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Microstructures of Porous Silica Prepared in Aqueous and Nonaqueous Emulsion Templates

Gi-Ra Yi and Seung-Man Yang*

Department of Chemical Engineering,
Korea Advanced Institute of Science and Technology,
373-1 Kusong-dong, Yusong-gu,
Taejon 305-701, Korea

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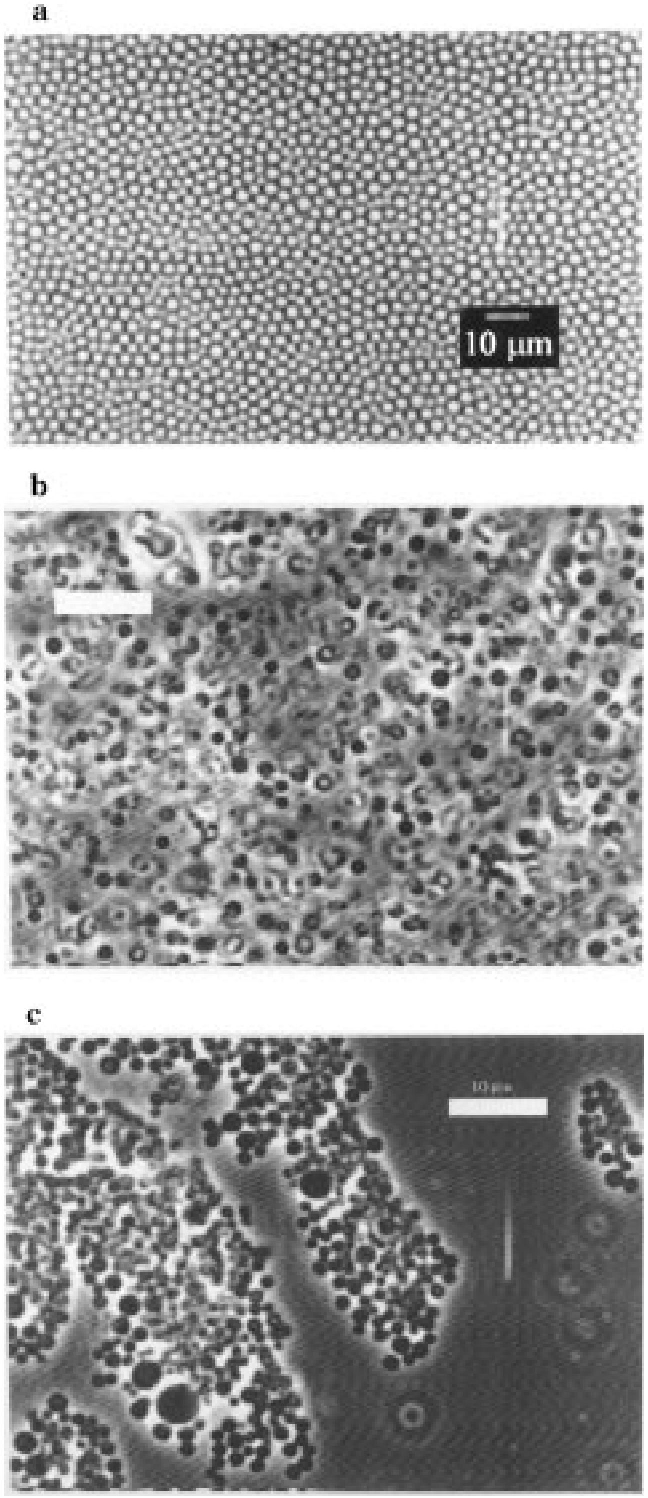

Figure 1. (a) Monodisperse silicone oil-in-water emulsion observed by optical microscopy and (b) and (c) optical microscopy images of mixture that contains emulsion and silica sols before and after gelation, respectively. Scale bars denote 10 μm in length.

