Plasmolysis-Inspired Nanoengineering of Functional Yolk–Shell Microspheres with Magnetic Core and Mesoporous Silica Shell

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Supporting Information

ABSTRACT: Yolk–shell nanomaterials with a rattle-like structure have been considered ideal carriers and nanoreactors. Traditional methods to constructing yolk–shell nanostructures mainly rely on multistep sacrificial template strategy. In this study, a facile and effective plasmolysis-inspired nanoengineering strategy is developed to controllably fabricate yolk–shell magnetic mesoporous silica microspheres via the swelling-shrinkage of resorcinol-formaldehyde (RF) upon soaking in or removal of n-hexane. Using Fe3O4@RF microspheres as seeds, surfactant-silica mesostructured composite is deposited on the swelled seeds through the multicomponent interface coassembly, followed by solvent extraction to remove surfactant and simultaneously induce shrinkage of RF shell. The obtained yolk–shell microspheres (Fe3O4@RF@void@mSiO2) possess a high magnetization of 40.3 emu/g, high surface area (439 m²/g), radially aligned mesopores (5.4 nm) in the outer shell, tunable middle hollow space (472–638 nm in diameter), and a superparamagnetic core. This simple method allows a simultaneous encapsulation of Au nanoparticles into the hollow space during synthesis, and it leads to spherical Fe3O4@RF@void-Au@mSiO2 magnetic nanocatalysts, which show excellent catalysis efficiency for hydrogenation of 4-nitrophenol by NaBH4 with a high conversion rate (98%) and magnetic recycling stability.

INTRODUCTION

As the basic units of living organisms, cells possess core–shell structure composed of cell membrane as the outer shell and cytoplasm protected nucleolus as the inner core. Cell plasmolysis, as a common biological phenomenon, is the process in which plant cells lose water in a hypertonic solution, causing protoplast to retract away from the cell wall (Scheme 1A). On the contrary, cell can absorb water by endosmosis in a hypotonic solution with a lower external osmotic pressure.

Through observation of plasmolysis and deplasmolysis, it is possible to determine the survival of cells and toxicity of the cell’s environment as well as the rate solute molecules cross the cellular membrane, estimating concentration of cell sap and guiding reasonable irrigation for crops.1–3 During the plasmolysis process, cells undergo transformation from core–shell to yolk–shell structure with the separation of cytoplasm and cell wall.

In the field of materials’ sciences, yolk–shell nanomaterials with rattle-like structures, as a kind of core–shell structure with a movable core, have been considered ideal carriers and nanoreactors4–12 due to their large void space for cargo storage and delivery. In the past decades, great efforts have been devoted to fabricating various yolk–shell nanomaterials.13–16 The construction of yolk–shell nanostructures is mainly achieved through templating methods by using silica, polymer resin, and carbon as the hard template, or surfactants as the soft template, followed by selective removal of the template via chemical etching, calcination, or solvent extraction treatment.17–25 These methods based on sacrificial templates usually require tedious and costly synthesis procedures, resulting in unavoidable template consumption and waste. In addition, template-free methods such as Ostwald ripening process26,27 and Kirkendall effect28–30 have also been reported to fabricate yolk–shell nanomaterials. However, the strategies are only suitable for the construction of metal or metal oxide yolk–shell structures with less controllable size and void space.31,32 Among various yolk–shell materials, yolk–shell microspheres with a porous outer shell attracted particularly increasing interest because they combine advantages of

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**Chemicals.** FeCl₃·6H₂O, trisodium citrate, sodium acetate, tetrathyl orthosilicate (TEOS), resorcinol, formaldehyde, NaBH₄ (99.0 wt%), 4-nitrophenol (4-NP, 99.0 wt%), ethanol, ethylene glycol, n-hexane, and concentrated ammonia solution (28 wt%) are all of analytical grade (Shanghai Chemical Corp.). Cetyltrimethylammonium bromide (CTAB) and chloroauric acid tetrahydrate (≥47.8 wt % Au) were supplied by Aldrich-sigma. Hydrophobic upconversion nanoparticles (NaGdF₄: Yb, Er@NaGdF₄) stabilized by oleylamine were synthesized according to a previous report. All other chemicals were used as received. Deionized water was used for all experiments.

