Conducting Materials

DOI: 10.1002/ange.200501446

# Rapid Synthesis in Ionic Liquids of Room-Temperature-Conducting Solid Microsilica Spheres**

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Herein, we report the rapid synthesis of monodispersed conducting solid microsilica spheres by hydrolyzing tetramethylorthosilicate (TMOS) and tetraethylorthosilicate (TEOS) in an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate, at room temperature. We also report the effect of varying experimental conditions such as the temperature and pH of the solutions on the synthesis and morphology of the silica spheres.

Metal oxide spheres have attracted much attention in fields such as optical materials and catalysts, as well as other nanotechnologies.[1–5] The sol–gel method is one of the most useful means to prepare metal oxide spheres and small particles with high densities.[6] Stöber et al. developed an excellent method to prepare monodispersed silica spheres from silicon alkoxides in alcoholic solutions.[7] This process was extended to the preparation of various metal oxides such as $Al_2O_3$, $TiO_2$, and $ZrO_2$.[8–10] While the original Stöber technique yields silica spheres with sizes in the range of 200–700 nm, a modified Stöber method yields larger spheres of 1–2 μm.[11] However, it is difficult to prepare monodispersed silica spheres larger than 2 μm in alcoholic basic media at room temperature,[7,11] while the synthesis of silica spheres in acidic media has been reported to produce spheres as well as irregularly shaped particles of 10–60 μm in size.[12] Controlling the size, shape, monodispersity, and yield of the desired product has become a challenge for material chemists.

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[**] We thank Dr. Yakov Langsam for SEM analyses, Michael Riboch for AFM measurements, and Dr. Boris Markovsky for conductivity measurements.

Room-temperature ionic liquids (RTILs) have received much attention as solvents, and significant progress has been made in their applications to biphasic reactions, chemical synthesis, electrochemistry, catalysis, polymerization, biocatalysis, liquid–liquid separations, extractions, dissolution, biopolymer, molecular self-assembly, and interfacial synthesis.[13,14] Recently, an ionic liquid was used as both a solvent and a template in the synthesis of zeolites.[15] Supermicroporous lamellar and well-defined inverse opal microstructured silicas have been prepared in ionic liquids, which serve as templates.[16,17] Hollow $TiO_2$ microspheres have been prepared in ionic liquids, and it was reported that their size was influenced by the rate of stirring and the reaction temperature.[14] Elsewhere, mesoporous silica nanoparticles of various morphologies that contained an ionic liquid were used as a controlled-release delivery nanodevice to discharge antibacterial ionic liquids against *Escherichia coli K12*.[18]

Moreover, owing to their diverse electrochemical properties, ionic liquids have been used as electrolytes for electrochemical devices such as lithium secondary batteries, electric double-layer capacitors, dye-sensitized solar cells, fuel cells, and actuators.[19] Several important properties of ionic liquids make them attractive substitutes for volatile organic solvents.[20] The properties of RTILs can be controlled over a wide range through variation of both the anion and cation as well as the chain lengths of the substituent groups. An increasing chain length in the cation alters the melting point of the ionic liquids and increases their viscosity and hydrophobicity.[21] Varying the anion also affects the property of ionic liquids; for example, salts based on the tetrachloroaluminate(III) anion are extremely water sensitive, whereas those based on the hexafluorophosphate anion are neutral and extremely hydrophobic.[22] Through careful consideration of the conducting properties and hydrophobicity of the ionic liquid, we chose 1-butyl-3-methylimidazolium hexafluorophosphate, $BMI^+PF_6^-$, as the solvent for the preparation of the silica spheres.

The hydrolysis of TMOS and TEOS in a fixed amount of ionic liquid under different reaction conditions (temperature, pH) were studied. The products were characterized by small-angle X-ray diffraction (SAXRD), energy-dispersive X-ray (EDX) spectroscopy, mass spectrometry, and Raman spectroscopy. An in-depth morphological study of the silica spheres prepared under different conditions was carried out by scanning electron microscopy (SEM), and the solid-state nature of the silica spheres was confirmed from the microtomed cross-section of the sample by transmission electron microscopy (TEM).