Materials with a spatial periodic dielectric constant are called photonic crystals or photonic band gap materials and have attracted much interest.[1] The main thrust of the intensive investigations stems from their wide variety of application areas ranging from microwave to optical devices.[2] Colloidal crystals with long-range periodicity at optical wavelength scales may have a photonic band gap;[3] however, although various colloidal crystals have been prepared successfully,[4] they may not be used as optical devices, since these systems lose their optical properties easily by external disturbances. Thus, it has been proposed to capture such self-organizing colloidal crystals via solidification of the continuous medium by sol−gel transition or polymerization.[5] In practice, macrocrystalline structures of monodisperse polystyrene beads,[6] or silica particles,[7] and emulsions[8] can produce solid materials with ordered macropores. These materials are also expected to exhibit unusual optical properties such as the reverse dielectric periodicity of the original colloidal crystals.[9] In addition, the readiness to control the pore size and uniformity may be of practical significance in various applications such as improved filters, membrane supports, catalytic materials and adsorbents, lightweight structural materials, and low dielectrics for ULSI semiconductors.[8,10] In this communication, we report useful information about the emulsion templates for the preparation of structured materials with uniform macropores. Although emulsion templates are attractive in many aspects including high deformability, they still have problems in efficiently preparing an ordered arrangement of monodisperse droplets and forming the inor-

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* To whom correspondence should be addressed. E-mail: smyang@kaist.ac.kr.

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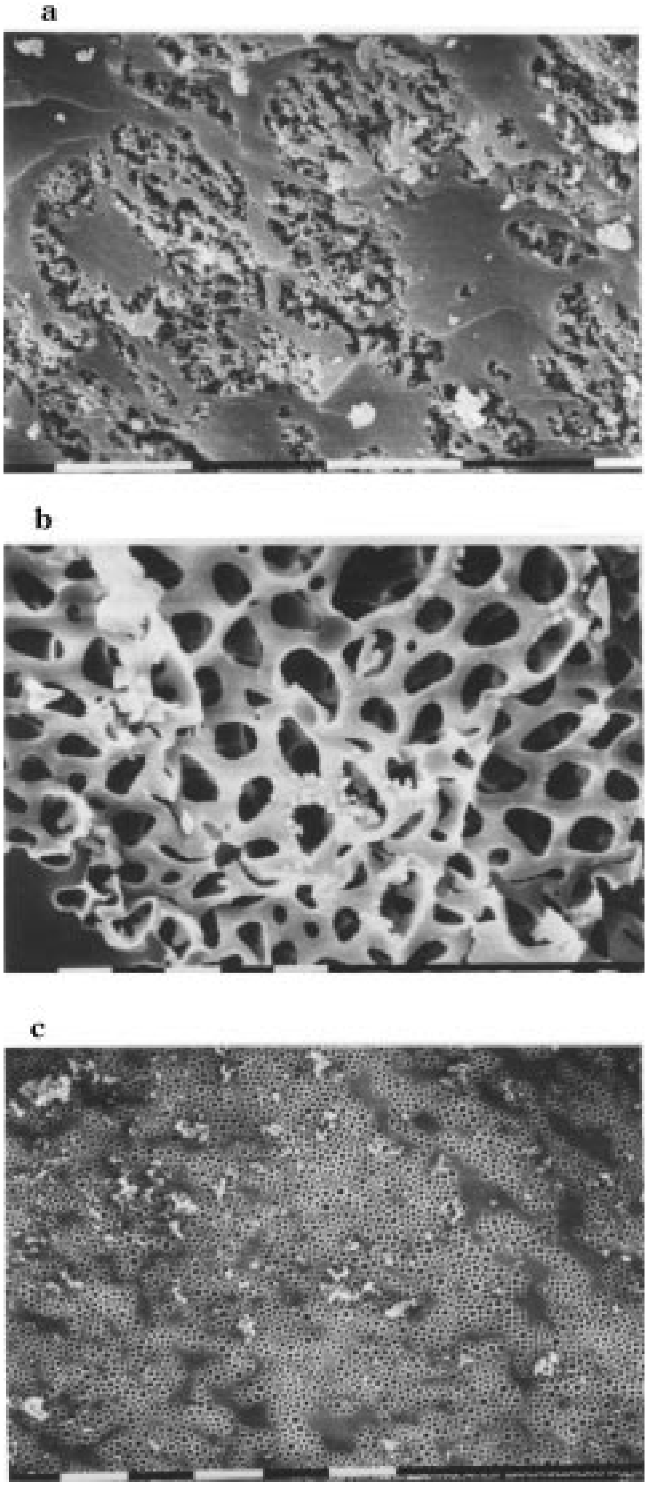

Figure 2. (a) SEM images obtained after gelation, in which emulsion-rich and emulsion-poor phases led to macropore-rich and macropore-free phases, respectively. Local ordered structures are shown in part b. (c) SEM image of macropore-rich structure obtained from the concentrated emulsion region. Scale bars denote 10 μm in length.

ganic matrix without altering the microstructure. To resolve these problems, we must select both the effective surfactant in the emulsion fractionations and the appropriate solvent in the capturing step.

