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The effect of cationic surfactant and some organic/inorganic additives on the morphology of mesostructured silica templated by pluronics

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ABSTRACT

Tri-block copolymers (poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), represented as $\text{EO}_x\text{PO}_y\text{EO}_x$), pluronics (F127 = $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$, P65 = $\text{EO}_{20}\text{PO}_{30}\text{EO}_{20}$, P85 = $\text{EO}_{27}\text{PO}_{39}\text{EO}_{27}$, P103 = $\text{EO}_{17}\text{PO}_{55}\text{EO}_{17}$, and P123 = $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) and cationic surfactants (cetyltrimethylammonium bromide (CTAB)), two surfactant systems, form complex micelles that self-assemble into mesostructured particles with distinct morphology depending on the pluronic type, the concentration of the cationic surfactant and the organic–inorganic ingredients in a siliceous reaction media under acidic conditions. The CTAB–P65 and CTAB–P85 systems form spheres, CTAB–P103 and CTAB–P123 systems form wormlike particles, and CTAB–F127 system form single crystals of mesostructured silica particles under very similar conditions. However addition of various salts (such as KCl and NaNO_3) into a CTAB–P103 or CTAB–P123 solution system and cyclohexane and KCl into a CTAB–P85 solution system produces the mesostructured silica spheres and wormlike particles, respectively. By controlling the hydrophilic–hydrophobic character of the pluronics, core–corona interface, by means of additives, such as small organic molecules or salts, one could obtain the desired morphology that is dictated by the shape of the micelles of the pluronic–cationic surfactant complex. The effects of the additives and the formation mechanism of those morphologies have been discussed using spectroscopy (FT-IR and Raman), diffraction (XRD) and microscopy (POM and SEM) data.

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1. Introduction

Since the discovery of mesoporous silica [1,2], there has been a tremendous effort devoted to functionalizing the mesoporous materials either by surface modification using various active chemicals or by controlling their morphology. Many research groups have synthesized spherical mesoporous silica [3–10] in all sizes for various purposes, from drug delivery systems to photonic crystals. Yano et al. [3] have established a method of making nanospheres with uniform size distribution using cationic surfactant in a water/methanol solution in basic media. Mesa et al. [8] have used pluronics, P123 and F127, to produce spherical beads using a cationic surfactant as a co-surfactant. However, in the cationic surfactant/pluronic systems, it is difficult to obtain a uniform size distribution [8–10] and yet the role of the cationic surfactant is not clarified.

Ozin et al. [11,12] investigated a surfactant–silica chemistry that yields various shapes including gyroids, ropes, toroids, discoids, shells, knots etc. Many groups have latter established methods to synthesize one shape in one pot [3–10,13–16]. Tang et al.

[13] have systematically investigated the topological transformation of mesostructured silica from gyroids to spheres using three surfactant systems, cationic (CTAB), anionic (Sodium Dodecyl Sulphate, SDS) and non-ionic (P123) and a co-surfactant (ethylacetate, EA). Three surfactant systems, CTAB–SDS–P123 and CTAB–SDS–P123–EA have been used to make spheres, ropes, and helical mesostructured silica materials [13,14]. Yang et al. [15] investigated a similar transformation of a rod-like to a vesicle-like mesoporous silica by increasing the hydrophobic content of the media in a tri-isopropylbenzene–P123 system. Stucky et al. [17] investigated the formation of single crystals and ropes from P108 and P123 systems, respectively, using various salts.

Synthesizing a single shape in one pot is important for many applications, such as catalysis, adsorption, separation, sensors and as a host for CVD for various purposes (optic, magnetic, photonic etc.). There are many efforts towards controlling the morphology [3–10,16,17]. Controlling the salt type and the salt concentration influences both the morphology [16] and structure of the mesophasers [18–20]. The presence of salt ions, especially the anions, influences the hydrophilicity of the pluronics both in liquid and liquid crystalline media [18–20]. We have investigated how the nitrate and perchlorate ions change the hydrophilic–hydrophobic balance of the pluronics during the synthesis of mesostructured silica films

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and monoliths [18]. Other than a few studies, [13–15] the current literature mainly focus on finding reaction conditions to produce one shape or to obtain uniform particle size distribution in one pot synthesis.

In this contribution, we have synthesized mesostructured silica spheres, wormlike particles and single crystals using P65, P85, P103, P123 and F127 with CTAB as a co-surfactant in an acidic media. Most of these samples have been synthesized for the first time, and investigated the role of CTAB molecules and some additives (such as salts and cyclohexane) using PXRD, SEM, EDS, FTIR and Raman spectroscopy techniques.

2. Experimental section

2.1. Synthesis

The procedure established by Mesa et al. [8] or its modified version have been used for the synthesis of mesoporous silica with different morphologies. By using a similar procedure mesostructured silica spheres, wormlike particles and single crystals were synthesized using P85, P65, P123, P103, and F127 tri-block copolymers with a cationic surfactant (CTAB). In a typical synthesis procedure, 0.123 g of cetyltrimethylammonium bromide (CTAB) was dissolved in a 0.14 M 50 ml HCl solution by continuous stirring. To this solution, a 0.620 g of P85 ($\text{EO}_{27}\text{PO}_{33}\text{EO}_{27}$) was added and slowly heated while stirring to obtain a clear solution. The experiments containing additional ingredients were conducted by following the same procedure. In these experiments various salts (KCl or NaNO_3) and organic molecules (cyclohexane) were added and completely dissolved before the addition of pluronic surfactant. Then the clear solution was cooled to room temperature (RT) and then a 1.25 g tetramethylorthosilicate (TMOS) was added by vigorous stirring. The final solution was stirred for another 3 min at RT and then kept in an oven at 95 °C for 5 days. The precipitate obtained from the above mixture was filtered, washed with excess water and kept in an oven at 60 °C to dry. Other compositions, changes in the CTAB/pluronic mole ratios, the amount of added salts and organic molecules have been described in the results and discussion section and tabulated in Table 1.

