



Encapsulation of Water-Soluble Dye in Spherical Sol-Gel Silica Matrices

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Abstract. The water-soluble, Lithol rubine B, dye was encapsulated into silica microspheres matrices. Encapsulation has been carried out by sol-gel process of W/O microemulsions formed from sodium silicate and dye aqueous solution in cyclohexane medium. The average particle size could be tailored from 1–10 μm , depending on the processing parameter such as homogenizing speed in the formation of W/O emulsion, the weight ratio of water to oil, and concentration of sodium silicate solution, etc. The pore size of dye-doped silica microspheres was measured by nitrogen adsorption-desorption isotherms. The leaching behavior of dye entrapped in silica matrices was investigated by UV/VIS and UV diffuse reflectance spectroscopy for the extract and solid powders after immersion for 24 h in water. The doping of GPTS (3-glycidoxypropyltrimethoxysilane) in sodium silicate and dye mixture solution greatly enhanced the stability against leaching of the dye. It was ascribed that GPTS serves simultaneously as an intermediate for the chemical bonding between the dye and silica, and as an agent for the formation of hybrid sol responsible for the shrinkage of pore size.

Keywords: encapsulation, sol-gel, dye-doped silica microspheres, leaching stability

1. Introduction

The incorporation of organic molecules into sol-gel system has been investigated widely [1–3]. In particular, inorganic-organic hybrids have attracted considerable attention as a subject of extensive research in materials chemistry, because of the potential of combining distinct properties of organic and inorganic characters [4, 5]. The molecules entrapped into sol-gel matrices are isolated in an individual cage, and not in direct contact with external materials. As a consequence, en-

capsulation of organics in sol-gel matrix offers much better protection of the molecules, allowing safer disposal or higher stability than the free molecule. In addition, silica matrix is thermally and photochemically stable without being hazardous to humans or the environment. They also exhibit higher mechanical strength and negligible swelling in organic solvents compared to most organic polymers. Another advantages of using silica as a host matrix of organics is the ability to modify the surface hydroxyls on silica surface with amines, thiols, methacrylate, and coupling agents such as dimethyldichlorosilane. Materials can be, also, tailored either to no leaching of

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the entrapped molecule from the matrix, or to slow release.

In the cosmetics, lots of chemicals like UV absorbers and dyes are being used to give a desirable performance. Such chemicals, which are generally synthetic organic compounds, would stimulate the skin to take allergies. Lithol rubine B is one of water-soluble red dye used in the cosmetics. Most of the reported sol-gel based silica powders incorporating dye were prepared by in-situ hydrolysis and condensation for tetraethoxysilane (TEOS) and dye mixtures solution under acid or base catalyst [6]. Then powders are obtained after gel formed is dried and pulverized. In that case, it is not easy to control the particle size and shape. Whereas, reverse microemulsions, organized assemblies by water, oil and surfactant have been successfully used as micrometer or nanometer sealed reactors to form monodisperse particles of inorganic materials [7]. In the water-in-oil microemulsion, water-soluble water glass (sodium silicate, Na_2SiO_3), which is widely used as the inexpensive production of silica sols, can be employed as solute [8]. One of the additional problems commonly encountered in dye-doped silica powder is that the dye encapsulated in silica matrices can be easily leached out in the dye-soluble solvent when the dye is physically trapped in the porous silica matrices. Therefore, it would be very valuable to prepare monodispersed dye-doped silica microspheres, enduring leaching to the solvent.

This paper describes the results on the preparation of dye-doped silica microspheres from water-in-oil microemulsions using the diluted sodium silicate solution as solute in aqueous phase. Another objective to be achieved here is the stabilization to leaching of water-soluble dye against water.

2. Experimental

2.1. Preparation of Dye-Doped Silica Microspheres

Water-in-oil microemulsions have been applied to prepare dye-doped microspheres. Nonionic surfactant, polyoxyethylene sorbitan monooleate (Tween 80, Juncei chemical co.), polyoxyethylene sorbitan monostearate (Span 60, Aldrich) were used as received. Cyclohexane (Aldrich), and sodium silicate solution (Aldrich) consisting of 27 wt% SiO_2 and 14 wt% NaOH were used as oil phase and silica precursor without further purification. Reverse microemulsions were prepared at room temperature by first mixing cyclohex-

ane, surfactant (Tween80/Span60 = 2/1 in mol ratio), and an aqueous sodium silicate solution dissolving dye (Lithol rubine B), and GPTS. The concentration of surfactant was set at 0.042 mol and weight ratio of water to oil (R) was in the range of 1/3 to 1/10. Dye concentration was fixed at 1.5×10^{-4} mol. Then the resulting mixtures were homogenized to form water-in-oil microemulsion. Aqueous solution of ammonium carbonate (Juncei, chemical co. 0.015 mol) as a gelling agent was added dropwise to microemulsions and stirred at room temperature for 2 h. The resulting dye-doped silica microspheres were filtered, and washed with acetone. Then, they were dried in convection oven kept at 80°C . Samples dried were redispersed in water and washed several times to remove residual surfactants.

