The Production of Hollow SiO$_2$ Nanoparticles (HSNPs) with a High Monodispersity

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We discuss the state-of-art synthesis of hollow SiO$_2$ nanoparticles with a high monodispersity (m-HSNPs). The template method using the Stöber process for m-HSNPs is introduced, and the advantages and mechanism of this method are described. Regarding the selection of templates, we suggest that the monodispersity of the templates should be faithfully pursued, while both positively and negatively charged templates can be considered as appropriate candidates. Particularly to negatively charged templates, we discuss their advantages for the dispersity of HSNPs, attributed to the no charge reverse SiO$_2$ coating. Moreover, the influences of the concentrations of NH$_3$ and H$_2$O in the Stöber process on the SiO$_2$ coating are discussed.

Keywords: hollow nanoparticles, silica, template method, Stöber process, monodispersity

1. Introduction

The structure of hollow SiO$_2$ nanoparticles (HSNPs) can be described as a void interior space surrounded by a SiO$_2$ layer (i.e., shell), with at least one of the following values in nanoscale: shell thickness, sizes of the interior space and the whole particle. Such a unique nanostructure endows the HSNPs with some physical properties different from solid SiO$_2$ particles, such as a low density and high specific surface area (SSA). In addition, the HSNPs shows their outstanding properties in the area of optical [1, 2], loading-releasing ability [3], heat insulation [4], etc. Therefore, considerable attention has been paid to developing facile and efficient synthetic methods of high-quality HSNPs. More specifically, free-standing SiO$_2$ nanoparticles, aggregated and broken HSNPs are not supposed to be contained in the high quality HSNPs, as these unfavorable species would degrade the characteristics expression of the hollow structure, and further reduce the credibility of performance evaluations.

Obtaining "high-quality" HSNPs can be equal to pursuing the high monodispersity of the HSNPs to some extent, that is, HSNPs show not only a high dispersity, but also a high uniformity in morphology (e.g., shape, particle size, shell thickness). There is no doubt that such a homogeneous morphology would make the analysis in terms of the relationship between the structure and performance easier and more convincing. Furthermore, a high monodispersity can endow the HSNPs with new attractive properties. Retsch et al. [1] found a visible Mie scattering phenomenon in observing monodispersed HSNPs (m-HSNPs) under illumination, which has never been reported when observing non-monodisperse HSNPs to the best of our knowledge. Deng et al. [5] demonstrated that m-HSNPs can be used to build a 2-D colloidal crystal for optical applications. Interestingly, such a colloidal crystal showed significant Fabry−Pérot fringes in its transmission spectrum, even when its thickness reached dozens of micrometers.

Considering the attractive properties and application potential of the m-HSNPs, previous studies on their synthetic method should to be summarized. This review deals with the most mature protocol for the synthesis of m-HSNPs, i.e., template method. The general process of the template method is introduced in the next section, with followed by pointing out a myth in the principle of the template selection. The influences of other parameters on the template method (i.e., concentrations of NH$_3$ and H$_2$O in the SiO$_2$ coating process) are also discussed in this review.

2. Overview of the template method

Figure 1 depicts the general process of the template method, which can be further divided into the SiO$_2$ coating step (step I) and template removing step (step II). In this process, the template@SiO$_2$ core−shell particles are intermediates, whereas they determined the morphology of finally produced HSNPs to a significant extent, while the step II can be simply seen as templates being replaced by void spaces. Therefore, the core issue of the template method is step I, while the quality of the SiO$_2$ coating directly affects the characteristics of the finally produced HSNPs (e.g., size, dispersibility, shell thickness and surface roughness).

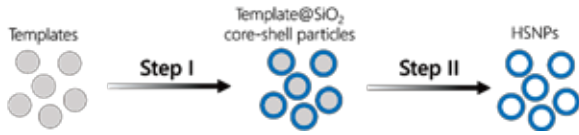Figure 1. Schematic diagram of the template method for the synthesis of HSNPs.

