

Synthesis of half-sphere/half-funnel shaped silica structures by reagent localization and the role of water in shape control

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Abstract: Shape control of silica structures is demonstrated by localization of the reagents. A uniform dispersion of reagents provided straight silica rods, while localization of the reagents in the emulsion droplet periphery provided a new type of structure—half-sphere/half-funnel. The effect of water concentration appeared to be related to the ease of diffusion of the silica precursor inside the emulsion droplet (i.e., the higher the water concentration, the lower the silica precursor diffusion).

The shape control of colloidal structures is an intriguing research area. Shape control by several strategies, including lithography, hard and soft templates, vapor–liquid–solid method, and manipulation of reaction conditions have been explored.^[1] Many of these shape control strategies have been employed for the synthesis of nanostructures, especially of noble metals.^[1,2] However, there have been only a few efforts to control the shapes of microstructures.^[3,4] Recently, Zhang's and Imhof's groups demonstrated the use of a polyvinylpyrrolidone-pentanol emulsion droplet system for the directional growth of silica microstructures (silica rods).^[4] Rod shape has been further modified by using strategies such as temperature- or alcohol-induced change in the emulsion droplet size and use of metal oxide nanoparticles.^[5–7] Similarly, cone shaped rods have been synthesized by etching the straight rods.^[8] Hydrophobic rods and nanowires have also been synthesized by depositing a layer of organosilanes on the growing rods.^[9] By combining the reaction pH with temperature manipulation, bent rods have also been synthesized.^[10] Similarly, complex hierarchical structures have been made by growing the rods on preformed particles such as silica, titania, and gold.^[11] Metal particles such as gold and silver have also been deposited on the preformed silica rods.^[12] Magnetic Janus rods have also been reported.^[13] The rods have been also self-assembled and grown on porous composites.^[14,15] By exploiting short-range order between silica rods, thermoreversible gels have also been synthesized.^[16]

However, a few efforts have been made to understand the underlying mechanisms related to the effects of different reagents on rod growth.^[5,6] Similarly, there are no reports in

the literature about shape control and formation of structures of increased complexity by localizing the reagents in the emulsion droplet.

In the present work: (1) We demonstrated an unprecedented phenomenon—the site-specific localization of reagents in the emulsion droplets—and employed this localization to induce anisotropic deposition of silica, which in turn led to the growth of structures of a completely new shape—half-sphere/half-funnel. Such structures were hard to achieve by previously reported strategies. (2) We investigated the role of ammonium hydroxide (NH₄OH) and water in rod growth and tried to understand the underlying mechanisms.

Polyvinylpyrrolidone (PVP; 0.5 g) dissolved in pentanol (5 mL) in the presence of sodium citrate (50 μL, 0.18 M) and water (140 μL) makes an emulsion droplet system. Addition of ammonium hydroxide (28–30% NH₃ in water, NH₄OH; 100 μL) solution followed by the addition of tetraethyl orthosilicate (TEOS; 50 μL) results in straight silica rods (Figure S1, supporting information). The straight rods resulted only when there was a uniform dispersion of reagents in the emulsion droplet. We assume that the uniform dispersion of reagents results in the uniform hydrolysis of the TEOS that leads to uniform deposition of silica on the rod initiation point (nucleus). However, when the reagents are localized in different parts of the emulsion droplet, silica deposition can be localized to specific areas of the emulsion droplet, which can lead to exotic new structures. Using this reagent localization hypothesis, we demonstrated that non-uniform distribution of water in the emulsion droplet led to unprecedented half-sphere/half-funnel shaped structures (Figure 1). Figure 1a shows the growth schematic and Figure 1b shows the scanning electron microscope (SEM) images of half-sphere/half-funnel shaped structures obtained when water was localized in the emulsion droplet periphery.

