Recent developments in materials synthesis in surfactant systems

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Abstract

The paper reviews the use of surfactant self-assembly to template the synthesis of polymers, ceramics with extended structures, and nanoparticles. The objective of the review is to highlight newer concepts linking self-assembly to materials nanostructure and to the realization of functional materials.
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1. Introduction

The self-assembly of surfactants to create hydrophobic and hydrophilic structured domains creates an opportunity to use these systems as media for the synthesis of materials with unique properties. The tremendous interest in functional nanostructured materials is an impetus to the development of surfactant-based templates for materials synthesis. In this paper, we review very recent developments over the last 2 years in the use of surfactant systems to direct the synthesis of ceramic and polymer structures. The literature in the field is vast, but the excellent recent review by Antonietti [1•] allows the reader to gain an essential understanding of the field prior to 2001.

There are many aspects to materials synthesis in self-assembled surfactant systems. The use of surfactant micelles and microemulsion based droplets that serve as nanoreactors for synthesis is perhaps the most ubiquitous direction in applications. The field of microemulsion polymerization and the synthesis of inorganic nanoparticles in water-in-oil microemulsions fall in this class. A second direction of intense fundamental and applied interest is the templating of mesoporous materials through the use of surfactant self-assembly, as exemplified through the development of mesostructured silicas and their variants synthesized in cationic surfactant systems. The remarkable aspect of such synthesis is the continuously evolving self-assembly as modulated by charge interactions between the surfactant and the inorganic structure and packing density considerations of the surfactant-ceramic complex during synthesis. The evolving self-assembly serves in a structure-directing role to ceramic synthesis. The review by Dabbs and Aksay [2] serves as an excellent background to work in this field.

Our objective in this summary of research in materials synthesis is to attempt to point out some newer correlations between materials structure and surfactant self-assembly. We try to link separate aspects of materials synthesis through the questions (a) Is there a clear link between the geometry of self-assembly and the final material structure? (b) Is there any new

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fundamental design principle for materials synthesis? (c) From the applications perspective, is there a clear link to a functional material? The last question is of particular interest in the translation of fundamental research to commercial applications, and there are an increasing number of papers which relate form and nanostructure to enhanced function.

To provide continuity with the review by Antonietti [1•], the paper is organized in an approximately equivalent manner.

2. Surfactant mediated ceramics synthesis

The literature on the synthesis of mesostructured silicas as mediated by cationic surfactants is large, and we do not attempt to be comprehensive. But we do wish to point out some truly fundamental advances in the understanding of the synthesis of these materials. Tolbert et al. [3•] have used time-resolved X-ray diffraction to follow changes in structure during synthesis. The study clearly delineates a smooth transition from the lamellar to the hexagonal phase of self-assembly upon heating a 20-carbon quaternary ammonium surfactant in solution with tetraethyl orthosilicate (TEOS). A discontinuous transition from the hexagonal to the lamellar phase is seen when following the same heating trajectory with a 16-carbon surfactant (CTAB) together with a cosolvent (1,3,5-trimethylbenzene, TMB) and TEOS. The authors draw an interesting correlation between interfacial curvature as influenced by the charge density and surfactant packing considerations. High charge densities obtained by partially hydrolyzed species favor close packing of surfactant to the lamellar structures. As polymerization proceeds, there is a lowering of the interfacial charge density allowing curvature to the less highly packed hexagonal shape. Such charge density considerations are coupled with the intrinsic packing parameter of the surfactants with the CTAB + TMB complex favoring higher packing parameters when the TMB is adsorbed to the CTAB tails, increasing the effective volume of the tail. The higher packing parameters favor lamellar structures at lower temperatures, while at higher temperatures, detachment of the TMB leads to smaller packing parameters and the introduction of interfacial curvature. It is interesting to note a complementary study by Fowler et al. [4] that describes the quenching of template driven synthesis of MCM-41 silica at early synthesis times to obtain nanoparticles of silica with structured interiors. The use of lyotropic liquid crystal mesophases with long range order have been used to synthesize mesoporous monolithic silicates with long range lamellar, cubic or hexagonal structures [5,6].

