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Modifying the Stöber Process: Is the Organic Solvent Indispensable?

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Abstract: The Stöber method is one of the most important and fundamental processes for the synthesis of inorganic (nano)materials, but has the drawback of using a large amount of organic solvent. Herein, we used ethanol as an example to explore if the organic solvent in a typical Stöber method can be omitted. We found that ethanol increases the particle size of the obtained silica spheres and aids the formation of uniform silica particles rather than forming a gel. Nevertheless, the results indicated that an organic solvent in the initial synthesis mixture is not indispensable. We discovered, an initially immiscible synthesis method, which can replace the organic solvent-based Stöber method to successfully synthesize silica particles with the same size ranges as the original Stöber process without addition of organic solvents. Moreover, this process can be of further value to be extended to synthesis processes of other materials based on the Stöber process.

Introduction

One of the most important methods for the synthesis of inorganic materials and nanomaterials is the Stöber process, proposed by Stöber et al. in 1968.[1] It was originally developed for the controlled synthesis of uniform submicron silica spheres, but has now been expanded into a huge system by a lot of extension methods for synthesizing diverse materials with different morphologies and microstructures for a variety of applications, such as aerospace, drug delivery, adsorption, and catalysis.[2] For example, ordered mesoporous silica, with tunable pore size and high surface area, has been synthesized via modified Stöber processes.[3] Also silica materials with core-shell structure, yolk-shell structure, etc., and even carbon materials and metal oxide materials with different structures were prepared by extension of the Stöber method.[4]

However, these classical or most modified methods always require the use of alcohols or other organic solvents to dissolve the silica precursors, which is neither economical nor environmentally friendly since a lot of organic solvent is wasted during the process.[5] For example, the most typical Stöber process, using 0.28 mol/L of tetraethyl orthosilicate (TEOS) in ethanol solution, consumes about 1 L of ethanol to synthesize only 17 g of SiO_2 spheres.[1] Therefore, it is important to find a way to reduce the organic solvent consumption.

A lot of attempts have been made and reported. It was discovered that the formation of bio-silica in diatoms and sponges occurs in aqueous solutions with the aid of proteins.[6] Subsequent studies found that silica with some specific structures could be synthesized without the addition of organic solvents in the presence of amino acids, surfactants, etc..[6-7] Based on these studies, Davis et al. proposed to use a lysine aqueous solution as a catalyst to replace typical ammonia to synthesize silica spheres.[8] However, the particle size was only ~5 nm, much smaller than that obtained by the Stöber method. Yokoi et al. performed similar research at the same time and 15–44 nm silica spheres were obtained.[9] In order to extend the size range, multi-steps seed regrowth processes were proposed and particles up to 200 nm could be synthesized.[10] Nevertheless, these modified methods are either only able to synthesize silica with specific structures, or the size range of samples obtained from them is still too small to replace the classic Stöber process.

Although TEOS can also react with water without organic solvents to form silica particles in a classic ammonia (instead of amino acid) catalyzed process, the product is often non-uniform and uncontrollable, rather than controlled uniform particles. The role of solvents has been studied. It was found that the type of solvent influences the silica particle sizes.[1,11] Furthermore, it has been reported that the alcohols not only regulate the miscibility of the system, but also participate in the reaction.[12] Although a lot of research has been done on the influence of solvent over decades, it has not yet been discovered that addition of organic solvents can actually be omitted in the ammonia Stöber process.

In this work, we found that uniform silica spheres with much larger and adjustable diameters can be synthesized without any organic solvents or amino acids (denoted as organic solvent-free method), as long as the ratio of reagents is controlled in an appropriate range. The particle size of the silica spheres synthesized by this method is controllable at the sub-micron scale, the same as the Stöber method. Moreover, the catalyst is the ammonia solution, just like the classic Stöber method (also in similar amounts), which is inexpensive and saves additional costs of other additives such

as amino acids. Due to the importance of the classical Stöber method for syntheses of inorganic materials, the success of this organic solvent-free controllable synthesis of silica can be of great significance in practical applications by extending it to other Stöber-based materials syntheses.

