

Anion-exchange Induced Phase Transformation of Mesostructured Silica

Mesostructured silica synthesized using cetyltriethylammonium (CTEA) ion as the pore-directing agent in acidic environments was ready to have interfacial anions exchanged at ambient temperature. In-situ small angle X-ray scattering (SAXS) was used to examine the structural changes of the as-made mesostructured materials and pyrene fluorescence quenching experiment was used to probe the variation in interfacial environment during the anion-exchange processes. About a half of the interfacial anions in between the silica framework and micelle were exchanged based on the fluorescence quenching experiments of pyrene, which was dissolved in the hydrophobic core of the micelle. Altering in the pore structure and the architecture of silica framework was observed when the interfacial anions were exchanged by anions of higher salting-in power. The resultant phase transformation was always toward pore structures of lower curvature. The influence of anion follows the Hofmeister series commonly encountered in macromolecular and biological systems.

The surfactant templated synthesis of the mesoporous silica was mainly divided into two routes: the alkaline synthesis of M41S families and the acidic synthesis of SBA phases.^[1-3] The latter processes using acidic medium, low temperatures and low concentrations of surfactants were more akin to the conditions for the synthesis of biorelevant composites. Under acidic condition with pH below the isoelectric point of silanol, the protonated silanols (I^+) are proposed to react with positive charged surfactants (S^+) via the counteranions (X) through a $\text{S}^+\text{X}\text{I}^+$ type interaction. Mesoporous materials of more versatile structures and morphologies were obtained in comparison to the alkaline synthesis, due to the weaker $\text{S}^+\text{X}\text{I}^+$ interaction between the silica and the micelles.^[4] However, the mechanism associated with this self-assembly process has not been directly proved. In the present study, the $\text{S}^+\text{X}\text{I}^+$ type assembly process is verified for the first time by examining the ion-exchange capabilities of the interfacial anions between the micelles and silica wall.^[5] Not only a remarkable structural transformation of the silica materials was observed accompanying with the anion-exchange, but also the influences of the anions in micelle morphology and silica architecture were clarified.

Beamline

17A1 W20-X-ray Powder Diffraction

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Mesoporous silica was prepared following the procedures in Ref. 4. The molar composition of the synthesis gel was $\text{TEOS}/\text{CTEABr}/\text{acid}/\text{H}_2\text{O} = 1/0.13/3/125$. The acids used in the present study were H_2SO_4 , HCl and HNO_3 . Typically, the aqueous solution containing CTEABr surfactant and acid was stirred at room temperature for one hour then at 0°C for another hour. To this solution, pre-cooled TEOS was added, and the mixture was stirred for 10 min. before it was aged at 0°C for 3 h. The resultant precipitate was filtered and transferred immediately to an aqueous solution of sodium salt. Salts including NaHSO_4 , NaH_2PO_4 , NaCl , NaBr , NaNO_3 , and NaSCN were used. To avoid leaching of the surfactant from the mesostructured silica, CTEABr was also added to the salt solutions except for NaSCN , in which the precipitate formed promptly upon adding CTEABr. To avoid interference from the

drying process, *in-situ* small angle X-ray scattering (SAXS) technique was used to examine the structural changes of the wet mesoporous materials during the anion-exchange processes. The experiments were conducted at National Synchrotron Radiation Research Center, Hsinchu, Taiwan. The reaction mixture was sealed in a Teflon container of 10 mm inner diameter and ca. 2 mm thickness with Kapton windows. The SAXS patterns were recorded in the transmission mode with $\lambda = 1.32 - 1.33$ nm radiation (1.5 GeV and 120-200 mA). The SAXS data were expressed in scattering vector q , where $q = 4\pi\sin\theta/\lambda = 2\pi/d$, and d is the d -spacing between scattering planes.

Figure 1(a) shows that 3D-hexagonal $P6_3/mmc$ phase was the mesostructured silica precipitated in H_2SO_4 , characterized by the (100), (101) and (002) scattering peaks at 1.25, 1.33, and 1.41 nm^{-1} , respectively. When the precipitate was immersed in the NaCl solution, the mesophase transformed gradually in 62 min to cubic $Pm3n$ characterized by the (200), (210) and (211) scattering

peaks at 1.19, 1.32, and 1.45 nm^{-1} , respectively. The phase transformation was from the mesopores of higher curvature to a lower one. The final cubic $Pm3n$ phase is also the mesostructure obtained in HCl solution. On the other hand, when immersing the precipitate formed in HCl into a $NaHSO_4$ solution, the three peaks of cubic $Pm3n$ disappeared and another set of three peaks corresponding to 3D-hexagonal appeared in 2 min (Fig. 1 (b)). As time prolonged, however, the peaks of 3D-hexagonal broadened and weakened, while those of cubic $Pm3n$ grew again and predominated the scattering patterns after 98 min. These results demonstrate that the interfacial anions between CTEA micelle and silica are exchangeable and the Cl^- ion is more dominant than HSO_4^- in influencing the final mesophase.