To localize the water at the periphery, water was introduced a few hours after all the other reagents were added. In the emulsion droplet, some water was present from the citrate solution and the aqueous NH₄OH solution (30% NH₃ and 70% water), which helped in partial hydrolysis of TEOS molecules and thus their penetration in the emulsion droplet. Therefore, TEOS molecules had already entered the emulsion droplet before water was added. From Figure 2c it appears that because of the high concentration of NH₄OH in the emulsion droplet, TEOS molecules get hydrolysed and crosslinked with each other as soon as they enter the droplet. This hindered further penetration of TEOS molecules into the center of emulsion droplet and resulted in a hollow spherical structure. On addition, water reaches the peripheral area first where the already partially hydrolysed TEOS molecules are present;

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therefore, TEOS hydrolysis and the condensation rate at the periphery accelerates, and the directional growth of hollow structures starts, which finally leads to the half-sphere/half-funnel shaped structures of about 1 μm size (Figure 1a: proposed schematic of structure growth and Figure 1b: SEM image of the structures). Another possible explanation for funnel growth upon water addition is that the water surrounding the spheres causes an osmotic effect and the shell of the hollow spheres break at one point and material (sodium citrate and NH_4OH) bursts out of the spheres and TEOS starts depositing at the borders of this burst and finally a growth of the funnel shaped structure starts. Or citrate and Na diffuse out of the porous shell and funnel growth starts at one point as it occurs in smooth rods. In some cases, we observed structures with two spheres and one funnel (Figure 1b). We assume that before the growth started, two emulsion droplets may have joined together.

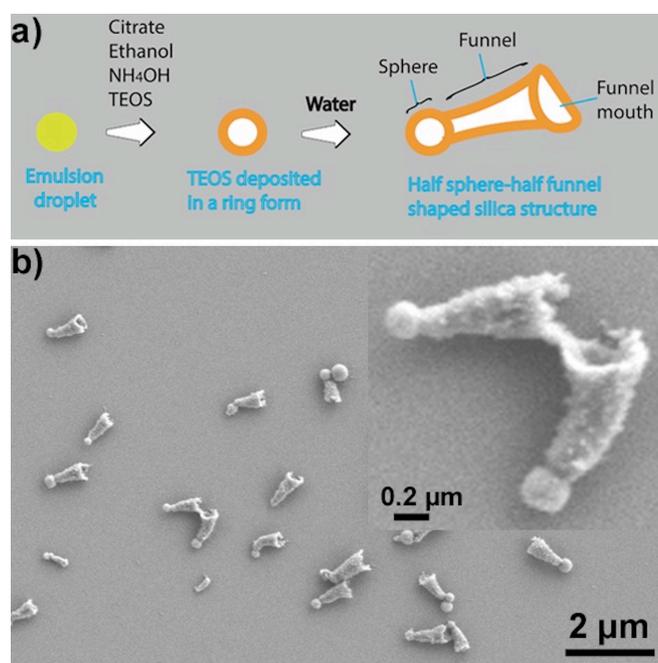


Figure 1. (a) Schematic demonstrating the growth of half-sphere/half-funnel shaped structures resulting from initial TEOS (then water) localization in the periphery of the emulsion droplet. (b) Low-magnification SEM image of half-sphere/half-funnel shaped structures and high magnification image of the structures (Inset).

To determine the crucial requirement for the growth of such structures, we added all reagents (citrate, ethanol, NH_4OH) except TEOS and water. After 3 hours, we added the TEOS and water together and allowed the mixture to react overnight. This resulted in straight rods similar to those obtained when all reagents were added together. The half-sphere/half-funnel shaped structures only grew when

TEOS was added with other reagents and water was added after a few hours.

Figure 2a (i) and (ii) are the scanning transmission electron microscope (STEM) image and energy dispersive X-ray spectroscopy (EDS) map of "Si" present in the half sphere- half funnel shaped structures. Figure 2a (i) and (ii) show that the structures are made of a hollow spherical structure joined with a hollow funnel shaped structure. Figure 2a (iii) shows the EDS map of "Na" present in the sodium citrate of the emulsion droplet. The presence of "Na" mainly (though some Na is distributed in the whole body of funnel) at the center of funnel mouth revealed that the emulsion droplet was attached at the funnel mouth, indicating that same directional growth occurred as was observed in straight silica rods.⁴ This also confirmed that in these half-sphere/half-funnel shaped structures, the spherical part was formed before the funnel part started growing.