**Scheme 1.** (A) Plasmolysis Process of Plant Cells upon Immersion in a Hypertonic Solution; and (B) Synthesis Procedure for the YS-MMS Microspheres

**Synthesis of Fe₃O₄@RF Microspheres.** Magnetite (Fe₃O₄) particles with a mean diameter of ~300 nm were synthesized as previously reported. First, 100 mg of Fe₃O₄ particles was dispersed in a mixture solution of ethanol (40 mL) and deionized water (20 mL) by ultrasonication. Into the resultant dispersion were added concentrated ammonia solution (1.2 g, 28 wt %), resorcinol (0.2 g, 0.09 mM), and formaldehyde (0.2 g, 37 wt %). After reaction for 10 h at 30 °C, the obtained core–shell Fe₃O₄@RF microspheres were collected, washed with ethanol and deionized water three times, respectively.

**Synthesis of Yolk–Shell Fe₃O₄@RF@Au-void@mSiO₂ Microspheres.** In a typical synthesis, 200 mg of Fe₃O₄@RF microspheres were dispersed in a mixed solution containing CTAB (0.5 g, 1.3 mmol), deionized water (80 mL), and concentrated ammonia solution (0.8 mL, 28 wt %) under ultrasonication treatment. 20 mL of n-hexane with dissolved TEOS (2.0 mL) was dropwise added into the water solution in 30 min. The reaction mixture was kept stirring for 12 h at 35 °C. The product was collected by a magnet, washed with ethanol and deionized water three times, respectively, and finally redispersed in 60 mL of ethanol for refluxing treatment at 70 °C for 12 h to remove CTAB templates. The solvent extraction treatment was repeated three times, and the obtained sample was then thoroughly washed with ethanol. Thus, yolk–shell magnetic mesoporous silica (Fe₃O₄@RF@Au-void@mSiO₂) microspheres, denoted as YS-MMS microspheres, were obtained. By changing the reaction temperature, a series of yolk–shell microspheres were obtained and denoted as YS-MMS-x, where x stands for the reaction temperature.

**Synthesis of Yolk–Shell Fe₃O₄@RF@Au-void@mSiO₂ Microspheres.** Oleylamine capped gold nanoparticles of about 10 nm were synthesized through a general one-pot organic phase method as previously reported. For fabrication of yolk–shell Fe₃O₄@RF@Au-void@mSiO₂ microspheres with encapsulated Au nanoparticles (Fe₃O₄@RF@Au-void@mSiO₂), the synthesis process is the same as above-mentioned for YS-MMS-35 microspheres except adding Au nanoparticles (10 mg) into n-hexane with dissolved TEOS (2.0 mL). The obtained yolk–shell Fe₃O₄@RF@Au-void@mSiO₂ microspheres are denoted as Au@YS-MMS microspheres.

**Catalytic Reduction of 4-Nitrophenol (4-NP) by Au@YS-MMS Microspheres.** To investigate the catalytic activity of Au@YS-MMS microspheres, the reduction of 4-NP was used as the model reaction. The catalytic reduction was carried out in a quartz cuvette and monitored by in situ measuring the UV–vis absorption spectra. At first, 0.3 mL of freshly prepared NaBH₄ solution (0.2 M) was added in the aqueous solution containing 0.03 mL of 4-NP (0.01 M) and 3.0 mL of deionized water. Subsequently, 0.02 mL of aqueous dispersion of Au@YS-MMS microspheres (0.02 wt %) was added, and the reaction started immediately. To study the recyclability of the catalysts, the used Au@YS-MMS microspheres were separated from the reaction mixture by a magnet at the end of each run, washed with absolute ethanol and deionized water, and then redispersed in water by ultrasonication and added in a fresh reaction solution. After reaction for 20 min, the solution was measured using UV–vis spectroscopy.