Results and Discussion

Examples of different sizes of SiO_2 spheres, as prepared by this organic solvent-free method, are shown in Figure 1. The amount of TEOS was fixed for all syntheses to 50 mL, whereas the size difference was induced by the use of different amounts of water and ammonia in the synthesis. The obtained silica spheres are uniform in size and shape when the sizes are in the range of approximately 100 nm–1 µm (Figure 1b–1e). An example of the particle size distribution obtained via SEM is shown in Figure S1a. However, when trying to reach even larger diameter particles (>1 µm) by only adjusting the ratio of reactants, the spheres lose uniformity, represented by small satellite particles present in the samples (Figure 1a). In addition, when the synthesis is not performed at an appropriate reactant ratio like discussed in this paper, agglomerated and non-uniform silica gels (Figure 1f), rather than uniform spheres, are being obtained. The volume and amounts of reactants of all the organic solvent-free syntheses in this work are listed in Table S1. Figure S2 shows the electron microscope images of all the obtained samples. The entry numbers of Table S1 and Figure S2 correspond to each other. Figure 1a-e correspond to the samples with entry numbers 5, 7, 19, 17, and 23 in Table S1, respectively. The amount of ammonia used in this process was in the same range as in a typical Stöber process, and its molar ratio to the resulting silica (NH_3/SiO_2) is 3.2–8.5, compared to 1–30 in the typical Stöber process.[1,13]
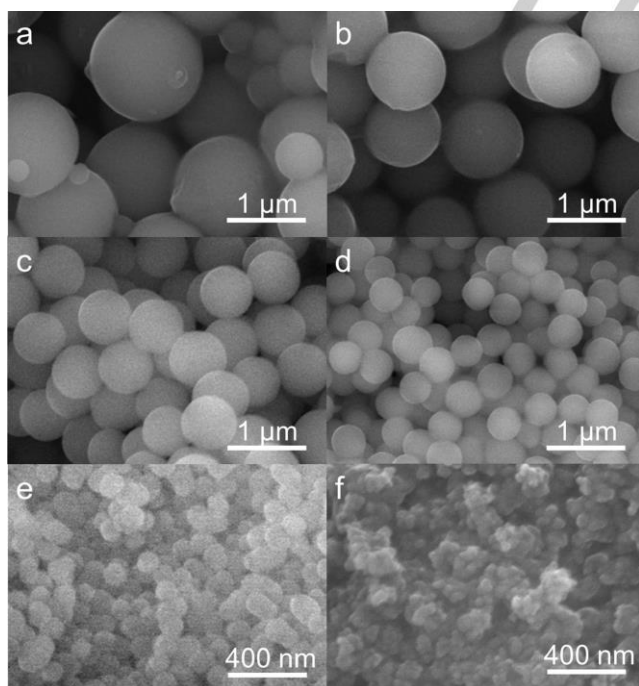

Figure 1. Scanning electron microcopy (SEM) images of silica with different sizes prepared by the organic solvent-free method. (a) Silica spheres with a diameter of ~1.3 µm. (b) Uniform silica spheres of ~1 µm. (c) Uniform silica spheres of ~710 nm. (d) Uniform silica spheres of ~430 nm. (e) Uniform silica spheres of ~100 nm. (f) Non-uniform and agglomerated silica gel.

