture of ethanol (61.75 mL), deionized water (D.I., 24.75 mL), and ammonium hydroxide aqueous solution (9.0 mL, 30 %). After stirring for 2 h, the silica particles were separated from the suspension through centrifugation, washed with ethanol several times and then re-dispersed in 10 mL of water. In a typical coating process, the as-prepared SiO₂ colloidal solution (1.0 mL) was sequentially combined with ammonium hydroxide aqueous solution (0.1 mL), D.I. water (27 mL), and an aqueous solution of CTAB (1 mL, 0.01 M), vigorously stirred for 30 min to ensure the complete adsorption of CTAB on the silica surface, and then mixed with resorcinol (0.05 g) and formaldehyde solution (0.07 mL). SiO₂@RF core-shell composites were collected after keeping the system under magnetic stirring for 16 hours.

Conversion to carbon shells. Briefly, carbon composites were obtained by heating the SiO₂@RF composites at 500 °C under N₂. After carbonization, the powder (0.2 g) was

etched in an aqueous solution containing NaOH (1.0 g in 10 mL water) under vigorous stirring at 51 °C for 3h. Aliquots were extracted, cleaned several times by centrifugation and water redispersion, and finally dispersed in water or dried into powder for various characterizations.

Coating RF spheres with silica. RF spheres were synthesized according to a procedure reported previously,² typically by mixing ethanol (8 mL), deionized water (20 mL), and ammonia aqueous solution (0.1 mL). After stirring for 1 h, resorcinol (0.1 g) and formaldehyde solution (0.14 mL) were added to the reaction solution and stirred overnight. The product was washed and centrifuged three times and diluted in D.I. water (10 mL). To modify the surface of RF spheres, 2 mL of RF colloidal dispersion was washed with acetic acid (1 M) three times. Then, an aqueous solution of polyamine (1 mL, 1 wt%) was mixed with the washed RF spheres and stirred for 2 h. The amine-capped RF spheres were centrifuged, redispersed in a mixture of water (3 mL) and ethanol (20 mL), mixed with ammonia solution (1.0 mL) and TEOS (0.1 mL) under vigorous stirring, and finally kept at room temperature for 3 h to complete the silica coating process. The product was collected by centrifugation.

Synthesis of C@C double layered hollow structures. To prepare multilayer structures, the silica spheres were first coated with RF resin by using CTAB as the surface modification agent, followed by the coating of another layer of silica, and then a additional layer of RF resin. The as-prepared SiO₂@RF@SiO₂@RF particles were carbonized, then etched in an aqueous NaOH solution at 51 °C for 2 hours.

Synthesis of α-Fe₂O₃@RF resin composites Ellipsoidal α-Fe₂O₃ (hematite) nanoparticles were prepared based on a previous report.³ Typically, a 250 mL aqueous solution containing 11.6 g of Fe(ClO₄)₃ · 6H₂O, 1.5 g of urea, and 0.16 g of NaH₂PO₄ was aged at 100 °C for 1 day in a Pyrex bottle. The solution was centrifuged three times with water and finally re-dispersed in 10 mL of water. For RF resin coating, 4 mL of as-prepared hematite spindles was first dispersed in 27 mL of H₂O, followed by the addition of 1 mL of CTAB (0.01 M) and 0.08 mL of ammonium hydroxide. The solution was stirred for 30 min before the introduction of 0.04 g of resorcinol and 0.056 mL of formaldehyde solution to ensure the complete adsorption of CTAB on the surface of hematite. The as-obtained α-Fe₂O₃@RF composites were collected by centrifugation and washed with deionized water and ethanol.

Synthesis of SiO₂@TiO₂@RF composites SiO₂@TiO₂ composite was first produced based on our recent reports.^{4,5} In a typical process, a certain amount of 360 nm SiO₂ spheres was dispersed in a mixture containing hydroxypropyl cellulose (HPC, 100 mg), ethanol (200 proof, 20 mL) and water (0.12 mL). The system was first stirred for 30 min, followed by the drop-wise addition of tetrabutyl titanate (TBOT, 1 mL of TBOT mixed with 4.5 mL of 200 proof ethanol) using a syringe pump (0.5 mL/min). After injection, the reaction system was heated to 85 °C and refluxed for 90 min. The precipitate, which contained SiO₂@TiO₂ nanocomposites, was collected using centrifugation, washed with ethanol and redispersed in D.I. water (10 mL). 4 mL of the as-prepared SiO₂@TiO₂ solution was then mixed with 27 mL of H₂O, 1 mL of CTAB (0.01 M) and 0.08 mL of ammonium hydroxide under stirring. 0.0425 g of resorcinol and 0.06 mL of formaldehyde was then injected to initiate the polymerization

process, which was conducted for 16 hours at room temperature. The final product was obtained by centrifugation and washed with water and ethanol three times.