Table 1

The type of pluronics, pluronic/acid/TMOS amounts, CTAB/Pluronic mole ratio, additive concentration used in the procedure given in the experimental section and the observed morphologies

Pluronics	CTAB/Pluronic (mole ratio)	Additives	Morphology
P65	0.00–3.00		Sphere
P85	0.00		Disordered
	0.18		Wormlike
	0.61		Wormlike and sphere
	1.22		Sphere
	4.00–6.64		Sphere and films
	10.0		Monoliths
	2.50	5 ml Cyclohexane	Wormlike
	2.50	1 g KCl	Wormlike
	2.50	1 g NaNO_3	Sphere
P103	3.34		Wormlike
P123	2.00		Wormlike
F127	0.0–1.67		Disordered
	2.50		Rhombododecahedron (major particles)
	Above 5.00		Rhombododecahedron (only product)

The pluronic (grams)/acid (molarity, ml)/TMOS (gram) amounts are 0.62/0.14 M, 50 ml/1.23 in all samples.

2.2. Characterization

The powder X-Ray diffraction (PXRD) patterns were collected on a Rigaku Miniflex diffractometer using a high power Cu $K\alpha$ source operating at 30 kV/15 mA. The XRD patterns of the samples were collected in the 1–10, 2θ range with a scan rate of

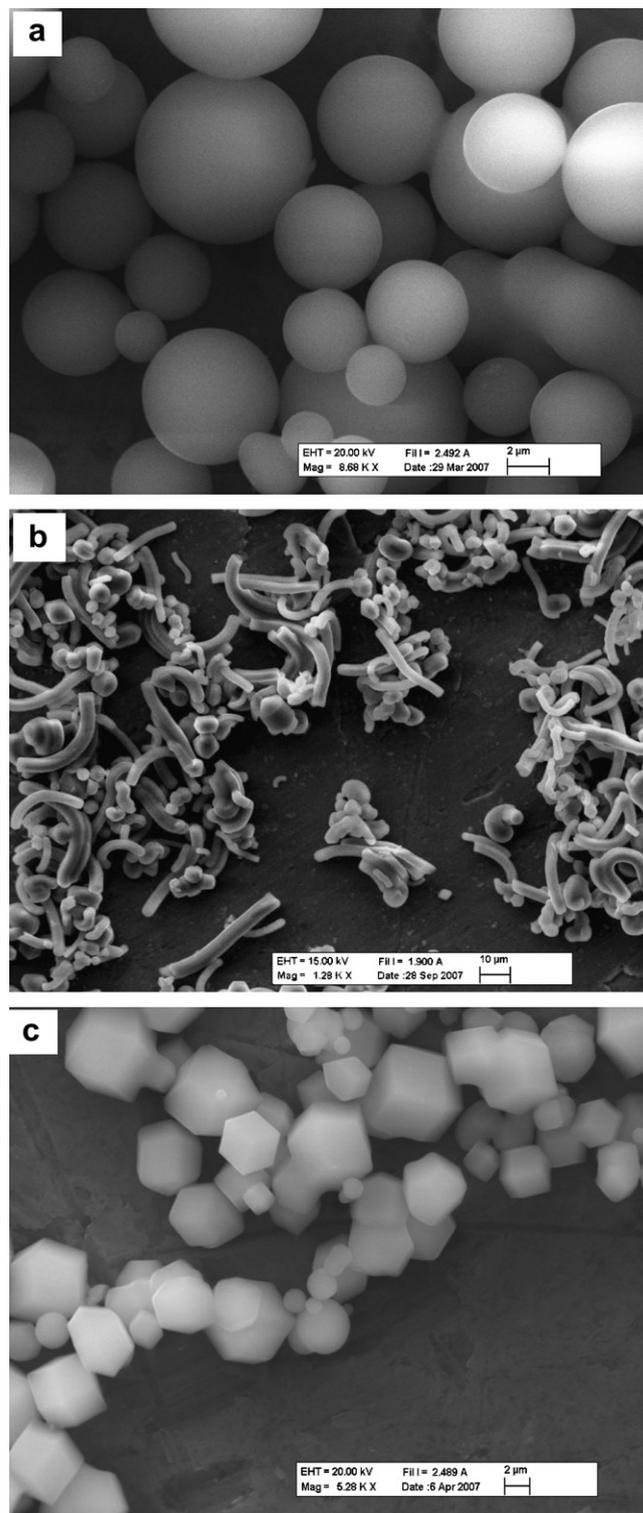


Fig. 1. The SEM images of mesostructured silica particles synthesized using (a) CTAB–P85 (CTAB/P85 mole ratio of 2.5), (b) CTAB–P103 (CTAB/P103 mole ratio of 3.0), and (c) CTAB–F127 (CTAB/F127 mole ratio of 5.0).

0.5°/min. The polarized optical microscopy (POM) images were recorded in transmittance mode on a Meije techno ML 9400 series Polarizing Microscope with transmitted light illumination, using convergent white light between parallel and cross polarizers. The FTIR spectra were recorded using a Bruker Tensor 27 model FTIR spectrometer. A DigiTect™ DLATGS detector was used with a resolution of 4 cm^{-1} and 256 scans in the $400\text{--}4000\text{ cm}^{-1}$ range for all samples. The micro-Raman spectra were recorded on a LabRam confocal Raman microscope with a 300 mm focal length. The spectrometer is equipped with a HeNe laser operated at 20 mW, polarized 500:1 with a wavelength of 632.817 nm, and a 1024×256 element CCD camera. The scanning electron microscopy (SEM) images of all samples were recorded on a ZEISS EVO40. The samples were prepared by dispersing the powders onto aluminum holders using acetone. Energy dispersive X-Ray scattering (EDS) maps were collected using the same SEM using Bruker AXS XFlash detector 4010.

3. Results and discussion

We have applied a modified version of the methods established by Mesa et al. [8] in the CTAB–Pluronic systems to synthesize mesostructured silica particles. In this investigation, five different pluronics, P65, P85, P103, P123, and F127 have been used with CTAB as a co-surfactant. The CTAB/Pluronic mole ratio was varied from 0.0 to 10.0 to optimize the reaction conditions and to elucidate the effect of CTAB in the formation of the mesostructured silica particles. The as-synthesized samples after washing and drying process were characterized by microscopy, spectroscopy and diffraction methods. Fig. 1 display the SEM images of the as-synthesized materials. The images clearly show that the particles are spherical in case of the CTAB–P65 (not shown) and CTAB–P85 systems, wormlike in the case of CTAB–P103 and CTAB–P123 (not shown) systems and single crystalline in the CTAB–F127 system in acidic media under our reaction conditions, Fig. 1. The wormlike morphologies from

