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Strategies for Spatially Separating Molecules in Mesostructured Sol-Gel Silicate Films

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Abstract. Three strategies for placing molecules in designated regions of mesostructured thin films made by the sol-gel dip-coating technique are demonstrated. These strategies all involve one-step syntheses where all of the components are present in the sol from which the substrate is pulled. Silicate films templated by ionic surfactants contain three spatially-separated regions: a silicate framework, an organic region formed by the hydrocarbon tails of the surfactants, and an intervening ionic interface formed by the charged surfactant head groups. The first method exploits lipophilic interactions between the molecule and the micelle to place it in the organic region. The second method uses chemical bonding of multiple trialkoxysilane groups in a three dimensional array on the molecule to place it in the silica framework. The third method uses multiple functionality at opposite sides of the molecule to enable it to span two regions. Luminescent molecules are used, and spectroscopy monitors the formation.

Keywords: sol-gel, mesostructure, luminescence, thin film

Deliberate and controlled placement of molecules in the spatially separated regions of mesostructured silicate materials is under active investigation [1–12]. The most commonly employed method involves backfilling or postdoping of MCM-41 type materials in which the silica is first templated with surfactants, then emptied of these structure-directing molecules by calcination or solvent extraction, and finally re-filled by diffusion of the desired guest molecules into the empty pores [13–18]. The location of the guest molecules is limited to the pores. An alternative method that allows one or more molecules to be placed in specified regions of the structure in a one-step dip-coating synthesis has recently been reported [1].

In the dip coating process a substrate is withdrawn slowly at a constant speed from a sol [12, 19, 20]. Upon withdrawal, a liquid film becomes entrained on the surface of the moving substrate. This film thins from gravitational draining, capillary-driven flows and evaporation. The film formation process is dynamic. Hydrolysis and condensation occur in tens of seconds, solvent evaporation is also rapid, and collapse of the gel network to the final film thickness (10^3 Å) occurs in less than a minute [12, 19, 20].

Figure 1 is a schematic diagram of the transformations that occur as the film is drawn from a sol that contains surfactant molecules. The regions identified in the diagram are not sharply defined but evolve continuously. The important assembly and chemical processes must occur sequentially and in the proper order; i.e., the micelles must form and achieve their long-range three-dimensional order before silicate condensation cements the structure in place. In dip coating, these processes are separated not only temporally but also spatially. This separation enables molecular probes to be used to monitor the assembly and the chemical changes that occur [12, 19, 20]. The first materials that contained luminescent molecules localized in specific regions (micelle interior, framework) were those formed during dynamic spectroscopic studies using molecular probes in evolving films [12].

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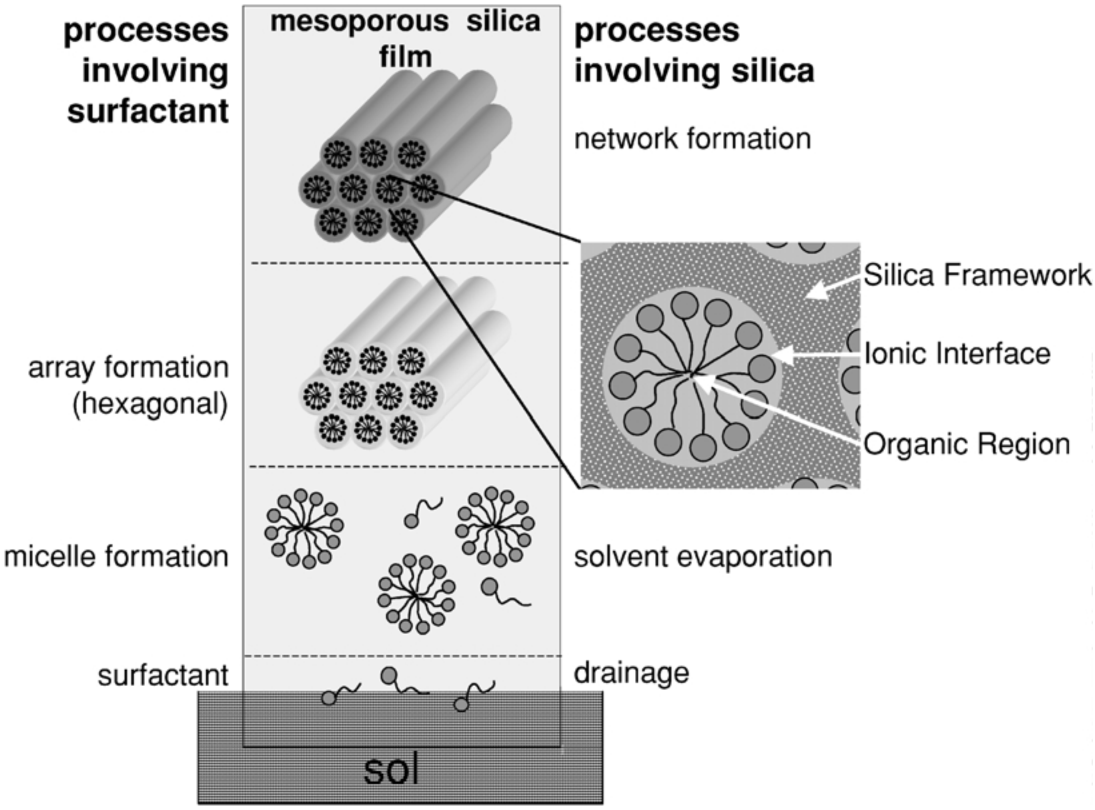