For the SiO$_2$ coating step, although there are several chemical reactions able to produce SiO$_2$ (e. g., Na$_2$Si$_3$O$_7$ + H$_2$SO$_4$ → 3 SiO$_2$ + Na$_2$SO$_4$ + H$_2$O, SiCl$_4$ + 2H$_2$ + O$_2$ → SiO$_2$ + 4HCl), the Stöber process [6] is believed to be the most promising and controllable one. In the Stöber process, the hydrolysis and condensation reactions over silicate esters (Si(OR)$_4$) successively occur by the catalysis of base (e.g., NH$_3$) in alkoxide solvent (e.g., ethanol) which contains a specific amount of H$_2$O. This sol-gel process can be described as follows,

Hydrolysis
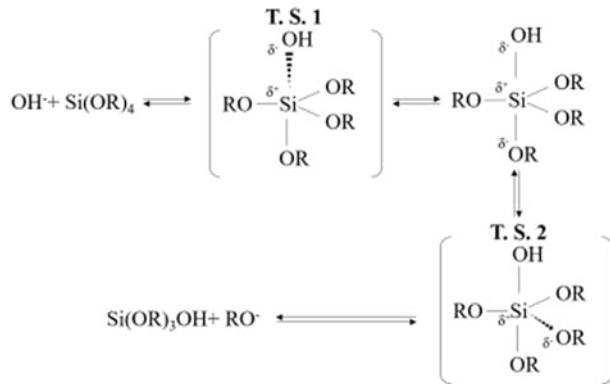
Condensation
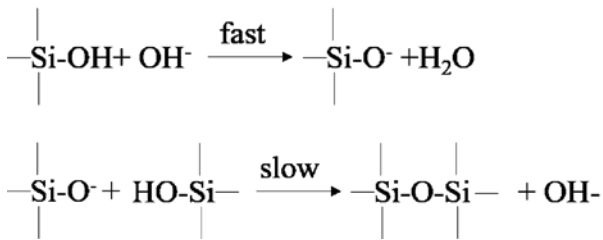
where R represents the carboxylic chain. The Stöber process was first developed for producing monodispersed SiO$_2$ microspheres as the nucleation and growth of SiO$_2$ microspheres in this process can be easily controlled by tuning the amount of precursor in the reaction system, as well as the concentration of H$_2$O and catalysts [7]. The formation of the monodispersed SiO$_2$ microspheres in the Stöber process can be explained by the model of LaMer and Dinegar [8, 9]. Figure 2 depicts the change in the silanol concentration ($c_{silanol}$) in the reaction system as a function of the reaction time. At the beginning of reaction, $c_{silanol}$ gradually increased

with the continuous hydrolysis of the silicate esters until it reached a critical concentration for nucleation (c_n). Since the condensation rate was much higher than that of hydrolysis, $c_{silanol}$ then stopped increasing and soon decreased to below c_n. Correspondingly, nucleus would not generate anymore, thus the generated nucleus started to synchronously grow (via heterogeneous nucleation). The growth procedure of the SiO$_2$ particles would finally stop when $c_{silanol}$ decreased to the concentration of the SiO$_2$ dissolve balance (c_s). Rationally, all the resulting SiO$_2$ particles had a similar size, thus achieving a high monodispersity.

To date, the Stöber process has been the most popular protocol for the SiO$_2$ coating using template method [10-16], thanks to its high controllability and operative under moderate conditions. Nevertheless, adopting the Stöber process is far from sufficient to achieve the high monodispersity of the HSNPs. Some condition parameters should be more strictly controlled, e.g., the template particles are supposed to be monodispersed, and the homogeneous nucleation of SiO$_2$ should be suppressed in the SiO$_2$ coating to avoid producing of aggregated HSNPs and free–standing SiO$_2$ nanoparticles.

3. Appropriate template materials for m-HSNPs

If there is no special demand for on the monodispersity of the HSNPs, the selection of the template particles can just be based on 1) the surface of the material is easy for SiO$_2$ decorating, and 2) this material can be removed without destroying SiO$_2$ shells. Accordingly, a number of materials has been used for the synthesis of HSNPs, e.g., CaCO$_3$ nanoparticles [10], polymer beads [11-13], ceramics powders [14], polymer emulsions [15], and micro-bubbles [16]. Nevertheless, there are only a smaller range of materials available for the synthesis of m-HSNPs, since the template particles should be fabricated to monodisperse.
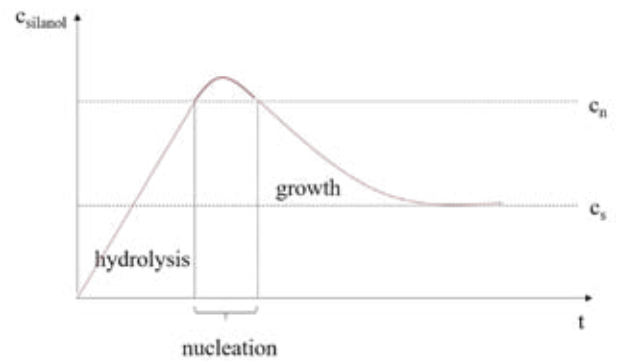