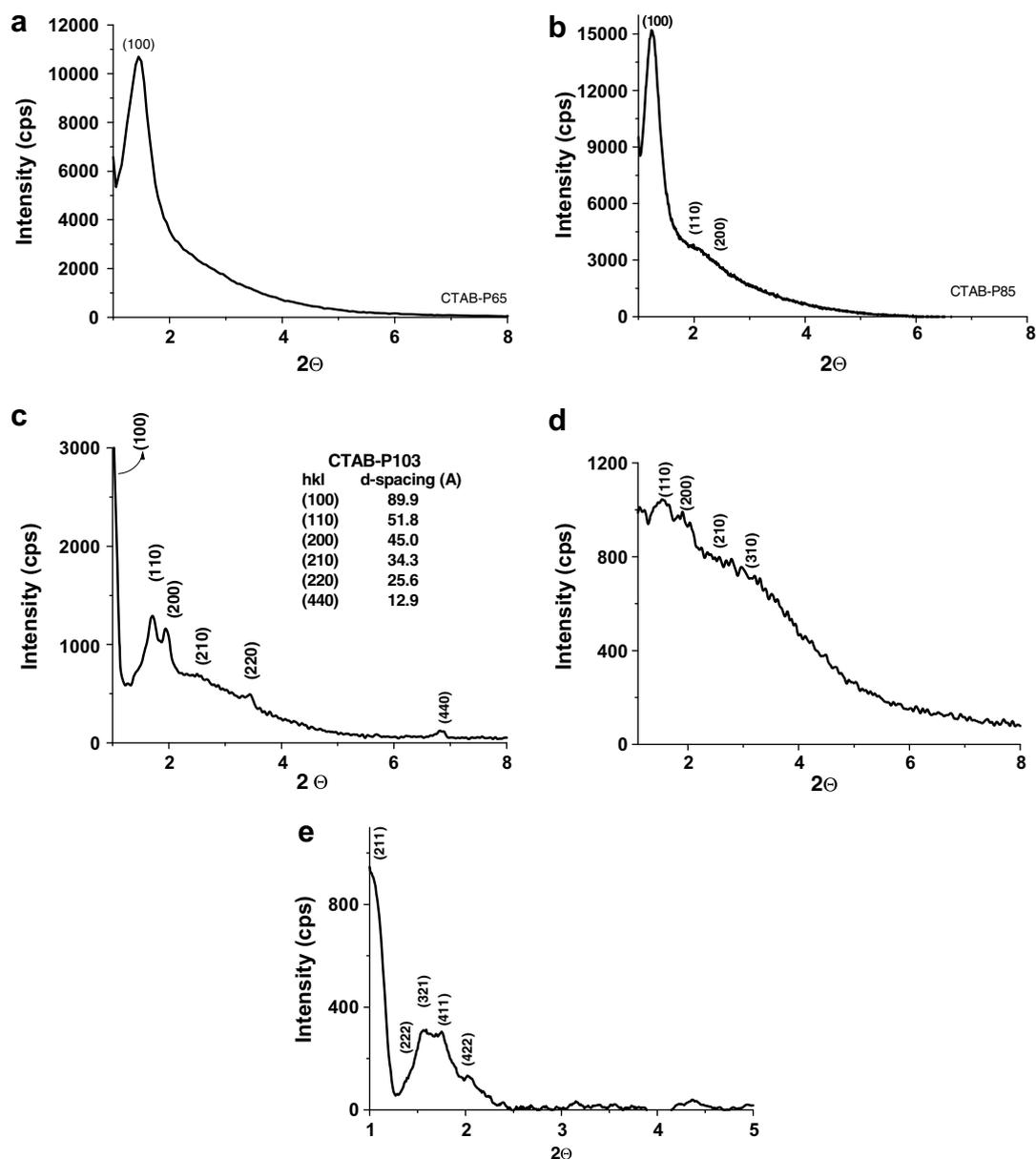


Fig. 2. The PXRD patterns of the mesostructured silica obtained from a system of (a) CTAB–P65 (CTAB/P65 mole ratio of 3.0), (b) CTAB–P85 (CTAB/P85 mole ratio of 2.5), (c) CTAB–P103 (CTAB/P103 mole ratio of 3.3), (d) CTAB–P123 (CTAB/P123 mole ratio of 2.0) and (e) CTAB–F127 (CTAB/F127 mole ratio of 6.0).

a CTAB–P85 system or spherical morphology from a CTAB–P123 can also be obtained upon the addition of an additive to the reaction media (see text latter). This control was achieved either by adding non-polar ingredients or alkaline metal salts. Each shape

can be obtained from a CTAB–Pluronic couple in a broad range of CTAB/Pluronic mole ratios.

Fig. 2 shows the PXRD patterns of various samples prepared using five different pluronics in the presence of various amounts