Figure 1. Schematic diagram of the film formation process (left.) The formation evolves continuously with the indicated steps occurring in the order shown from bottom to top as the substrate is withdrawn from the sol reservoir. The magnification (right) shows the three distinct regions into which mesostructured thin films may be subdivided.

The mesostructured thin films made with ionic surfactants, the subject of this paper, contain three distinct regions: the silica framework, the organic non-polar region in the hydrophobic interior of the micelle, and the ionic interface between the charged surfactant head groups and the silica pore surface. These regions are sketched on the right side of Fig. 1.

In this paper we define and demonstrate three one-step methods to synthesize hybrid mesostructured silica thin films in which a desired molecule is deliberately placed in a specified region of the mesostructure. These strategies are succinctly termed "philicity" (or like dissolves like), chemical bonding, and bifunctionality. Each of them is defined in general and then illustrated with specific molecular examples. Finally, we use these strategies to achieve multiple placement where two molecules are simultaneously placed in the film, each in a different region, in a one-step process.

Experimental

The sol was prepared and films were dip coated onto silicon as described previously [1].

Preparation of Sols to Exploit Philicity

Films containing dodecyl perylene diimide were prepared by dissolving 3.5 wt% of cetyltrimethylammonium bromide (CTAB, the surfactant) and about 10^{-4} g of the diimide in 32.6 ml of TEOS sol prior to pulling the films. Films with paraterphenyl were prepared by dissolving approximately 10^{-4} g of paraterphenyl in 27.7 ml of sol containing 3.5% CTAB by mass.

Preparation of Films to Exploit Bonding

4,4′-Hydroxymethyl-2,2′-bipyridine ($bpy(CH_2OH)_2$) [21] and $[Ru\{bpy(CH_2OH)_2\}_3](PF_6)_2$ [22] were

Table 1. Deliberate placement: Strategies and results.

Strategy	Molecular example	Luminescence (nm)	Lattice spacing (Å)
Philicity	Dodecyl perylene diimide	532, 574, 632	38
Philicity	Paraterphenyl	343	40
Bonding	Ru$\{$bpy(CH$_2$OH)$_2\}_3$(PF$_6$)$_2$	615	39
Bonding [1]	Eu^{3+} complex	616.6	38
Bifunctionality [1]	MPS-PPV	460	43
Bifunctionality [1]	Ru(bpy)$_2$ATT^{2+}	650	36

prepared as described in the literature. Ru$\{$bpy(CH$_2$ OH)$_2\}_3$ (PF$_6$)$_2$(72.2 mg, 0.0694 μmol) and a slight excess of isocyanatopropyltriethoxysilane ($\sim$100 μl, 0.4 mmol) were added to $\sim$10 ml anhydrous DMF under nitrogen followed by 20 hours of reflux. The solvent was removed under vacuum at elevated temperature yielding the ruthenium complex derivatized with $-$Si(OMe)$_3$ groups. The stock solution (5.0 mL), water (0.20 mL) and HCl (0.07 N, 0.6 mL) were mixed and stirred for 15 min before the addition of the Ru complex/EtOH solution (11.6 mL, Ru:Si $\sim$ 1:15). CTAB (3.5 wt% to the final mixture) was then added slowly with stirring and the resulting sol was used for dip coating.