2.2. Characterization

Specific BET surface areas and pore size distribution measurements were performed on an ASAP 2400 (micromeritics) device, after the samples were outgassed overnight at 80°C . Particle size and morphology of non-doped and dye-doped silica microspheres were determined from photographs by scanning electron microscope (Philips XL 30S SEM/Phoenix EDS). For the leaching experiments, about 1 g of dye-doped silica microspheres were immersed in 100 ml water for 24 h. The extract was collected, and the amount of dye in extract was determined by UV-Vis spectroscopy (UV-Vis 2401 PC, Shimadzu). The dye remaining in the silica microspheres after leaching by water was characterized by UV diffuse reflectance spectroscopy.

3. Results and Discussion

In water-in-oil microemulsions, the aqueous phase containing the water-soluble sodium silicate i.e. water glass is dispersed as microdroplets surrounded by a monolayer of surfactant molecule in the continuous oil phase. As may be expected, the particle size and shape will be strongly influenced by the concentration of solute, the ratio of surfactant to oil, and the ratio of water to oil [7, 8].

Figure 1 shows the silica microspheres prepared in homogenizing speed of 11,000, 13,000, 22,000, and 24,000 rpm at 4 mol of sodium silicate solution, 1/3 of water to oil ratio (W), and 10 of water to surfactant ratio (R). It was observed that size of silica microspheres decreased with the increase of homogenizing speed and

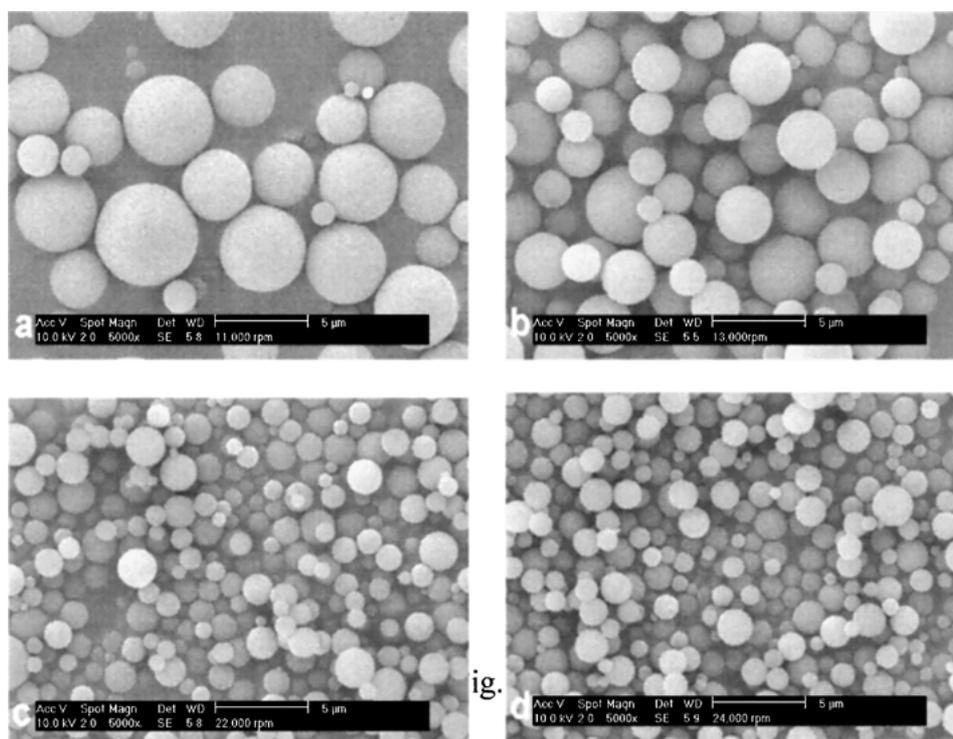


Figure 1. Scanning electron micrographs of silica microspheres prepared after homogenizing in speed of (a) 11,000, (b) 13,000, (c) 22,000, and (d) 24,000 rpm.