Some novel aspects of the synthesis of mesoporous silicas and other oxides are described. While a significant objective has been the realization of monolithic silicas with mesostructure allowing fabrication to membranes and thin films, other 3D morphologies have also been explored. Fowler et al. report the synthesis of hollow silica spheres where the shell is mesoporous [7] and mesostructured [8]. The use of amino acid based surfactants represent novel trends in inducing silica self-organization to mesostructured materials [9]. Further application of biologically relevant templates involve the use of tobacco mosaic virus liquid crystals in silica synthesis [10]. Biologically relevant ceramics such as calcium carbonate have been synthesized in the presence of surfactant-dendrimer complexes [11]; the use of cationics induced the formation of vaterite, while anionics inhibited growth due to complexation with Ca^{2+}. The dendrimers with long alkyl tails are able to incorporate both cationic and anionic surfactants, thereby facilitating a systematic study of surfactant mediated calcium carbonate crystallization.

Other interesting ceramic architectures through surfactant mediation have been described. The use of laurylamine hydrochloride as the cationic surfactant leads to the formation of entangled nanotubules of silica, indicating that the final step of assembly to hexagonal order is absent in these systems [12]. In nonaqueous systems of water-in-oil microemulsions formed by cationic surfactants, reticulated silica rod-like structures are observed [13]. Harada et al. develop a sequential templating process where initial colloidal particles of silica condense to colloidal stringlike aggregates which further transform to rods and then translate to a network system of interconnected rods. It would be interesting to correlate the evolution of the surfactant template geometry in these essentially nonaqueous systems to the evolution of the template in aqueous systems conducive to the synthesis of mesostructured silicas. A particularly fascinating approach is the superposition of flow during mesostructured materials synthesis as shown by Kim and Yang [14•]. Taylor instabilities during Couette flow generated by rotating coaxial cylinders leads to coil-spring streamlines in the fluid. When the fluid contains a cationic surfactant (CTAB) together with the silica precursor, the wormlike micelles adopt the streamline structure and acts as a template during silica synthesis. The coil-spring morphology is preserved in the silica, which additionally reveals ordered mesoporosities.

The translation from form to function in mesostructured materials has also been demonstrated in the recent literature. Wirnsberger et al. [15•] have shown that a pH sensitive dye (fluorescein isothio-

cyanate) incorporated into thin films of mesostructured silica exhibits a rapid photoluminescent response to environmental pH changes. Mesostructured V−Mg−O materials with potentially enhanced catalytic properties have been synthesized through templating mechanisms [16]. The grafting of cyclodextrin groups into mesostructured silica leads to a functional material that shows an enhanced ability for the removal of organic compounds [17•]. A second example in separations technology involves the synthesis of arylene and ethylene bridged polysilsequioxane materials through base catalyzed hydrolysis and condensation in the presence of the cationic CTAC (cetyltrimethylammonium chloride) [18]. These mesoporous organic−inorganic hybrids are found to be very effective in the adsorption of phenols. Mesostructured nickel/nickel oxide electrodes synthesized through surfactant templated mechanisms show an enhanced redox charge capacity and an extremely rapid charge transfer, evidently due to the mesostructured porosities which allow rapid ionic diffusion [19•]. Related work on the electrodeposition of semiconductor films in lyotropic liquid crystalline media may be a novel method to combine and correlate electrooptical properties with nanoarchitecture [20].

3. Polymer architectures templated by surfactants

The generation of polymer latexes in surfactant emulsion and microemulsion systems is not considered here as this is an independent and vast research area that is commercially important. Rather, we focus on the generation of polymers with unique architectures that are obtained as a result of synthesis in surfactant systems. It has often been stated that goal of such polymerization is to rigidify and preserve the morphology of self-assembly, thereby creating structures that are ordered over several length scales. This is rather difficult in cases where monomers are doped into surfactant systems; the resulting polymerization often leads to phase separation and morphologies independent of the surfactant assembly. Polymerizable surfactants appear to hold promise as structure preserving systems. A recent report by Summers et al. [21•] examines a range of microstructures (microemulsion droplets and lyotropic liquid crystals) obtained prior to polymerization of systems containing polymerizable single and double chain cationics. Neutron scattering, electron microscopy, and polarized optical microscopy are used to correlate structures prior to polymerization and after polymerization.

