Formation Mechanism and Size Control in One-Pot Synthesis of Mercapto-Silica Colloidal Spheres

Zhenda Lu, Lei Sun, Kevin Nguyen, Chuanbo Gao, and Yadong Yin*
Department of Chemistry, University of California, Riverside, California 92521

ABSTRACT: Mercapto-silica spheres with controllable size from ~150 nm to ~3.5 μm and narrow size distribution have been prepared in water using a one-pot synthesis, in which 3-mercaptopropyltrimethoxysilane (MPS) was used as the sole silica source and ammonia as the base catalyst. The hydrolysis of MPS at the early stage of the reaction produces amphiphilic silicate species which initiate the self-emulsification of the system and lead to the formation of oil-in-water emulsion droplets. Further hydrolysis and condensation promote the nucleation and growth of the mercapto-silica spheres inside the emulsion droplets. These mercapto-silica spheres are both structurally and functionally different from typical silica particles prepared from silicon alkoxides. Understanding the formation mechanism allows systematic tuning of the size of mercapto-silica spheres in a wide range by changing the amount of precursor, the concentration of ammonia, the amount of additional surfactants, and the reaction time. We find that Ostwald ripening may occur quickly if the spheres are kept in the reaction solution, resulting in significant broadening of the particle size distribution. In order to obtain uniform and stable samples, it is important to quench the growth of the mercapto-silica spheres by separating them from the original reaction mixture and then storing them in solvents that can prevent further ripening.

1. INTRODUCTION
Surface functionalization provides a powerful means of tuning the properties of nanostructured materials for their application in catalysis, adsorption, separation, optics, and many other areas. Colloidal silica has been one of the most popular materials suitable for introducing surface functionality to nanostructures because of its chemical inertness, controllable porosity, convenient processability, optical transparency, and possibility of postfunctionalization. In addition to the conventional grafting method for introducing functional groups to the silica surface, recent efforts have been made to directly use organosilane precursors for producing organosilica nanostructures containing functional surfaces. The unhydrolyzable organic group on a typical organosilane will be automatically incorporated into the silica network, rendering the silica surface with a high density of functional groups that is difficult to achieve using conventional grafting methods. In particular, mercapto-silanes such as 3-mercaptopropyltrimethoxysilane (MPS) have been employed to produce thiol-functionalized silica, and used for adsorbing highly toxic heavy metals ions, such as mercury, silver, and lead in contaminated water and organic solvents. The strong thiol−metal interaction also allows binding of various nanoparticles, including Au, CdS, and CoFe₂O₄ to silica supports. Moreover, thiol-functionalized silica has been used for the immobilization of oligonucleotides and proteins for bioanalysis.

In contrast to pristine silica that can be easily produced by sol−gel processes such as the well-known Stöber method, the colloidal chemistry of organosilane as the sole precursor to organosilica has not been fully developed, although considerable efforts have been made along this direction. Trau et al. have explored a two-step procedure for the synthesis of mercapto-silica spheres of several to tens of micrometers in size. Nakamura et al. further reported a number of one-pot procedures for the preparation of mercapto-silica spheres with sizes ranging from a few hundred nanometers to several micrometers. They pointed out that mercapto-silica spheres of narrower size distributions are favored in a base-catalyzed aqueous hydrolysis reaction rather than the Stöber process, which takes place mainly in alcohol solutions. However, the products suffer from high polydispersities, even when using recent procedures that involve colloidal synthesis at a high temperature (100 °C). In addition, although various synthesis conditions have been explored, these prior studies have not been able to clarify the mechanisms for how these organosilica particles nucleate, grow, and ripen and how these processes are affected by the reaction conditions. This understanding is very important for producing organosilica particles of well-controlled morphology, size, and uniformity.

In this paper, we carry out systematic studies of the colloidal synthesis of mercapto-silica spheres by hydrolyzing MPS precursor in a basic aqueous solution, and propose that the mercapto-silica spheres form through an emulsion-based process.