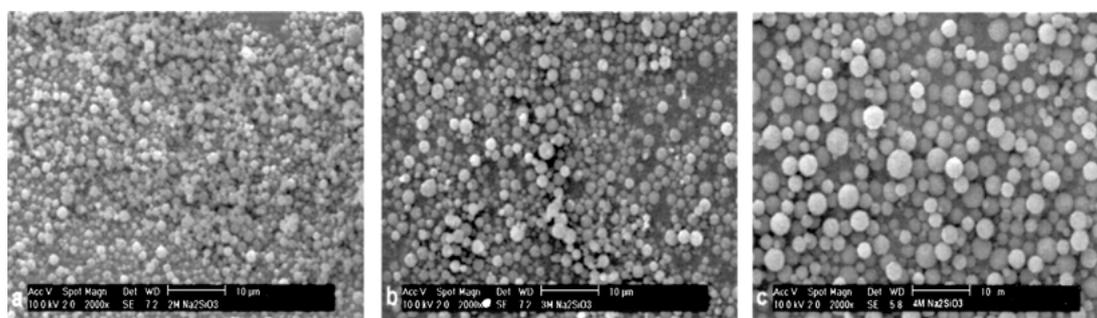


Figure 2. Scanning electron micrographs of silica microspheres prepared from Na_2SiO_3 solution in mole concentration of (a) 2, (b) 3, and (c) 4.

was not changed above 22,000 rpm. As can be easily expected, this suggests that a high shear rate caused the formation of smaller droplets in W/O microemulsion, resulting in smaller sizes of silica microspheres.

Figure 2 presents SEM photographs of silica microspheres prepared as a function of concentration of sodium silicate solution at a fixed $W (=1/3)$, $R (=10)$, and homogenizing speed ($=13,000$ rpm). As the concentration of sodium silicate solution was increased to 2, 3, and 4 mol, the particle size of silica microspheres

also increased to around 1, 1.5, and 3 μm . This may be the results from both the growth of emulsion droplet due to the increase in the viscosity of an aqueous solution and the decrease in the concentration of water during the drying process. Here, the maximum concentration of water glass that could be stabilized in the microemulsions was less than 4 mol.

Figure 3 shows SEM photographs of silica microspheres prepared as a function of water to oil at a fixed condition. The average particle size of the silica

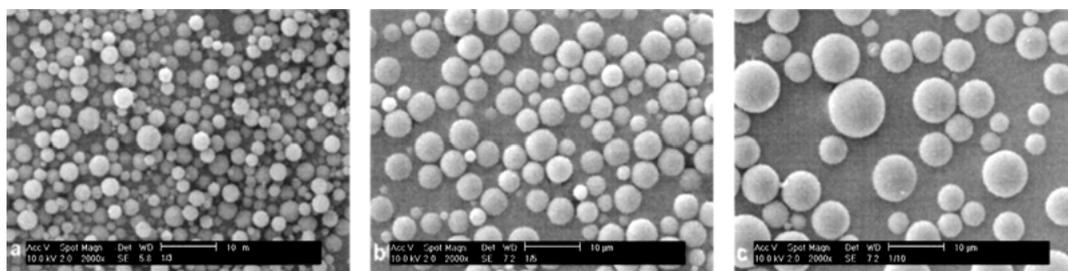


Figure 3. Scanning electron micrographs of silica microspheres prepared from water to oil ratio (W) of (a) 1/3, (b) 1/5, and (c) 1/10.

