Silica Nanostructures

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Formation of Hollow Silica Colloids through a Spontaneous Dissolution–Regrowth Process**

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The chemistry of silica in aqueous solution remains an actively investigated topic despite vigorous research for over a century because of its relevance to various fields such as biology, geology, and health science, and to many technical applications including water purification, adsorbents, separation, optical devices, and catalysis.[1–3] The existence of a large number of silicate species and their rich chemical interactions makes the dissolution and growth of silica challenging to study. However, this complexity also provides enormous opportunities for the development of materials with new structures and functionalities. For example, systematic investigation of the dissolution and formation of silica nanoparticles has made it possible to control the nucleation and growth, and subsequently the crystal size and shape, of zeolite materials.[4–6] Herein, we report that amorphous silica colloids, when dispersed in an aqueous solution of $NaBH_4$, undergo a spontaneous morphology change from solid to hollow spheres. Concurrent but separate core-dissolution and shell-growth processes appear to be responsible to the formation of the hollow structures. Besides the interesting fundamental aspects of this spontaneous process, this work also provides an effective self-templated route for the preparation of hollow silica nanostructures, which may find immediate applications in fields such as catalysis and drug delivery.[7–12] Since silica can coat many nanostructures through simple sol–gel processes, our discovery also allows convenient transformation of core–shell particles into yolk–shell structures, which are promising for use as nanoscale reactors and controlled-release vehicles. Compared to widely adopted methods using polymer beads and micelle and emulsion droplets as sacrificial templates,[13–20] this process is very simple, effective, scalable, and able to produce highly monodisperse samples.

The formation of hollow silica spheres proceeds spontaneously when amorphous silica colloids are mixed with $NaBH_4$ in aqueous solution (Figure 1 a). Monodisperse amorphous silica colloids with controllable sizes (ca. 100–800 nm) were first prepared using the well-known Stöber process; a typical transmission electron microscopy (TEM) image of the products is shown in Figure 1 b. After mixing with $NaBH_4$ at appropriate concentration at 51 °C for 6 h, all solid SiO_2 spheres were converted into well-defined hollow nanostructures (Figure 1 c). In this process, poly(vinylpyrrolidone) (PVP) is usually added in the reaction system as a surfactant to prevent the aggregation of hollow spheres. The rate of solid-to-hollow conversion was found to increase steeply with reaction temperature. For example, the conversion was completed within 5 h at 56 °C and 3 h at 61 °C. A higher reaction temperature also increased the roughness of the silica shells: the shells obtained at 51 °C were relatively smooth, while those at 56 °C showed clearly increased grain size and discernable pores (Figure 1 d). The ability to tune shell porosity by simply controlling the reaction temperature is promising for applications requiring size-selective transportation of molecules through the shell.

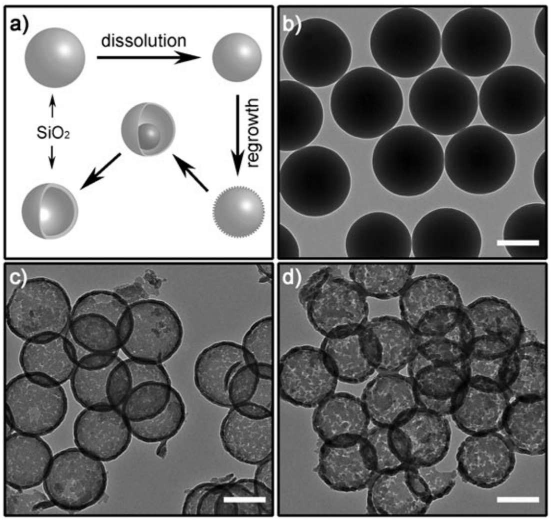

Figure 1. a) Schematic illustration of the spontaneous formation of hollow SiO_2 spheres. b) TEM images of as-prepared SiO_2 spheres. c,d) Samples after reacting with 0.06 $g\,mL^{-1}$ $NaBH_4$ for 6 h at 51 °C (c), and 5 h at 56 °C (d). Scale bars are 200 nm.