Received: December 3, 2010
Revised: January 27, 2011
Understanding the formation and ripening mechanism allows us to produce high-quality mercapto-silica spheres of uniform size ranging from \(~\sim 150\) nm to \(~\sim 3.5\) \(\mu\)m. The emulsion-based mechanism is consistent with the one proposed by Trau et al. for their two-step process (acid-catalyzed hydrolysis and condensation followed by base-catalyzed condensation) for the synthesis of large microspheres (>2.5 \(\mu\)m),\(^{42}\) although our focus in this work is on the formation of submicrometer spheres through a one-pot base-catalyzed synthesis. We show that the size of the mercapto-silica spheres can be tuned systematically by changing the amount of precursor, the concentration of ammonia and additional surfactant, and the reaction time. All these effects can be explained well by using the emulsion-based mechanism. We also demonstrate that the change of sphere size at the later stages of the reaction is due to Ostwald ripening, and further point out that the key for preparing uniform mercapto-silica spheres in this reaction process is to separate the products from the reaction mixture right after their solidification to avoid ripening, and then disperse them in solvents that can prevent particle dissolution and materials transfer.

2. EXPERIMENTAL SECTION

2.1. Materials. MPS precursor, sodium hydroxide, ammonium hydroxide solution (\(\text{NH}_3\cdot\text{H}_2\text{O}, \sim 28\% \text{NH}_3\) in water), and sodium dodecyl sulfate (SDS) were purchased from Aldrich. Ethanol was obtained from Fisher Scientific. All chemicals were used as received without further treatment.

2.2. Synthesis of Mercapto-Silica Spheres. Mercapto-silica spheres were prepared by using a one-pot procedure. In a typical synthesis, MPS precursor in the amount of 0.05–2.00 mL (final concentration between 0.009 and 0.36 M) was added to 1% \(\text{NH}_4\text{OH}\) aqueous solution (0.05 M) to a total volume of 30 mL and vigorously shaken for 1 min using an IKA MS3 minishaker at a speed of 2500 rpm. The resulting mixture was then incubated at room temperature for several hours. The final products were washed with ethanol a few times. For spheres with sizes less than 200 nm, washing was performed with 0.01 M \(\text{NaOH}\) aqueous solution first to prevent aggregation and then with ethanol several times. The incubation time decreased with increasing precursor concentration: 2 h for the concentration above 180 mM, 3–5 h for the concentration between 36 and 90 mM, and 12 h for the concentration less than 18 mM. We also prepared the particles by varying only the concentrations of catalyst (\(\text{NH}_3\)) and surfactant (SDS), and keeping the rest of the parameters unchanged to investigate their influence on product size and uniformity.

2.3. Characterization. The morphology of the nanostructures was investigated using a Philips Tecnai 12 transmission electron microscope (TEM) with a 120 keV beam energy. UV–vis absorption spectra measurements were carried out using a Varian Cary 50 spectrophotometer. Dynamic light scattering (DLS) analysis was performed on a ZetaPALS system. Before each measurement, 100 \(\mu\)L of sample was diluted with 3 mL of water, and the time was counted at the point of dilution. Optical images were taken using a Zeiss AXIO Imager optical microscope.