The influence of the volume and molar ratios of water and ammonia, at constant volume of TEOS, on the silica sizes in the organic solvent-free method was studied. The results are shown in Figure 2. Since the concentration of the ammonia solution is 25%, the curve for each ammonia content has a corresponding minimum content of water instead of 0 mol. Additionally, only in a narrow range of water content, depending on the amount of ammonia added, this organic solvent-free method is able to prepare SiO_2 spheres. Otherwise a non-uniform gel is produced (yellow area in Figure 2). Another conclusion that can be deduced from the figure is that the lower the water content used in the synthesis, the larger the diameter of the SiO_2 spheres obtained. Ammonia contents below 1.33 mol allow a wider range of particle sizes than the higher ammonia contents. Comparing different curves along the Y-axis, it is found that in most cases, at a certain water content, increasing the amount of ammonia can increase the particle size. However, when the water content is small (~4 mol water), the particle size rises first and then drops with the increase of ammonia content. Some models of silica formation and growth in typical Stöber process have been proposed and studied.[14] Although there is no consensus yet on many details (e.g. the formation process of primary particles, the rate determining step of particle growth), it is generally accepted that different water and ammonia contents change important features, such as the solvation, electrostatic interactions, hydrolysis and condensation rates, that can influence the final particle size.[15] The equations for the hydrolysis and condensation of TEOS are shown in Figure S3. In the synthesis process, TEOS undergoes hydrolysis first, to produce monomers with one or more silanol groups and releasing ethanol into the solution (Figure S3 (Eq. 1)). Then, the condensation between silanol groups (Figure S3 (Eq. 2)) or between silanol groups and ethoxy groups (Figure S3 (Eq. 3)) generates oligomers with siloxane bonds. The oligomers separate from the continuous phase to form nuclei, which become primary particles and grow further into the stable final particles through aggregation or monomers addition.[15-16] The influence of water content is that more water enables enhanced interactions between polymer segments and the continuous phase and dilutes the monomer concentration, which can reduce the final particle size. For the effect of ammonia, with increasing NH_3 concentration, there is a balance between the tendency to produce larger particles (due to the increase of charge shielding ability) and the tendency to produce smaller particles (due to the enhancement of solvation).[17] This might be a reason for the apparent plateau value observed at low water content and with the increase of ammonia, where the particle size starts to drop after rising first. The particle size at high water content cannot reach this plateau value due to the limitation of the maximum ammonia concentration. As the effect of water and ammonia on the particle size shows a similar trend for the organic solvent-free process as for the typical Stöber method, they may have similar mechanisms and growth models, which need to be further studied and verified.
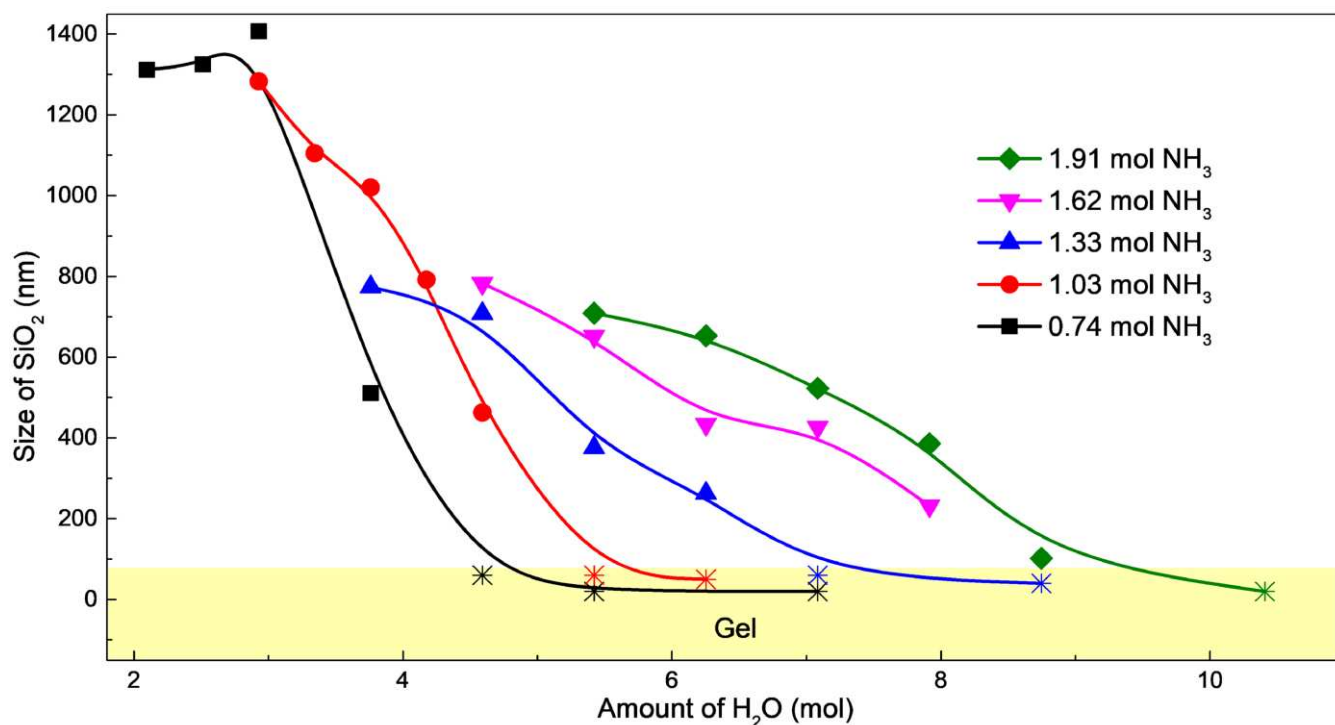
Figure 2. Particle sizes synthesized by modified organic solvent-free Stöber method with different water and ammonia content. 50 mL of tetraethyl silicate (TEOS) is used with various amounts of water and ammonia without addition of ethanol. The amount of water includes the water content in the ammonia solution and the water directly added. Uniform spheres smaller than 100 nm cannot be synthesized in these cases, non-spherical and non-uniform gels are formed instead (yellow segment).