Results and Discussion

The three strategies for incorporating molecules and directing them to any one of the regions in Fig. 1 are demonstrated with luminescent molecules that can be studied spectroscopically. Philicity exploits the physical affinities of the active ingredients for a particular environment (for example, that of a lipophilic dye for surfactant micelles) to place the molecule in the desired region. Both lipophilic molecules (resulting in placement in the micelle) and hydrophilic molecules (resulting in placement in the ionic region or pores in the framework) can be used. The former is illustrated in this paper. Bonding involves the use of functional groups on the molecule that will chemically bond to the desired region. In this paper, the molecules that are used contain alkoxysilane groups that surround each molecule in three dimensions and form the silicate network during condensation. Bifunctionality requires that the molecule possess two different groups that simultaneously interact with two different regions of the mesostructure. For example, if the molecule contains a condensable alkoxysilane group on one side and an ionic group on the other, it can chemically bond to the pore wall with the ionic group penetrating the ionic interface region.

All of the mesostructured sol gel silica films discussed in this paper have a 2-d hexagonal structure that is templated by using 3.5 wt% CTAB in the final sol. All of the films that are discussed show x-ray diffraction patterns with peaks at 2θ values of 2.2 ± 0.1 and 4.4 ± 0.1 degrees, with a lattice spacing of approximately 40 Å [23].

Table 1 summarizes the data discussed below.

1. *Philicity*. This first strategy utilizes the guest molecule's affinity for a certain type of environment that directs it to the desired region of the film. The interaction that is exploited here is lipophilic interaction of the dopant molecule with the micelle. Because the first step in the formation of the film is micelle formation, hydrophobic molecules will be incorporated into the film at this early stage in the formation process. At the critical micelle concentration (CMC), the individual surfactant molecules aggregate to form micelles and the lipophilic dopant molecule is incorporated therein.

   Dodecyl perylene diimide and paraterphenyl are insoluble in the polar precursor sol but are emulsified by the surfactant and incorporated into the organic region. This incorporation is verified by strong emission from mesostructured films that is absent from amorphous films without surfactant. The emission of dodecyl perylene diimide in the mesostructured film (Fig. 2) is similar to that from the molecule in nonpolar solution. The XRD shows that incorporation of the diimide does not affect the long-range order. The behavior of paraterphenyl is similar; its spectrum in the mesostructured film is discussed in Section 4.
2. *Bonding.* The second strategy involves the formation of chemical bonds between the molecule and the framework. The molecules discussed here are

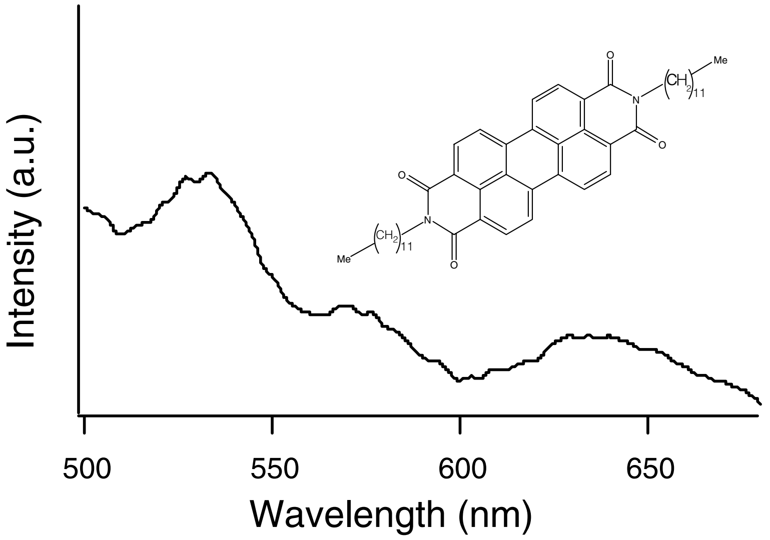

Figure 2. Emission spectrum (351 nm excitation) of dodecyl perylene diimide in the organic region of a mesostructured sol-gel thin film, illustrating the philicity strategy for incorporation in the organic region.