In the present work, the porous structured materials were prepared from the templates of aqueous and nonaqueous emulsions. The porous materials from the *aqueous* emulsions were obtained following the procedure reported by Imhof and Pine.[8] Figure 1a shows the optical microscopic image of the silicone oil-in-water emulsions prepared by repeated fractionation technique as described by Bibette.[11] As noted, the emulsion contained a few larger or smaller emulsion droplets, and its polydispersity was about 0.005 that was obtained by dynamic light scattering. In this case, the surfactant of sodium dodecyl sulfate (SDS, Aldrich) was used as a stabilizer in the preparation of stock emulsions, and subsequently as a flocculant in the fractionation of the emulsion droplets. The silica sol was made by mixing tetramethoxysilane (TMOS; Aldrich, 98% purity) or tetraethoxysilane (TEOS; Aldrich, 98% purity) and hydrochloric acid with the volume ratio of 1:3 under agitation with a magnetic stirrer. Gelation was then induced by adding ammonium hydroxide (Aldrich, 30% NH_3 content). The final porous materials were prepared by calcining the gelled emulsion at 550 °C and thereby evaporating the drop phase.

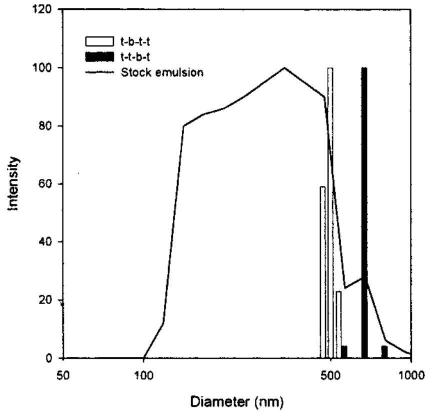

Figure 3. Size distributions of polydisperse stock emulsion and monodisperse emulsions prepared by the repeated purification technique.

The microscopic photographs of the emulsion and silica–sol mixture taken before and after the gelation are shown in parts b and c of Figure 1, respectively. As noted in Figure 1c, during gelation, emulsion droplets in an aqueous medium migrated into local regions in which the local macrocrystalline structure was captured. Owing to the migration and flocculation of emulsion drops, the prepared porous materials did not have uniform pore distribution, but exhibited nonhomogeneous microstructures separated into porous phase and nonporous silica gel matrix phase, see Figure 2a. To overcome the formation of nonhomogeneous pore structure, the emulsion drops were concentrated by depletion flocculation. However, the phase separation and nonuniform distribution of pores still appeared, although the structure was improved considerably as shown in Figure 2c. In addition, to examine the effect of pH change in mixing of emulsion at pH 7 and silica sol at pH 2, we observed the phase stability of emulsion in acidic or neutral pH condition through an optical microscopy. However, no morphology change or flocculation did occur. This suggested that the local nonhomogeneity of sol–gel transition rate led to the migration of emulsion droplets into more mobile regions. The emulsion drop migration was responsible for the nonuniform distribution of pores. These morphologies