Figure 2. $c_{silanol}$ changes as a function of the reaction time in the Stöber process for the monodispersed SiO$_2$ microspheres.

Taking into account the convenience of fabrication, monodispersed polymeric beads (MPBs) have become a commonly used template material for the synthesis of the m-HSNPs, which can be easily obtained by either soap–free emulsion polymerization or dispersion polymerization [17]. Besides, it is also easy to varying the size, hydrophilicity and surface charge (signal and density) of MPBs. Another highlight of the MPBs is that they can be removed by calcination in air, which is convenient on operation and would have little effect on the SiO_2 shell structure. However, the disadvantage of using MPBs is also significant—CO_2 emission in the template-removing step, which means that the production of m-HSNPs using MPBs templates is not very "green". Based on this issue, a great effort has been made to find alternative materials of MPBs. Fuji et al. [15] fabricated SiO_2-coated polymer emulsions with an improved monodispersity, and further obtained m-HSNPs by washing the composites with water. Wang et al. [14] synthesized monodispersed hematite colloidal nanoparticles with high monodispersity and variable particle shape. They proposed that these hematite colloidal nanoparticles are appropriate for the synthesis of m-HSNPs, since SiO_2 exhibited high affinity to the surface of hematite and such template particles could be easily removed by acid etching.

In previous studies, the sign of charge on the surface was also an important factor to judge whether or not these template particles are appropriate for SiO_2 coating. Since electrostatic attraction is believed to be the driving force for the SiO_2 coating, as well as the negatively charged SiO_2 particles came from Stöber process, positively charged templates were chronically believed to be much more advantageous for the SiO_2 coating than the negatively charged ones. As reported by [18], when negatively charged monodispersed polymer beads (n-MPBs) were used for the SiO_2 coating, the SiO_2 particles generated in the bulk solution instead of depositing on n-MPBs, further leding to the failure in obtaining the m-HSNPs. However, these studies may be more reasonable if the surface charge density of the n-MPBs and reaction parameters for the SiO_2 coating have been varied. In fact, there have been some studies that indirectly demonstrated the possibility of a SiO_2 coating on n-MPBs. Graf et al. [12] found SiO_2 shell could be constructed on the surface of n-MPBs with the assistance of polyvinylpyrrolidone (PVP). Indeed, PVP would not reverse the charge sign of the n-MPBs, thus in that study the SiO_2 shell was successfully constructed on a negative surface, though the authors did not point out if there was a possibility of the SiO_2 coating on the n-MPBs without the assistance of PVP. Deng et al. [5] obtained n-MPB@Vinyl-SiO_2 core-shell particles using vinyltrimethoxysilane (VTMS) as the precursor of SiO_2, and further confirmed the high yield of the SiO_2 coating on the n-MPBs. Although the authors deduced that the coating of SiO_2 in this case resulted from the interaction between the vinyl ligands of VTMS and the hydrophobic surface of the n-MPBs, they also pointed out the negative charges carried by n-MPBs would not suppress the coating of SiO_2. Therefore, for addressing whether or not the SiO_2 coating on the surface of n-MPBs via the typical Stöber process is feasible, a further analysis is supposed to be conducted based on additional experiments, while more facts (e.g., surface charge density of n-MPBs, reaction parameters) should be taken into account for the appropriate conclusion.