Synthesis of $ZrO_2@RF$ resin To prepare ZrO_2 particles, zirconium(IV) butoxide (TBOZ, 0.6 mL, 80 wt. % in 1-butanol) was dissolved in ethanol (4.5 mL), which was then slowly added into a mixture of ethanol (25 mL) and water (0.1 mL) using a syringe pump (0.25 mL/min). After injection, the reaction mixture was stirred overnight to obtain a white precipitate, which was collected using centrifugation, washed with ethanol and redispersed in D.I. water (10 mL). 2 mL of the above-mentioned ZrO_2 solution was mixed with CTAB solution (1 mL, 0.01 M) and 0.08 mL of ammonium hydroxide. After stirring for 30 minutes, 0.04 g of resorcinol and 0.056 mL of formaldehyde was added into the reaction system, which was further stirred for 16 h to produce the final brownish product.

Synthesis of $Fe_3O_4@RF$ resin composites Superparamagnetic Fe_3O_4 spheres were synthesized using a high-temperature hydrolysis reaction that we reported previously.⁶ In a typical process to make $Fe_3O_4@RF$ resin composites, solid Fe_3O_4 together with 0.1 mL of ammonium hydroxide was dispersed in 27 mL of water by sonication. 0.05 g of resorcinol and 0.07 mL of formaldehyde were then added under vigorous stirring. The reaction system was kept at room temperature for 16 h to ensure the complete polymerization of RF resin. The as-prepared brownish product was finally washed with D.I. water several times.

Characterization. The sample morphology was characterized by using a transmission electron microscope (TEM, Tecnai T12). FTIR measurements were conducted on a Bruker aquinox 55 FTIR spectrometer at room temperature under N_2 flow with a resolution of 4cm^{-1} , using the KBr method. The nitrogen adsorption isotherm was obtained at 77K using a nitrogen sorption instrument (Micromeritics ASAP 2010). Zeta potential measurements of the colloidal dispersions were performed by using a Beckman Coulter Delsa Nano C Zeta Potential Analyzer.

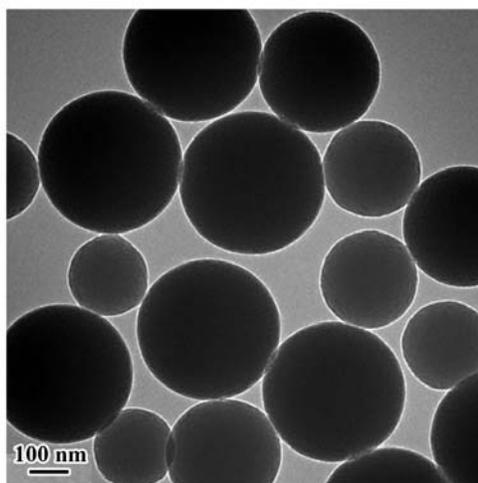


Figure S1. TEM image of the product after RF coating without any surface modification. Only free RF particles could be obtained, as indicated by the smaller particles in the image.

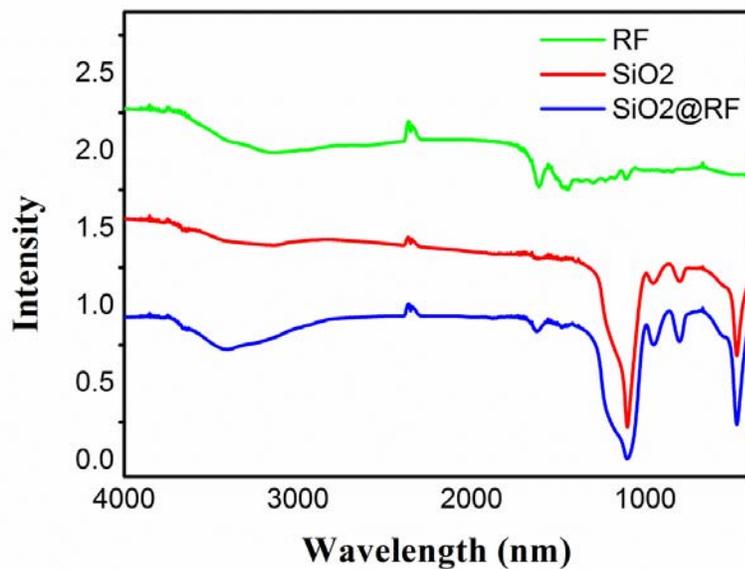


Figure S2. FT-IR spectra of RF sphere, SiO₂ particles and SiO₂@RF composite. The SiO₂@RF shows a peak at 1606 cm⁻¹ which represents the aromatic groups, and a peak at 1475 cm⁻¹ which corresponds to the -CH₂- groups. Both peaks are expected for samples with an RF coating.