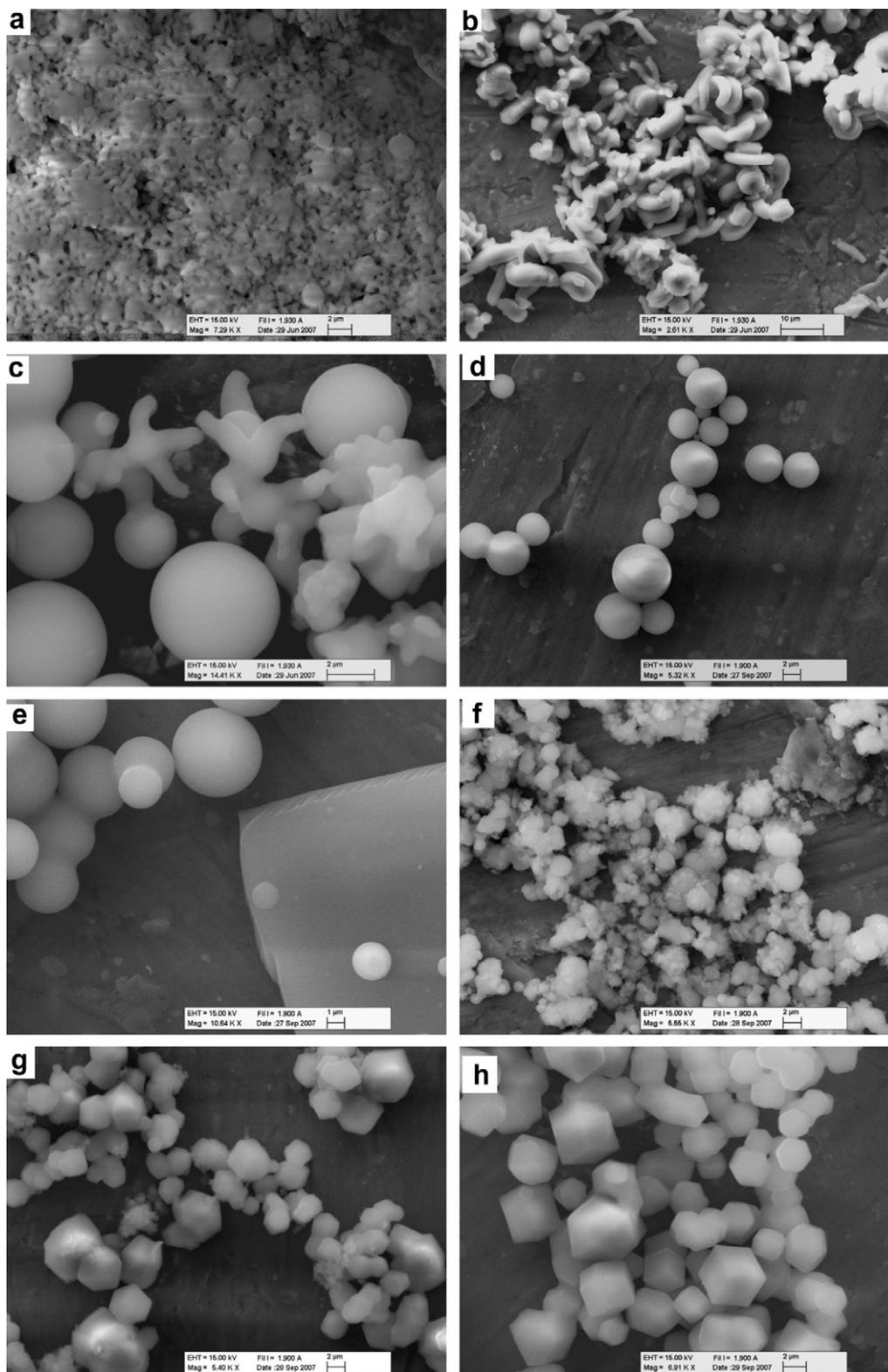


Fig. 3. The SEM images of the mesostructured silica obtained from CTAB–P85 systems with a CTAB/P85 mole ratio of (a) 0.00, (b) 0.18, (c) 0.61, (d) 1.22 and (e) 2.50 and of CTAB–F127 with a CTAB/F127 mole ratio of (f) 1.67, (g) 3.33, and (h) 5.00.

of CTAB. The use of P65, P85, P103, and P123 enables us to tune the unit cell diameters in the spheres in a broad range, from 6 to 10 nm. The CTAB–P65 or CTAB–P85 systems and the CTAB–P103 or CTAB–P123 systems produce 2D hexagonal mesostructures with a P6mm space group with either spherical or wormlike morphologies, respectively. However, only the wormlike structures are birefringent under POM between the crossed polarizers, indicating that the channels are oriented along the rope axis rather than random as in the spheres. The samples obtained from the CTAB–P103 system display up to six diffraction lines, which can be indexed to (100), (110), (200), (210), (220), and (440) planes of 2D hexagonal structure with a P6mm space group, Fig. 2. The mesostructured CTAB–F127 samples have a crystalline morphology with a rhombododecahedron shape. The XRD pattern of the crystalline sample has diffraction lines at 2.04, 1.76, 1.56, 1.44, 1.02° , 2θ corresponding to (422), (411), (321), (222), and (211) reflections of Im3m space group of cubic symmetry with a unit cell parameter of a equals to 21.2 nm. Note also that the samples prepared without CTAB do not diffract at small angles, indicating that the mesostructure is disordered or does not form in the absence of CTAB under our reaction conditions.

The effect of CTAB to the CTAB–P85 and CTAB–F127 systems has been investigated by carrying out the following experiments. The cationic surfactant to pluronic mole ratio was varied from 0.0 to 6.6 in the CTAB–P85 and 0.0 to 10.0 in CTAB–F127. In the absence of the cationic surfactant, one gets aggregated small particles with a distinct but not well defined morphology, Fig. 3a. In the presence of enough CTAB, at lower CTAB concentrations, the particles are only wormlike (CTAB/P85 mole ratio of 0.1–0.6), spherical at intermediate concentrations (CTAB/P85 mole ratio of 0.8–4.0) and a mixture of films and spheres at high concentrations (CTAB/P85 mole ratio of 4.0–6.6), Fig. 3. The addition of a small amount of CTAB prevents aggregation of the particles indicating that the CTA^+ ions are also on the surface of the growing particles. The CTA^+ ions form a complex at intermediate concentrations (CTAB/P85 mole ratio of 0.8–2.5) and the excess CTA^+ ions go to the air–water interface to produce mesostructured silica films, Fig. 3e. Note that the samples prepared using high CTAB concentrations contain a large amount of film samples, formed in the air water interface. Those film samples diffract at small angles characteristic of a film samples prepared using pure CTAB. If one prepares

with even larger quantities of CTAB, one obtains monoliths at the bottom of the reaction vessel. Therefore, we did not further investigate those samples.

Fig. 4 displays the Raman difference spectra of the silica spheres obtained from the CTAB–P85 (CTAB/P85 mole ratio of 0.46, 1.66 and 3.33) system and silica particles obtained from pure P85 system under similar reaction conditions. Notice that the peaks marked on the difference spectra at 2852 cm^{-1} correspond to the dissolved CTAB (see later) and all the other peaks at 2881, 2940 and 2978 cm^{-1} correspond to asymmetric $\nu\text{-CH}_2$, symmetric and asymmetric $\nu\text{-CH}_3$ groups of the PO units [21], respectively. The spectral changes are in the PO block of the P85 molecules and the dissolved CTAB signals become visible in the difference spectra, which suggests that the CTA^+ ions interact with the PO units of the P85 molecules and are involved in the assembly process. Most likely, the interaction of the alkyl tail of the CTAB molecules within the PO core of the CTAB–P85 micelles influences the conformation on the PO blocks and as a result alters the intensity of the CH_2 and CH_3 groups of the PO units. We have further investigated the CTAB–P85 system in various conditions to discover the interactions between the CTAB and P85 and also to determine the functions of the CTA^+ ions in the mesostructured silica assembly process.