Most recently, Chen et al. [12] directly demonstrated that the negatively charged particles can also be appropriate for the SiO_2 coating, thus can be used as the templates for the synthesis of m-HSNPs. In that study, the SiO_2 coating via the Stöber process on n-MPBs (i.e., Poly (Styrene-*co*-acrylic acid) microspheres from soap-free emulsion polymerization) was studied. Three kinds of n-MPBs with different surface charge densities were used, while all the other reaction components were preserved the same as for the typical Stöber process, i.e., using tetraethyl orthosilicate (TEOS) as the precursor of SiO_2, NH_3 as the catalyst and ethanol as the solvent. Results in that work indicated when the charge density of n-MPBs was high (zeta potential reached to -45.6mV in water), SiO_2 can form a uniform shell on the surface of n-MPBs rather than yielding free-standing SiO_2 particles, Interestingly, the SiO_2 coating became much harder to perform when the surface charge density of the n-MPBs was reduced, in other words, being more "positive", resulting in a considerable number of free-standing SiO_2 particles in production (see Figure 3). Since there was no surfactant used, i.e., the surface charge density was only adjusted by varying the content of the poly (acrylic acid) chains in n-MPBs, that study directly showed the feasibility of the n-MPBs using as the template particles for the SiO_2 coating and m-HSNPs synthesis. Figure 4 shows the morphology and size distribution of the as-obtained m-HSNPs. As noted, the m-HSNPs were endowed with a considerably high monodispersity as they were uniform in both the size and shell thickness and there were neither aggregated particles nor free-standing SiO_2 particles produced.
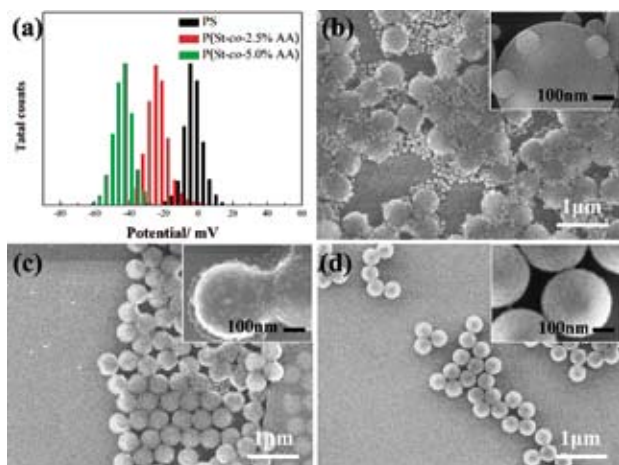
Figure 3. (a) zeta potential (in water) distribution histograms of the as-synthesized n-MPBs with different contents of acrylic acid; SEM images of SiO2 coated n-MPBs with low (b), middle (c) and high (d) surface charge (negative) densities; inserts of (b)~(c) are high-magnification SEM images; image reprinted from ref. [12].
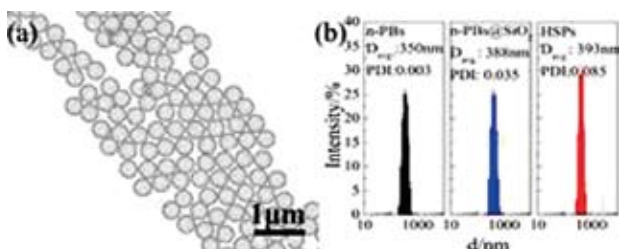

Figure 4. (a) STEM image of m-HSNPs synthesized using n-MPBs; (b) size distribution histograms of templates, SiO2 coated templates and m-HSNPs; image reprinted from ref. [12].

As demonstrated by Chen et al. [12] using n-MPBs as the templates is more advantageous for preventing the aggregation of m-HSNPs, since the mechanism of the SiO2 coating in this case is different from that on positively charged surface. The most important argument for that difference is there was no "surface charge reversal" occurred in the process of SiO2 coating on n-MPBs. In this process, as seen in Figure 5, the zeta potential of subject (i.e., n-MPB/ SiO2 composites) gradually increased from -17.2 mV along with the deposition of SiO2, then remained constant at around -36.7 mV after the SiO2 shells formed. Before starting the Stöber process, the zeta potential of the n-MPBs in ethanol reduced from -17.2mV to -11.9 mV after ammonia solution was added. This phenomenon can be attributed to the adsorption of NH_4^+ ions on the surface of n-MPBs. This phenomenon that they observed is opposite that of the SiO2 coating on the positively charged surface, in which the surface charge of the subject particles would reverse

from positive to negative, and the NH_4^+ cations would not likely be absorbed on the surface of the template particles as well. In any case, the reversal of surface charge implies that there is a certain stage when the apparent surface charge of the particles was equal to zero (i. e., zeta potential=0). While, rationally, particles at this stage were under the risk of aggregation. Therefore, Chen et al. [12] believe that the "no-charge reversal" SiO2 coating process is an important advantage of using n-MPBs for m-HSNPs and can be seen as the main reason for the high monodispersity of the resulting m-HSNPs, besides the high monodispersity of templates.

