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Part 1. Formation of Silica Structures Utilizing A Cationically Charged Synthetic Polymer At Neutral pH and Under Ambient Conditions

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Summary

The formation of uniquely synthesized well-structured nanometer and micrometer sized silica spheres utilizing a cationically charged synthetic polymer at neutral pH and under ambient conditions is reported. The products were characterized using Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Fourier Transform Infra Red Spectroscopy (FTIR) and X-Ray Diffraction (XRD). Evidence was found that the final silica structures incorporated the polyallylamine hydrochloride (PAH), the cationically charged synthetic polymer used here. It is proposed that PAH facilitates the formation of silica structures by a similar mechanism to that described previously in the literature for the formation of silica by the silicatein proteins.

Introduction

It is of great interest to synthesize and characterize controlled structures at nanometer and micrometer size scales for emerging technologies. Such materials have tremendous potential applications in the field of materials science, in areas such as electro-optics, nano-composites, ceramics, rubber technology and biomedical materials but they are also useful in catalysis and separations. In this investigation, we report well-structured silica nano spheres uniquely synthesized at neutral pH and ambient conditions, using an organosilicon precursor and a cationically charged synthetic organic polymer.

The sol-gel synthesis of novel silica structures has been studied thoroughly under severe conditions of pH and / or temperature[1, 2, 3]. It was discovered recently that in diatoms the formation of ornate silica structures is catalyzed by silaffin proteins[4]. It has also been described how these macroscopic silicatein filaments show catalytic activity in addition to structure directing behavior. The macroscopic filaments were found to serve as scaffolds, which facilitates the formation of novel silica and silsesquioxane structures. In particular, they were found to behave as templates that direct the growth of product structures over the surface of the protein filaments[5].

In this investigation, we have successfully synthesized similar silica structures using polyallylamine hydrochloride (PAH), which is a cationically charged synthetic organic polymer at neutral pH and under ambient conditions. The results presented herein show that the previously believed concept that the specific enzymes / peptides catalyze the silica synthesis due to their particular chemical structure and activity[4, 6-8], may also be applicable to synthetic macromolecules. This is further supported by the evidence of formation of similar silica structures synthesized using other synthetic organic polymers that include polyallylamine and polyethyleneimine [9]. We propose that the cationically charged synthetic polymer investigated here (PAH) facilitates the formation of silica structures by a similar mechanism to that described above.

Related behavior has also been seen recently for organogel-silica composites[10]. Another investigation revealed that synthetic diblock copolypeptides were able to catalyze the formation of ordered silica *in vitro*[11]. It was also reported that a silica gel is formed in a few minutes, for an inorganic silicate precursor at pH 8.5, in the presence of a polymer catalyst, but the structure and morphology of the resulting material were not reported for this system[12].

Experimental

The synthesis experiments were carried out by adding a solution (0.01 to 10 M) of tetramethoxysilane (TMOS) pre-hydrolyzed in 1 mM HCl to a PAH solution (1-50 mg/ml) and buffering the mixture to pH 7.0[9]. These conditions for the range of TMOS and PAH concentrations studied resulted in the precipitation of silica particles within 5 minutes. The non-catalyzed control mixtures did not precipitate silica, even after centrifuging, and were observed to form a transparent gel in a few hours.

After just a couple of minutes of the reaction time, this reaction mixture was seen to contain silica particles, in the colloidal phase as well as in the precipitate. The reaction mixture was then centrifuged and the precipitate was washed thoroughly with de-ionized ultra filtered (DIUF) water, in order to remove the remaining PAH, and thus avoid further polymerization of silica particles.

Results and Discussion

The micrographs obtained by Scanning Electron Microscopy (SEM), show that these precipitates were made up of silica spheres of nanometer and micrometer sizes (see Figure 1). It was also found that the silica spheres were composed of smaller particles (30 nm or less), which are the condensed sol / colloidal silanol particles present in the pre-hydrolyzed TMOS solution[9]. Further, the product composition was studied using Energy Dispersive Spectroscopy (EDS) and Fourier Transformed Infra Red (FTIR) spectroscopy. These results showed the presence of silica like structures (I.R. peaks near 1100 cm^{-1} and strong Si and O signatures in the EDS)[9]. We also found evidence in above spectra, for the first time, that the final silica structures incorporated the PAH. The IR spectra showed the C – H and N – H stretching modes of the PAH and EDS showed C, Cl and N peaks in addition to the silica signatures seen by both the methods. This indicates that the polymer is not only catalyzing the reaction but also acting as a structure-directing agent or template as described by Tacke for the formation of silica by the silicatein proteins[5].