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The solid-to-hollow transformation also occurs at room temperature without the involvement of surfactant PVP. In this case, the reaction is much slower, and the conversion is typically completed within ten days, thus allowing for careful monitoring of the hollowing process. Figure 2 shows a complete cycle of morphology change of silica colloids reacting with $NaBH_4$ at room temperature. Gradual dissolution of the spheres was observed during the first two days of reaction of $0.03\,g\,mL^{-1}$ colloid with $0.06\,g\,mL^{-1}$ $NaBH_4$ at room temperature. Compared to the as-prepared sample, the colloidal particles remained uniform and spherical with only a change in average diameter from approximately 400 to 292 nm (Figure 2a,b). Immersion of the sample in $NaBH_4$ solution for an additional day further decreased the average size of the spheres. Interestingly, a very thin shell can be observed around each sphere at this stage. In TEM images, the shells appear to have collapsed onto the carbon grid, presumably during drying, thus suggesting that they are very soft at this stage of reaction (Figure 2c). The average shell diameter is estimated from images to be approximately 360 nm. The actual value adopted in solution is likely to be somewhat smaller, as it is reasonable to guess that the soft shells flatten partially against the TEM grid after drying. Continued reaction further shrunk the core spheres to approximately 147 nm on day five and to about 127 nm on day six, while the thickness of the shells increased considerably such that they were rigid enough to maintain the three-dimensional spherical structure after drying (Figure 2d,e). It appears that the shells were also rigid enough that the measured diameters should correspond closely to the values in as-prepared solution; this accounts for the apparent small decrease in shell diameter in comparison to the softer shells of Figure 2c. The silica cores eventually disappeared after about ten days of reaction, leaving behind hollow shells with perfectly round shapes and an average diameter of approximately 353 nm (Figure 2f). Longer reaction times (e.g. 14 days) produced no observable changes in the morphology and thickness of the hollow structures.

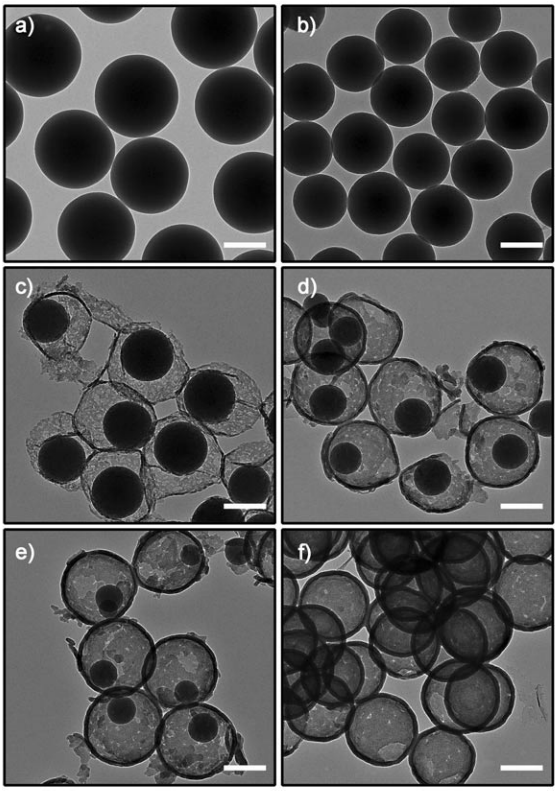

Figure 2. TEM images of a) as-prepared SiO_2 spheres, and samples after reacting with $0.06\,g\,mL^{-1}$ $NaBH_4$ at room temperature for b) 2 days, c) 3 days, d) 5 days, e) 6 days, and f) 10 days. Scale bars are 200 nm.

The composition and elemental distribution of the hollow structures was mapped through energy dispersive X-ray spectroscopy (EDS) by displaying the integrated intensity of silicon and oxygen signals as a function of the beam position when operating the transmission electron microscope in the scanning mode (STEM). Mapping of elements including silicon, oxygen, boron, and sodium against hollow spheres with and without cores (Figure 2d,f) indicates that both samples are composed of Si and O only (Figure 3a–d). The quantity of B is below the instrument detection limit (atomic ratio B:Si < 0.02) and Na concentration is negligible (atomic ratio Na:Si ≈ 0.02). The strong signal obtained from the edges of the shells suggests their hollow structure, confirming contrast-based TEM observations. As shown in Figure 3a,b, the shell and the remaining core display similar signal responses at different mapping energies, suggesting their identical compositions. The integrated EDS spectrum of a single hollow sphere (Figure 3e) further confirms Si and O as the only components, and the calculated atomic ratio of Si to O is 0.5 ± 0.027. The strong signal of carbon and weak signals