Figure 2b shows the STEM image and EDS maps taken after 10 min. when an aqueous solution (140 μL) of potassium chloride (KCl; 0.1M) instead of pure water was added with all other reagents (citrate, ethanol, ammonium hydroxide, and TEOS). We added KCl to find out how the water is dispersed in the emulsion droplet by EDS mapping of K^+ ions. Figure 2b (i) and (ii) show that TEOS (Si) is uniformly dispersed in the emulsion droplet. Figure 2b (ii) further shows that a silica nucleus that grows into straight silica rods is formed on one side of the emulsion droplet. Figure 2b (iii) shows that K^+ ions (i.e., water) get uniformly dispersed if added in the beginning along with other reagents. Figure 2c shows the STEM image and EDS maps taken 10 min. after addition of water containing KCl to the sample in which all of the other reagents (citrate, ethanol, NH_4OH , and TEOS) had been combined 3 hours earlier.

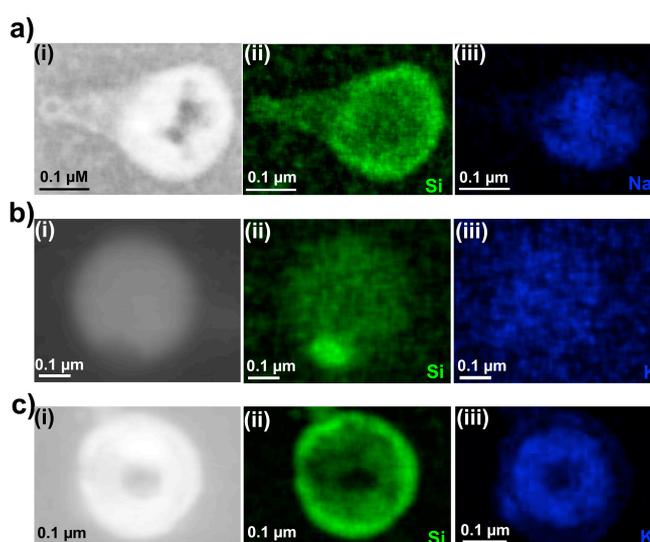


Figure 2. STEM and EDS images showing the emulsion droplet position, the hollow nature of structures, and the difference in initial nucleation point. (a) STEM image showing a hollow half-sphere/half-funnel structure (i), EDS map showing the location of "Si" of silica (ii), and EDS map showing the position of "Na" of citrate of the emulsion droplet. (b) When all reagents are added together. STEM image of emulsion droplet (i), EDS map showing the uniform distribution of "Si" of silica and nucleation of silica rod in the emulsion droplet corner (ii), and EDS map showing the uniform distribution of "K" present in the aqueous KCl solution. (c) When water is added after 3 hours and images are taken within couple of minutes of water addition. STEM image of emulsion droplet after addition of aqueous KCl solution (i), EDS map showing the peripheral localization of "Si" of silica (ii), and EDS map showing the localized distribution of "K" present in aqueous KCl solution (iii).

Figures 2c (i and ii) show that silica gets deposited in a ring-shaped structure. Similarly, STEM images after 3 hours of growth in the absence of water showed that the ring structures get formed even when no water was added (Figure S2, supporting information). This ring formation was quite different from the solid silica nucleus formation in one corner of the emulsion droplet [Figure 2b (ii)] when water is uniformly dispersed in the emulsion droplet. This difference in initial nucleus shape resulted from the high concentration of NH_4OH in the emulsion droplet. The increased NH_4OH concentration resulted due to lack of any dilution caused by water. Figure 2c (iii) shows that when an aqueous KCl solution (instead of pure water) is added after 3 hours, it did not disperse uniformly in the emulsion droplet; it was confined at the periphery.

Additionally, we investigated the effect of water and NH_4OH concentrations on the shape of silica structures (rods), and tried to correlate their effect to the underlying mechanism. We worked on three hypotheses to understand what controls the shape of structures when all the reagents are added together and only concentrations are changed: (1) hydrolysis rate (2) emulsion droplet size, and (3) diffusion of TEOS in emulsion droplet. To test hypothesis 1, we investigated the effect of low NH_4OH concentration. In a 5 mL PVP-pentanol solution, addition of 5, 50, 65, and 100 μL of the NH_4OH solution resulted in spherical (no directional growth), crooked, straight thin, and straight thick structures, respectively (Figure 3a, Figure S3 of supporting information). As NH_4OH is known for its catalytic role in increasing the hydrolysis rate of TEOS, we assumed that a very low hydrolysis rate led to simple spherical deposition of silica on the emulsion droplet, a moderate hydrolysis rate led to a half directional and half-spherical growth (i.e., a transition point), and a high hydrolysis rate led to a complete directional growth.