SAXRD results revealed a lack of organization of the pores for the as-prepared silica spheres, whereas some extent of order could be observed in a sample that was calcined at 1000 °C. EDX spectroscopy showed the presence of phosphorus and chlorine from the encapsulation of the ionic liquid, $BMI^+PF_6^-$, and aqueous HCl solution within the silica spheres in the as-prepared sample, whereas their absence was noted in the sample calcined at 1000 °C. Desorption chemical ionization mass spectrometry indicated the presence of 1-butyl-3-methylimidazole (BIM-H) in the sample, while the Raman spectrum of the as-prepared silica spheres revealed C–H stretching and ring-stretching vibration bands that confirmed the presence of the entrapped ionic liquid as well as O–H stretching bands from water molecules. The entrapped ionic liquid remained intact in the silica spheres even after several washings with acetone. The D and G bands in the Raman spectrum indicate the carbon content of the sample annealed at about 1000 °C.

The size distribution of the microspheres was confirmed by SEM, which revealed diameters in the range of 50–85 μm. The surface area measured for the as-prepared sample was $3.17\ m^2\,g^{-1}$, while that for the calcined sample ranged from 8–$12\ m^2\,g^{-1}$, which is much higher than reported values.[12] The increase in surface area is a result of the evaporation or decomposition of the entrapped molecules of water and ionic liquid inside the silica spheres; upon removal of the entrapped species, empty pores are left behind. Thermogravimetric analysis of the silica spheres showed a weight loss of about 9.6 % at 150 °C due to the removal of water, whereas a weight loss of 17 % at 550 °C was attributed to the decomposition and removal of the entrapped ionic liquid, as confirmed by Raman spectroscopy.

The proposed mechanism for the formation of the different morphologies of the spheres is shown in Figure 1. As a result of the hydrophobicity of the ionic liquid, microsized droplets of aqueous HCl solution are formed under vigorous stirring. Molecules of the silica precursor (TMOS, TEOS) enter these aqueous acidic microdroplets and are hydrolyzed, leading to the formation of microspheres. Aggregated and overgrown dimeric silica spheres also result from the above mechanism, as hydrolysis of the silica precursor takes place inside two attached microdroplets of water.

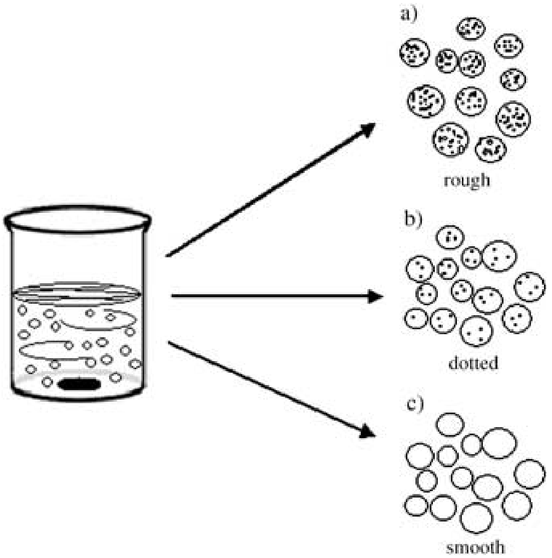

**Figure 1.** Schematic representation for the formation of different morphologies of silica spheres under different experimental conditions.

The formation of silica spheres with rough surfaces (Figure 1 a) depends on the reaction time and the temperature. With a longer reaction time, microdroplets of water adhere to the fully grown silica spheres and the silica precursor is hydrolyzed in those microdroplets to yield a rough surface, as depicted in Figure 2. Changes in the reaction time, the pH of the aqueous solution, the temperature, and the hydrophobicity of the ionic liquid (all under stirring) have an important effect on the preparation and the peripheral morphology of the silica microspheres. By decreasing the reaction time (Figure 1 b,c), silica spheres with smoother surfaces were obtained as shown in Figures 3 and 4.