Figure 1(c) is an example of consecutive phase transformation on the silica material precipitated in H_2SO_4 and ion-exchanged with a NaSCN solution. After immersing the solid in the NaSCN solution for 2 min, the three peaks of 3-D hexagonal $P6_3/mmc$ phase of the as-made precipitate weakened and new scattering peaks corresponding to 2-D hexagonal and cubic $la3d$ phases appeared. As time prolonged to 8 min, the peaks of original 3-D hexagonal phase vanished. The peaks of 2-D hexagonal reached a maximum at 5 min and then declined gradually until completely disappeared after 27 min. On the other hand, the peaks of cubic $la3d$ phase grew stronger and retained till the end. Therefore, the 2-D hexagonal phase was only an intermediate phase before equilibrium.

Figure 2 summarized the silica mesophases obtained in different acids and those after ion-exchange with various anions of sodium salts. The phase transformation usually reaches equilibrium in 3 h, and the final silica mesophase is a function of the counteranions of the sodium salts. The mesophase was cubic $Pm3n$ in $NaHSO_4$, NaH_2PO_4 , and NaCl, 2-D hexagonal in NaBr and $NaNO_3$, and cubic $la3d$ phase in NaSCN. It is also noticeable that the phase transformations induced by interfacial anion-exchange are all from porous structure of higher curvature to that of lower one. On the other hand, the silica mesostructures prepared in different acids show different tolerances toward phase transformation upon anion-exchange. For the 2-D hexagonal mesostructure synthesized in HNO_3 , no phase transformation was observed, except in NaSCN. In contrast, the 3-D hexagonal $P6_3/mmc$ mesostructure synthesized in H_2SO_4 always has phase transformation upon anion-exchange. The final mesophase of the silica is determined by the anion species in the interface, and the influence of anions in phase transformation increases in the order of $HSO_4^- <$

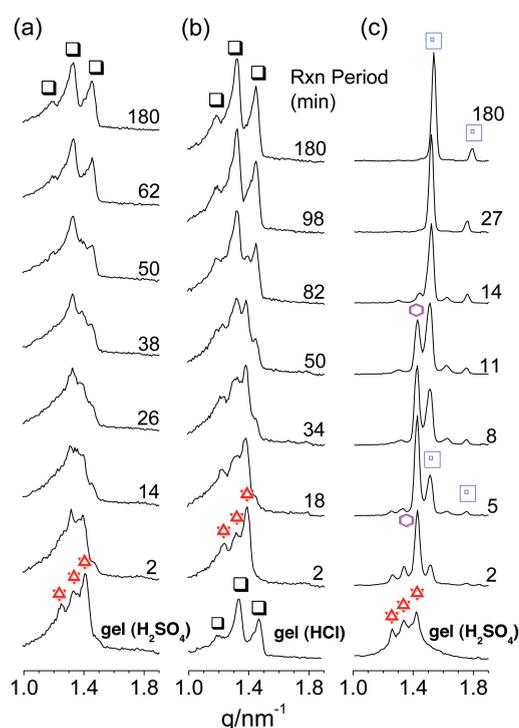


Fig. 1: The *in-situ* SAXS patterns of mesostructured silica precipitated in (a) H_2SO_4 then ion-exchanged with NaCl solution, (b) HCl then ion-exchanged with $NaHSO_4$ solution, and (c) H_2SO_4 then ion-exchanged with NaSCN (\blacktriangle : 3-D $P6_3/mmc$, \blacksquare : cubic $Pm3n$, \circ : 2-D $p6m$, \blacksquare : cubic $la3d$).

$\text{H}_2\text{PO}_4^- \sim \text{Cl}^- < \text{Br}^- \sim \text{NO}_3^- < \text{SCN}^-$, which follows the Hofmeister series of salting-in.^[6] The ions on the right usually lead to increased solubility of proteins and induce protein denaturation. They are usually larger, with significant polarizability and exhibit weaker interactions with water. In contrast, the ions on the left of the series, generally called salting-out ions, water-structure-makers, or kosmotropic ions, reduce the solubility of proteins by inducing their crystallization.

Fluorescent aromatic hydrocarbons such as pyrene (Py) have been widely used to probe the micro-environment of organized host media, such as micelles, microdroplets, vesicles, etc.^[7] For the purpose of *in-situ* detecting the interfacial anions between the micelle and silica wall, pyrene was dissolved in the CTEA micelles and the fluorescence lifetime (τ) of pyrene was measured by time-correlated single-photon counting apparatus at ambient temperature. Samples were excited with 338 nm light source and the detection was made at 395 nm. The

Table 1: Mesophases and lifetimes (τ) of pyrene in the silica precipitated in different acids and after ion-exchanged with various salt solutions for 3 h.