In order to test this assumption, we kept the NH_4OH amount low (50 μL instead of 100 μL) and added an additional amount of water (190 μL instead of 140 μL). Instead of crooked structures, straight rods were obtained (Figure S4, supporting information). This indicated that the decrease in NH_4OH concentration decreased the TEOS hydrolysis rate and led to crooked structures, while addition of water increased the hydrolysis rate and thus

compensated for the loss resulting from decreased NH_4OH concentration. We interpreted that if a similar level of hydrolysis is maintained, similar structures can be obtained by using different combinations of reagents, and that it is the hydrolysis rate that determines the anisotropic or isotropic growth of structures. However, at a low NH_4OH concentration, an increase in hydrolysis rate by high temperature did not make straight rods (Figure S5, supporting information). Similarly, a low temperature should have resulted in crooked structures, but instead it resulted in thick rods (Figure S6, supporting information). This ruled out the assumption that the TEOS hydrolysis rate was controlling the shape of silica structures when NH_4OH concentration was changed.

Similarly, a small decrease in the amount of NH_4OH (65 μL instead of 100 μL) resulted in long-thin rods. Addition of 35 μL water while the thin rods were growing resulted in a corresponding increase in rod thickness [from ≈ 240 to ≈ 320 nm; $\approx 33\%$ increase; Figure 3b (i) and (ii)]. There were two

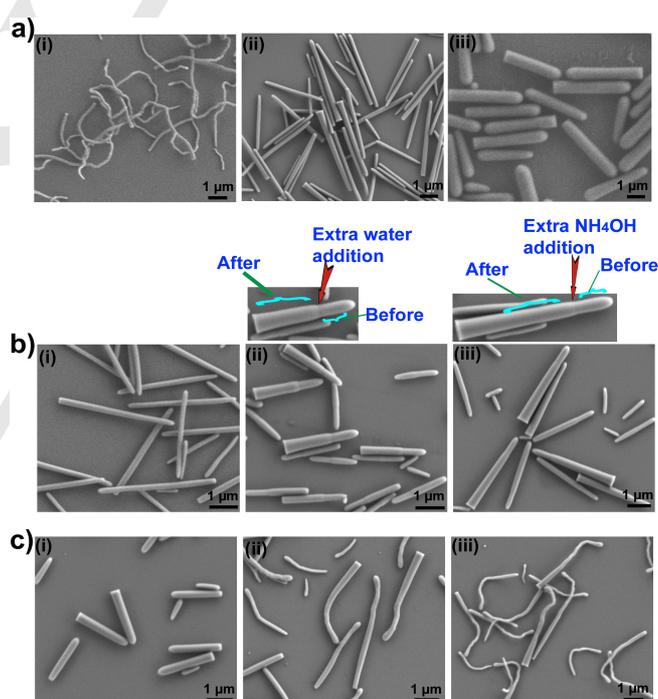


Figure 3. The role of water and NH_4OH in controlling the silica structure shape. (a) The effect of NH_4OH concentration on the structure shape. Crooked structures formed when 50 μL of NH_4OH was added (i); thin rods formed when 65 μL of NH_4OH was added (ii); and thick rods formed when 100 μL of NH_4OH was added (iii). (b) The effect of additional water and NH_4OH on the rods growing at low concentration of NH_4OH . Thin rods formed when 65 μL of NH_4OH was added (i); rods become thick when 35 μL of water was added to the growing rods after 3 hours (ii); rods become less thick when 35 μL of NH_4OH was added to the growing rods after 3 hours (iii). (c) The effect of water concentration on the structure shape. Thick rods formed when 140 μL of water was added (i); less crooked rods formed when 90 μL of water was added (ii); highly crooked rods formed when 60 μL of water was added (iii). Note: Preparation conditions for all the above structures are provided in the supporting information.