The spectral changes, shown in Fig. 4 and the observed morphology, shown in Fig. 3a–e, are consistent with each other such that, the difference spectra display almost no change above 3.33 CTAB/P85 mole ratios, indicating that the excess CTAB molecules are not part of the mesostructured silica. Moreover, in the CTAB–F127 systems, one needs more cationic surfactant to observe the effect. The single crystals form at a CTAB/F127 mole ratio as low as 3.33, but the pure crystals form at higher concentrations, CTAB/F127 mole ratio of 5.0 and above, Fig. 3f–5h. The CTAB–P123 and CTAB–P103 systems usually produce wormlike morphology in a broad range of CTAB concentrations. However at higher CTAB/Pluronic ratios, the spherical particles can also be obtained from the CTAB–P123 (CTAB/P123 mole ratio of 5.0) and CTAB–P103 (CTAB/P103 mole ratio of 3.3) systems.

The spherical morphology is usually obtained at relatively lower CTAB/Pluronic mole ratios in smaller pluronics, such as P65 versus P85 and P103 versus P123. The CTAB–P85 system also produce wormlike particles if the CTAB/P85 mole ratio is below 0.5, however the CTAB–P65 system gives spherical particles at a mole ratio as low as 0.1. Similarly, the CTAB/P103 gives only spherical particles, if the CTAB/P103 mole ratio is higher than 2.5. However, the spherical and wormlike particles with a much smaller aspect ratio coexist in the CTAB–P123 system with a CTAB/P123 mole ratio as high as 3.33. In all CTAB–Pluronic systems, the CTA^+ ions influence the hydrophilicity of the pluronics by incorporating the alkyl tail of the cationic surfactant into the polypropylene oxide core and carrying the negatively charged counter anions together to the polypropylene oxide–polyethylene oxide region of the pluronics. This makes the PPO–PEO interface more hydrophilic, see Scheme 1. Notice that the PEO/PPO mole ratio is higher, 1.64 and 1.33, in both P65 and P85, respectively, than that of 0.62 and 0.57 in P103 and P123, respectively. Therefore in both P65 and P85 systems, the media is hydrophilic enough, such that there is no need for large amounts of cationic surfactant to produce spherical particles. However, F127 is even more hydrophilic than P65 and P85, still one needs high CTAB concentrations in the CTAB–F127 system, therefore the size to charge ratio of the CTAB–Pluronic micelle complex is also as important.

The interaction and formation of a complex between cationic surfactant and pluronics, were further investigated using Raman and FTIR spectroscopy methods. Fig. 5a and b display a series of Raman spectra of a water–CTAB, water–P85, and water–CTAB–P85 systems in various stages of the water evaporation. Notice that

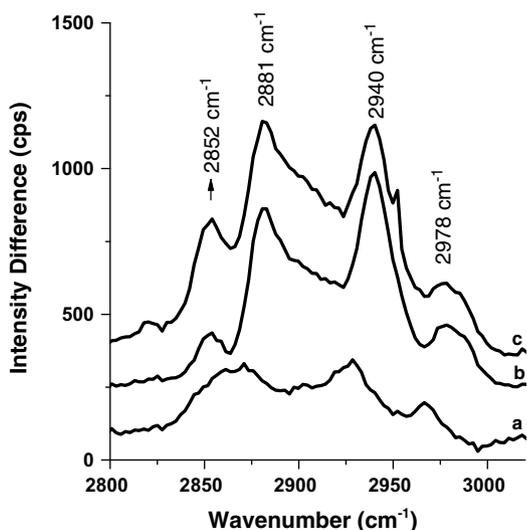


Fig. 4. Micro-Raman difference spectra between mesostructured silica obtained from CTAB–P85 systems and pure P85 (CTAB/P85 = 0.0, X) (a) the CTAB/P85 mole ratios of 0.46 – X, (b) CTAB/P85 mole ratios of 1.66 – X, and (c) CTAB/P85 mole ratios of 3.33 – X.