3. RESULTS AND DISCUSSION

3.1. Formation of Mercapto-Silica Spheres. Mercapto-silica spheres are prepared using a MPS precursor as the only silica source, similar to the way tetraethyl orthosilicate (TEOS) is used in the Stöber method. However, unlike the standard Stöber process, water instead of alcohol is used as the main solvent. The precursor MPS is dispersed initially as large oil droplets in water so that the solution appears clear upon one minute of mixing. Within several minutes, the solution starts to appear milky, indicating the formation of emulsion droplets that can scatter visible light. After several hours, solid mercapto-silica spheres form, which can be recovered by centrifugation. Nakamura et al. suspected that the growth process of mercapto-silica particles may differ from that of TEOS; however, no mechanism was clearly proposed.\(^{40}\) Our observations suggest that the mercapto-silica particles form through a process similar to the emulsion polymerization process that has been widely employed for the preparation of polymer latex particles. The base-catalyzed hydrolysis of MPS precursor produces mercaptopropylsilicate monomers or oligomers which have an amphiphilic structure due to the presence of both hydrophilic silanol groups and relatively hydrophobic mercaptopropyl chains. At the early stage of the reaction, the hydrolyzed mercaptopropylsilicate species act as surfactants to emulsify the remaining precursor droplets,
producing an oil-in-water emulsion. Further hydrolysis and condensation of MPS lead to the formation of solid spheres through a mechanism analogous to the well-studied emulsion polymerization process. Interestingly, a similar self-emulsification process has been reported for the formation of polydimethylsiloxane (PDMS) colloidal particles through the hydrolysis of dimethyldiethoxysilane (DMDES) in water, which contains two nonhydrolyzable hydrophobic methyl groups.44,45 Scheme 1 further illustrates the proposed mechanism. It begins with the formation of precursor mini-droplets through the deformation of the interface of MPS precursor/aqueous phase due to the shear force provided by the quick shaking method. With ammonia as a catalyst, MPS precursor is partially hydrolyzed to form monomers and oligomers of mercaptopropylsilicate, which emulsify the precursor to produce smaller oil-in-water emulsion droplets. Hydrolysis and condensation continue inside the emulsion droplets, which subsequently grow through coalescence of droplets and the mass transfer of more precursor from the mini-droplets. Analogous to the classic emulsion polymerization process, the mini-droplets are believed to act as reservoirs by providing MPS precursor to the growing emulsion droplets. After a certain reaction period, the precursor mini-droplets disappear and most of the MPS species are located in the emulsion droplets. At this point, the emulsion droplets can only grow through coalescence, which becomes more difficult as the condensation of the silica proceeds at the later stage. After extensive condensation, the emulsion droplets convert into a uniform population of MPS solid spheres, as shown in the highlighted step in Scheme 1. It is worth noting that this is not the final state for the mercapto-silica spheres if they are kept in the reaction solution. As will be discussed later, the well-known Ostwald ripening process may occur, leading to the growth of larger spheres at the expense of the relatively smaller ones and thus gradually increasing the polydispersity of the mercapto-silica spheres.46 Understanding of the formation and ripening mechanism of the mercapto-silica spheres has helped us to significantly improve the quality of the products and harvest size-controlled monodisperse spheres.

The growth of mercapto-silica spheres was monitored by DLS, as shown in Figure 1a, for a sample prepared with the MPS and ammonia concentrations of 0.036 and 0.50 M, respectively. Right after mixing, no droplets can be detected by DLS due to the invisibility of the MPS precursor in water. Within 2 min, a small portion of the MPS precursor was hydrolyzed, yielding amphiphilic species that eventually allowed the emulsification of the system. As indicated in DLS measurements, emulsion droplets with an average size of ∼180 nm started to form after 2 min, with size increasing gradually to about 600 nm in ∼20 min and remaining constant afterward. The growth of the emulsion droplets can be attributed to either the mass transfer from the precursor reservoir or interdroplet coalescence, both of which are due to the liquid nature of the precursor and hydrolyzed monomer and oligomers at the initial stage of the reaction.42 As the hydrolysis and condensation proceed in the presence of the base catalyst, a three-dimensional Si–O–Si network is gradually established, which turns the emulsion droplets into rigid spheres. Because the coalescence becomes difficult, the particle size remains at ∼600 nm after ∼20 min and remaining constant afterward. The formation of silica spheres can also be monitored by the optical transmittance of the solution because colloidal silica particles scatter visible and near-IR light. As more liquid silane is converted to solid silica, the overall transmittance decreases accordingly. Figure 1b shows the evolution of the transmittance value at a wavelength of 900 nm during the reaction, while the inset shows the corresponding transmission spectra. Again, no obvious

Figure 1. (a) Average diameter of mercapto-silica colloids characterized by DLS as a function of time. (b) Evolution in the transmittance of the solution at 900 nm during the colloid formation process. Inset is a plot showing the transmittance spectra of the aqueous solution. The concentrations of MPS and ammonia are 0.036 and 0.50 M, respectively.