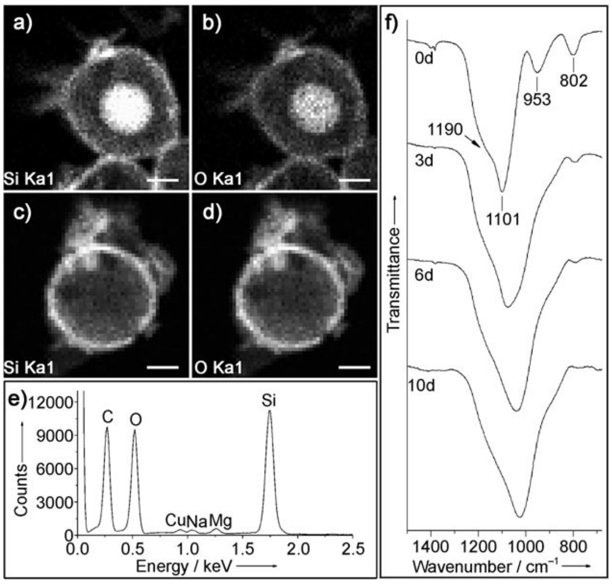

Figure 3. a–d) Mapping of Si and O in core–shell (a, b) and hollow SiO_2 structures (c, d) by EDS. e) EDS spectrum of hollow SiO_2 structures. f) FTIR spectra of as-prepared SiO_2 spheres (0d), and samples after reacting with $0.06\,g\,mL^{-1}$ $NaBH_4$ at room temperature for 3 days, 6 days, and 10 days. Scale bars are 100 nm.

of copper, sodium, and magnesium originate from the supporting carbon film and the copper grid. On the basis of the above measurements, we can conclude that the solid SiO_2 spheres have been transformed into hollow shells with the same chemical composition. In addition, X-ray diffraction (XRD), high-resolution TEM (HRTEM), and electron diffraction measurements all confirm that both solid and hollow spheres are amorphous.

FTIR spectroscopy was used to characterize the structural change of SiO_2 spheres upon the reaction with $NaBH_4$ solution. Weak absorption bands attributed to the C–H bending vibration in unhydrolyzed OEt groups are observed between 1350 and 1500 cm^{-1} for as-synthesized solid colloids (Figure 3 f, 0d). Bands located at 1190, 1101, 953, and 802 cm^{-1} are associated with the longitudinal-optical (LO) mode and transverse-optical (TO) mode of the Si-O-Si asymmetric bond stretching vibration, the Si–OH stretching vibration, and the network Si-O-Si symmetric bond stretching vibration, respectively.[21] After exposing silica spheres to $NaBH_4$ solutions and with prolonged reaction time, the intensity of the bands related to C–H bending vibration decreases gradually and finally becomes indistinguishable, thus indicating that the residual OEt groups in as-prepared solid SiO_2 spheres have been completely hydrolyzed during the reaction. The TO mode of the Si-O-Si asymmetric stretching vibration band shows a distinct red shift from 1101 to 1026 cm^{-1} during the solid-to-hollow conversion, while the band corresponding to the LO mode does not change significantly. Moreover, the Si-O-Si symmetric stretching vibration band at 802 cm^{-1} also shifts to 783 cm^{-1} and gradually decreases in intensity. The red shift of the Si-O-Si bands suggests a more open SiO_2 network structure with lower internal stress in the newly formed silica shells.[21,22] The Si–OH stretching vibration band at 953 cm^{-1} cannot be easily discerned because of its overlap with the red-shifted Si-O-Si asymmetric stretching vibration band.