**Measurements and Characterization.** Transmission electron microscopy (TEM) measurements were conducted on a JEOL 2011 microscope (Japan) under an operation voltage of 200 kV. Field-emission scanning electron microscopy (FESEM) images were acquired on the Hitachi model S-4800 field emission scanning electron microscope (Japan). Regular scanning electron microscopy functional cores and porous shells with high surface area and accessible pore channels, which are beneficial for target capture and guest molecule delivery and enrichment. Despite the above-mentioned advances in fabricating core–shell and yolk–shell microspheres, until now, it still remained a great challenge to synthesize yolk–shell microspheres through mild and nonsacrificial scaffold routes or methods. Herein, we report a novel, facile, and mild plasmolysis-inspired nanoengineering strategy to synthesize uniform yolk–shell mesoporous silica microspheres. The feature of the synthesis is that the hollow space is created by mimicking cell plasmolysis process based on the swelling-shrinkage of resorcinol-formaldehyde (RF) upon soaking in or removal of organic solvent. The yolk–shell magnetic mesoporous silica microspheres (Fe₃O₄@RF@void@mSiO₂) are synthesized through deposition of a mesoporous silica layer on the presynthesized RF resin coated Fe₃O₄ core. The solvent extraction treatment was repeated three times, and the obtained sample was then thoroughly washed with ethanol. Thus, yolk–shell magnetic mesoporous silica (Fe₃O₄@RF@void@mSiO₂) microspheres, denoted as YS-MMS microspheres, were obtained. By changing the reaction temperature, a series of yolk–shell microspheres were obtained and denoted as YS-MMS-x, where x stands for the reaction temperature.
TEM images of Fe₃O₄ and Fe₃O₄@RF microspheres. SEM observations indicate the resultant Fe₃O₄@RF microspheres possess regular spherical morphology with uniform diameter of about 420 nm (Figure 1b). The obtained well-dispersed uniform microspheres tend to assemble into three-dimensional ordered structures during sampling on a silicon wafer. TEM images indicate the distinct core–shell structure with uniform RF shell thickness of about 60 nm (Figure 1b, inset). In the water/n-hexane mixture synthesis system at 35 °C, the coassembly of CTAB and silicate oligomers from the hydrolysis of TEOS in the presence of Fe₃O₄@RF microspheres as seeds gives rise to yolk–shell structural Fe₃O₄@RF/CTAB-SiO₂ composites after washing (Figure S1). It indicates the void between RF and outer shell directly formed after CTAB/SiO₂ shell deposition and the subsequent washing and separation process. After further solvent extraction treatment with ethanol, the obtained YS-MMS-35 microspheres exhibit uniform spherical morphology and excellent dispersity with a mean diameter of about 750 nm (Figure 1c). Interestingly, a clear core–shell structure with bright core and gray shell was observed for each YS-MMS microsphere. Such a phenomenon is probably attributed to the presence of hollow space that enhances contrast between the magnetic core and mesoporous silica shell under SEM (Figure 1c, insets). TEM observations show distinct uniform yolk–shell structure with outer shell thickness of about 90 nm, middle hollow space with a mean diameter of about 570 nm, and the well-retained Fe₃O₄@RF as the inner core (Figure 1d,e). The high-resolution TEM image shows clear radially aligned mesopore channels with pore size of about 5.0 nm in the outer shell (Figure 1f).

Nitrogen adsorption–desorption isotherms (Figure 2a) of YS-MMS-35 microspheres show representative type-IV curves with a sharp capillary condensation step in the partial pressure (P/P₀) range of 0.55–0.75, suggesting cylindrical pores with uniform mesopores. The pore size distribution curve (Figure 2b) derived from the adsorption branch indicates that YS-MMS microspheres have a mean pore size of 5.4 nm. Such a pore size is much larger than that (2.0–3.0 nm) of traditional mesoporous silica materials obtained by using CTAB as the template, due to the presence of expanding solvent n-hexane. The BET surface area and total pore volume of YS-MMS and Au@YS-MMS microspheres is depicted in Scheme 1B. First, water-dispersible Fe₃O₄ particles were synthesized through one-pot synthesis in water/n-hexane solution using TEOS as a silica precursor and CTAB as a structure-directing agent at 35 °C. After extraction treatment by ethanol, the CTAB template and n-hexane can be removed, and yolk–shell mesoporous silica (YS-MMS) microspheres were thus obtained.

