

Effect of Reaction Parameters on the Hydrolysis of Tetramethyl Orthosilicate and Tetraethyl Orthosilicate and their Surface Morphology in an Ionic Liquid

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Silica with different morphologies is found to be an interesting class of material that receives significant attention nowadays. Here, we report a simple and efficient method for the room-temperature synthesis of silica spheres (20–80 μ m sizes) in room-temperature ionic liquids (1-butyl-3-methylimidazolium hexafluorophosphate). The effect of reaction parameters such as pH, temperature, time, and solvent on the hydrolysis products and their morphology is described in this research paper. The morphology of the hydrolysis products of tetramethoxy silane and tetraethoxy silane are studied with the help of scanning electron microscopy. These results demonstrate a practical method for synthesizing smooth and rough surface silica spheres by modifying the reaction conditions. The confinement of the ionic liquid in the silica is studied with the help of Raman spectroscopy and mass spectroscopy.

I. Introduction

The sol-gel method is one of the most useful methods for preparing silica (SiO₂) particles with different structures. Toward the end of 1956, Kolbe described the formation of silica particles by reacting tetraethyl silicates in alcohol solutions with water in the presence of certain bases,¹ and noted that a very pure reactant gives uniform spherical silica particles. In 1967, Stober, Fink, and Bohn carried out a systematic study to prepare monodispersed silica spheres.² This simple hydrolysis process was later extended, and today the preparation of various metal oxides such as Al₂O₃, TiO₂, ZrO₂, etc. is conducted in a similar way.³⁻⁵

Previously, sol–gel synthesis and alcohol–water solutions, as solvent mixture, were used for hydrolysis, and these reactions were mostly acid or base catalyzed.^{1,6–9} Recent research by Adachi *et al.*¹⁰ describes the use of a nonalcoholic diglyme solution, whereas cyclohexane as a solvent was used by Roy *et al.*¹¹ for sol–gel silica synthesis. Herein, we explain the importance of room-temperature ionic liquids (RTILs) as solvents for the sol–gel preparation of silica. The application of RTILs has reached different fields in chemistry, such as biphasic reactions, chemical synthesis, electrochemistry, catalysis, polymerization, biocatalysis, liquid/liquid separations, extractions, dissolution, biopolymer, molecular self-assembly, and interfacial synthesis of opal microstructure silica,²³ super-microporous lamellar silica,²⁴ zeolite,²⁵ and hollow TiO₂ microspheres.²² In all these synthetic examples, the RTILs also act as templates.

The properties of RTILs can be designed according to the type of anion and cation, and according to the chain length of

the substituent groups. An increase in the alkyl chain length of the cation results in a change in the melting point and an increase in the viscosity, as well as hydrophobicity, of the ionic liquid (IL).²⁶ In our sol-gel synthesis, we used 1-butyl-3-methylimidazolium as the cation and hexafluorophosphate as the anion. This molecule shows neutral and extremely hydrophobic properties.²⁷ The conductive properties of RTILs are the source of conductivity of the synthesized products.²⁸ The additive property of the IL and the physical confinements of the IL in the formed product enabled us to obtain spherical silica with conducting properties^{29,30} in the sol-gel synthesis. In a previous report, we emphasized the conductive properties of the silica prepared by using IL as the solvent.²⁸ In the current paper we extend the previous report, and discuss the effect of temperature, time, pH, and the effect of an IL solvent on the synthesized product, as well as its morphology. We have also demonstrated herein the control reactions, which lead to different morphologies of the hydrolysis product in the absence of an IL, and the hydrolysis of the silica precursors in water, which gives an aggregated precipitate. In this article, scanning electron microscopy (SEM) is used as a tool for characterizing the morphological changes that the product undergoes as a function of the reaction parameters. Raman and mass analyses assist in the detection of the presence of IL in the sphere samples.