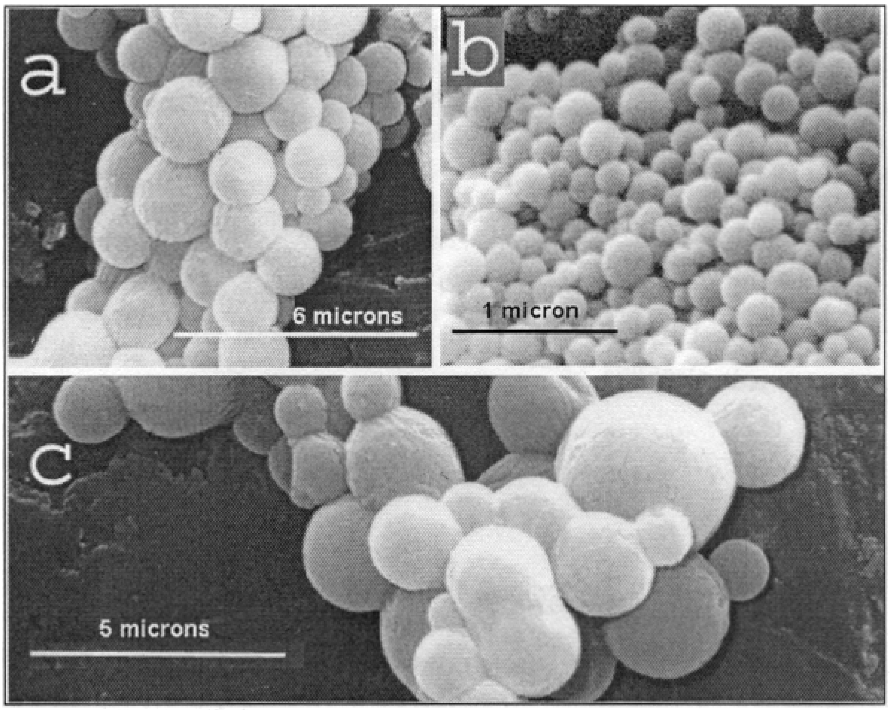

Figure 1. Representative SEM micrographs of silica nanometer and micrometer sized structures formed using PAH at neutral pH and under ambient conditions.

It was observed that adjusting the pre-hydrolysis time, reaction time, buffer, molecular weight of the polymer, TMOS concentration, polymer concentration and density of active sites on the polymer chain could each control the size and morphology of the silica structures. Some of these parameters were found to significantly influence the silica synthesis and are discussed briefly below. Further detailed studies are still in progress and the results will be presented in due course[9].

1. Effect of Pre-hydrolysis Time

As expected, the longer the pre-hydrolysis time for the TMOS solution, the larger is the particle size up to a certain point in time. But at a very large pre-hydrolysis time (90 min), very few large particles (2-10 μm) were found. Instead, large numbers of very small particles (~200 nm) were seen. We observed the formation of interconnected structures that are made up of small particles and these tiny particles did not condense further to form larger particles, as were seen for any other samples. It was also seen that longer pre-hydrolysis time produces smoother particle surfaces.

2. Effect of the Reaction Time

The reaction time also affects the silica particles. In particular, no large particles (> 2 μm) were observed for shorter reaction times (less than 5 minutes). However, smaller particles (30-50 nm) in addition to large particles were seen for the samples with longer reaction times (5-20 minutes). In addition, the increase in particle size with the reaction time shows that the silica particles are the agglomerates of smaller particles wherein the smaller particles are allowed to come together over a longer period of time and form bigger particles. This is supported by the evidence that the half broken larger particles were seen by SEM (not included here) to be made up of smaller particles of sizes between 50-200 nm[9]. It was also observed that larger particles had smaller particles sticking on their surfaces. This clearly suggests that the particle growth is by continuous nucleation.

3. Effect of Buffer

Different buffers (even near pH 7.0) were found to affect the silica synthesis. For example, PAH is not fully soluble in phosphate-citrate buffer, which was the buffer adopted in previous studies[4, 6]. This may be due to the three acid groups per molecule of the citric acid binding together different polymer chains through hydrogen bonding. This idea was supported by the fact that PAH was found to be soluble in sodium citrate buffer, wherein all the hydrogen atoms are replaced by sodium atoms. It is interesting to note that there was gel formation (but no ordered precipitation) when deionized ultra filtered (DIUF) water (pH 7.0) was used instead of buffer, even in presence of polymer. As the chain conformation of PAH is governed by the buffer[13], we propose that a buffer affects the silica synthesis and the product structure. Hence, here we chose potassium phosphate buffer, which formed solutions with PAH over a considerable range of polymer concentration. In addition, the ions present in the buffer and their quantity affect the synthesis. In the case of diatoms, it has been proposed that the ratios of Si to P, C and N (i.e. the nutrients in the medium) are secondary factors affecting the silica synthesis[14].

We are currently quantifying the effects of all the above-mentioned process variables in this system and attempting to synthesize different silica geometries other than the spheres. Further investigations employing a few more polymers will provide an insight to the mechanism of silicification at neutral pH and under ambient conditions. The results of these investigations will be reported later[9].

Conclusion

We report the formation of uniquely synthesized well-structured silica nano and micro spheres utilizing a cationically charged synthetic polymer at neutral pH and under ambient conditions, for the first time. We propose that the cationically charged synthetic polymer investigated here (PAH) facilitates the formation of silica structures by a similar mechanism to that described by Tacke for the formation of silica by the silicatein proteins[5]. We also found evidence that the final silica structures incorporated the PAH. These results obtained under such modest conditions may be useful for the economical industrial synthesis of controlled silica structures.

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