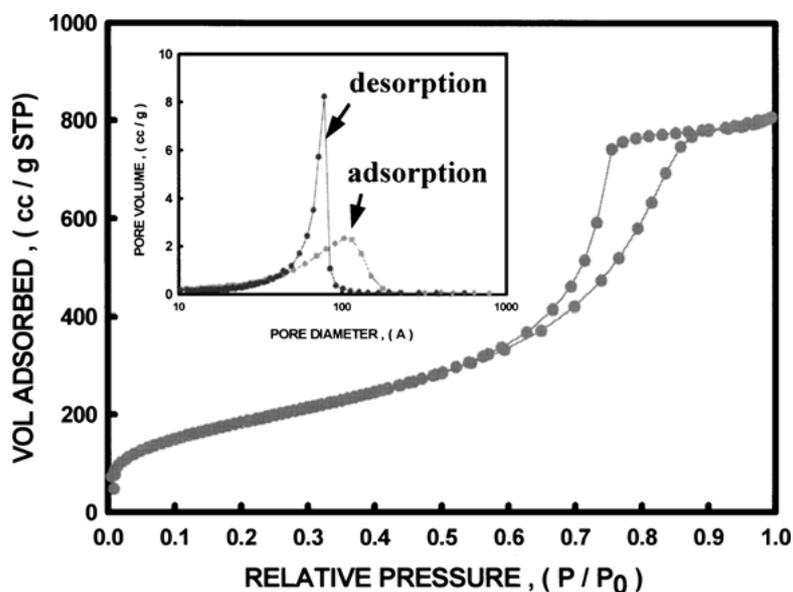
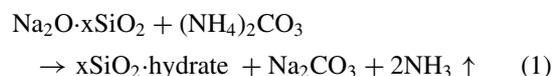


Figure 4. Nitrogen adsorption-desorption isotherms and pore distribution of silica microspheres.

microspheres, corresponding to the initial size of microemulsion, decreased as W increases. This implies that the size of microemulsion droplets decreases steadily with the decrease in the water concentration, as observed by C-L Chang et al. [7].

Figure 4 shows the representative nitrogen adsorption-desorption isotherms on the powders prepared from microemulsion method without doping the dye and GPTS. This isotherm can be classified as type IV by IUPAC classification [9] with its hysteresis loop, which indicated mesoporous property associated with capillary condensation. The average pore size was about 80 Å, and BET specific surface area was around 800 m²/g. For the other powders prepared by varying the processing parameter in microemulsions, similar behaviors were observed, even though there is a little difference in the value of surface area, pore

size, and volume. It was known that silica particles were produced by the reaction between sodium silicate and ammonium carbonate as following.



Thus, SiO₂ powders produced from sodium silicate solution would have higher specific surface area, pore size, and pore volume than that of silica powders prepared from tetraethoxysilane (TEOS), because Na₂CO₃ can be washed out, remaining the pore in it. As a consequence, this means that the dye entrapped within silica matrices produced from sodium silicate solution can be more easily leached out by the dye soluble solvent. Generally, it was expected that with the increase of silica level in initial solution, the silica

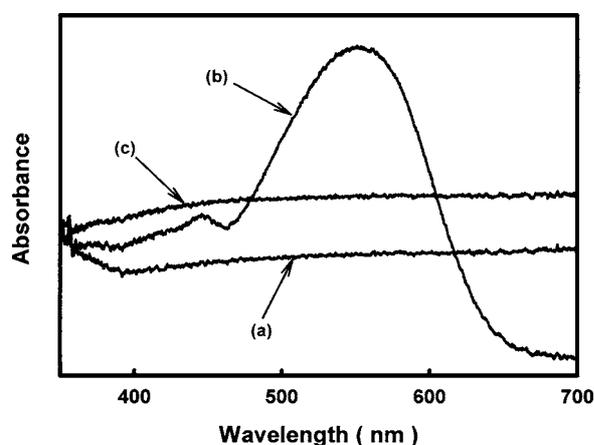


Figure 5. UV-diffuse reflectance spectra of dye-doped silica microspheres dried after leaching in water for 24 h. Dye-doped silica microspheres were prepared (a) without GPTS, (b) by adding 0.02 mol GPTS, and (c) by immersing a commercial silica spheres in dye-dissolved solution.

network become denser by condensation [10], resulting in the enhanced stability to leaching.

Figure 5 exhibits the UV diffuse reflectance spectra for the dye-doped silica microspheres leached by water after being prepared with 3 different methods. Then, the fraction of the dye remaining in silica microspheres after leaching was compared. Here, it was noted in Fig. 5(b) that the broad absorption band peaked at around 540 nm was caused by red dye, i.e. Lithol rubine B. In Fig. 5(a), the dye entrapped in silica microspheres prepared from sodium silicate solution without GPTS was completely leached out after immersing in water for 24 h. Comparable result was also obtained in Fig. 5(c) when the dye molecules are physically entrapped into the commercial silica spheres by dipping in the dye dissolved solution. This result suggests that the dye doped in silica spheres is absorbed simply on the surface of pore, which can be easily leached by water. Based on the above observation, even when silica microspheres were prepared by in-situ microencapsulation process from dye and sodium silicate solution, the dye was not completely incorporated in the silica network or close pore. However, surprisingly, it was found in Fig. 5(b) that dye in silica microspheres prepared with doping a small amount of GPTS was not leached out at the same condition. This result implies that GPTS doped in silica network plays an important role for the incorporation of the dye in silica matrices.