The concentration of $NaBH_4$ was found to determine the formation of SiO_2 hollow structures. At room temperature, we varied the concentration of $NaBH_4$ over the range 0.03–0.06 $g\,mL^{-1}$ while keeping the concentration of silica colloids fixed at 0.03 $g\,mL^{-1}$. At the low $NaBH_4$ concentration of 0.03 $g\,mL^{-1}$, the SiO_2 spheres were still solid after six days, but their average diameter was slightly reduced by approximately 9 nm from the original value of approximately 416 nm (Figure 4 a). With the concentration of $NaBH_4$ increased to 0.045 $g\,mL^{-1}$, a thin shell formed on the surface of SiO_2 cores after six days (Figure 4 b). The outer part of the cores shows apparently reduced contrast, thus suggesting a lower density material. With the $NaBH_4$ concentration further increased to 0.05 and 0.06 $g\,mL^{-1}$, the diameters of the core/shell were decreased to approximately 230/393 nm and 127/354 nm, respectively, after six days, and the core–shell structure became more regular and distinguishable (Figure 4 c, d). We noticed that all the silica colloids eventually transformed into hollow structures if the concentration of $NaBH_4$ was kept above 0.045 $g\,mL^{-1}$ and the reaction proceeded for long enough time (see the Supporting Information). Figure 4 e, f summarizes the change in the diameters of cores and shells as a function of the reaction time at various concentrations. At a low $NaBH_4$ concentration of 0.03 $g\,mL^{-1}$, the core diameter showed no obvious change with the reaction time except a 12-nm reduction after three days. At $NaBH_4$ concentrations at or above 0.045 $g\,mL^{-1}$, the core diameter decreased almost linearly with the reaction time with a higher rate at higher concentration. It took approximately 21 days to fully transform original solid spheres to hollow shells in a 0.045 $g\,mL^{-1}$ $NaBH_4$ solution, and only ten days in a 0.06 $g\,mL^{-1}$ solution. For samples at all $NaBH_4$ concentrations, there was no apparent shell growth in the first two days so that the core and shell share the same diameter, which shrunk rapidly. After two days, thin shells started to form on the surfaces of the core particles so that the values for outer diameters increased on day three and then remained almost constant as the reaction time increased. For samples with $NaBH_4$ concentrations above 0.03 $g\,mL^{-1}$, the shell thickness increased gradually as the cores dissolved slowly. Furthermore, smaller shells were obtained at higher $NaBH_4$ concentrations, in agreement with the rapid dissolution of silica spheres in the early stage of the reaction under such conditions.

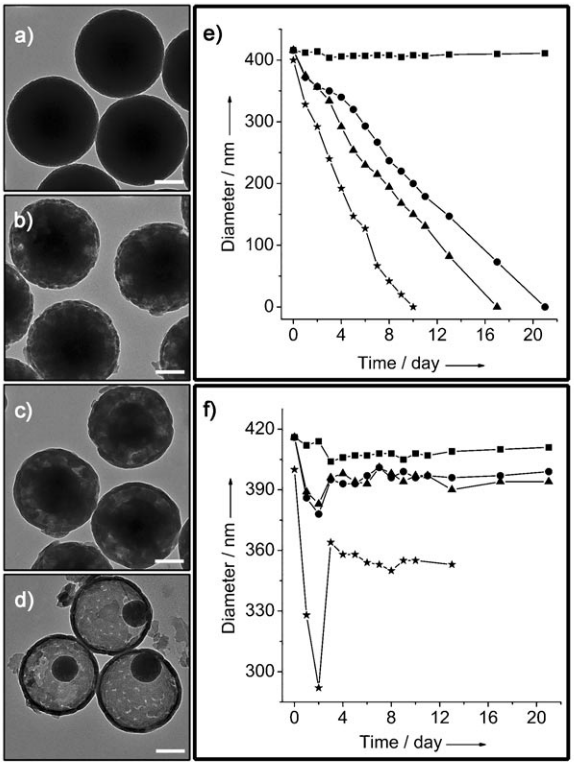

Figure 4. a–d) TEM images of SiO_2 spheres reacted with a) 0.03 b) 0.045, c) 0.05, and d) 0.06 $g\,mL^{-1}$ $NaBH_4$ at room temperature for 6 days. e,f) Dependence of the diameter of SiO_2 core (e) and shell (f) on time after reacting the silica spheres with various concentrations of $NaBH_4$ (■ 0.03 $g\,mL^{-1}$, ● 0.045 $g\,mL^{-1}$, ▲ 0.05 $g\,mL^{-1}$, ⋆ 0.06 $g\,mL^{-1}$).