The water-dispersible Fe₃O₄ particles were synthesized through the well-established solvothermal method. SEM image (Figure 1a) shows that the obtained magnetic Fe₃O₄ particles exhibit spherical morphology with uniform size of ~300 nm. TEM characterization indicates that Fe₃O₄ particles are composed of numerous magnetic nanocrystals (Figure 1a, inset). This unique structure endows the particles fast magnetic responsiveness because their thermal motion in solutions can be suppressed by the applied magnetic field. By virtue of the strong complexation between iron ions in Fe₃O₄ particles’ surface and phenolic hydroxyl groups, the polymerization of resorcinol and formaldehyde can occur in the solid–liquid interface of Fe₃O₄/reaction solution, leading to core–shell Fe₃O₄@RF microspheres.

■ RESULTS AND DISCUSSION

Synthesis and Characterization. The fabrication procedure of YS-MMS and Au@YS-MMS microspheres is depicted in Scheme 1B. First, water-dispersible Fe₃O₄ particles were coated with a protective shell of RF resin through interface sol–gel polymerization of resorcinol and formaldehyde in an alkaline solution, resulting in Fe₃O₄@RF microspheres. Next, a shell of CTAB/silica composite with mesostructure was deposited on the n-hexane swelled Fe₃O₄@RF microspheres through one-pot synthesis in water/n-hexane solution using TEOS as a silica precursor and CTAB as a structure-directing agent at 35 °C. After extraction treatment by ethanol, the CTAB template and n-hexane can be removed, and yolk–shell mesoporous silica (YS-MMS) microspheres were thus obtained.

The inset in panel (a) and (b) is the corresponding TEM image of Fe₃O₄ and Fe₃O₄@RF microspheres.

Figure 1. SEM images of Fe₃O₄ (a), Fe₃O₄@RF (b), and YS-MMS (c) microspheres and TEM images (d–f) of YS-MMS-35 with different magnification. The inset in panel (a) and (b) is the corresponding TEM image of Fe₃O₄ and Fe₃O₄@RF microspheres.
crystalline phase, indicating that the magnetite particles were well retained. Low-angle XRD patterns for the YS-MMS-35 microspheres reveal hexagonal mesopore symmetry (Figure S2b), and only (100) diffraction can be clearly indexed, implying a low structure ordering because of the curved mesoporous silica shell. The magnetic property characterization at 300 K by using a superconducting quantum interference device (SQUID) reveals that Fe3O4@RF and YS-MMS-35 microspheres possess superparamagnetic behavior without remanence when the applied magnetic field is removed, and they have a high magnetization saturation value of 71.2 and 40.3 emu/g, respectively (Figure S3), which is favorable for a fast magnetic separation process. The superparamagnetism is mainly due to the fact that magnetite particles are composed of magnetite nanocrystals (<10 nm), avoiding the irreversible aggregation of magnetic materials after removal of magnetic field.

It is worth noting that the size of hollow space (i.e., void diameter) can be tuned by simply changing the reaction temperature. At the reaction temperature of 25 °C, the obtained YS-MMS-25 (Figure 3a) exhibits spherical morphology and well-retained Fe3O4@RF core and void diameter of 470 nm, and the gap between Fe3O4@RF core and mesoporous silica shell is about 25 nm. As the reaction temperature increases to 30 and 40 °C, the void diameter increases to 525 and 670 nm, respectively (Figure 3b,c). Notably, the YS-MMS-45 sample (Figure 3d) obtained at 45 °C exhibits interesting finger-like morphology with Fe3O4@RF core and mesoporous shell with highly radially aligned mesopores (Figure S4a,b), and the largest void diameter (675 nm) of YS-MMS-45 is close to that of YS-MMS-40. It suggests that the YS-MMS-45 sample experiences a slightly different formation process at 45 °C. Further increasing the reaction temperature results in a small reduction of the void size into 664 nm for YS-MMS-55 and 635 nm for YS-MMS-65, respectively (Figure 3e,f). In addition to the void size, the thickness of mesoporous silica shell increases slightly from 70 to 95 nm with the reaction temperature from 25 to 65 °C. It is mainly due to the promoted hydrolysis–condensation of TEOS at higher temperature that favors a quick formation of a thick CTAB/silica composite on Fe3O4@RF microspheres via interface coassembly. Some little silica residues were observed due to the unavoidable homogeneous nucleation of silica oligomers despite that the interface heterogeneous nucleation was the dominant process (Figure 3a,e,f). Moreover, by using Fe3O4@RF microspheres with 150 nm sized Fe3O4 core and thicker RF layer (235 nm) as the seed for growth of CTAB/silica composite shell, the void size can reach 960 nm (Figure S5a,b), much larger than that (640 nm) of YS-MMS microspheres obtained using the same whole size of Fe3O4@RF microspheres but with a thinner RF layer (110 nm) (Figure S5c,d). It implies that thicker RF is favorable for the formation of larger voids at the same reaction temperature.