II. Results and Discussion

The general procedure for the preparation of silica spheres is presented in our previous report.²⁸ In this article, we present several hydrolytic reactions. The brief procedure is as follows: the hydrolytic reaction was carried out in a Teflon vessel of 15 mL. The 0.5 mL of tetramethoxy silane (TMOS)/tetraethoxy silane (TEOS) (Aldrich Chemical Co., 99%, Israel) precursors for silica, with 3 g of IL (BMI⁺BF4⁻, Aldrich Chemical Co., 96%), were stirred for 1 min in a Teflon vessel to form a homogeneous transparent solution. To this solution, 0.25 mL acidic water is added under stirring condition. The hydrolytic precipitation reaction is carried out with stirring under different experimental conditions, by varying the acidic concentration, temperature, and time. The volume of the silica precursors, IL, and the acidic water remains the same for all reactions. The reaction product in all cases, and under all conditions, is silica. Our conclusion is based on the identification of the silicon and oxygen peaks in an energy dispersive X-ray spectrum of the asprepared and calcined products.

The obtained results are categorized according to the different experimental conditions. The morphologies of the as-synthesized products as a function of various experimental conditions such as time, pH, temperature, and solvent medium were obtained from SEM measurements and are discussed in various sections throughout this paper. Explanations are provided as to the way in which these parameters correlate with each other.

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(1) Hydrolysis of TMOS and TEOS under Different Experimental Conditions; Time Dependence on the Hydrolysis of TMOS and TEOS at 50°C

SEM images of the hydrolysis of TMOS as a function of reaction time are presented in Fig. 1. The duration time of the reaction plays an important role in determining the surface morphology when all other parameters are kept constant (amount of IL, amount of water, and the amount of the silica precursor). The decrease in the reaction time changes the surface morphology of the spheres. The SEM images illustrate that for shorter reaction periods, smoother surfaces are observed. Lengthening the reaction time leads to an increase in surface roughness. The SEM images as a function of reaction time are shown in Figs. 1(a)–(d). The surface of the spheres after 60 min of reaction (Fig. 1(a)) is described as rough-dotted. After 30 min (Fig. 1(b)) and 15 min (Fig. 1(c)) of reaction, dotted surfaces are

observed. A single sphere with a rough surface is presented in Fig. 1(e). After only 5 min, a smooth surface is obtained (Fig. 1(d)). It is clear that by extending the reaction time, more precipitated dots appear on the surface. The size distribution of the spheres is calculated (using the Scion image program) from the SEM images of the respective reactions, and the inset graph depicts the size distribution for the 60, 30, 15, and 5 min reaction times. Particles with the largest diameter are obtained in the 60 min reaction. Almost the same width of size distribution is obtained for all reaction times. This can be explained as follows: the size distribution is dependent on the formation of microdroplets of water and their sizes. On the other hand, the size of the microdroplet depends on the stirring rate. Because all the hydrolytic reactions were carried out under the same stirring conditions, almost the same distribution width is obtained. It is clear that time also affects the surface morphology, where short



Fig. 1. Hydrolysis of tetramethoxy silane with a 0.25*M* acidic solution in an IL solvent at different time intervals: (a) 60 min; (b) 30 min; (c) 15 min; and (d) 5 min, showing different surface morphologies; (e) presents a single, rough-dotted sphere. The inset picture shows the size distribution of the spheres.



TMOS, 0.01M, 5min, 50 °C

Fig.2. Hydrolysis of tetramethoxy silane (TMOS) and tetraethoxy silane (TEOS) at different acidic concentrations at 50°C with a constant time parameter: (a) TMOS, 0.1M, 5 min, 50°C; (b) TEOS, 0.1M, 5 min, 50°C; (c) TMOS, 0.01M, 5 min, 50°C.

reaction times result in a smooth surface, and lengthening the reaction time leads to a rougher surface. This is because when a fully grown sphere is formed during the hydrolytic reaction, water droplets simultaneously adhere to the sphere leading to its hydrolysis, where precipitation occurs, forming rough-dotted spheres. The formation of the precipitate dots is strongly dependent on reaction time and does not appear in the 5 min reaction. All the phenomena described for TMOS are also observed for TEOS cases with a decrease in reaction time. The same behavior is observed for the hydrolysis reaction of TEOS at different reaction times.