Salts	Acids		H ₂ SO ₄		HCl		HNO ₃	
	τ /ns	mesophase	τ /ns	mesophase	τ /ns	mesophase	τ /ns	mesophase
-	199	3-D P6 ₃ /mmc	203	Cubic Pm3n	72	2-D p6m		
NaHSO ₄	199	Cubic Pm3n	197	Cubic Pm3n	146	2-D p6m		
NaCl	211	Cubic Pm3n	213	Cubic Pm3n	156	2-D p6m		
NaNO ₃	147	2-D p6m	152	2-D p6m	71	2-D p6m		

fluorescence decay profiles were analyzed with a nonlinear least-squares iterative reconvolution method. Table 1 shows the mesophases and the τ values of mesostructured silica precipitated in different acids in comparison to those after ion-exchange in various salt solutions for 3 h. The lifetimes were 199, 203, and 72 ns for the silica precipitated in H₂SO₄, HCl, and HNO₃, respectively. These results show that NO₃⁻ ion is the most efficient in quenching pyrene fluorescence among the three counteranions, while HSO₄⁻ and Cl⁻ ions have similar quenching abilities.

For the silica precipitated in H₂SO₄ and ion-exchanged with NaNO₃, τ decreased markedly from 199 to ca. 147 ns, which is a value between those observed in H₂SO₄ and HNO₃. On the other hand, for the silica precipitated in HNO₃ and post-treated in NaHSO₄, τ increased from 72 to 146 ns. Noticeably, the lifetimes of the final products in these two experiments were close. Similar phenomenon was also observed for the silica precipitated in HCl then ion-exchanged with NaNO₃ (τ = 152 ns) and that precipitated in HNO₃ and post-treated in NaCl (τ = 156 ns). These results infer that there should be an equilibrium distribution of the original interfacial anion and the counteranion of sodium salt. Assuming a linear relationship between the τ value and the anion concentration, it is estimated by linear equation in one variable that 42-46% molar ratios of the interfacial anions were exchanged. These results demonstrate that the chaotropic anions would determine the final mesostructure even though they only occupy about one-half of the interfacial anion sites.

The Hofmeister anion effect on the mesostructured silica has been attributed to that the chaotropic ions bind strongly and closely to the headgroups of the surfactants, partially reduce the electrostatic repulsion between the charged surfactant headgroups, therefore resulting in micelles of low curvature. The present study demonstrates that the hydrated anions instead of the net anions should

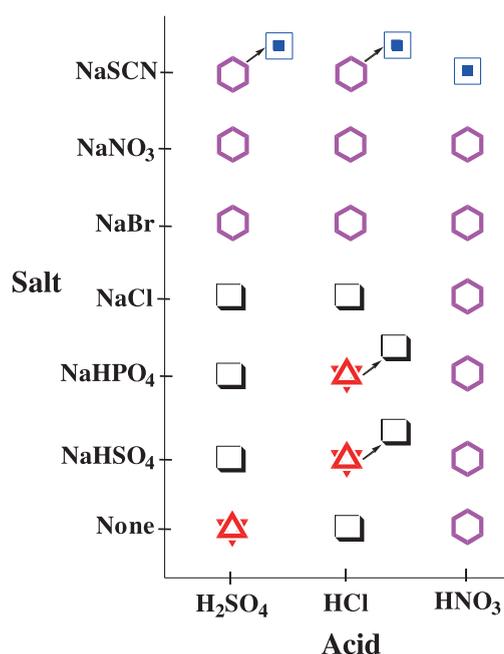


Fig. 2: The phase diagram of the mesoporous silica materials formed in different acids and ion-exchanged with various sodium salt solutions based on *in-situ* SAXS data. (\blacktriangle : 3-D P₆₃/mmc, \blacksquare : cubic Pm3n, \hexagon : 2-D p6m, \blacksquare : cubic Ia3d).

be considered in their binding strength to the headgroups of the surfactants. The kosmotropic ions on the left of the Hofmeister series have higher solvation energies either due to the smaller size or stronger hydrogen bond and form larger hydrated anions, which bind weakly to the headgroups of the surfactants. Contrarily, the chaotropic ions on the right of the series have lower solvation energies and form smaller hydrated anions, which bind strongly to the headgroups of the surfactants and have stronger influence on the final phase of the mesostructured silica. The mesophase transformation induced by the interfacial anion-exchange also provides a unique technique to study anions which are not yet included in the Hofmeister series and their influence in the systems of biological macromolecules, like proteins, DNA and lipids may be predicted.^[5]

Experimental Station

SAXS patterns recorded in the transmission mode end station

References

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