In order to study the influence of ethanol on the silica synthesis, the process without ethanol and typical Stöber method with ethanol were compared under the same conditions (Figure 3). The amount of ethanol varies with the amount of ammonia or water, but always dilutes the final concentration of TEOS to 0.28 mol/L as reported.[1] The specific amounts of ethanol and reactants used are shown in Table S2. Another set of experiments presented in Figure 3b used 1/10 of the ethanol content of a typical process as a control experiment. As shown in Figure 3, the two processes with or without ethanol have similar trends in the effect of ammonia on the particle size, but with a broader size range in the organic solvent-free method (Figure 3a). However, for water the effect differs (Figure 3b). The particle size of silica in the presence of ethanol remains the same or slightly increases first and then decreases with the addition of water, which is consistent with reports in the literature of a typical Stöber process.[18] When only 1/10 of the classic ethanol amount is added, the size of the silica particles starts to decrease at a lower water content. However, in the organic solvent-free process, a monotonic decrease of particle size with the increase of water can be observed. Furthermore, in most cases, adding ethanol leads to larger particle sizes up to a certain particle size limit (similar to the maximum particle size of silica synthesized without ethanol). The role of ethanol is complex.[19] It is difficult to study it as an independent variable since ethanol is both a solvent and a by-product of a reversible reaction (Eq. 1 in Figure S3).[20] The effects of the amount of reactants and the type of solvent have been extensively studied, but few studies have focused on the amount

of solvent, and these few papers do not have a consistent conclusion.[21] However, as shown in Figure 3b, compared with the quite small effect on the variation in particle size when reducing the amount of ethanol with a factor of 10, the effect of the presence or absence of ethanol in the initial synthesis mixture is large. This suggests that, although there are other effects, the more important role of ethanol in the synthesis is as a solvent to dissolve two immiscible phases, TEOS and water, into one phase. Figure S4 supports this hypothesis, as the process with ethanol added as a solvent has a shorter induction period (the part where the conductivity rises). The shorter induction period indicates that the dissolution of all reagents into one phase enables the reactant molecules to better contact and react with each other, improving the efficiency of hydrolysis and condensation, which could be one of the reasons for the larger particle size caused by ethanol.[15] In the organic solvent-free process, the hydrolysis of TEOS will gradually release ethanol, which can also dissolve the two phases of water and TEOS into one phase. This might also explain why at low water content, the particle size of silica prepared by the organic solvent-free process is similar to that of particles synthesized with the addition of ethanol. The particle prepared by the organic solvent-free process is much smaller at high water content, probably because the gradually released ethanol is too little relative to water to regulate the miscibility of water and TEOS. In addition to the above particle size measurements by electron microscopy, N_2-sorption and dynamic light scattering (DLS) measurement (see Figure S5 and Figure S6) were used to prove that there is no structural difference (including particle size