assumptions, the first, a decrease in NH_4OH resulted in a decrease in TEOS hydrolysis, and therefore further condensation only occurred on the previously formed silica, leading to thin rods. Deposition of TEOS molecules preferably occurs on the already-deposited silica because hydrolysis of ethoxy groups present on deposited silica occurs faster than the hydrolysis of those present on free TEOS molecules. When concentration is high, hydrolysis rate is high, and initial deposition can occur on a wide area due to the presence of a sufficient number of hydrolyzed TEOS molecules. Addition of extra water increased the hydrolysis rate (compensated for the loss that resulted from the reduced NH_4OH concentration) and increased the rod thickness. If increased hydrolysis rate was the cause of this enhanced rod thickness, then an increase in temperature should also have increased the rod thickness. However, an increase in temperature always resulted in crooked structures. Therefore, the change in hydrolysis rate does not seem to be a plausible cause for the increased rod thickness, further indicating that the hydrolysis rate is not affecting the rod thickness.

The second assumption was that a decrease in NH_4OH resulted in a corresponding decrease in water content because NH_3 is only 30% and 70% is water in NH_4OH solution. To investigate this assumption, we made samples by keeping the standard amount of NH_4OH while decreasing the amount of water. The SEM images showed that a decrease in water resulted in crooked rods even though the NH_4OH concentration was constant (Figure 3c). The rods became more crooked with decreasing water content.

To further confirm that it is the water content inside the ammonia solution rather than the NH_4OH or hydrolysis rate that changes the rod thickness, we added 35 μL extra NH_4OH instead of extra water to a sample in which rods were growing at low (65 μL) concentration of NH_4OH for 3 hours. Only a slight increase in rod thickness occurred [≈ 270 nm to ≈ 325 nm; $\approx 20\%$ increase; Figure 3b (iii)]. The increase in thickness was less than that obtained with the addition of the same amount of pure water [Figure 3b (ii)] because only 70% of water is added to the system (NH_4OH : is 30% NH_3 and 70% water). This further indicated that it is not the NH_4OH or the hydrolysis rate, but the water content in the NH_4OH that controls the rod thickness.

These experiments indicated that effective water concentration is the most crucial element affecting the final shape of structures. We assumed that this effect of water concentration results from its indirect control of the emulsion droplet size (more water yields a larger emulsion droplet). Therefore, the underlying controlling factor is the initial emulsion droplet size—a very small emulsion droplet results in no rod growth, an intermediate size droplet results in crooked growth, and a large droplet results in straight rod growth.

To determine whether such rod growth is controlled by emulsion droplet size (hypothesis 2), we checked the direct effect of water addition on the emulsion droplet size. A solution of PVP-pentanol and sodium citrate was somewhat turbid; a clear solution resulted when water was added to

the solution. (Figure 4a). This indicated that water reduces the size of the emulsion droplets. To further confirm the effect of water content on the emulsion droplet size, we measured (using TEM imaging) the emulsion droplet size at different concentrations of water while keeping the NH_4OH concentration constant. For example, at a constant NH_4OH amount (100 μL), additions of 140 μL , 90 μL , and 40 μL of water resulted in emulsion droplets of 208 ± 91 , 289 ± 81 , and 352 ± 189 nm, respectively (Figure 4b). These measurements revealed that an increase in water content results in a corresponding decrease in the emulsion droplet size. However, this was opposite to our assumption that an increase in effective water concentration should increase the size of emulsion droplets.

The hypothesis 3 was that the presence of water in the emulsion droplet reduces the diffusion of TEOS molecules further inside the emulsion droplet, and thus molecules start depositing on the edges in addition to the central part. Therefore, we assumed that this hindrance to the diffusion of TEOS molecules results in a corresponding increase in the silica rod thickness. To check this, we made two emulsion systems, one with 40 μL and other with 140 μL of water, while keeping the other reagents as in standard conditions.