Stability to leaching of the dye against water, which was analyzed by UV-Vis spectrophotometer, was investigated as a function of GPTS amount doping in

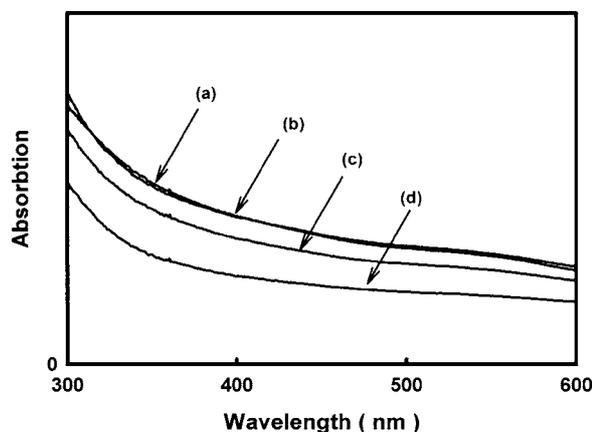


Figure 6. UV-Vis spectra of the extract obtained after immersion dye-doped silica microspheres in water for 24 h. Dye-doped silica microspheres were prepared by adding GPS of (a) 0.002, (b) 0.01, (c) 0.015, and (d) 0.02 mol into sodium silicate and dye mixture solution.

silica matrices. Figure 6 shows the results on the UV-Vis absorption spectra for the extract after leaching the dye-doped silica microspheres prepared with different amount of GPTS in water. In this figure, peaks caused by red dye, i.e. Lithol rubine B were not observed. This indicates that water-soluble dye was never extracted by water regardless of GPTS amounts doped in silica matrices. In order to investigate possible causes for the dramatic increase in leaching stability, porosity was measured for the dye-doped silica microspheres prepared with different amount of GPTS.

Figure 7 shows the variation of pore size for the dye-doped silica microspheres prepared as a function

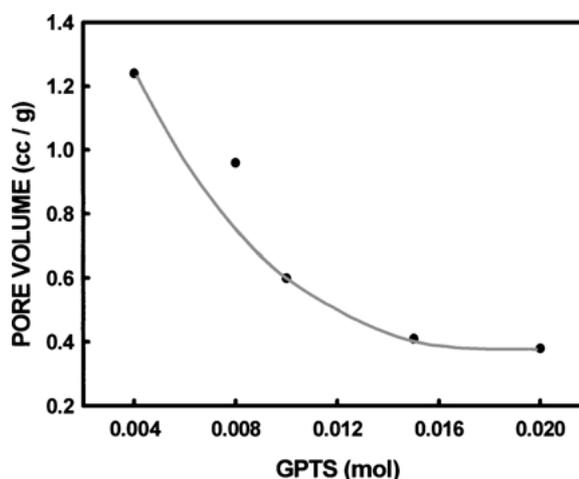


Figure 7. The variation of pore volume measured as a function of GPTS amount.

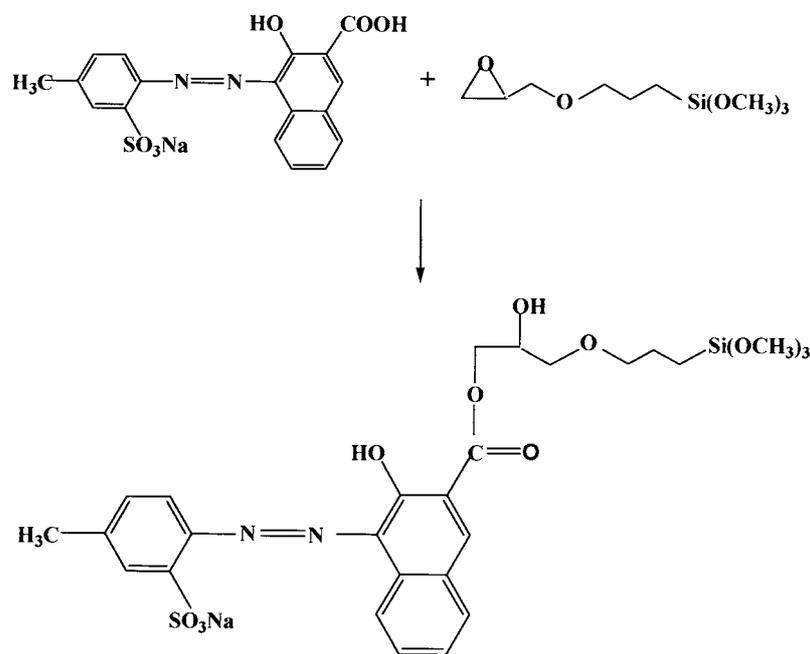


Figure 8. Possible reaction scheme between Lithol rubine B and GPTS.