Figure 2. Average particle diameter (determined by DLS) as a function of MPS precursor concentration.
change in transmittance occurred in the first 2 min, which is consistent with results from DLS analysis. Then, the transmittance decreased gradually due to the hydrolysis and polymerization of the MPS precursors, and reached 40% after 20 min. Interestingly, unlike the size of droplets, the transmittance continued decreasing as time elapsed. It suggests that hydrolysis and condensation still proceed inside the emulsion droplets even though their coalescence has effectively stopped as the surface hardens at the later stage of the reaction. As more liquid silane is converted to solid silica, the refractive index of particle increases and the overall transmittance decreases accordingly.

3.2. Effect of the Precursor Concentration. To determine the critical factors that influence the mercapto-silica sphere formation, we carried out reactions by systematically varying the parameters, such as the concentrations of the precursor, catalyst ammonia, and the additional surfactant SDS, as well as the reaction time. A strong dependence of the size of the mercapto-silica spheres on precursor concentration has been observed. In a series of syntheses, we varied only the concentration of the MPS precursor (0.009–0.36 M) but kept the rest of the parameters unchanged: 30 mL of total volume containing 0.50 M NH₃ prepared in a 50 mL centrifuge tube under shaking for 1 min at 2500 rpm. Figure 2 plots the change of average droplet size at different precursor concentrations. The data were obtained by DLS after three hours of incubation to ensure that the spheres were fully grown. The sphere size increases as the precursor concentration increases, allowing a wide range of tuning from 170 nm to 3.5 μm. The larger sphere size at higher precursor concentrations is due to more extensive growth of emulsion droplets supported by the availability of more MPS precursor. No particles or droplets can be detected if the precursor concentration is lower than 0.005 M, suggesting that the hydrolyzed monomers or oligomers remain soluble species in solution. At a precursor concentration of 0.72 M or even higher, mercapto-silica particles still can form but with a significantly greater polydispersity.

The size and morphology of mercapto-silica spheres were further characterized using optical and electron microscopy.

Figure 3. Dark-field optical microscopy images of mercapto-silica particles prepared at different MPS concentrations: (a) 0.36 M; (b) 0.18 M; (c) 0.090 M; (d) 0.054 M; (e) 0.036 M. Scale bars are 10 μm. Insets are corresponding TEM images with scale bars of 2 μm. (f) Average sphere diameter as a function of MPS concentration measured from optical microscopy images.
As Figure 3 shows, the spheres with sizes larger than 500 nm can be clearly monitored using an optical microscope (OM) operated in dark-field mode. They can easily self-assemble into two-dimensional close-packed arrays on the glass substrate during the drying process, demonstrating a high degree of monodispersity. Insets are corresponding TEM images of the mercapto-silica spheres for the smaller samples, confirming their spherical morphology and narrow size distribution. Figure 3f summarizes the sphere sizes measured from microscopy images as a function of the precursor concentration, which is consistent with the results obtained from DLS analyses. Small mercapto-silica spheres (less than 300 nm) were evaluated only by TEM, as shown in Figure 4. The average diameter of spheres and the coefficient of variation (cv) measured from corresponding TEM images are listed in the figures. When low concentrations (0.018 and 0.009 M) of precursors were used, the average sphere size decreased to 210 and 151 nm and the size distribution was slightly broadened. This may be explained by the higher relative inhomogeneity associated with the fewer occasions of coalescence during the formation of smaller spheres. It is found that the sphere size from the images is slightly smaller than that measured by DLS characterization, especially in the case of the small spheres. This is due to the fact that DLS results account for the contribution of the solvation layer of the spheres extended in the solution, while such a layer has been removed under vacuum during TEM observations. Overall, the DLS, OM, and TEM measurements show consistent results, which confirm that uniform mercapto-silica spheres with sizes ranging from 150 nm to 3.5 μm can be easily produced by controlling the concentration of the MPS precursor.