The above observations allow us to partially conceive the mechanism of the transformation from solid silica spheres to hollow structures, although a complete understanding is not possible at this point owing to the complex nature of silicate species involved in the reaction. From our observations, it is clear that dissolution and redeposition of silica proceed simultaneously during the reaction to yield the hollow shells:

the dissolution process proceeds at an appreciable rate from the beginning of reaction until the consumption of the cores, while silica redeposition, in comparison, appears to have a delayed onset. It is well known that the reaction between $NaBH_4$ and water slowly produces H_2 and sodium metaborate $NaBO_2$. At the beginning of the reaction, a high pH value (greater than 11.0) is quickly established (see the Supporting Information) so that the amorphous surface silica is destroyed by dissociating Si–O bonds and then dissolved into solution in the form of monosilicate and polysilicate species with various compositions.[1,23–26] This procedure is similar to the dissolution of silica in aqueous NaOH solution, in which no hollow SiO_2 nanostructures but only solid spheres with reduced sizes can be found during the dissolution process.[25] Regrowth of silica only occurs after reacting colloids in $NaBH_4$ solution for about two days, leading to the formation of thin shells with diameters slightly larger than those of the shrinking cores. The $NaBO_2$ resulting from gradual decomposition of $NaBH_4$ seems to contribute to the redeposition of a silica layer. When pure $NaBO_2 \cdot 4H_2O$ with a boron concentration equivalent to 0.06 $g\,mL^{-1}$ $NaBH_4$ was mixed with silica colloids and aged for two days, many sheet-like thin fragments in addition to the shrunken colloids can be found in the products (see the Supporting Information). With the reaction time prolonged to ten days, some hollow SiO_2 structures similar to those obtained from the reaction with $NaBH_4$ can be found. On the basis of the above observations, we can propose the following possible pathway for the solid-to-hollow transformation (Figure 1 a). The high pH value of $NaBH_4$ solution may simply dissolve the surface layer of colloids in the initial stage. Monosilicate and polysilicate species are released into the solution, which eventually becomes supersaturated. At the same time, the concentration of $NaBO_2$ also increases gradually as a result of the decomposition of $NaBH_4$, thus causing the silicate species to precipitate and redeposit on the core surfaces. In this case, the deposition of the silicate species on the surface of the remaining silica spheres as the result of heterogeneous nucleation is energetically favored over the formation of new solid particles through the homogeneous nucleation. The further growth of shells and dissolution of cores may be facilitated through Ostwald ripening.[27] Obviously, the unique properties of $NaBH_4$ (high pH and slow decomposition) provide the optimal conditions for the growth of hollow shells. It is expected, however, that such reaction conditions can be mimicked by using NaOH to achieve a high pH value for silica dissolution and a later gradual addition of $NaBO_2$ for regrowth to produce hollow silica shells. Work in this direction is currently in progress.

The simple process reported herein can be conveniently used to produce hollow nanostructures not only from pure solid SiO_2 colloids but also from various silica-coated composite particles with various shapes. Silica is well-known for its ability to coat many colloidal structures to form core–shell structures.[28–31] We further demonstrate that such structures can be converted into hollow silica spheres containing movable cores.[32] For example, monodisperse Au@SiO_2 core–shell particles can be converted into yolk–shell nanostructures by mixing them with $NaBH_4$ (Figure 5 a). The gold nanoparticles are no longer located at the center of the hollow silica spheres because of the consumption of the original silica shell and its replacement with a void surrounded by a thinner silica shell. For applications in catalysis, the individual encapsulation of metallic nanocatalysts within a porous shell should significantly improve both activity and