of varying GPTS in the presence of constant amount of the dye. In this figure, it is notable that the pore size decreases with increasing GPTS in the mixture solution of sodium silicate and dye. Shrinkage of pore size by the introduction of GPTS is supposed to be related with the formation of hybrid sols, which lead to higher gel density, by the surface modification of silica sols [11]. Therefore we propose that the shrinkage of pore size with doping GPTS influences the stability to leaching of the dye by trapping in narrow pores. A larger pore volume will allow better penetration of the leaching agent, i.e. water, loss of the dye by leaching would be more pronounced. As seen in Fig. 6, however, the amount of leachable dye is not reduced slowly with doping of GPTS. Instead, the dye in dye-doped silica particles was never leached by water after doping of GPTS for the entire sample. This suggests that additional factors are responsible for the leaching stability of the dye. As can be seen in Fig. 8, it was reported [12] that the dye containing function groups such as Lithol rubine B could be modified with glycidoxyl group of GPTS by adding GPTS. It might be supposed that GPTS acts as a coupling agent to react between Si-OH on silica and Si-OH on GPTS, which is simultaneously hydrolyzed by water and modified with the dye. Thus, the investigations show that the use of alkyl silane having an ability to bind with the dye is

crucial to encapsulate the water-soluble dye into silica microspheres without leaching in water.

4. Conclusions

Dye-doped silica microspheres were prepared by combining the water-in-oil microemulsions and sol-gel process. The average particle size of these microspheres decreased as the homogenizing speed for formation of W/O emulsion and the weight ratios of water to oil increase, and increased as the concentration of sodium silicate solution increases. Physical entrapment of dye in silica matrices was insufficient to the stability to leaching in dye-soluble solvent. Dye i.e. Lithol rubine B in silica microspheres was not leached by introducing GPTS into sodium silicate and dye mixture solution. It was deduced that GPTS might serve as either physical entrapment with the decrease of pore size and covalent entrapment in silica matrices.

References

1. J.E. Mark, Y.C. Lee, and P.A. Branconl (eds.), *Hybrid Organic-Inorganic Composites*, ACS Symp. Ser. vol. 585 (Am. Chem. Soc., Washington, DC 1995); B.K. Coltrain, C. Sanchez, D.W. Schaefer, and G.L. Wikes (eds.), *Better Ceramic Through Chemistry VII: Organic/Inorganic Hybrid Materials*, Mat. Res. Soc. Symp. Proc., vol. 435 (MRS, PA, 1996).

2. L.L. Hench and J.K. West, *Chem. Rev.* **90**, 33 (1990).
3. C. Rottman, A. Turniansky, and D. Avnir, *J. Sol-Gel Sci. Tech.* **13**, 17 (1998).
4. J. Livage, *Current Opinion in Solid State & Mat. Sci.* **2**, 132 (1997).
5. P.G. Romero, *Adv. Mater.* **13**(3), 163 (2001).
6. J.-C. Panitz and F. Geiger, *J. Sol-Gel Sci. Tech.* **13**, 473 (1998).
7. C.-L. Chang and H.S. Fogler, *Langmuir* **13**, 3295 (1997).
8. M. Jafelicci Jr, M.R. Davolos, F.J. Santos, and S.J. Angrade, *J. Non-Cryst. Solids* **247**, 98 (1999).
9. S.J. Gregg and K.S.W. Sing, *Adsorption, Surface Area and Porosity* (Academic Press, New York, 1982).
10. T. Gerber, B. Himmel, and C. Hubert, *J. Non-Cryst. Solids* **170**, 160 (1994).
11. H.K. Schmidt, *J. Sol-Gel Sci. Tech.* **8**, 557 (1997).
12. S. Hofacker and G. Schottner, *J. Sol-Gel Sci. Tech.* **13**, 479 (1998).