3.3. Effect of Ammonia. Analogous to the classic sol–gel process, ammonia was used as a base catalyst for the hydrolysis of the MPS precursor. A higher concentration of ammonia produces more monomers and oligomers of silicates, which emulsify the precursor more effectively, leading to a decrease in the size of emulsion droplets. On the other hand, ammonia also catalyzes the condensation reaction of the hydrolyzed species, promotes the formation of three-dimensional silica networks, and eventually accelerates the solidification of the mercapto-silica spheres. As shown in Figure 5, increasing the ammonia concentration indeed leads to a decrease in the size of mercapto-silica spheres. In a reaction system containing 0.054 M precursor, the sphere size can be tuned between 1.7 μm and 200 nm by changing the ammonia concentration from 0.1 to 15 M. The cv values of the final spheres evaluated by DLS are relatively small when the ammonia concentration is in the range 0.25–1 M. Out of this range, the polydispersity also increases. We note that an ammonia concentration of 0.5 M seems to be optimal for producing narrowly distributed mercapto-silica spheres for a wide range of precursor concentrations.

3.4. Effect of Additional Surfactant. To further understand the formation process and control the size of the mercapto-silica spheres, we added different amounts of additional surfactant, SDS, to a reaction mixture containing 0.036 M precursor and 0.5 M ammonia. SDS, as a typical surfactant, can be adsorbed on the surface of oil droplets to effectively lower the interfacial tension and introduce electrostatic repulsion. The growing process of mercapto-silica spheres with SDS is similar to that without SDS, as shown in Figure 6a. The emulsion droplets can be detected at about 2 min after initial mixing. Unlike the reaction without SDS in which the particle size remained constant after 20 min, there...
was a slight size increase between 20 and 40 min for the reaction in the presence of SDS. Because the small size change is unlikely to be caused by coalescence, we believe the growth of droplets/spheres at the later stage of the reaction is mainly due to the uptake of the precursor from mini-droplet reservoirs or monomer/oligomer silicates dissolved in solution. Consistent with this understanding, we observed a decrease in the transmittance of the emulsion systems even after the droplet/sphere diameter reached a maximum, and a slower change in the transmittance when a higher concentration of SDS was used (Figure 6b). More importantly, the final mercapto-silica spheres show average sizes of 590, 280, and 196 nm when prepared with different SDS concentrations (0, 0.003, and 0.067 mg/mL, respectively). The trend of decreasing sphere size with increasing SDS concentration has been further proven by a series of preparations containing 0.054 M precursor with various SDS concentrations. Figure 7 plots the average sphere diameter against the SDS concentration. Interestingly, we notice that the initial addition of tiny amounts of SDS can dramatically decrease the size of the mercapto-silica spheres, for example, from 1.1 μm to 620 nm only by adding 0.01 mg of SDS to 30 mL of reaction mixture. Further increasing the SDS concentration leads to a gradual decrease in the sphere size. When the concentration is higher than 3 mg/mL in the mixture, no droplets can be effectively detected by DLS: the mixture stayed clear even after 5 days of incubation. The reduction in product size can be easily understood as the result of the higher emulsification power of SDS than that of the hydrolyzed silicates. However, as suggested in Figure 6b, the emulsion droplets prepared in the presence of SDS remained “soft” for a much longer time compared to the samples without SDS, giving more chances for interdroplet coalescence and subsequently yielding particles with broader size distributions. The insets in Figure 7 show typical TEM images of mercapto-silica particles prepared at two SDS concentrations, both with cv higher than 30%. We therefore conclude here that adding additional surfactants allows a high degree of tuning of the size of mercapto-silica spheres, which is accompanied by an increase in size distribution.