Doping self-assembled surfactant microstructures with monomers to synthesize nonparticulate polymers with unusual morphologies remains a fascinating objective. Faul et al. describe interesting work where

polyelectrolyte-surfactant complexes are doped with vinyl monomers subsequent to which free-radical polymerizations are conducted [22]. The resultant polymers show wire and cigar shaped morphologies which appear related to the structure of the complex. Doping hydrophobic monomers in vesicles to produce hollow polymer shells also represents continuing efforts to induce morphology into polymer structures through surfactant templating mechanisms. In recent years, this approach has been used in spontaneously formed vesicles such as those formed by mixtures of cationic and anionic surfactants (catanionic vesicles) [23]. The report by McKelvey et al. uses styrene crosslinked with divinylbenzene leading to a hardened shell structure [23]. On the other hand, styrene polymerization in dioctadecyldimethylammonium bromide (DODAB) vesicles leads to phase separation and the generation of parachute morphologies with bead structures of the polymer tethered to the vesicle [24]. Krafft et al. [25•] have demonstrated the polymerization of isodecylacrylate (ISODAC) in vesicles of perfluoroalkylated phosphatidylcholine and in the conventional vesicles of phosphatidylcholine. While phase segregation and beadlike structures were observed in the conventional vesicles, shell structures were observed in the perfluorinated vesicle system. The authors attribute the difference to the extreme confinement offered by the perfluorinated vesicles. Polymer growth is confined to a narrow hydrophobic region within the bilayer and the polymer is excluded from the fluorinated surfactant tails which are strongly organized to maintain vesicle structure.

Hydrogel structures have also been synthesized in surfactant systems to generate highly porous structures that may also have the requisite mechanical characteristics for biomedical and membrane applications. Lester et al. [26] show accelerated kinetics of polyacrylamide photopolymerization in lyotropic liquid crystalline phases of nonionic surfactants. Puig et al. [27] have synthesized crosslinked particles of polyacrylamide in AOT water-in-oil microemulsions. Following this, the particles are transferred to an aqueous phase containing monomer some of which diffuses into the particle. Further polymerization leads to a hydrogel with nodes of highly crosslinked particulates. These microstructured hydrogels have larger Young's modulii than conventional hydrogels.

The connection between form and function is brought about by a second example. The electropolymerization of aniline in the inverse hexagonal mesophase of AOT has been recently reported [28]. In this interesting report, the applied electric field aligns domains of the inverse hexagonal structure parallel to the field through electro-osmotic flow. The electrodeposition leads to nanowire arrays of polyaniline growing normal to the electrode surface. These con-

ductive polymers are of significant commercial interest in electrooptical device development.

4. Surfactants and nanocrystal synthesis and assembly

The templated crystallization of inorganic nanoparticles in surfactant systems is a third area where progress has been made over the last couple of years. Spherical nanoparticle synthesis in water-in-oil microemulsions continues to be a much-studied area with new variants. Au/Pd and Au/Ag bimetallic particles have been synthesized in AOT water-in-oil microemulsions [29,30]; the papers are of interest as they show the formation of true bimetallics and not particles of individual species. Calandra et al. [31] demonstrate an interesting approach to ZnS nanoparticle synthesis by contacting the precursor salts (Na_2S) and $ZnSO_4$ which are suspended in water free AOT micelles; this is done by dissolving the precursors in water containing microemulsion droplets, then evaporating off all solvents followed by resuspension in the nonpolar solvent. In these cases, it is important to understand the nature of the counterion attached to AOT and if there is counter-exchange upon salt incorporation influencing the precipitation of ZnS. Casson et al. show a significant influence of the bulk solvent on growth rates of copper nanoparticles in AOT water-in-oil microemulsions [32]. While the synthesis of ferromagnetic and superparamagnetic nanoparticles has been clearly demonstrated in AOT water-in-oil microemulsions, a recent development is the synthesis of molecule based magnets such as cobalt hexaferrocyanate in these systems [33].