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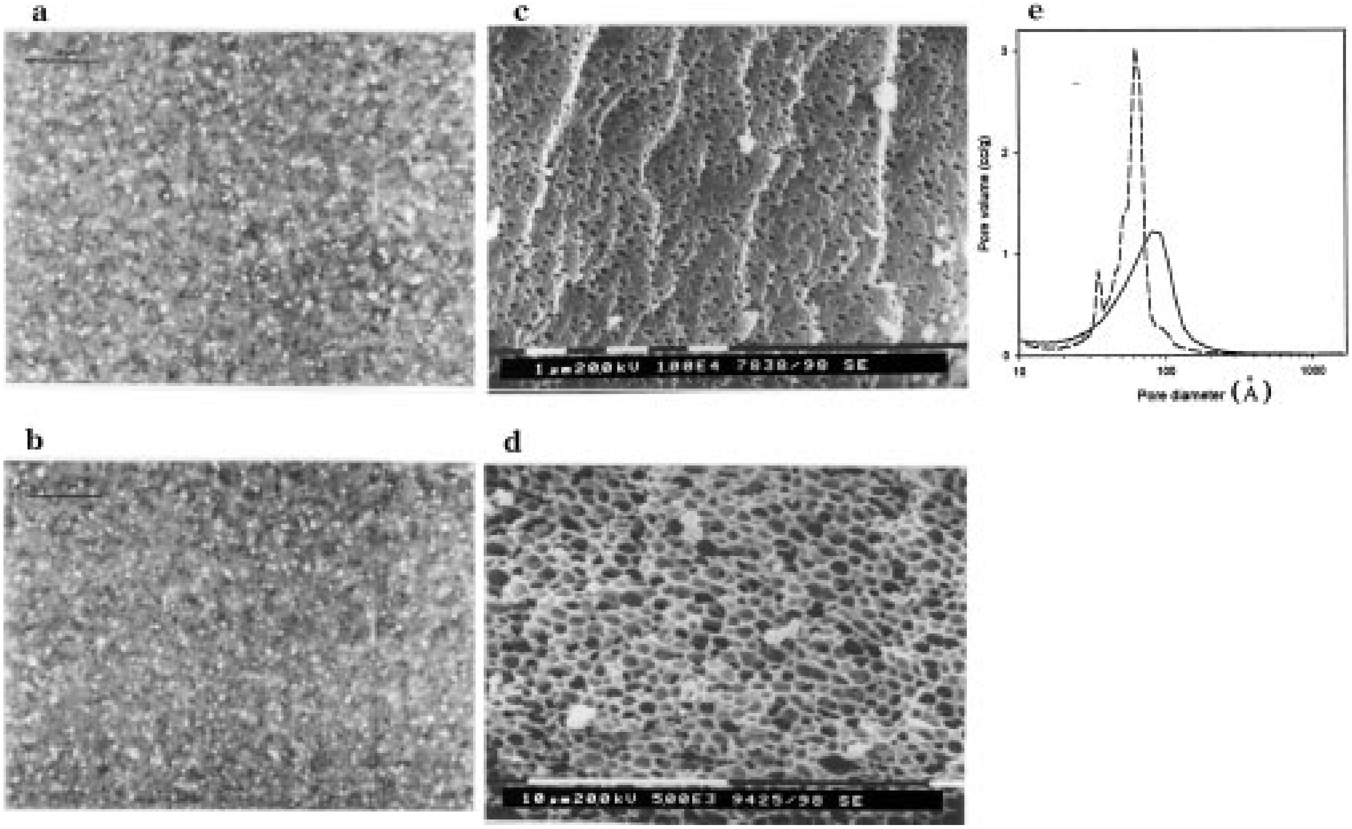

Figure 4. (a and b) Optical microscopic images of the mixture of isooctane-in-formamide emulsion and silica sol before and after gelation, respectively; (c) SEM image of porous silica produced by flocculation−densification; (d) ordered macroporous silica produced in the emulsion densified by centrifugation; and (e) pore size distribution of silica structure, in angstroms, determined from the nitrogen sorption isotherm. (Solid line: adsorption, dotted line: desorption).

may be undesirable for optical and acoustical applications, and especially for low dielectric materials which require well-distributed isolated cell structure. Thus, a special route that would not affect the microstructure of the emulsion crystals should be considered for the templating process. Addition of oxalic acid or formamide has been known as a novel route for creating the spatially uniform reaction and thereby preventing nonuniform particle growth.[8,12,13] Here, we substituted formamide for water as the solvent to ensure its effect on preparations of structured materials.

We used the isooctane-in-formamide emulsion as a system congruous with formamide. In this case, the isooctane-in-formamide emulsions were stabilized by a triblock copolymer, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (hereafter $EO_{20}PO_{70}EO_{20}$) containing 30 wt % ethylene glycol ($H(-OCH_2CH_2-)_x[-OCH(CH_3)CH_2-]_y(-OCH_2CH_2-)_z$-OH, $\bar{M}_n$; ~5800, Aldrich). In the same manner as the previous aqueous emulsions, the monodisperse isooctane-in-formamide emulsions were prepared from the nonaqueous stock emulsions. It is noteworthy, however, that different surfactants should be used as a flocculant for the efficient fractionation, because the $EO_{20}PO_{70}EO_{20}$ is like a paste at room temperature and difficult to handle. Moreover, it is less soluble in formamide. Thus, SDS with favorable solubility in formamide was used as a flocculant, and the triblock copolymer was used as a stabilizer.[14]