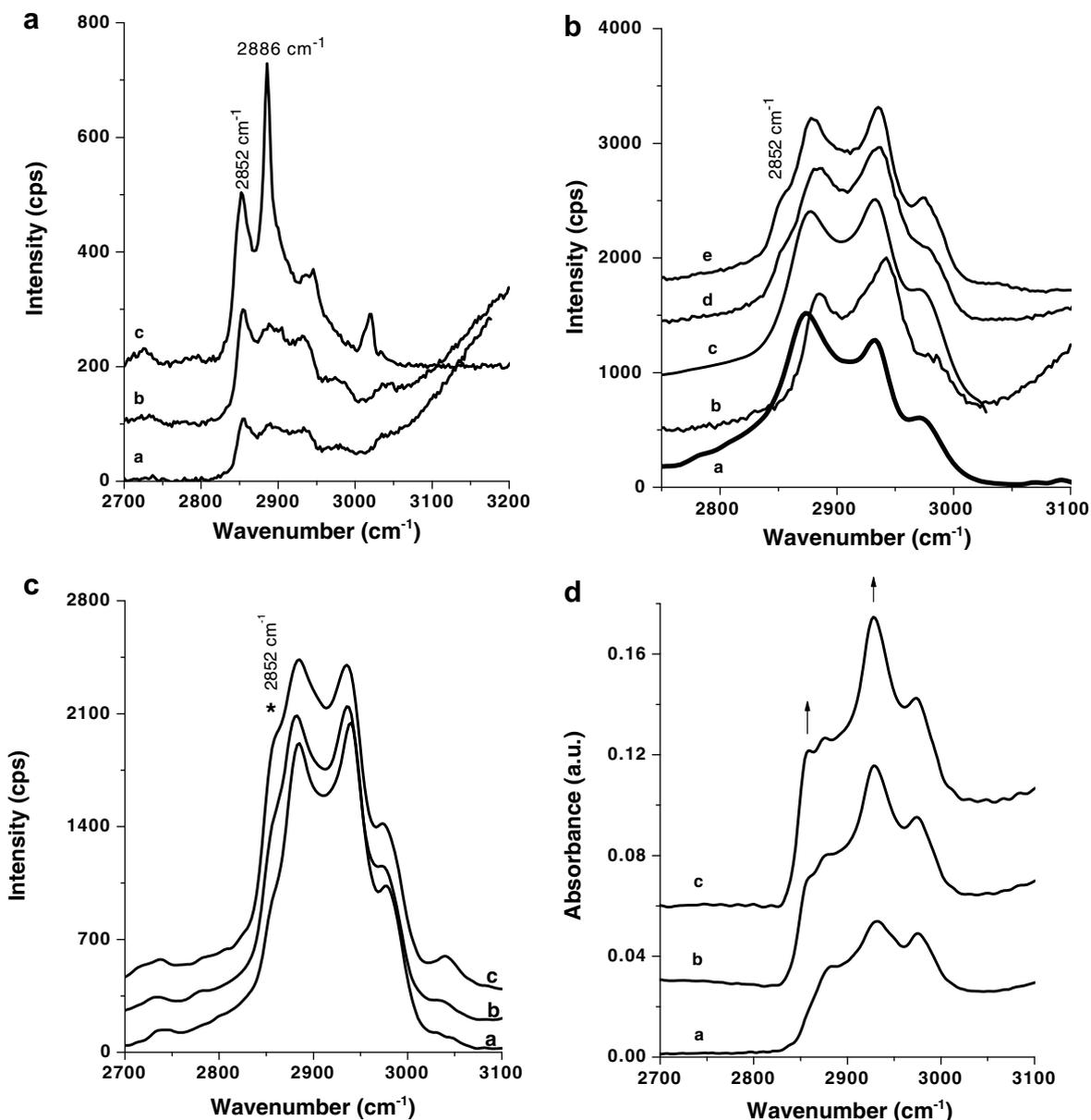
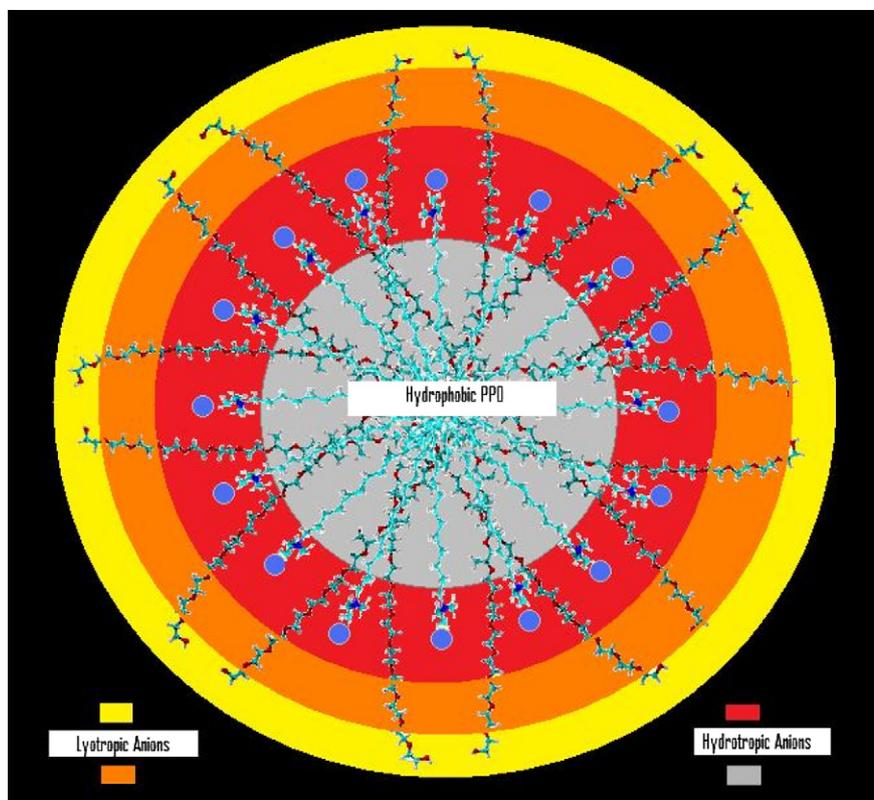


Fig. 5. The Raman spectra of (A) water–CTAB mixture with water evaporation; a through c, (B) (a) pure P85, (b) 10% w/v P85 + H₂O mixture, (c) mesostructured silica synthesized using P85 as structure directing agent, (d) mixture of 10% w/v CTAB + P85 + H₂O, and (e) mesostructured silica synthesized from CTAB–P85 system and (C) micro-Raman and (D) FTIR spectra of mesostructured (a) CTAB–P65–SiO₂, (b) KCl–CTAB–P65–SiO₂ and (c) NaNO₃–CTAB–P65–SiO₂.

the spectra of the water–CTAB changes drastically upon evaporation of water, Fig. 5a. The peak at around 2886 cm⁻¹ that originates from the asymmetric stretching mode of CH₂ groups of CTA⁺ ion is very sensitive to dissolution. The spectrum of the CTAB–P85 complex (see Scheme 1) in the presence of a small amount of water closely resembles that of the spectrum of the mesoporous silica materials prepared using CTAB and P85, indicating that both surfactants are present in the channels. Note also that the spectrum of the dissolved P85 is quite different from the spectra that contain CTAB and P85 mixtures. The peak at 2852 cm⁻¹ appears only in the presence of CTAB in all spectra (the spectra of CTAB–P85–H₂O, CTAB–P85–SiO₂ and CTAB–P85–[Zn(H₂O)₆](NO₃)₂ mixtures) without the intense asymmetric stretching mode of the CH₂ units of CTAB crystals at around 2885 cm⁻¹, indicating that the CTAB is completely dissolved in all cases, in a form of a CTAB–P85 complex. The FTIR spectra of the mesoporous silica prepared using P85 in the

presence and absence of CTAB are also presented in Fig. 5b for comparison purpose. Notice that these two spectra differ slightly from one another. The difference spectrum of the two spectra shows peak related to the dissolved CTAB. Based on our IR and Raman observations we suggest that the CTAB–P85 complex in the micelle form before interaction with the silica species in the self-assembly process. The complexing of CTAB–Pluronic makes the micelles positively charged, thus enhances the surfactant–silica assembly process.

As discussed above, the CTAB molecules play important roles in the silica assembly process. The formation of a complex between the CTA⁺ ions and pluronic provides positive charges to each micelle, Scheme 1. Therefore, the unit cell parameters of the particles are determined by the size of the pluronic micelles, Fig. 2. The complex formation has been investigated using FTIR and Raman spectroscopy techniques in this work using as-synthesized



Scheme 1.

mesostructured silica particles, water–CTAB, water–CTAB–P85, and CTAB–P85–[Zn(H₂O)₆](NO₃). Note also that the CTAB–P85–[Zn(H₂O)₆](NO₃) mixture form liquid crystalline mesophases that closely resembles the structure of mesostructured silica, CTAB–P85–SiO₂. Note that the interaction of surfactants (non-ionic, cationic and anionic) with pluronics has been widely investigated in aqueous solutions and in liquid crystalline phases using light scattering, calorimetry, small-angle X-ray scattering and NMR techniques [22–26]. It is a common conclusion that the cationic surfactant molecules interact with pluronics to form charged complex micelles in an aqueous media [22–24], which is consistent with our proposal.