3

distribution width) between silica spheres synthesized with and without ethanol. The numbers in the figures correspond to the entry numbers of the samples in Table S1 and S2. Comparing the silica spheres with similar particle size synthesized by the organic solvent-free process and the typical Stöber process, there is no significant difference in N_2-sorption and DLS results. Moreover, the diffuse reflectance infrared Fourier transformations (DRIFT) and thermogravimetric analysis (TGA) were combined to compare the surface properties and amount of silanol groups of similar particle size silica spheres synthesized by the two processes. The DRIFT spectra (Figure S7) show that they present similar surface hydroxyl (929 cm^{-1}, 3800–3000 cm^{-1}) groups, Si–O–Si (817 cm^{-1}, 1110 cm^{-1}) and surface water (1630 cm^{-1}), although there are slight differences (e.g. the less visible Si-OH signal at 929 cm^{-1} at 200 °C in the particles prepared by classical Stöber method and the shape of the broad band at 3800–3000 cm^{-1}). Their TGA curves (Figure S8) further display two weight losses of the desorption of surface water (RT to 200 °C) and of the condensation of hydroxyl groups (200–800 °C), which are respectively almost overlapping for the two samples. This suggests that they have similar amount of surface water and silanol groups, i.e. similar surface properties. More detailed analysis about their DRIFT and TGA results can be found in the supporting information.
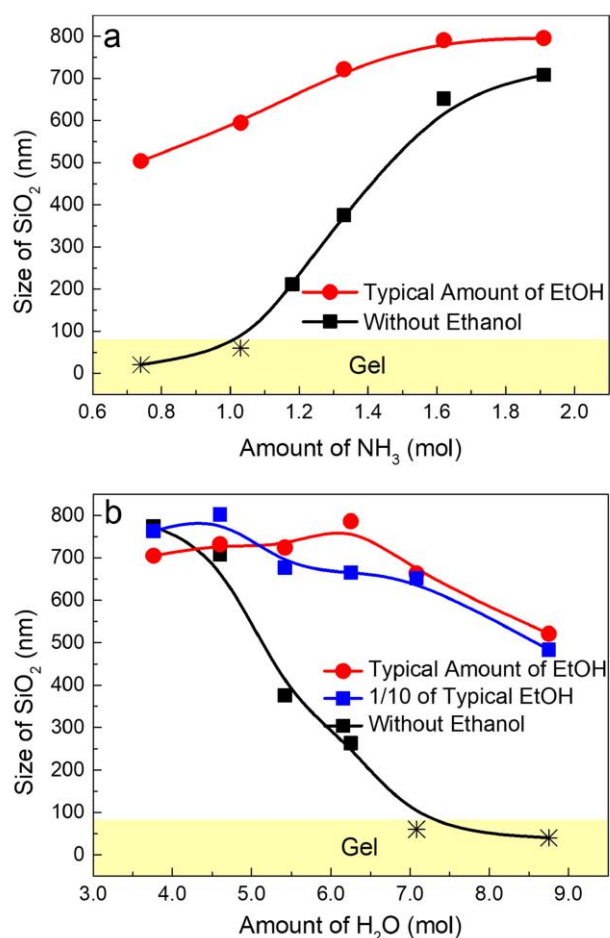
(a) Particle sizes variation with NH_3 in 5.42 mol of H_2O. (b) Particle size variation with H_2O in 1.33 mol of NH_3.