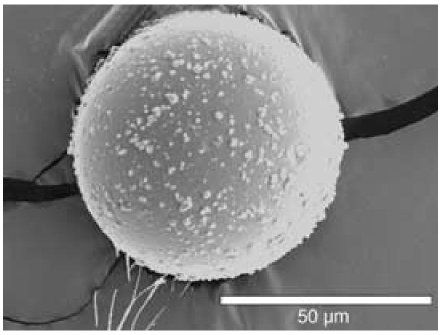

***Figure 2.*** Silica spheres with rough surfaces as synthesized from TMOS at 50 °C for 1 h in aqueous HCl solution (0.25 M).

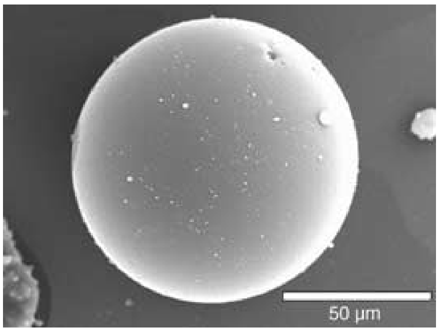

***Figure 3.*** Silica spheres with a dotted morphology as synthesized from TMOS at 50 °C for 1 h in aqueous HCl solution (0.1 M).

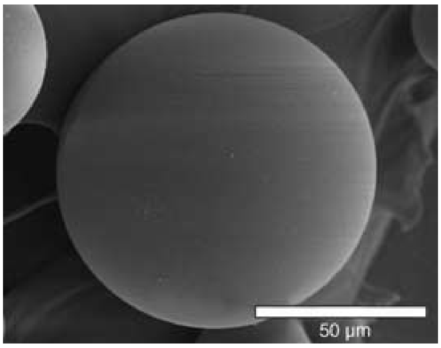

***Figure 4.*** Silica spheres with smooth morphology as synthesized from TMOS at 50 °C for 5 min in aqueous HCl solution (0.25 M).

It was observed that the pH of the acidic solutions as well the temperature affect the rate of hydrolysis. Reactions were carried out at pH 1–2 (0.25–0.01 M HCl) at room temperature and at 50 °C under vigorous stirring. Under similar reaction conditions (room temperature, 0.1 M HCl, 30 minutes), a clear solution was observed for the TEOS precursor whereas silica spheres formed in the case of TMOS which suggests that the rate of hydrolysis of TMOS is faster than that of TEOS. This difference in rate was also confirmed upon hydrolysis of TMOS at room temperature with 0.01 M HCl for 30 minutes by which smooth silica spheres were obtained; under the same reaction conditions with TEOS, a clear solution was obtained. Thus, variation of the reaction conditions leads to the formation of different morphologies of silica.

To determine whether the silica spheres were hollow or solid we microtomed the products, and studied the cross-section of a sample (Figure 5). The TEM image shows a smooth outer layer and small particles arranged inside to form a solid microsilica sphere.