designed with eighteen condensable —OR groups directed in three dimensions. These molecules can condense to form the framework, but in practice some TEOS is necessary in order to produce films with long-range order and well defined XRD peaks. The results of the bonding strategy using a ruthenium complex of a newly designed disubstituted bipyridine ligand are shown in Fig. 3. The luminescence spectrum of the mesostructured film is the same as that of the amorphous films with no

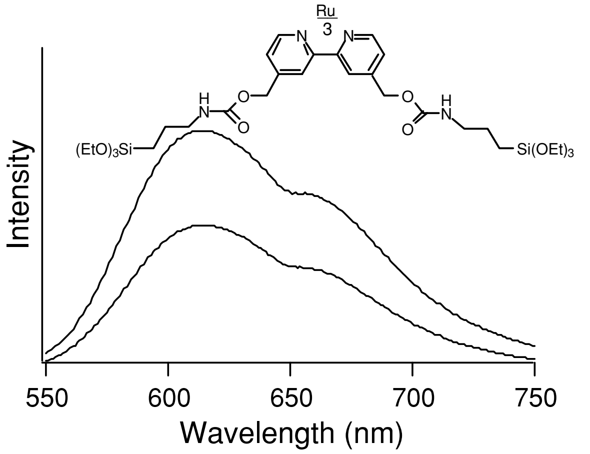

Figure 3. Ruthenium emission spectra (470 nm excitation) in a mesostructured thin film (top) and an amorphous thin film (bottom), illustrating the bonding strategy for incorporation in the silica framework region.

surfactant. This ligand can be used to place almost every transition metal in the framework.

Lanthanide complexes can also be deliberately placed in the framework by using the tridentate ligand containing eighteen condensable —OR groups described previously [3, 24]. An example is discussed in the "Multiple Placement" section below.

3. *Bifunctionality*. Two examples employing this strategy were discussed in detail in Ref. [1]. These examples used a ruthenium complex and a conducting polymer.
4. *Multiple Placement*. The generality of the placement strategies makes it possible to place deliberately one molecule in one region and a second in a different region of the same film. Both of the guest molecules are present in the starting sol and are guided to the desired region of the final mesostructure based on their type of interaction. As an example, a mesostructured film containing a lanthanide ion, Eu^{3+}, in the framework (by using the bonding strategy) and a p-terphenyl laser dye in the organic region (by using the lipophilic strategy) is formed. The luminescence spectrum in Fig. 4 verifies that both molecules are present. The intensities and the wavelengths of the band maxima verify their locations.

The three strategies discussed in this paper can be applied generally toward the incorporation of organic, inorganic and biomolecules in selected regions

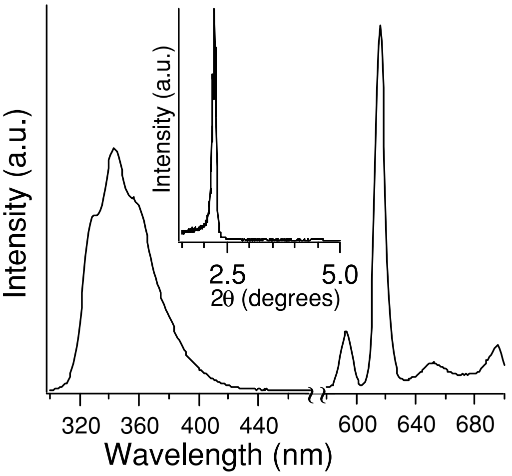

Figure 4. Emission spectrum (266 nm excitation) from a hexagonal mesostructured thin film containing both an Eu complex (peaks greater than 590 nm) in the framework and paraterphenyl (maximum at 343 nm) in the organic region. Inset shows the XRD pattern.

of mesostructured sol-gel thin films. The synthesis conditions must be carefully developed in order to avoid disruption of the long range order. Further elaboration of this methodology may lead to the chemical synthesis of highly complex nano-architectured materials.

Acknowledgments

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