The use of surfactant systems to synthesize nonspherical inorganic nanoparticles is also of interest since shape anisotropy may have pronounced effects on nanoparticle function. Pinna et al. report the formation of triangular CdS nanocrystals in the $Cd(AOT)_2$/isooctane/water system [34]. Interestingly, the particles are of the hexagonal wurtzite structure but are unstable and revert to aggregated particles of the FCC cubic structure It is often difficult to correlate the shape of the nanoparticle to template geometry. In an extensive study of the $Cu(AOT)_2$/isooctane/water system, Pileni [35•] shows evidence of spherical, rod-shaped, and irregularly shaped particles, as a consequence of synthesis at various system compositions where the system shows very sensitive changes in microstructure from independent reverse micelles to interdigitated micelles, clusters of micelles, and even lamellar and vesicular structures. The shape of the copper nanoparticles is further influenced by the nature of the salt, and the concentration of the precursor ionic species. Exclusivity of nanoparticle shape and the

ability to control particle shape in ambient temperature surfactant mediated synthesis remains an important issue. Two groups [36,37] have shown a remarkable transformation from Au nanoparticles to nanorods of controllable aspect ratio, simply by the addition of CTAB to the system. Johnson et al. [37•] have elucidated the role of CTAB in inducing this transformation to surfactant adsorption on side/edge faces of isometric crystals allowing growth along the [1 1 0] axis. Simmons et al. [38] have reported the synthesis of high aspect ratio CdS nanorods in reverse micelles of AOT and phosphatidylcholine (lecithin). There are several possibilities that affect the transformation from spheres in the AOT system to rods in the AOT + lecithin system. These include micellar distortions due to curvature modifications introduced by lecithin which has a lower spontaneous curvature, adsorption of lecithin on specific crystal faces to break symmetry, and micellar cluster formation which allows further growth of nucleated particles. The transformation from the FCC zinc blende structure in AOT micelles to the hexagonal wurtzite structure in the AOT + lecithin micelles is another evidence of surfactant mediated symmetry breakage in crystal formation. In a very nice experiment to understand the role of the micellar template, Summers et al. [39] have used single and double chained polymerizable surfactants (surfmers) to vary interfacial curvature of reverse micelles in the synthesis of $BaSO_4$. These researchers show that in the unpolymerized case with flexible interfaces, spherical nanoparticles of $BaSO_4$ are formed. When the micellar curvature is made more rigid through polymerization, cylindrical particles are observed with aspect ratios varying from 1 to 2.

Ordered arrays of high aspect ratio nanowires and nanorods have been synthesized through electrodeposition in surfactant systems [40•,41]. This work, by Huang et al. is especially interesting, as it illustrates long range order of nanowires through alignment of the inverse hexagonal liquid crystalline structure formed by AOT at high concentrations. Again, electro-osmotic flow may be responsible for domain alignment and electrodeposition in the aqueous cylindrical channels of the inverse hexagonal structure. The system is simple and the templating of materials structure is very nicely illustrated both in these papers on inorganic nanowire synthesis and in the accompanying work on the electrodeposition of polyaniline [28].