To acquire more detailed information about the formation of the yolk–shell structure, the intermediate sample was withdrawn from the synthesis system for YS-MMS-35 after reaction for 8 h. TEM characterization reveals that the sample is core–shell–shell microspheres without a hollow structure. The microspheres are about 900 nm in diameter, comprising Fe3O4 core, RF shell, and CTAB-silica composite outer shell (Figure S6). Particularly, the RF layer thickness was significantly increased from 60 nm for Fe3O4@RF microspheres to 180 nm for the intermediate sample Fe3O4@RF@CTAB-silica microspheres, indicative of a dramatically swelled RF shell (Figure S6b). As a result, the RF shell became loose after deposition of CTAB-silica in the reaction, as compared to the pristine Fe3O4@RF microspheres with a dense RF shell. To investigate the function of n-hexane during the construction of yolk–shell mesoporous silica microspheres, a control experiment was conducted without using swelling agent n-hexane, and we maintained other conditions the same as those for YS-MMS-35 microspheres. The obtained microspheres exhibit dense core–shell–shell structures with perpendicular aligned mesopore channels on the surface (Figure S7). These results indicate that n-hexane is crucial for the formation of yolk–shell structures. To further study the surface property of Fe3O4@RF microspheres, a control experiment was performed by adding Fe3O4@RF microspheres to the water/n-hexane mixture made of water and n-hexane with dissolved hydrophobic upconversion nanoparticles (NaGdF4:Yb, Er@NaGdF4, UCNPs). As shown in Figure S8a, the upper n-hexane in the water/n-hexane biliquid phase shows typical blue fluorescence, and no fluorescence was observed in the lower water layer upon irradiation of 980 nm light. However, after Fe3O4@RF microspheres were added in the water layer, it was found that the water layer also shows blue light after mixing for 4 h (Figure S8b). The fluorescence spectrum (Figure S8c) of the lower layer of aqueous Fe3O4@RF microspheres dispersion shows the same emission peaks as UCNPs/n-hexane solution, indicative of the presence of UCNPs in the water phase. The recycled Fe3O4@RF microspheres from the water phase were found to absorb numerous UCNPs on the surface (Figure S8d). Furthermore, dynamic light scattering (DLS) technique was employed to study the swelling effect of n-hexane on the RF shell of Fe3O4@RF microspheres, the microspheres were dispersed in water/n-hexane solution under gentle stirring at 40 °C, and their hydrodynamic diameters were measured using DLS. The hydrodynamic diameter of Fe3O4@RF microspheres was increased from 880 to 1020 nm and almost remained constant after stirring for 4 h (Figure S9a), further confirming that Fe3O4@RF microspheres can be swelled by n-hexane. However, when the Fe3O4@RF microspheres were treated at 100 °C for 12 h and then used for swelling experiment, their size was found to be reduced to about 540 nm and remained around 550 nm in the biliquid system of n-hexane and water even after stirring for 4 h (Figure S9b). Furthermore, when using Fe3O4@RF microspheres that were treated at 100 °C for 12 h as seeds for the synthesis of YS-MMS-35 microspheres, dense sandwich structures of Fe3O4@RF@mSiO2 microspheres (Figure S10) were obtained, and no middle voids were observed. It suggests that the increased cross-linking density can slightly decrease the size of the Fe3O4@RF microspheres.