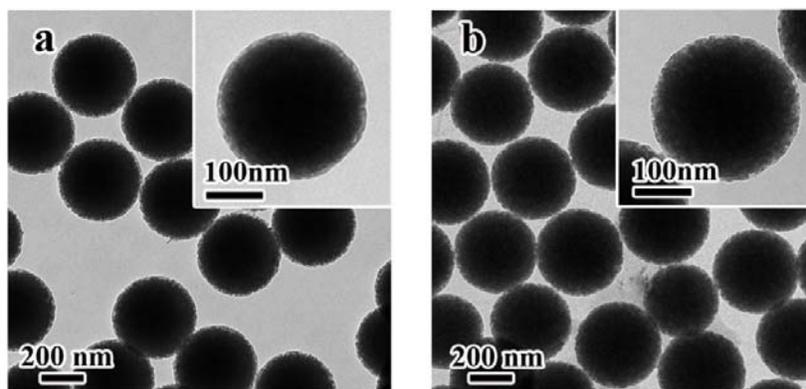


Figure S3. TEM image of SiO₂@RF before a) and after b) carbonization

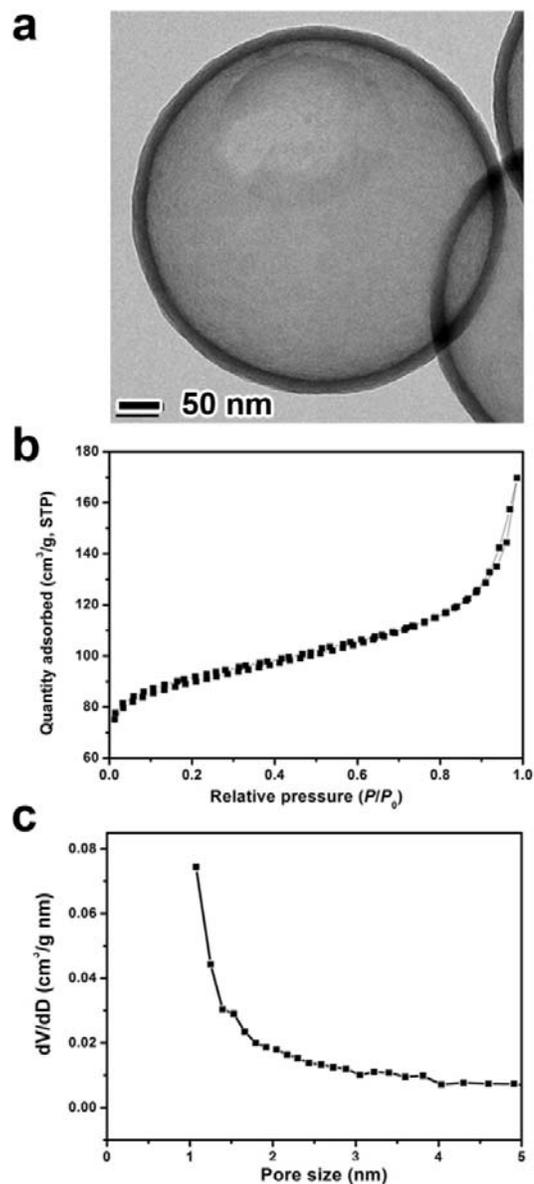


Figure S4. TEM images of a) a high magnification TEM image of a carbon shell after etching of the silica core, and b) N₂ adsorption/desorption isotherms and c) pore size distribution of the hollow carbon shells. A typical sample of hollow carbon shells displays a Brunauer-Emmett-Teller (BET) surface area of 406.875 m²g⁻¹, a total pore volume of about 0.22 cm³g⁻¹, and an average pore size of 1.114 nm.

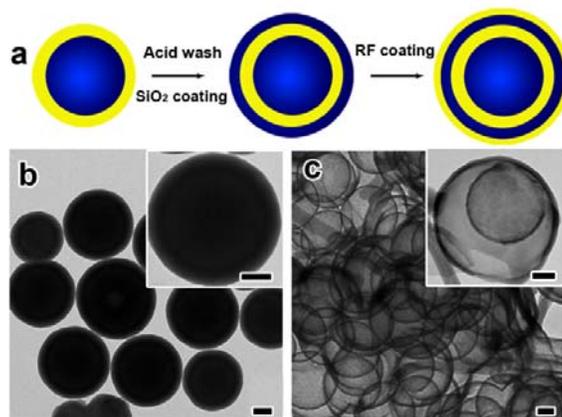


Figure S5. a) Schematic illustration of multilayer coating of SiO₂@RF@SiO₂@RF nanoparticle. TEM images of: b) RF@SiO₂, and c) hollow double layer carbon shells. All scale bars are 100 nm.

References

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