(2) Effect of pH (Acidic Concentration H^+) on the Hydrolysis of TMOS and TEOS at 50°C With a Constant Time Parameter

In addition to varying the reaction time, which was shown above to affect the morphology of the products, the pH also plays an important role in shaping the final product. The effect of pH on the rate of hydrolysis of the TMOS and TEOS at a constant temperature, 50°C, is demonstrated in Fig. 2. When the solution is acidified from 0.01 to 0.25M, and the reaction time is increased, the SEM results depict an increase in the roughness of the surface of the spheres of TMOS and TEOS. As we have already observed from the hydrolysis of TMOS versus time (Figs. 1(a)–(d)), the decrease in the hydrolysis reaction time at a higher acidic (0.25M) aqueous solution leads to the formation of spheres having a smooth-surface morphology. This can also be confirmed from Fig. 2, which illustrates smooth silica spheres obtained by a 5-min-hydrolysis reaction at different acidic concentrations. Furthermore, it should be noted that the influence of time on the structure is more important than the acidity, because smooth surfaces are obtained for short times (5 min) even if the acidity is increased (0.25M). In general, the hydrolysis of TMOS is faster than TEOS. This is obtained when the reaction is conducted at $0.01M \text{ H}^{+1}$ for 5 min (Fig. 2(c)). Under these conditions, when silica precipitates from the TMOS solution, no reaction is detected for TEOS. For all reactions, the size distribution of the silica spheres is calculated and appears in the graphs in Fig. 2. The largest particles measured are 50–60 µm (Fig. 2(a)), obtained for the reaction conducted for 5 min at $0.1M \text{ H}^{+1}$ for TMOS at 50°C reaction times.

(3) The Temperature Effect on the Hydrolysis of TMOS and TEOS

We have also examined the effect of temperature on the morphology of the products. The SEM images depicting the results are presented in Fig. 3. They illustrate the difference in the structure of the products obtained at 50°C and at room temperature (RT) under different acidic concentrations and reaction times. The temperature effect is demonstrated by comparing Fig. 1(b) (TMOS, 0.25M HCl, 30 min, 50°C) and Fig 3(a) (TMOS, 0.25M HCl, 30 min, RT). At a high temperature, we observed a rough-dotted surface (Fig. 1(b)), while at RT the surface of the spheres was smooth (Fig. 3(a)). The same smooth surface at the RT reaction was also observed for TEOS. This phenomenon is also reflected in the case of the hydrolysis of TEOS (see Fig. 3(b) 0.25M HCl, 30 min). No reaction, even high acidity, is observed (for TMOS and TEOS) at RT for 5 or 15 min reaction times. Silica with a completely different structure is obtained (see Fig. 3(e)) for the TEOS products reacting under a $0.1M \text{ H}^{+1}$ acidic aqueous solution for 30 min. A small amount of silica is obtained, showing minute spherical aggregated particles in the 0.2–0.3 µm range. According to our interpretation, these small particles illustrate the seed for the micrometer-size spheres obtained under different reaction conditions. A careful observation of the size distribution graphs for all the different





TEOS, 0.1M, 30min, RT

Fig. 3. Scanning electron microscopic images of the hydrolysis of tetraethoxy silane (TMOS) and tetraethoxy silane (TEOS) at room temperature under different reaction conditions: (a) TMOS, 0.25*M*, 30 min, RT; (b) TEOS, 0.25*M*, 30 min, RT; (c) TMOS, 0.1*M*, 30 min, RT; (d) TMOS, 0.01*M*, 30 min, RT; (e) TEOS, 0.1*M*, 30 min, RT.

hydrolysis reactions for TMOS and TEOS shows that larger silica particles are observed in the TMOS reactions than in TEOS. This perhaps reflects the higher rate of hydrolysis measured for TMOS. Overall, we found that the RT reactions are best for developing smooth-surface silica spheres, as confirmed by the SEM images at different acid concentrations.

We have also compared the morphology of the products described above with those obtained for products of a reaction conducted under the same conditions without an IL. These control reactions and others are presented below.