![Figure 3. TEM images of YS-MMS microspheres synthesized at (a) 25, (b) 30, (c) 40, (d) 45, (e) 55, and (f) 65 °C. (g) The void diameter of YS-MMS microspheres versus the reaction temperature.](image-url)
and inhibit the swelling of RF shell. Similarly, colloidal RF microspheres (RF-30, Figure S9B, inset) were also synthesized via the sol–gel reaction of resorcinol and formaldehyde in ethanol–water system at 30 °C. DLS measurements (Figure S9B) indicate that the diameter of RF-30 increases continuously from 209 to 380 nm upon soaking in water/n-hexane solution, while the diameter of RF-100 obtained after treatment of RF-30 at 100 °C remained around 190 nm. To understand the reversibility of the low-cross-linking RF layer, DLS measurements were performed on Fe₃O₄@RF microspheres after cyclic soaking in n-hexane and washing with ethanol. The hydrodynamic diameter of Fe₃O₄@RF microspheres demonstrated a reversible size change from about 1000 nm (after soaking with n-hexane-H₂O for 3 h) to about 570 nm (after washing with ethanol three times) (Figure S9C). These results confirm that the RF layers undergo a reversible swelling–shrinkage process. On the basis of these results, it is reasonable to speculate that YS-MMS microspheres can also undergo the similar reversible swelling and shrinkage process, going back and forth between the compact core–shell and yolk–shell states.

Comparatively, when hydrophilic Fe₃O₄@SiO₂ microspheres obtained by sol–gel depositing silica on Fe₃O₄ particles were used to replace Fe₃O₄@RF microspheres for the synthesis of YS-MMS-35 microspheres, the mesoporous silica shell of the obtained sample after solvent extraction treatment was found to grow directly on the surface of Fe₃O₄@SiO₂ microspheres, forming a sandwich Fe₃O₄@SiO₂@mSiO₂ core–shell structure and radially aligned mesopore channels (Figure S11), and no such yolk–shell magnetic mesoporous silica microspheres were observed because the inorganic dense silica shell of Fe₃O₄@SiO₂ microspheres is not swellable. All of these results further indicate that Fe₃O₄@RF microspheres with swellable RF shell as the core play a key role in constructing yolk–shell structure in the water/n-hexane mixed synthesis system.

Typical resorcinol-formaldehyde resin produced by basic catalyst usually has a highly cross-linked three-dimensional network with methylene-bridged novolac structures because of the active substitution at C₂, C₄, and C₆ positions of resorcinol rings with formaldehyde at high temperatures. However, in our study, the RF microspheres derived from the sol–gel reaction in ethanol–water system at low temperatures (e.g., 30 °C) was found to possess a considerable amount of unreacted benzyl methylene groups due to the polymerization at low temperature, as proved by the solid ¹³C NMR (Figure S12a). For comparison, uniform RF microspheres (RF-30) synthesized via a polymerization of resorcinol and formaldehyde were further treated at 100 °C for 12 h. As compared to RF-30, the solid ¹³C NMR of the obtained RF-100 exhibits obvious reduced signals at 65–75 ppm attributed to benzyl methylene and significantly increased signals at 20–60 ppm assigned to the diaryl methanes (Figure S12b). The molecular structure and composition analysis results further confirmed that the RF resin obtained in study has a relatively lower cross-linking density with unreacted benzyl methylene moieties.

**Formation Mechanism.** On the basis of the above results, we proposed a formation mechanism similar to the cell plasmolysis process. As depicted in Figure 4, at the beginning, Fe₃O₄@RF microspheres were dispersed in an aqueous solution containing CTAB surfactant and ammonia–water. Next, n-hexane with dissolved TEOS was slowly added dropwise. The droplets of n-hexane-TEOS tend to interact with RF surface due to the hydrophobic interaction between the hydrophobic backbone of RF and n-hexane (Figure 4a). Because the RF resin in this study has a loose three-dimensional structure due to the low cross-linking degree, the n-hexane droplets with dissolved TEOS can easily enter into the RF resin shell and expand the polymer framework (Figure 4b) via the hydrophobic interaction. After swelling by n-hexane–TEOS solution, the dissolved TEOS in n-hexane can be hydrolyzed into silicate oligomers at the interface of n-hexane swelled RF and aqueous solution by ammonia–water, coassemble with CTAB micelles, and deposit on the swelled Fe₃O₄@RF microspheres through a radial alignment (Figure 4c,d). After the mesostructure was fixed with cross-linked silica framework, the microspheres can be magnetically separated and washed with ethanol. During washing with ethanol (Figure 4e), the n-hexane “dissolved” in RF shell can be easily washed away because it is miscible with ethanol, which causes the RF shell to shrink inward due to the strong complexation between iron ions in Fe₃O₄ particles’ surface and phenolic hydroxyl groups from RF layer. However, the outer silica shell is much rigid and remains stable without significant shrinkage during the washing process, which generates the yolk–shell structured microspheres. This process is similar to the cell plasmolysis that cells
lose water in a hypertonic solution, leading to the separation of cytoplasm and cell wall and the formation of yolk–shell structure. Finally, the template CTAB molecules can be removed by ethanol extraction, and magnetic mesoporous silica microspheres with radially aligned mesopore channels can be obtained.