It is known that the presence of anions also influences the conformation, as a result the hydrophilicity, of the ethylene oxide groups of the pluronics [27–29]. The anions of metal salts influence the solubility, conformation of the surfactants in both liquid and liquid crystalline media [27–29]. It has also been shown that the anions of the salts have a great effect on the morphology of the mesostructured silica in dilute and concentrated media [14,16,30]. Some anions, on the left hand side of the Hofmeister's series [31] ($\text{SO}_4^{2-} > \text{HPO}_4^{2-} > \text{CrO}_4^{2-} > \text{CO}_3^{2-} > \text{Cl}^-$), are known to be lyotropic and make the surfactant molecules more hydrophobic, and the others, on the right hand side of the series ($\text{Br}^- > \text{NO}_3^- > \text{I}^- > \text{ClO}_4^- > \text{SCN}^-$), are known to be hydrotropic and make the surfactant molecules more hydrophilic [27–29].

We have further investigated the role of hydrophilic–hydrophobic balance in the PPO core and PEO corona interface by other additives. For this purpose, the effect of two different anions, Cl^- (lyotropic) and NO_3^- (hydrotropic) and cyclohexane as a hydrophobic additive have been tested in our reaction conditions. The addition of KCl or cyclohexane to the CTAB–P85 system, even at 2.5 CTAB/P85 produces a wormlike morphology, Fig. 6a and b. Note that both Cl^- and cyclohexane make the P85 micelles more hydro-

phobic. The Cl^- ions occupy the hydrophilic regions of P85 complex micelles and enhance the contribution of the PPO block of P85, similarly cyclohexane molecules go to the PPO region of the micelles and enhance the hydrophobic interactions. However, in the presence of NaNO_3 , one gets a spherical morphology, Fig. 6c. The FTIR and Raman spectra of the three samples prepared using CTAB–P65 system and presence of chloride and nitrate salts are displayed in Fig. 5c and d. The amount of dissolved CTAB molecules (difference spectra between the samples with and without salts display spectrum similar to dissolved CTAB) in the mesostructured silica is enhanced in the presence of both Cl^- and NO_3^- anions, Fig. 5c and d. However, the amount of dissolved CTAB is noticeably higher in the nitrate case.

The lyotropic anions occupy the aqua media close to the EO tail; however, the hydrotropic anions occupy the ethylene oxide–propylene oxide interface making the media more hydrophilic, see Scheme 1. Sachs et al. [32] have studied the dynamics of anion penetration into the hydrophobic domains of lipids where the hydrotropic anions penetrate further, thereby disrupting the hydrocarbon packing. Sachs et al.'s finding is consistent with our observations and model. The addition of salts of the lyotropic anions have an effect similar to increasing the PO units of the pluronics, enhancing the hydrophobicity of the media or the hydrophobic interactions, see Scheme 1. Similarly, the addition of salts of hydrotropic anions makes the pluronics more hydrophilic and has the effect of increasing the EO units. The distribution of the anions in the EO units from the PO core towards EO corona influences the conformation on the EO units in the pluronics, as a result the effectiveness of the ethylene oxide groups. The distribution of the anions also affects the hydrating (hydrotropic ions wet) and dehydrating (lyotropic ions dry) of the PO units and, as a result, the conformation in the PO core and EO corona of the micelles.

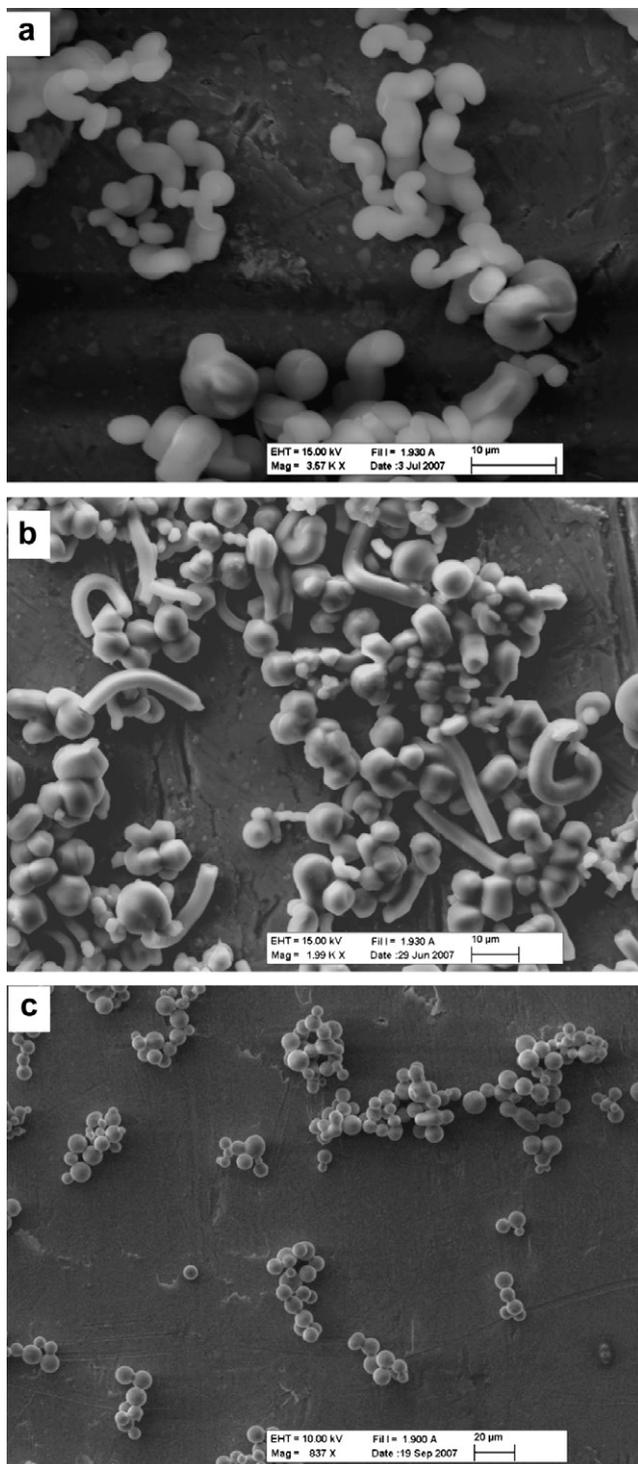


Fig. 6. The SEM images of mesostructured silica obtained from CTAB–P85 system with a CTAB/P85 mole ratio of 2.50 in the presence of (a) 1 g KCl, (b) 5 ml Cyclohexane, and (c) 1 g NaNO_3 .