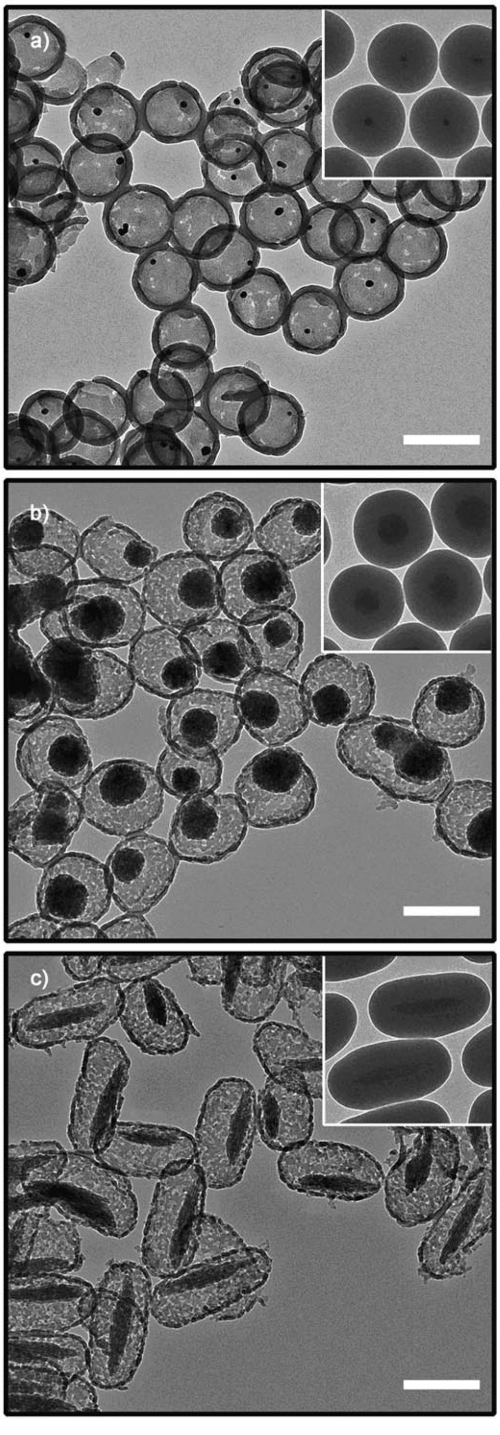

Figure 5. TEM images of yolk–shell structures produced by reacting core–shell a) Au@SiO_2 spheres, b) Fe_3O_4@SiO_2 spheres, and c) α-Fe_2O_3@SiO_2 ellipsoids with $NaBH_4$ solution at 51 °C for 10 h, 6 h, and 10 h, respectively. The corresponding initial core–shell particles are shown in the insets. Scale bars are 200 nm.

selectivity by minimizing catalyst sintering and secondary reactions of the products.[32]

We have also demonstrated that superparamagnetic Fe_3O_4 colloids recently developed in our group can be coated with a layer of silica and then transformed into yolk–shell structures with Fe_3O_4 particles inside hollow silica shells (Figure 5b).[33] Such hollow composite structures can be effectively manipulated using external magnetic fields. The combination of strong magnetic response of Fe_3O_4 colloids and the hollow and porous structure of silica shells makes these composite materials ideal candidates for biomedical applications such as targeted drug delivery.[34–36]

The spontaneous growth of silica shells occurs not only for spherical particles but also for nonspherical colloids. As an example, we have synthesized ellipsoidal α-Fe_2O_3@SiO_2 core–shell particles[37–39] and successfully converted them into yolk–shell type structures by treating with $NaBH_4$ solution. The elliptical shape of the composite colloids was retained for both the α-Fe_2O_3 core and the silica shell after the conversion (Figure 5c), again supporting the proposed growth mechanism. Such hollow composite ellipsoids might find applications in fields such as optical rotational diffusion studies.[40]

In summary, we report the spontaneous transformation of silica colloids from solid spheres to hollow structures with high morphological fidelity in aqueous solutions of $NaBH_4$. After the transformation, the hollow structures are still composed of SiO_2, but they possess a more open silica network then the original solid spheres. The hollowing process has been found to be general to silica colloids of various sizes and shapes. The porosity of the shells can be conveniently tuned by the reaction temperature, thus providing a possibility to control the diffusion of molecules through the shell according to their sizes. The high pH value and gradual decomposition of $NaBH_4$ facilitate the formation of hollow structures first by partial dissolution of the silica cores and then by redeposition of the silicate species back onto the core surfaces to form shells. While more work is required to fully reveal the details of the mechanism behind this spontaneous process, this work provides an extremely simple, mild, and effective recipe to transform silica or silica-coated composite materials into hollow structures with various functions.

Experimental Section

Monodisperse SiO_2 spheres were prepared using a modification of the procedure originally described by Stöber et al.[41–43] In a typical process, SiO_2 spheres (0.3 g) were first dispersed in aqueous PVP (10 mL, 2.91%). $NaBH_4$ (0.6 g) was added to the system and the mixture was heated at 51, 56, or 61 °C for 6, 5, or 3 h, respectively. Aliquots (0.1 mL) were extracted and cleaned several times by centrifugation and water redispersion and finally dispersed in water or dried into powders for various characterizations. The reaction can also occur at room temperature without the presence of PVP under otherwise similar conditions. The procedures for the synthesis of Au@SiO_2, Fe_3O_4@SiO_2, and α-Fe_2O_3@SiO_2 yolk-shell structures are provided in the Supporting Information.

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