(4) Control Reactions

(A) Hydrolysis of TMOS and TEOS in the Absence of an IL: The control hydrolysis of TMOS and TEOS, 0.5 mL each,

was carried out in the absence of ILs at 50° C for 60 min in a 0.25*M* aqueous solution of HCl. A silica-gel product was obtained for the TMOS reaction, whereas TEOS did not show any corresponding gel formation. This indicates that TMOS is more facile for hydrolysis as compared with TEOS. The morphology obtained from the SEM image shows irregular solid shapes composed of flat surfaces assembled from large and small aggregated particles.

(B) The Hydrolysis of TMOS and TEOS without Water, Under Neutral Conditions: A second series of control hydrolysis of TMOS and TEOS, 0.5 mL each, was carried out in the absence of an acidic aqueous solution, but with a 3 g IL at 50° C. After 60 min of reaction time, a small amount (8 mg) of silica particles was obtained in the TMOS reaction, whereas no product was observed for TEOS. Even this small amount was



Fig. 4. Small angle X-ray analysis curve for (a) an as-prepared sample and (b) a calcined sample (1000°C).

obtained due to the open-air conditions under which the reaction was conducted, where the presence of water vapor caused this reaction to occur. The SEM image of the product is similar to that observed in Fig. 3(e), and the particles are more irregular in shape, as compared with Fig. 3(e). The particle sizes are in the range of $\sim 0.2 \,\mu$ m. As stated above, according to our interpretation these particles act as seeds under acidic conditions to form fully grown spheres.

The following controlled reactions indicate the importance of both the IL as a solvent, as well as the acidic solution, to obtain fully grown, sphere-shaped structures. Up to this point we have demonstrated, with the help of SEM, the effect of different reaction conditions on the synthesized products, as well as on their morphology. Now we will describe the chemical composition of their products and their physical properties.

(5) Small Angle X-Ray Analysis (SAXRD)

The SAXRD pattern of the reaction products is recorded on a Bruker AXS D8 Advance X-ray powdered diffractometer (Bruker Scientific Israel Ltd., Israel) (CuK α radiation $\lambda = 1.5418$ Å). The SAXRD curves are given in Figs. 4(a) and (b). The SAXRD analysis for the as-prepared products shows the lack of organization of the pores (Fig. 4(a)), whereas some sort of order can be observed from the SAXRD curve for the calcined sample at 1000°C (Fig. 4(b)). Inset figures with a 20 range of 2–4 are shown. The inset for Fig. 4(a) shows a smooth curve, whereas the inset in Fig. 4(b) shows some shoulders or peaks at 2.45 and 2.85 (20). These diffraction peaks are marked with arrows. Perhaps a kind of wormhole-like framework structure is formed upon calcination. The transition from unorganized to organized pores is due to the role of the RTIL, which induces the formation of the surrounding silica. Upon its decomposition, poorly organized pores remain. The wide-angle XRD patterns show the amorphous nature of the silica. The microtome cross-section of the calcined silica spheres is given in Figs. 5(a) and (b). The images elucidate that the sphere consists of tiny micrometer-size particles precipitated together with an IL, which is entrapped in between the tiny particles. After calcination, the cross-section image shows an empty space left between the particles (Fig. 5b). This evidently signifies the role of IL in binding the small micro particulates of precipitate silica to get a large size sphere of silica.

(6) Raman Spectroscopy and Mass Spectroscopy (MS) (DCI)

It is difficult to determine whether the alkoxy groups have been completely removed from the silica surface under these acidic conditions. This is because silica entraps IL in its structure, and the Raman bands of the ILs appear in the same energy range as those of the alkoxy groups. However, some support for the complete removal of the alkoxy groups is obtained from the thermogravimetric analysis (TGA) measurements coupled to a mass spectrometer. We have not detected any residues equal in mass to the alkoxy group upon heating the silica product. This negative result substantiates the assumption of the complete removal of the alkoxy group. Raman spectra were recorded on a Jobin Yvon Horiba Raman System (France). The 524 nm line of an Ar⁺ laser was used as the excitation source. Raman spectroscopy was used to analyze the entrapped IL and the water molecules in the as-prepared spheres. The Raman spectrum for the as-prepared, sphere-shaped products confirms the presence of the vibration bands for C–H stretching (2968, 2880 cm^{-1}) and



Fig. 5. Transmission electron microscopic images for (a) microtome cross-section of calcined silica sphere, and (b) magnified image of the cross-section of calcined silica sphere.