In summary, the high monodispersity of the template particles should be seen as the most important principle for template selection. Meanwhile, recent work has encouraged the application of the negatively charged templates for the synthesis of the m-HSNPs, and thus the surface charge sign should not be a manipulate criteria for selection.

4. Influence of c_{NH3} and c_{H2O} in SiO2 coating

During the Stöber process for synthesizing monodispersed SiO2 microspheres, the influences of the concentration of NH3 (c_{NH3}) and the concentration of H2O (c_{H2O}) in reaction system have been intensively investigated [7, 19]. It was found that NH3 in the Stöber process acted as the catalyst, since both the hydrolysis and condensation over silicate esters are nucleophilic reactions, the rate of which would increase with the increasing pH of the reaction system. In addition, increasing the concentration of the reactant H2O would also accelerate the Stöber process. Therefore, adjusting the c_{NH3} or c_{H2O} would vary the hydrolysis rate of the silicate esters, as well as the rate of the following condensation, thus further affect the nucleation and growth of the SiO2 particles. As a highlight, G.H. Bogush et al. [19] systemically studied the influence of c_{NH3} and c_{H2O}, followed by successfully proposing an equation to predict the size of the resulting monodispersed SiO2 microspheres.
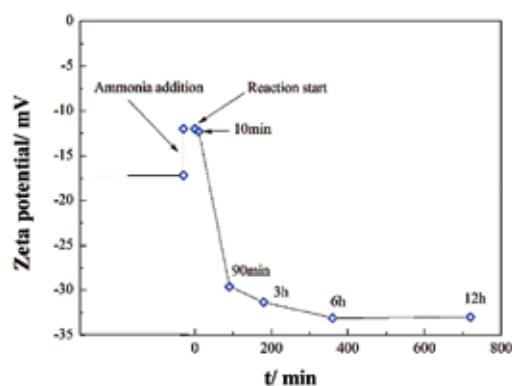

Figure 5. The change in zeta potential (in ethanol) before and in the course of SiO2 coating on n–MPBs; image reprinted from ref. [12].

Although the role of NH_3 in the Stöber process for the monodispersed SiO_2 microspheres has been clarified, it is still important to discuss the influence of c_{NH3} on the SiO_2 coating in the template method. Yun et al. [11] observed the SiO_2 coating on positive MPBs with the varying c_{NH3} in the Stöber process. They found that the roughness of the SiO_2 shells increased with the increasing c_{NH3}, which could be attributed to the fast growth of the SiO_2 particles in their transition from the bulk solution to the surface of templates due to such a high c_{NH3}. Takai et al. [20] demonstrated that the structure of the SiO_2 shell formed on the surface of positive MPBs depended on the c_{NH3} (i.e., pH in the solution). They also observed the effects of c_{NH3} on the TEOS conversion rate, shell thickness and dispersity of the m-HSNPs. In summary regarding to the SiO_2 coating process on the positively charged templates, c_{NH3} is supposed to be controlled at a considerably low level in order to suppress the generation of aggregation and free-standing SiO_2 particles, as well as to reduce the roughness. Nevertheless, since NH_3 acts as the catalyst for the SiO_2 production, a low c_{NH3} would also result in a low conversion rate of the SiO_2 precursor, thus leading to thin, loose, or even incomplete SiO_2 shells on the templates, which would finally result in a low mechanical strength of the m-HSNPs. Therefore, when positive templates are used for the m-HSNPs, optimizing experiments for c_{NH3} are necessary to balance the robustness and monodispersity of the m-HSNPs.