Other recent aspects of nanoparticle synthesis in surfactant systems include the placement and manipulation of nanoparticles both on surfaces and in 3D geometries. This is the next level of nanocrystal assembly—addressing the use of nanoparticles synthesized in surfactant systems? Cobalt nanoparticles synthesized in $Co(AOT)_2$ reverse micelles have been

deposited onto surfaces through solvent evaporation in the presence of a magnetic field. The films formed on the surface take on varying structures and exhibit distinct magnetic properties depending on whether the external magnetic field applied during deposition is oriented parallel or orthogonal to the surface [42]. An excellent paper by Pileni [43•] summarizes various methods of depositing nanoparticles with optical and/or magnetic properties onto surfaces, the supracrystalline thin film morphologies and the collective optical and magnetic properties of such films. In semiconductor based nanoparticles, thiol functionalization is important to obtain ordered 2D films. Typically, in magnetic materials, the easy axes of the nanoparticles become oriented along the direction of the applied magnetic field. A paper by Bonini et al. [44] describes a hybrid concept wherein flame spraying of microemulsions containing nanoparticles leads to deposition of thin films. The method is an alternative to laser-assisted ablation and other thermal methods to evaporate metallic substrates and condense the vapors to thin films. Firestone et al. [45] show how functionalization of silver nanoparticles can allow spatial positioning of these nanoparticles into various regions (the aqueous, the hydrocarbon, or the interfacial region) of a mesoscopically ordered lamellar gel phase of a polymer-grafted lipid based system. By such positioning, it may be possible to influence collective behavior of the nanoparticles and modulate their electronic, magnetic or optical properties. A particularly fascinating article by Davis et al. [46] describes strategies employed in the assembly of nanoparticles during biomineralization. The realization of materials with higher ordered architectures is termed as nanotectonics and involves various strategies of matrix confinement of nanoparticles, programmed assembly, engineering of substrates for nanoparticle attachment, shape-directed assembly of nanoparticles and slow transformations of nanoparticle morphologies. Lessons drawn from nature may be used effectively in the fabrication of functional materials, especially in polymer-nanoparticle composites.

The final level of nanocrystal assembly is incorporation into a device to create a truly functional material. An excellent review by Shipway and Willner [47••] describes several potential applications of nanoparticles and nanoparticle arrays, the design of field-responsive materials for use as sensors etc.

5. Further aspects of surfactant self-assembly and materials synthesis

The fact that surfactant self-assembly leads to nanoscale hydrophobic and hydrophilic domains has allowed synthesis of hybrid functional materials such as mesoporous ceramics containing polymers within the pores, nanoparticles in polymer matrices for device applications, etc. A notable example is the incorporation of conjugated polydiacetylenes in mesoporous silicas through co-synthesis of polymerizable surfactants that provide the template for silica condensation [48•,49]. The conjugated polymers exhibit novel chromatic changes in response to thermal, mechanical and chemical stimuli and the silica provides the mechanical integrity for device fabrication. Moy et al. [50] show that the incorporation of ruthenium (II) complexes in polymerized bicontinuous microemulsions dramatically increases the photoluminescence as a consequence of rigidifying the photochromic groups.

Finally we mention functional materials made through the self-assembly of small molecules that are able to gel organic liquids, the so-called organogelators. These are to some degree, the analogues of wormlike micelles in aqueous media, but constitute the reverse structure with the hydrophobic moieties facing the organic solvent. The self-assembly of these low molecular weight compounds to gelate organic liquids is based not on electrostatic interactions, but on hydrogen bonding and van der Waals interactions [51•,52]. Gronwald et al. [51•] has written a very recent and lucid review on this novel class of materials and their applications as templates for polymerization and as matrices for molecular recognition. An example of such self-assembly is the transformation of AOT inverse micelles to organogels upon the addition of para-substituted phenols [52]. The spherical micelles undergo transformation to strands which further assemble to fibers and to fiber bundles as shown in the schematic of Fig. 1a. Fig. 1b is an AFM image of these organogels. The transformation from reverse micelles to strands implies that nanoparticles synthesized in reverse micelles undergo transcription to the gel strands, potentially leading to new functional materials.