It can also be observed in Figure 3 that compared to the typical Stöber method, the organic solvent-free process is only able to produce monodisperse silica spheres within a certain narrow range of water to ammonia ratio. At low ammonia or high water content, which is expected to produce particles smaller than 100 nm, a non-uniform gel is formed. Nevertheless, literature reported silica spheres as small as 50 nm could be produced via a typical Stöber process.[1] In those cases where small particles are produced such as at lower concentrations of ammonia, the hydrolysis of TEOS is less efficient, resulting in monomers with fewer silanol groups. These monomers tend to condense loosely to larger siloxane clusters and branched networks first, and then collapse into smaller and dense particles.[15] The two steps can be carried out well in ethanol solution. However, in the organic solvent-free process, it was observed that the liquid was absorbed by the polymer networks to form a non-flowing gel, so that the reaction cannot proceed to the next step to produce dense particles. We hypothesize that this is due to the much smaller liquid volume of the organic solvent-free process than the typical process with ethanol does not have sufficient space to accommodate and disperse the loose polymer networks formed at the beginning of the reaction, leading to the polymer segments and networks can contact and condense with each other. Therefore, based on the data, another proposed role of ethanol in the typical Stöber process seems to be the dispersion of the monomers, oligomers and nuclei produced by the reaction, to avoid the formation of non-flowing and non-uniform gels.

However, the roles of ethanol are not indispensable. In the organic solvent-free process, although the reactants are immiscible, the initial reaction under stirring will gradually produce ethanol from hydrolyzed TEOS at the interphase of the two phases (Eq.1 and Eq.3 in Figure S3) and dissolve the reactants progressively. Therefore, as long as the ratio and volume of water and ammonia are appropriate, uniform silica spheres larger than 100 nm are able to be produced. Moreover, keeping the above in mind, when synthesizing silica particles smaller than 100 nm, the problem of gel formation due to insufficient space can be avoided by reducing the concentration of TEOS to decrease the amount of monomers. Figure 4a shows the results of using the same amounts of ammonia and water while reducing the amount of TEOS. The process with lower TEOS concentration results in smaller relatively uniform particles. Furthermore, it confirms that particles smaller than 100 nm can indeed be obtained instead of formation of a gel network. High angle annular dark field scanning transmission electron microcopy (HAADF-STEM) and electron tomography were applied to study the morphology and size of these particles with a diameter smaller than 100 nm. As shown in Figure 4b1 and 4b2, the particle size is still relatively uniform (see also the Figure S1b for the particle size distribution of ~50 nm particles), but the sphericity is lower than what was observed for larger particles. The 3D reconstruction obtained by electron tomography (Figure S9) shows that the particles with a diameter of ~50 nm are not perfect spheres, but have a rather oval shape in combination with aggregates of smaller (spherical) particles. The relatively irregular morphology of the smaller particles is hypothesized to be due to that in their synthesis processes, the primary particles were already in a larger size (resulting from the stronger interaction between the polymer segments and the

Figure 3. The comparison between the typical Stöber method with ethanol and the organic solvent-free method of this work. For syntheses with added ethanol, the typical amount of ethanol to dilute TEOS to 0.28 mol/L has been used as well as 1/10th of that amount. The amount of TEOS in all syntheses is 50 mL.

continuous phase), while the final particles are smaller.[15,16] Therefore, the growth process, from the larger primary particles to the small final particles, might be shorter, e.g. fewer primary particles aggregated together or less monomer was added on the primary particles. In this case, smaller particles formed from aggregation/addition of fewer and larger primary particles had rougher surfaces and more irregular shapes than larger particles formed from more and smaller primary particles.
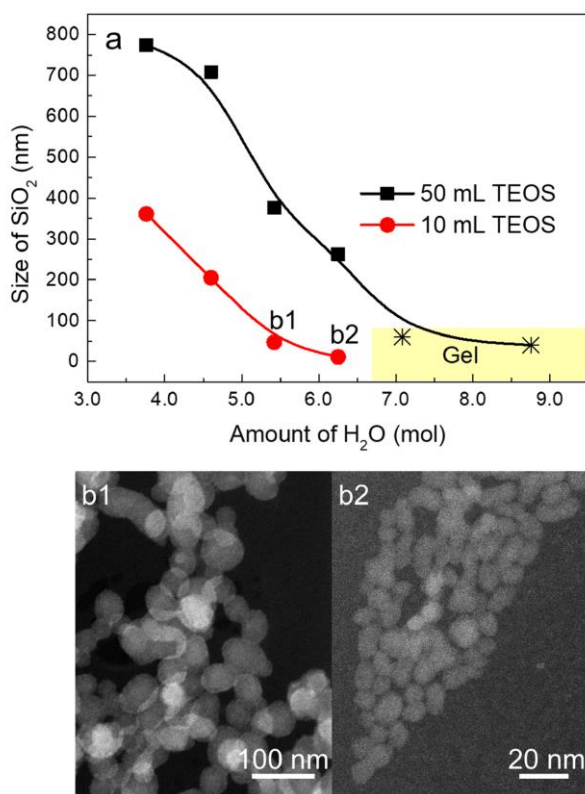