Fig. 6. Raman spectra of (a) an as-prepared sample and (b) calcined silica spheres at 1000°C.

ring stretching (3175, 3068 cm^{-1}) for the entrapped IL, as well as O-H stretching (3441 cm⁻¹) for water molecules. A Raman spectrum is also recorded for the calcined spheres (1000°C). The D (1346 cm⁻¹) and G (1586 cm⁻¹) bands in the Raman spectrum indicate the presence of carbon³¹ in the calcined sample due to the decomposition of the IL annealed at 1000°C. The spectra for the as-prepared, as well as the calcined samples, are shown in Fig. 6.

MS (DCI, FAB, at 200°C) of the as-prepared material further confirmed the presence of 1-butyl-3-methylimidazole (139 m/z) entrapped in the spheres.

(7) **TGA**

A TGA graph is given in Fig. 7. The TGA data support the Raman analysis, which reveals that the weight loss is due to the complete evaporation of water molecules at 150°C, with the subsequent evaporation and decomposition of the IL at 550°C, both of which are entrapped in the sphere-shaped structures. The silica spheres showed a weight loss of about 9.6% water at 150°C and 17% IL at 550°C. The graph shows a total $\sim 26\%$ weight loss from the total weight of the as-prepared sample.

III. Conclusions

In this research, we have extended a previous report on the preparation of conductive silica using ILs. With the current data, we have emphasized the surface morphology of the silica spheres and the parameters that control it. The precipitation reactions carried out at RT as well as in a short time frame, led to the formation of smooth-surface spheres. In most cases it was found that the TMOS precursor is both easier to handle and easier for obtaining larger size silica spheres. We also observed the formation of spheres at low temperature when TMOS was hydrolyzed, whereas TEOS did not show any results at low temperature. The explanation for the different reactivities of TMOS can be explained as follows: with TMOS it is easy for the water molecule to attack the silicon backbone, as compared with TEOS, as the methoxy group in TMOS is relatively small and



Fig. 7. Thermogravimetric analysis graph for an as-prepared sample.

provides a less sterically hindered environment, as compared with that of the ethoxy group.³² A previous paper of ours reported that hydrolyzability decreases from TMOS to TEOS in an acidic medium, in accordance with the current results.³³ It is worth mentioning that TEOS and TMOS both dissolve in the IL, and if the formation of the silica spheres is related to phase separation, this is due to the IL/water immiscibility. Thus our effective methodology yields silica spheres with a different surface morphology in addition to the conductive property.

References

¹W. Stöber, A. Fink, and E. Bohn, "Controlled Growth of Monodisperse Silica Spheres in Micron Size Range," J. Colloid Interface Sci., 26 [1] 62-9 (1968).

²T. Ogihara, H. Nakajima, T. Yanagawa, N. Ogata, K. Yoshida, and N. Matsusita, "Preparation of Monodisperse Spherical Alumina Powder from Alkoxide," J. Am. Ceram. Soc., 74 [9] 2263-9 (1991).

³(a) J. H. Jean and T. A. Ring, "Nucleation and Growth Of Monosized TiO₂ Powder from Alcohol Solution," *Langmuir*, **2** [2] 251–5 (1986). (b) K. Chen, Y. Chen, "Synthesis of Spherical Titanium Dioxide Particles by Homogeneous Precipitation in Acetone Solution," J. Sol-Gel Sci. Tech. 27[2] 111-7 (2003)

T. Ogihara, N. Mizutani, and M. Kato, "Processing of Monodispersed ZrO2 Powders," Ceram. Int., 13 [1] 35-40 (1987).

⁵H. Yang, G. Vovk, N. Coombs, I. Sokolov, and G. Ozin, "Synthesis of Mesoporous Silica Spheres Under Quiescent Aqueous Acidic Conditions," J. Mater. Chem., 8 [3] 743-50 (1998).