6. Challenges in surfactant-mediated synthesis

Amphiphilic molecules form soft aggregates in solvents, held together by van der Waals and ionic forces. Physical templating would require conservation of this morphology during materials synthesis, as well as formation of materials that directly conform to this structure. This has been demonstrated in the formation of mesoporous silica as well as in some cases where amphiphiles have been immobilized by polymerization. For most surfactant-mediated synthesis applications, the connection between the mor-
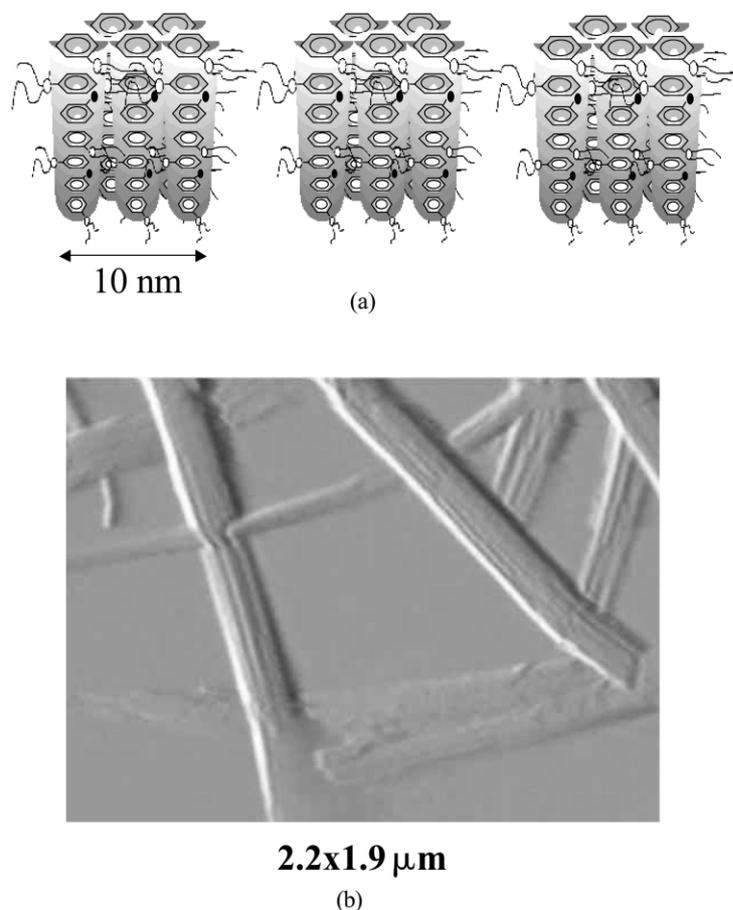
Fig. 1. (a) Schematic of organogel of self-assembly from strands to fibers to fiber bundles. (b) Atomic force micrograph of a self-assembled organogel.

phology of the surfactant aggregates and the resulting particle structure is much more complex, being affected by a host of conditions prevailing in the local microenvironment surrounding the growing particle. These include the pH, composition, and ionic strength, as well as surfactant head group spacing. As reaction takes place within these microenvironments, many of these factors are liable to change. The decoupling of each of these effects still remains a challenge, and provides interesting new opportunities in this field.

Surfactant aggregates associate (or dissociate) with time scales that can range over several orders of magnitude. If the time scale associated with particle formation is small compared to the time scale for this transformation, intermediate, non-equilibrium aggregate structures afford additional opportunities for templated materials synthesis. The fast kinetics associated with several solution-based precipitation processes is ideally suited for this application. The control of solution conditions and surfactant architecture to exploit non-equilibrium surfactant morphologies remains an interesting scientific challenge.

The assembly of particles formed in these structures into precisely tailored, technologically important, 3D structures is another important challenge. In situ reactions in a well-organized and immobilized amphiphilic matrix represent one approach towards this goal. Use of shear on liquid crystalline systems tends to produce alignment of microscopic domains into macroscopic regions in the direction of shear, or other interesting morphological transitions. Reactions within these shear-induced structures represent an interesting opportunity for combining and controlling the rheological behavior displayed by these complex fluids with materials synthesis. A more active approach is the use of engineered peptides to direct the self-organization of nanoparticles into important structures [53]. External stimuli provide great promise, and the next few years will be certain to show progress in using light, electric and magnetic fields to organize particles into 3D matrices. The real test of self-assembly and materials synthesis will be the generation of functional structures with unique and useful properties.

Acknowledgements

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