Figure 4. Experiments to synthesize silica particles smaller than 100 nm by the organic solvent-free method. (a) The particle sizes comparison of silica synthesized with two different amounts of TEOS by the organic solvent-free method. (b1, b2) HAADF-STEM images of silica particles with a diameter of ~50 nm (b1) and ~10 nm (b2) synthesized by the organic solvent-free method. The amount of NH_3 is 1.33 mol in all experiments. The b1 and b2 data points in Figure 4a correspond to Figure 4b1 and Figure 4b2, respectively.

The results thus show that particle size ranges of silica that can be prepared by the organic solvent-free process are the same as the typical Stöber method, which can be controlled between about tens of nm and 1 µm. The solid content obtained by the modified process for silica particles smaller than 100 nm is ~17 g/L to ~19 g/L, which is similar with that of the typical Stöber method. The larger particles, however, can be synthesized at a solid content of ~53 g/L to ~123 g/L, making it more suitable for large scale fabrication than the typical Stöber processes. In addition, Nagao et al. reported an extension of the Stöber method to synthesize silica particles larger than 1 µm, which introduced electrolytes in the hydrolysis of alkyl silicates.[22] We preliminary studied if this extended method of adding electrolytes still works in the organic solvent-free process. As shown in Figure S10, the diameters of silica increased from ~380 nm to ~1.8 µm and from ~710 nm to

~2 µm, respectively, by the addition of 0.1 g (4.14×10^{-4} mol) of $Cu(NO_3)_2 \cdot 3H_2O$, while still remaining uniform. It shows that this modification based on the Stöber method is also feasible for the organic solvent-free process. Therefore, it's a reasonable expectation that more syntheses of various other materials based on the typical Stöber method, such as porous materials, aerogels, carbon materials, and metal oxide materials, are also applicable to the organic solvent-free alternative method described here.

Conclusion

In summary, we found that although ethanol plays an important role in the Stöber method to control particle size and avoid gelation, it is not indispensable. A modification of the Stöber method was described, able to synthesize spherical silica particles with a controllable size without any organic solvents addition to the initial synthesis mixture. The particle size range of the SiO_2 spheres that can be prepared by this organic solvent-free process is the same as the typical Stöber method and even with a more sensitive particle size adjustment depending on the smart combination of water and ammonia content. This method can save a lot of organic solvent use and produces a higher solid content, which is more economical and environmentally friendly. Moreover, because the Stöber method is the foundation for materials synthesis of a variety of important structures, this organic solvent-free improvement will open new doors for all related fields when extended to other synthesis processes based on the Stöber method.

Experimental Section

Synthesis of silica particles

The organic solvent-free process is similar to the Stöber method except there is no additional organic solvent added. Ammonia solution (wt % = 25%) and deionized water were mixed in a beaker and agitated at 400 rpm at room temperature. The calculation of the amount of water in the synthesis included the water content in the ammonia solution and the water directly added. Then, 50 mL of tetraethyl orthosilicate (TEOS) was added into it quickly. The mixture was kept stirring at room temperature for 24 h. The silica spheres were collected by centrifugation without washing. Subsequently, they were dried at 353 K for 24 h. The details on the volumes and amounts of reactants of all the organic solvent-free syntheses in this work are listed in Table S1.