⁶K. Kosuge and P. Singh, "Rapid synthesis of Al-Containing Mesoporous Silica Hard Spheres of 30-50 mu m Diameter," Chem. Mater., 13 [8] 2476-82 (2001).

⁷B. Karmakar, G. De, and D. Ganguli, "Dense Silica Microspheres from Organic and Inorganic Acid hydrolysis of TEOS," J. Non-Cryst. Solids, 272 [2-3] 119-26 (2000).

⁸H. Nishimori, M. Tatsumisago, and T. Minami, "Growth Mechanism of Large Monodispersed Silica Particles Prepared from Tetraethoxysilane in the Presence of Sodium Dodecyl Sulfate," J. Sol-Gel Sci. Tech., 9 [1] 25-31 (1997)

K. Adachi, T. Iwamura, and Y. Chujo, "Novel Synthesis of Submicrometer Silica Spheres in Non-Alcoholic Solvent by Microwave-Assisted Sol-Gel method,' Chem. Lett., 33 [11] 1504-5 (2004).

¹⁰J. Dupont, G. S. Fonseca, A. P. Umpierre, P. F. P. Fichtner, and S. R. Teixeira, "Transition-Metal Nanoparticles in Imidazolium Ionic Liquids: Recyclable Catalysts for Biphasic Hydrogenation Reactions," J. Am. Chem. Soc., 124 [16] 4228-422 (2002).

¹¹T. Welton, "Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis," *Chem. Rev.*, **99** [8] 2071–83 (1999).

¹²F. Endres, M. Bukowski, H. Hempelmann, and H. Natter, "Electrodeposition of Nanocrystalline Metals and Alloys from Ionic Liquids," Angew. Chem. Int. Ed., 42 [29] 3428-30 (2003).

¹³(a)P. Wasserscheid and W. Keim, "Ionic Liquids—New "Solutions" for Transition Metal Catalysis," Angew. Chem., Int. Ed., 39 [21] 3772-89 (2000). (b) D. Zhao, M. Wu, Y. Kon, E. Min, "Ionic Liquids: Applications in Catalysis," Today. 74 157-89 (2002).

¹⁴(a) C. Hardacre, D. J. Holbreg, S. P. Katdare, and K. R. Seddon, "Alternating Copolymerisation of Styrene and Carbon Monoxide in Ionic Liquids," Green Chem., 4 [2] 143-6 (2002). (b) A. J. Carmichael, D. M. Haddleton, S. A. F. Bon, K. R. Seddon, "Copper(I) Mediated Living Radical Polymerisation in An Ionic Liquid," *Chem. Commun.* **14** 1237–1238 (2000). ¹⁵R. A. Sheldon, R. Maderia Lau, M. J. Sorgedrager, F. Rantwijk, and K. R.

Seddon, "Biocatalysis in Ionic Liquids," Green Chem., 4 [2] 147-51 (2002).

 ¹⁶R. P. Swatloski, A. E. Visser, W. M. Reichert, G. A. Broker, L. M. Farina, J. D. Holbrey, and R. D. Rogers, "On the Solubilization of Water with Ethanol in Hydrophobic Hexafluorophosphate Ionic Liquids," *Green Chem.*, 4 [2] 81–7 (2002).

¹⁷L. A. Blanchard, D. Hancu, E. J. Beckmann, and J. F. Brennecke, "Green processing Using Ionic Liquids and CO₂," *Nature*, **399** [6731] 28–9 (1999). ¹⁸R. P. Swatloski, S. K. Spear, J. D. Holbrey, and R. D. Rogers, "Dissolution of

Cellose with Ionic Liquids," J. Am. Chem. Soc., 124 [18] 4974-5 (2002).

¹⁹N. Kimizuka and T. Nakashima, "Spontaneous Self-Assembly of Glycolipid Bilayer Membranes in Sugar-Philic Ionic Liquids and Formation of Ionogels," Langmuir, 17 [22] 6759-61 (2001).