### 3.5. Ostwald Ripening

The growth of mercapto-silica spheres has also been monitored by characterizing samples collected at different reaction times by using TEM and DLS. We first looked at the reaction containing 0.054 M of MPS precursor and 0.5 M ammonia. One hour after mixing, monodisperse spherical objects can be observed under optical microscope, but they collapse and fuse with each other when dried on the substrate. Also, no isolated solid spheres can be recovered after washing. All these observations suggest that the condensation in the droplets/spheres at this stage is not extensive enough to reinforce them against the capillary forces experienced during drying or the mechanical treatment during washing, although they are rigid enough to prevent coalescence in the original solution. We find that a 4 h period allows sufficient condensation in most cases. As can be seen in Figure 8a, after 4 h of reaction, the product contains uniform solid spheres with a cv of ~1%. The spheres remain in the isolated form after washing for a few times and then drying on the carbon grids. Further prolonging the reaction time to 1 day leads to broader size distribution with the cv value increasing to 5%. The appearance of the smaller spheres in Figure 8b suggests the occurrence of the Ostwald ripening process, which cannot be ignored if the mercapto-silica spheres are left in the reaction mixture for one day. After 3 days, a large number of small spheres with diameters less than 200 nm can be observed through both TEM and DLS analysis, as shown in Figure 8c. Note that the presence of many small particles might also be due to the
reprecipitation of dissolved silicate species when the solvents evaporates during TEM sampling process. Some of the original spheres grow larger to about 1.4 μm at the expense of the small ones. Therefore, a long incubation time is detrimental to the monodispersity of the products. In their earlier works, Nakamura et al. reported their synthesis of polydisperse thiol-organosilica
particles which were collected from the reaction solution after one or three days. We suspect the broad size distribution in their cases is probably due to the Ostwald ripening, which occurred during the unnecessarily long incubation. To prevent ripening, it is necessary to separate the MPS spheres from the reaction mixture as soon as they become solidified, and then keep them in a solvent in which the spheres have a low solubility. Ethanol is a good candidate for this purpose because the mercapto-silica spheres can be well-dispersed in ethanol but there is no significant solubility over time. Figure 8d shows a typical TEM image and corresponding DLS result of mercapto-silica spheres which were collected after 4 h of incubation, then washed with ethanol several times, and finally redispersed and stored in ethanol for 3 days. The nearly unchanged diameter and size distribution clearly suggests the high stability of the spheres in ethanol. We therefore further conclude the requirements for preparing uniform mercapto-silica spheres: they need to be separated from the reaction mixture right after their solidification and before the occurrence of Ostwald ripening, and then stored in ethanol or other solvents in which the mercapto-silica spheres have a good dispersibility but a low solubility.

We also studied the stability of smaller spheres prepared with an MPS precursor concentration of 0.018 M while keeping all other parameters unchanged. As shown in Figure 9, after 6 h of incubation, uniform mercapto-silica spheres can be collected. Again, longer incubation time leads to a broader size distribution. Compared with the larger mercapto-silica spheres in Figure 8, the spheres with smaller sizes (∼210 nm) need about 6 h to solidify, but obvious Ostwald ripening occurs in just 24 h (Figure 9c). Therefore, the optimal incubation window for obtaining smaller mercapto-silica spheres is much narrower. When the mercapto-silica sphere is further reduced to below 200 nm, the solidification process and the ripening process may start to overlap, making it difficult to obtain stable particles with uniform sizes. This could explain why monodisperse mercapto-silica spheres with small sizes are generally much harder to produce.

4. CONCLUSION

In summary, high-quality mercapto-silica spheres have been successfully synthesized through a one-pot process in which MPS was used as the single silica source. The formation of the spheres follows an emulsion-based process in which the silicate species hydrolyzed at the early stage act as surfactants to emulsify the remaining MPS precursor in water, and further hydrolysis and condensation inside the emulsion droplets lead to the formation of solid mercapto-silica spheres. On the basis of the emulsion mechanism, we demonstrate systematic control over the size of mercapto-silica spheres by changing the concentration of precursor, ammonia, and additional surfactant and the reaction time. We also revealed that Ostwald ripening may occur quickly if the spheres are kept in the reaction solution, which results in significant broadening of the size distribution of the products. As a final remark on preparing uniform and stable mercapto-silica spheres, we emphasize the importance of quenching the growth of the mercapto-silica spheres by separating them from the original reaction mixture and then storing them in solvents that can prevent further ripening.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: yadong.yin@ucr.edu.

■ ACKNOWLEDGMENT

We thank the U.S. National Science Foundation (Grant No. DMR-0956081) for support of this research. Yin also thanks the Research Corporation for Science Advancement for the Cottrell Scholar Award, 3M for the Nontenured Faculty Grant, and DuPont for the Young Professor Grant.

■ REFERENCES

(41) Stober, W.; Fink, A.; Bohm, E. J. Colloid Interface Sci. 1968, 26, 62.