The synthesis with ethanol, executed as a control experiment, is the classic Stöber method. Ammonia solution (wt % = 25%) and deionized water were dissolved in 300 mL of ethanol to prepare a solution A and agitated at 400 rpm at room temperature. An ethanol solution B containing 50 mL of TEOS was added into it quickly. The specific amounts of ethanol and reactants are shown in Table S2. The amount of ethanol in solution B is equal to the total amount of ethanol minus the amount of ethanol in solution A. For samples 34-39 in Table S2, the amount of ethanol in the solutions during the synthesis was one-tenth that of the other samples. The mixture was kept stirring at room temperature for 24 h. The silica spheres were collected by centrifugation without washing, and subsequently the spheres were dried at 353 K for 24 h.

Characterization

The topography of silica particles larger than 100 nm was investigated by a field emission scanning electron microscope (FEI Quanta 250 SEM) operating at 20 kV. The sample powder was sputter-coated with gold

before the SEM observation. The particles smaller than 100 nm were analyzed with high angle annular dark field scanning transmission electron microcopy (HAADF-STEM) using a Thermo Fisher Tecnai Osiris electron microscope operated at 200 kV and 60 pA beam current. For HAADF-STEM imaging, the powder was diluted with ethanol, then a few drops from the suspension was dropped on a carbon coated polymer film on a copper grid. The particle sizes were calculated by measuring all the visible particles in the SEM or STEM images and averaging them. To prevent beam damage on the samples, a fast tomography technique was used. Tomography series were acquired by using the Fischione model 2020 single-tilt tomography holder over a tilt range from −50° to +70°, with tilt increments of 2°. The reconstruction of the tilt series was performed using the Astra Toolbox. Visualization and segmentation were performed using Amira 5.4.0 software. The conductivity was measured during the synthesis by a Metrohm 644 Conductometer. Nitrogen sorption measurements were carried out at -196 ℃ on a Quantachrome Quadrasorb SI automated gas sorption system. Before the measurements, the samples were degassed for 16 h under high vacuum at a temperature of 200 ℃. Prior to DLS measurements, the powders were dispersed in deionized water to prepare a suspension. Then, the particle size and agglomeration was measured by dynamic light scattering using a Zetasizer NanoZS (Malvern, UK) analyzer. Thermogravimetric analyses (TGA) and differential thermal analysis (DTG) were measured on a Mettler Toledo TGA-DSC 3+ in a continuous 80 mL/min flow of Ar, and the samples were flushed for 30 min prior to the measurement to ensure an inert gas atmosphere. A heating ramp from 30 ℃ to 1000 ℃ with a heating rate of 10 ℃/min was applied. The diffuse reflectance infrared Fourier transform (DRIFT) were performed on a Nicolet 6700 Fourier Transform IR spectrometer, equipped with a DRIFT Praying Mantis High Temperature Reaction Chamber (Harrick, USA). The measurement parameters included a resolution of 4 cm^{-1} and the accumulation of 100 scans for each spectrum. KBr was used as a background, and samples for the measurements were diluted by KBr to 2 wt%. The spectra for each temperature were obtained after heating to that temperature, stabilizing for 30 min and cooling back to room temperature, to exclude the thermal effects at high temperature. The heating and cooling processes were completed in the chamber after the samples were diluted with KBr, except that the samples for the spectrum of 1000 ℃ were heated and coolded before mixing with KBr, since KBr would melt at 1000 ℃.

Conflicts of interest

There are no conflicts to declare.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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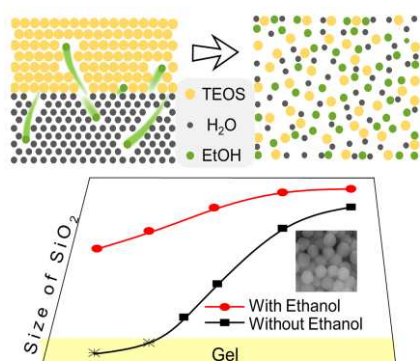
Organic solvents are not indispensable in the Stöber method and its extensions. Ethanol produced from the hydrolysis of tetraethyl orthosilicate (TEOS) already makes the reactants miscible and completes the synthesis. A simple organic solvent-free alternative to the Stöber process enables the synthesis of controllable uniform silica spheres, and has the potential to be extended to other Stöber process-based material synthesis.