T. Nakashima and N. Kimizuka, "Vesicles in Salt: Formation of bilayer Membranes from Dialkyldimethylammonium Bromides in Ether-Containing Ionic

²¹T. Nakashima and N. Kimizuka, "Interfacial Synthesis of Hollow TiO₂ Microspheres in Ionic Liquids," *J. Am. Chem. Soc.*, **125** [21] 6386–7 (2003).
²²Y. Zhou and M. Antonietti, "A Novel Tailored Bimodal Porous Silica with

Well-Defined Inverse Opal Microstructure and Super-Microporous Lamellar Nanostructure," *Chem. Comm.*, **20**, 2564–5 (2003). ²³Y. Zhou and M. Antonietti, "Preparation of Highly Ordered Monolithic Su-

per-Microporous Lamellar Silica with a Room-Temperature Ionic Liquid as Template Via the Nanocasting Technique," *Adv. Mater.*, **15** [17] 1452–5 (2003). ²⁴E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald, and

R. Morris, "Ionic Liquids and Eutectic Mixtures as Solvent and Template in Synthesis of Zeolite Analogues," Nature, 430 [7003] 1012-6 (2004).

²⁵J. D. Holbrey and K. R. Seddon, "The Phase Behaviour of 1-Alkyl-3-Methylimidazolium Tetrafluoroborates; Ionic Liquids and Ionic Liquid Crystals,' ²⁶C. M. Gordon, J. D. Holbrey, A. R. Kennedy, and K. R. Seddon, "Ionic ²⁶C. M. Gordon, J. D. Holbrey, A. R. Kennedy, and K. R. Seddon, "Ionic

Liquid Crystals: Hexafluorophosphate Salts," J. Mater. Chem., 8 [12] 2627-36 (1998).

²⁷H. Tokuda, K. Hayamizu, K. Ishii, Md. A. B. H. Susan, and M. Watanabe, "Physicochemical Properties and Structures of Room Temperature Ionic Liquids. 1. Variation of Anionic Species," J. Phys. Chem. B, 108 [42] 16593-600 (2004).

²⁸D. S. Jacob, A. Joseph, S. P. Mallenahalli, S. Shanmugam, S. Makhluf, J. Calderon-Moreno, Y. Koltypin, and A. Gedanken, "Rapid Synthesis in Ionic Liquids of Room-Temperature-Conducting Solid Microsilica Spheres," Angnew.

Chem. Int. Ed., **44** [40] 6560–3 (2005). ²⁹M. A. Klingshrim, S. K. Spear, J. D. Holbrey, and R. D. Roger, "Ionic Liquids as Solvent and Solvent Additives for the Synthesis of Sol-Gel Materials,' J. Mater. Chem., 15 [48] 5174-80 (2005).

³⁰F. Shi, Q. Zhang, D. Li, and Y. Deng, "Silica-Gel-Confined Ionic Liquids: A New Attempt for the Development of Supported Nanoliquid Catalysis,' " Chem.

Eur. J., **11** [18] 5279–88 (2005). ³¹S. Shanmugam and A. Gedanken, "Generation of Hydrophilic, Bamboo-Shaped Multiwalled Carbon Nanotubes by Solid-State Pyrolysis And its Electrochemical Studies," J. Phys. Chem. B, 110 [5] 2037-44 (2006).

32J. Hyeon-Lee, G. Beaucage, and S. E. Pratsinis, "Aero-Sol-Gel Synthesis of

 J. Hyeon-Lee, G. Beaucage, and S. E. Fratsinis, Acto-sol-Get synthesis of Nanostructured Silica Powders," *Chem. Mater.*, 9 [11] 2400–3 (1997).
³³T. N. M. Benard, M. J. Van Bonmel, and A. H. Boonstra, "Hydro-lysis-Condensation Processes of the Tetra-Alkoxysilanes TPOS, TEOS and TMOS in some Alcoholic Solvents," *J. Non-Cryst. Solids*, 134 [1–2] 1–13 (1991).