During the synthesis of yolk–shell microspheres, the higher reaction temperature in the range of 25–40 °C helps to expand the RF shell, and therefore leads to larger void sizes (470–670 nm). However, when the temperature reaches 45 °C, the liquid n-hexane “dissolved” in the RF shell tends to escape from the RF due to the decreased interaction between them at high temperatures, which can cause the expanded RF to deform under the shearing force of mechanical stirring, and finally leads to formation of fig-like YS-MMS-45 microspheres (Figure 3d, Figure S4). The swelling agent, a small portion of n-hexane, can escape from the RF shell when the reaction temperature (55–65 °C) is above 45 °C. It results in spherical swelled RF shell and finally a spherical void of about 660 nm (Figure 3e,f). The thicker RF is favorable for much expanded polymer shell upon interaction with n-hexane, and thus can generate YS-MMS microspheres with a large void (Figure S5).

Interestingly, this one-pot water/n-hexane mixture synthesis is applicable for construction of multicomponent yolk–shell microspheres with well-controlled compartmentalization of each component. For example, by introducing hydrophobic oleylamine capped Au nanoparticles (∼15 nm, Figure 5a) in the n-hexane solution containing TEOS for the synthesis of YS-MMS-35 microspheres, yolk–shell mesoporous silica microspheres (∼735 nm in diameter) with encapsulated Au nanoparticles inside the voids can be readily synthesized (Figure 5b,c). Strikingly, all Au nanoparticles are selectively and homogeneously deposited on the RF surface inside the hollow space of the obtained Au@YS-MMS-35 microspheres, and no free Au nanoparticles were observed outside the yolk–shell nanoparticles, indicating an effective encapsulation of guest nano-objects. To the best of our knowledge, such a facile introduction of functional nanoparticles (typical functional nanocatalysts) in the yolk–shell microspheres has not been reported before. High-angle annular dark field scanning transmission electron microscopic (HAADF-STEM) characterization of a single Au@YS-MMS-35 microsphere confirms the yolk–shell structure of the microspheres. The corresponding energy dispersive X-ray (EDX) mapping (Figure 6) of the elements clearly reveals that gold nanoparticles are the Au nanoparticles exclusively distributed in the voids, especially on the RF shell, of the yolk–shell microspheres. The Au content was measured to be 1.20 wt % by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Similarly, by replacing the hydrophobic Au NPs with the same amount of ∼12 nm sized UCNPs (NaGdF4: Yb, Er@NaGdF4) (Figure S13a), they were also wrapped into the middle hollow space by replacing Au NPs with UCNPs in the synthesis system of Au@YS-MMS-35 microspheres. UCNPs can be readily encapsulated in the middle voids, forming a multifunctional yolk–shell magnetic silica, denoted as UCNPs@YS-MMS-35 microspheres (Figure S13b,c). These results confirm the versatility of this plasmolysis-inspired nanoengineering method in producing various yolk–shell nanoparticles with different functional nanocomponents.