When SDS was used as a flocculant, the monodisperse emulsions were obtained after several purification steps. The drop size distributions of stock emulsion and fractionated emulsions were measured using a dynamic light scattering, and the results are shown in Figure 3.[15] It can be readily seen in Figure 3 that polydisperse stock emulsions were fractionated in size successfully. The optical microscopy images captured before and after the gelation step are shown in Figure 4 a and b, respectively. Indeed, the microscopic images remained unchanged throughout gelation. Furthermore, the SEM image in Figure 4c, for the captured macropore structure, showed the morphology similar to the fractionated emulsion. However, as noted in Figure 4c, the macropores contained in the silica matrix were not arranged in macrocrystalline structure. This was primarily due to the low volume fraction of emulsion drops. Therefore, further densification of the prepared emulsions by other

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(14) $EO_{20}PO_{70}EO_{20}$ surfactant in the formamide formed self-assembled micelles in very low concentrations (10^{-3} mol/L). In addition, the cmc (critical micelle concentration) of SDS in formamide was somewhat high, around 0.06 mol/L. The micelle sizes of triblock copolymer and SDS in formamide were the same order of magnitude (10^{-8} m).

(15) In Figure 3, letters “t” and “b” indicate the top and bottom phases, respectively. For example, sample “t−t−b−t” was prepared by four steps of fractionation; the sample was taken in the first two steps from the top, in the third step from the bottom and finally, in the fourth step from the top phase. Thus, from the sample titles, its fractionation history in purification process can be figured out. As expected, emulsion “t−t−b−t” had larger droplets than emulsion “t−b−t−t”.

means such as centrifugation was required to increase the volume fraction. During centrifugation at 8500−12000 rpm, the emulsions sustained its phase stability. By utilizing the concentrated emulsion templates, the silica with uniform macropores could be synthesized, and the captured SEM image was shown in Figure 4d. Indeed, the macropores with narrow size distribution can be seen from the SEM image.

Nitrogen sorption isotherms of the porous structure prepared from the densified emulsion templates are shown in Figure 4e. It can be noted from the isotherms that micropores smaller than 50 nm were constructed and the BET internal surface area was about 390 m^2/g, which was not sensitive to the macropores. The results demonstrated that further densification of the silica matrix was required for optical applications for which the matrix should be as dense as possible in order to achieve the maximal contrast in the refractivity between the matrix and the macropores. Of course, silica of a low refractive index (∼1.5) is not appropriate as useful photonic crystals. It is known that materials with high refractive index (>2.5) may be effective for photonic crystals. However, even macroporous-structured materials with a refractive index below 2.5, such as silica, may have measurable photonic band gaps. Thus, silica with the densified macropores would have higher refractivity than coarse macroporous silica.

In conclusion, the effects of solvent properties in the emulsion templating process were investigated by employing two distinctively different systems of aqueous and nonaqueous emulsions. The present reports provide the experimental evidence of how the solvent properties influence the captured pore morphology of the microstructured materials prepared via the emulsion templating. First, in silicone oil-in-water emulsion templating process, the emulsion drops migrated and formed self-assembly in relatively mobile local regions. This deteriorated the uniformity of macropore structure although a local macrocrystalline pore structure was formed. Meanwhile, for the nonaqueous emulsion of isooctane-in-formamide, the uniform porous materials were produced successfully from the emulsion templating due to the effect of formamide on the sol−gel reaction. In the presence of formamide, the network was grown uniformly during gelation. However, when the emulsion density was low, the captured macropores did not possess a desired level of ordered or macrocrystalline structure. To concentrate the emulsion for a satisfactory template, additional densification such as centrifugation was required. Finally, we are currently undertaking a systematic investigation on the macrocrystalline structure of captured pores by employing various stabilizers and flocculants. For example, one possible candidate as a flocculant is a triblock copolymer ($EO_{40}PO_{20}EO_{40}$) which occurs in powder form at room temperature, containing 80 wt % ethylene glycol ($\bar{M}_n$; ∼5800, Aldrich). Owing to its high solubility in formamide, $EO_{40}PO_{20}EO_{40}$ is more effective than SDS as a flocculant, although not desirable as a stabilizing agent. This is a very useful result when the stabilizing agent is not favorable as a flocculant to induce the depletion attraction due to its poor solubility in the organic solvent.

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