In the case of using n-MPBs as the templates, rationally, c_{NH3} also significantly affects the conversion rate of the SiO_2 precursor, and thus a high c_{NH3} is advantageous for constructing thick SiO_2 shells on the templates [12]. However, different from the case using positive templates, the increasing c_{NH3} would not likely cause the increasing surface roughness of the m-HSNPs. As seen in Figure 6, all the obtained m-HSNPs with using the same n-MPBs but applying different c_{NH3} value show similar surface roughnesses, whereas the shell thickness increases with the increasing c_{NH3}. Figure 6 also shows that the m-HSNPs synthesized with a high c_{NH3} contained neither aggregates nor SiO_2 nanoparticles. This phenomenon is believed to be another significant difference between using negative templates and using positive templates for the synthesis of the m-HSNPs.

As already discussed, the influence of c_{NH3} towards the morphology of the obtained m-HSNPs depends on the charge signal of the template surface, possibly due to the SiO_2 coating mechanisms on the positive or negative templates are different from each other. On the contrary, an increasing c_{H2O} would always exert a negative influence on the morphology

of the m-HSNPs in both of these cases. When positive templates were used for the SiO_2 coating, a high c_{H2O} would lead to a high growth rate of the SiO_2 particles and further lead to the occurrence of aggregation and the production of free-standing SiO_2 nanoparticles [11]. On the other hand, using negative templates, as proposed by [12], a high c_{H2O} would suffer from the adsorption of NH_4^+ on the surface of the templates, and further result in the homogeneous nucleation of SiO_2 in the bulk solution. Rationally, in this case, only a part of the produced SiO_2 could transfer onto the surface of the templates, thus resulting in an incomplete SiO_2 coating.
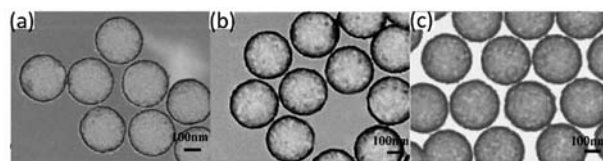

Figure 6. STEM images of m-HSNPs synthesized with low (a), middle (b) and high (c) C_{NH3}; image reprinted from ref. [12].

5. Conclusion

This review deals with the template method for the synthesis of monodispersed HSNPs. The Stöber process is the appropriate technique for achieving the SiO_2 coating on templates, thanks to its high controllability and operability under moderate conditions. Furthermore, to endow the HSNPs with a high monodispersity, the following principles are supposed to be maintained for selecting the appropriate materials of the template particles: (i) the surface of this material easily undergoes a SiO_2 decorating; (ii) this material can be removed without destroying SiO_2 shells; (iii) it is easy to obtain highly monodispersed particles of this material. According to previous studies, monodisperse polymer beads, polymer emulsions and monodisperse hematite colloidal nanoparticles are all competitive materials for the template particles, while the latter two can also lead to the "green" production of the m-HSNPs. In terms of the surface charge of the templates, we suggest both negatively and positively charged templates can be taken into consideration. Specific to negatively charged templates, such templates show their advantages towards the dispersity of the m-HSNPs, possibly attributed to the fact that the corresponding SiO_2 coating on them is a "no-charge reversal" process. However, it seems that the negative templates are suitable for the SiO_2 coating only when their surface charge density is considerably high. We also discussed the influence of c_{NH3} and c_{H2O} in the SiO_2 coating process on the morphology of the m-HSNPs. As discussed, both a high and low c_{NH3} are unfavorable for SiO_2

coating on the positively charged templates, as the former would lead to a rough surface of the SiO2 shells, as well as producing aggregates and free-standing SiO2 nanoparticles, while the latter would reduce the mechanical strength of the SiO2 shells. On the other hand, for the SiO2 coating on negatively charged templates, a high c_{NH3} is advantageous for constructing thick SiO2 shells, while unfavorable phases of SiO2 (i.e., aggregates and free-standing particles) would not likely to be produced in this case. On the contrary, a high c_{H2O} is always undesirable for the SiO2 coating, no matter on the positively or negatively charged templates.

Considering the attractive properties of the HSNPs and their additional characteristics due to their high monodispersity, we anticipating there will be a significant improvement in the synthetic protocol of m-HSNPs. We also suggest some issues not considered in this review, such as the hydrophilicity and mass concentration of the templates in the SiO2 coating system, need to be addressed in the future.

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