**Catalytic Hydrogenation of 4-Nitrophenol.** Yolk–shell magnetic mesoporous silica microspheres with Au nanoparticles encapsulated in the hollow space (Au@YS-MMS-35 microspheres) are ideal heterogeneous catalysts because of the following merits. First, the outer radially aligned and open mesopore channels can facilitate the diffusion and transport of reactants and product molecules. Second, the middle large hollow space provides a large space for reaction. Third, the well-dispersed catalytically active Au nanoparticles can move freely inside the hollow space upon immersion in liquid solutions. Fourth, the inner magnetic core enables the Au@YS-MMS-35 microspheres to be easily separated and recycled with applied magnetic fields. The catalytic performance of Au@YS-MMS-35 microspheres was investigated by using the solution-phase hydrogenation of 4-nitrophenol (4-NP) by NaBH4 to 4-aminophenol (4-AP) as a model reaction (Figure 7A). After adding NaBH4 into the 4-NP aqueous solution, the UV–vis absorption peak shifts from 319 to 401 nm due to the deprotonation of 4-NP (Figure 7B). No obvious change of UV–vis absorption spectra was observed after 24 h, implying that the hydrogenation reaction cannot happen in the absence of catalysts. The addition of Au@YS-MMS-35 microspheres into the reaction solution initiated the reduction immediately, and the intensity of absorption peak at 401 nm gradually decreased and eventually disappeared with the increase of time (Figure 7C). At the same time, an absorption peak around 300 nm appeared gradually due to the formation of 4-AP, and the color of the reaction system turned from light yellow to a colorless transparent solution, indicating the complete reduction of 4-NP. The linear relationship between log(C/C0) and
reaction time \( t \) is shown in Figure 7D. Herein, \( C_t \) and \( C_0 \) stand for the concentration of 4-NP at reaction time \( t \) and 0 min, which were measured by the relative intensity of absorbance \( A_t \) and \( A_0 \), respectively. After reaction for 20 min, the conversion of 4-NP reaches 98%. The catalytic reduction reaction matches the first-order kinetics and the rate constant \( k \) of the reaction and is calculated to be 0.14 min\(^{-1}\), reflecting a high catalytic reactivity by Au@YS-MMS-35 microsphere catalysts. Because the diffusion of reactants can influence the catalytic kinetics, a series of Au@YS-MMS microsphere with different mesoporous silica shell thickness from 90 to 160 nm, obtained by changing the TEOS amount from 2.0 to 3.5 mL in the synthesis system of Au@YS-MMS-35, were employed to investigate the catalytic performance. The catalysts with a thicker mesoporous shell were found to exhibit much slower catalytic kinetics (Figure S14), probably due to the longer diffusion distance for reactants from the solution to the hollow space of microspheres as compared to those that possess a thinner outer shell. By virtue of the magnetic responsiveness of the yolk–shell microspheres, the Au@YS-MMS-35 catalysts can be conveniently recycled by magnetic separation. The conversion of 4-NP can be maintained above 93%, and the morphology of the recycled catalyst remains unchanged (Figure S15) even after reuse 10 times (Figure 7e), indicating a high recycling stability of the catalysts due to the stably encapsulated Au nanoparticles.

**CONCLUSIONS**

A plasmolysis-inspired nanoengineering approach was developed for the tailor-made construction of uniform yolk–shell microspheres based on the interface coassembly of CTAB and silica oligomers on the solvent swelled \( \text{Fe}_3\text{O}_4@\text{RF} \) core, the subsequent RF shell shrinkage, and the separation of RF shell and mesoporous silica shell. The obtained microspheres have high surface areas (439 m\(^2\)/g), well-defined yolk–shell structure with perpendicular mesopores of 5.4 nm in the silica shell, a tunable hollow space size of 472–638 nm, and a phenolic resin protected superparamagnetic core. A plasmolysis-like formation mechanism was proposed for the yolk–shell microspheres. The low-cross-linking density of RF resin was found to be the key factor in the construction of hollow space because such RF shell is apt to be swelled by \( n \)-hexane. Through the plasmolysis-like synthesis, catalytically active Au nanoparticles (12 nm) were simultaneously encapsulated into the hollow space without blocking the mesopore channels. The obtained Au@YS-MMS microspheres exhibit an excellent performance in catalytic hydrogenation of 4-NP with a conversion of 98% in only 20 min. The yolk–shell magnetic catalysts were found to possess good catalytic stability with retained high conversion of above 93% even after running 10 times. Considering the mild and facile synthesis, it is believed that this novel plasmolysis-like strategy can be widely used to design various functional yolk–shell structured materials for applications in smart drug delivery system, nanocatalysts in tandem reactions, and so on.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b09055.

**S Supporting Information**

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**Notes**

The authors declare no competing financial interest.

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