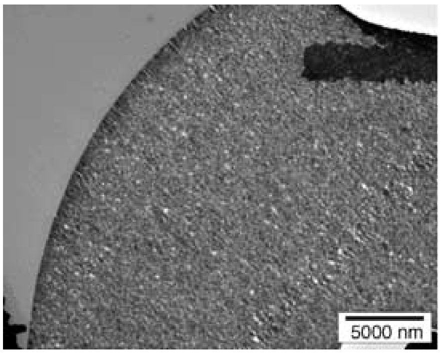

***Figure 5.*** TEM image of the cross-section of single silica spheres.

Control hydrolysis reactions (1 h) in the absence of ionic liquids were also carried out to study the morphology of the hydrolyzed products of TMOS (0.5 mL) and TEOS (0.5 mL) with aqueous HCl solution (0.25 M) under vigorous stirring at room temperature as well as at 50 °C. Clear solutions were observed for the reactions performed at room temperature, but silica gels were observed at 50 °C, which suggests that the ionic liquid accelerates the rate of reaction at room temperature and plays an essential role in the formation of the spheres. A second control reaction (1 h) in the presence of the ionic liquid but in the absence of aqueous HCl solution was performed to study the morphology of the hydrolysis products of TMOS (0.5 mL) and TEOS (0.5 mL) under vigorous stirring at 50 °C. In both cases, dustlike particles (1-micron particles as well as aggregates) were observed. These results demonstrate that in the presence of aqueous HCl solutions, the dustlike particles play a significant role by functioning as seeds for the formation of fully grown silica spheres. These dustlike silica particles tested positive for antibacterial activity (*E. coli*, Gram-negative). Reactions carried out for shorter periods of time and in the absence of aqueous HCl solution resulted in clear mixtures, which substantiate the roles of the acidic solution and the reaction time. The above findings demonstrate the necessity of the ionic liquid and the aqueous HCl solution under vigorous stirring in order to develop silica microspheres.

It is known that silica acts as an insulator and that the conducting properties of silica can be improved through doping with electrolytes.[23] Interestingly, with our synthetic route to the silica microspheres, the entrapped molecules of the ionic liquid induce their conducting properties at room temperature.[24] The bulk conductivity as determined by impedance measurements for pristine 1-butyl-3-methylimidazolium hexafluorophosphate $BIM^+PF_6^-$ is reported as $3.8\times10^{-2}\,S\,cm^2\,mol^{-1}$.[19] The conductivity of the silica spheres was also measured by the impedance method over the frequency range 5–50 kHz at room temperature and 60 °C. The conductivities observed at 5 kHz at different time intervals are $7.87\times10^{-6}$, $8.50\times10^{-6}$ (72 h), and $9.83\times10^{-6}\,S\,cm^{-2}$ (144 h) at room temperature. The conductivity decreased after 192 h to $6.77\times10^{-6}\,S\,cm^{-2}$. Thus, the presence of entrapped ionic liquid and water were needed to improve the conductive properties of our synthesized silica spheres. The observed increase in the conductivity with increasing time was due to adsorption of water molecules on the silica.[25] The conductivity was found to increase with an increase in temperature, with values of $8.14\times10^{-6}$ (194 h) and $9.76\times10^{-6}\,S\,cm^{-2}$ (216 h) measured at 60 °C. These results are interpreted as a result of the increased mobility of entrapped molecules of the ionic liquid.[24]

The conductivity of the silica spheres will hopefully gain importance for their applicability in electrochemistry and sensors.[26a–c] The conductivity is most probably due to a special oriented alignment of the molecules of ionic liquid along the surface. A detailed study of the conductivity of an individual silica sphere is in progress and will be reported soon. The current process for the synthesis of silica spheres in an ionic liquid has opened new directions and opportunities to explore their application in several fields, however more research has to be carried out to address the challenges that remain and to explore the importance of ionic liquids in other fields.

## Experimental Section

In a typical synthesis, TMOS (0.5 mL, 0.516 g, 3.38 mmol; Aldrich Chemical Co, 99 %) and $BMI^+PF_6^-$ (3 g, 0.01 mol; Aldrich Chemical Co., 96 %; density = 1.37 g cm$^{-3}$) were stirred in a 15-mL teflon vessel for 1 min at room temperature to form a homogeneous transparent solution. Then, 0.01 M aq. HCl (0.25 mL) was added under stirring. (Milli-Q water was used to prepare the acid solution and a 0.2-µm Whatman Anotop 25 filter was used for filtration). The reaction mixture was stirred vigorously at room temperature for 30 min and then quenched by the addition of acetone. The white spheres were separated by centrifuging at 9000 rpm for 10 min, and the product was washed with acetone several times to remove excess ionic liquid, then centrifuged at 9000 rpm for 10 min, and dried under vacuum for 24 h. The size of the silica spheres obtained ranged from 50 to 85 µm.

Received: April 27, 2005

**Keywords:** conducting materials · hydrolysis · ionic liquids · silica · synthesis design

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