4. Conclusion

Three different morphologies were investigated under a similar reaction condition in a CTA–Pluronic–Silica system, namely spheres, wormlike particles and single crystals. Increasing the ethylene oxide units in the pluronics changes the morphology from wormlike particles to spherical particles and to single crystals in the presence of cationic surfactant. The mesostructures in the

spheres and wormlike particles are 2D hexagonal while the single crystals are cubic. The addition of a cationic surfactant influences the hydrophilic–hydrophobic character of the pluronics and affects the morphology. The cationic surfactant–pluronic interaction makes the pluronics more hydrophilic and provides positive charge to their micelles, which influences the assembly of the silica species. The amount of the cationic surfactant required for one type of morphology is low in the smaller pluronics, at a CTAB/P65 mole ratio as low as 0.1 in the CTAB–P65 system, and large in the larger pluronics, at a CTAB/F127 mole ratio as high as 5.0, in the CTAB–F127 system. Most likely some cationic surfactant molecules remain in the solution and modify the surface of the growing silica particles.

The addition of lyotropic anions, such as Cl^- and non-polar organic molecules makes the pluronic micelles more hydrophobic such that the effect is equivalent to decreasing the ethylene oxide units in the pluronics. One can obtain all three morphologies by influencing the hydrophilic character of the pluronics using salts or organic compounds in the reaction media. Further studies are required to expand the concept using other pluronics, oligo(ethylene oxide) type nonionic surfactants and may be anionic surfactant instead of cationic surfactant.

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References

- [1] T. Yanagisawa, T. Shimizu, K. Kuroda, C. Kato, *Bull. Chem. Soc. Jpn.* 63 (1990) 988.
- [2] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* 359 (1992) 710.
- [3] K. Yano, Y. Fukushima, *J. Mater. Chem.* 13 (2003) 2577.
- [4] Y. Yamada, T. Nakamura, M. Ishi, K. Yano, *Langmuir* 22 (2006) 2444.
- [5] M. Mizutani, Y. Yamada, K. Yano, *Chem. Commun.* 11 (2007) 1172.
- [6] L. Qi, J. Ma, H. Cheng, Z. Zhao, *Chem. Mater.* 10 (1998) 1623.
- [7] R.I. Nooney, D. Thirunavukkarasu, Y. Chen, R. Josephs, A.E. Ostafin, *Chem. Mater.* 14 (2002) 4721.
- [8] M. Mesa, L. Sierra, B. Lopez, A. Ramirez, J.L. Guth, *Solid State Sci.* 5 (2003) 1303.
- [9] J.P. Hanrahan, A. Donovan, M.A. Morris, J.D. Holmes, *J. Mater. Chem.* 17 (2007) 3881.
- [10] W.J.J. Stevens, K. Lebeau, M. Mertens, G.V. Tendeloo, P. Cool, E.F. Vansant, *J. Phys. Chem. B* 110 (2006) 9183.
- [11] H. Yang, N. Coombs, G.A. Ozin, *Nature* 386 (1997) 692.
- [12] H. Yang, G.A. Ozin, C.T. Kresge, *Adv. Mater.* 10 (1998) 883.
- [13] B. Wang, W. Shan, Y. Zhang, J. Xia, W. Yang, Z. Gao, Y. Tang, *Adv. Mater.* 17 (2005) 578.
- [14] B. Wang, C. Chi, W. Shan, Y. Zhang, N. Ren, W. Yang, Y. Tang, *Angew. Chem. Int. Ed.* 45 (2006) 2088.
- [15] G. Zhou, Y. Chen, J. Yang, S. Yang, *J. Mater. Chem.* 17 (2007) 2839.
- [16] J. Wang, J. Zhang, B.Y. Asoo, G.D. Stucky, *J. Am. Chem. Soc.* 125 (2003) 13966.
- [17] C. Yu, B. Tian, J. Fan, G.D. Stucky, D. Zhao, *J. Am. Chem. Soc.* 124 (2002) 4556.
- [18] A.F. Demirörs, M. Arslan, Ö. Dag, *Micropor. Mesopor. Mater.* 98 (2007) 249.
- [19] A.F. Demirörs, B.E. Eser, Ö. Dag, *Langmuir* 21 (2005) 4156.
- [20] C. Albayrak, G. Gülten, Ö. Dag, *Langmuir* 23 (2007) 855.
- [21] C. Guo, J. Wang, H.Z. Liu, J.Y. Chen, *Langmuir* 15 (1999) 2703.
- [22] Y. Li, R. Xu, S. Couderc, D.M. Bloor, J.F. Holzwarth, E. Wyn-Jones, *Langmuir* 17 (2001) 5742.
- [23] J. Jansson, K. Schillen, G. Olofsson, R.C. da Silva, W. Loh, *J. Phys. Chem. B* 108 (2004) 82.
- [24] J. Jansson, K. Schillen, M. Nilsson, O. Söderman, G. Fritz, A. Bergmann, O. Glatter, *J. Phys. Chem. B* 109 (2005) 7073.
- [25] D. Löf, A. Niemiec, K. Schillen, W. Loh, G. Olofsson, *J. Phys. Chem. B* 111 (2007) 5911.
- [26] K. Aramaki, Md.K. Hossain, C. Rodriguez, M.H. Uddin, H. Kunieda, *Macromolecules* 36 (2003) 9443.
- [27] H. Schott, *J. Colloid Interface Sci.* 192 (1997) 458.
- [28] T. Iwanaga, M. Suzuki, H. Kunieda, *Langmuir* 14 (1998) 5775.
- [29] C. Rodriguez, H. Kunieda, *Langmuir* 16 (2000) 8263.
- [30] E. Leontidis, *Curr. Opin. Colloid Interface Sci.* 7 (2002) 81.
- [31] F. Hofmeister, *Arch. Exp. Pathol. Pharmacol.* 24 (1888) 247.
- [32] J.N. Sachs, T.B. Woolf, *J. Am. Chem. Soc.* 125 (2003) 8742.