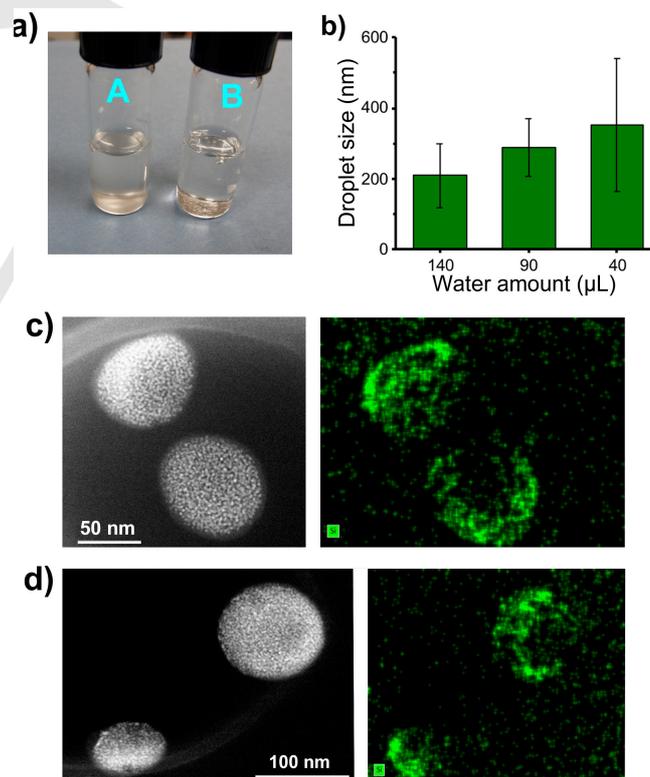


Figure 4. The effect of water amount on the droplet size and TEOS diffusion inside the droplet. (a) Photo showing a PVP-pentanol solution with citrate alone (A) and with citrate and water (B). (b) Plot showing an increase in emulsion droplet size with a decrease in water content. (c) STEM and corresponding EDS maps of "Si of TEOS" taken after 3 min. of TEOS addition

to a sample with 40 μL of water. d) TEM and corresponding EDS maps of "Si of TEOS" taken after 3 min. of TEOS addition to a sample with 140 μL water. Note: Preparation conditions for all the above structures are provided in the supporting information.

The TEOS was added, and the grids were prepared just after 3 min. EDS mapping showed that TEOS entered the emulsion droplet more quickly (though difference is small) when there was small amount of water than when there was large amount of water (Figure 4c,d). This indicated that the impedance in TEOS diffusion results in the change in the thickness of the silica structures. The higher the diffusion rate, the thinner the structure. This rate of TEOS diffusion indirectly may relate to the effect of temperature (thinner or crooked rods at high temperature and thick rods at low temperature). These studies do not confirm anything about the maximum diffusion rate below which a straight growth can occur; other factors, such as concentrations of citrate, NH_4OH , and TEOS may play a role in controlling the final growth. However, certainly a correlation appears between TEOS diffusion in the emulsion droplet and silica structure shape (thick, thin, or crooked). Additional experiments involving a table for main experiments, effect of citrate and water concentration, effect of delayed addition of sodium citrate, water, and NH_4OH are included in the supporting information under the section on additional experiments.

In summary, we have demonstrated that localized growth could be induced by localizing the reagents at different sites within the same emulsion droplet and employed this phenomenon to synthesize a new type of structure—half-sphere/half-funnel. The correlation of NH_4OH concentration with the silica structure shape (e.g., crooked, straight, thin, thick) appears to result from the water present in NH_4OH , and not from the NH_3 content. This effect of water on the structure shape is also correlated to the ease of diffusion of TEOS in the emulsion droplet size. The more the water, the slower the diffusion of TEOS in the droplet. To our surprise, an increase in water content resulted in smaller emulsion droplets. Under the explored conditions, it can be concluded that the emulsion droplet size does not relate to the silica structure shape; it may be the ease of diffusion of TEOS inside the droplet that controls the silica structure shape and thickness. We anticipate that these studies will provide a better understanding of the shape evolution of silica structures and the underlying mechanisms controlling the various shapes, which will make the synthesis of such structures (made of other materials also) more predictable and reproducible.

Acknowledgements

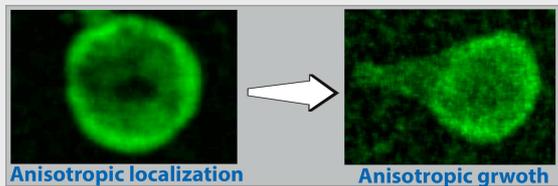
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