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Transparent thin films and monoliths prepared from dye-functionalized ordered silica mesostructures

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Micelle templating and co-condensation of tetraethoxysilane and 3-(2,4-dinitrophenylamino)propyltriethoxysilane in the presence of hexadecyltrimethylammonium bromide has been used to synthesize transparent yellow thin films and monoliths of organic dye-functionalized MCM-41 silica: these hierarchical materials consist of covalently linked inorganic–organic networks with mesoscale periodicity and macroscale organization.

Considerable attention has been focused on the functionalization of silica-based ordered mesoporous materials, designated as M41S,[1] by covalent coupling of organic moieties,[2] because such structures could have important uses in optical applications,[3] catalysis,[4–6] metal-ion extraction[7,8] and adsorption processes.[9] Functionalization with organic groups can be achieved either by post-synthetic grafting[10–12] or *via* direct routes involving co-condensation of tetraalkoxysilanes and organo-functionalized trialkoxysilanes.[13–17] The one-pot synthesis should offer several advantages such as a better control of the organic functionality content and a homogeneous dispersion of organic moieties in the final materials. Moreover, it has been recently reported that this approach was appropriate to prepare multi-component inorganic–organic hybrids and their ordered mesoporous derivatives.[18]

The covalent attachment of dye molecules into ordered porous MCM-41 type materials could be of general importance in a number of areas such as optics, sensor and membrane technologies. A preliminary study[3] based on the synthesis of mesostructured 3-(2,4-dinitrophenylamino)propyl-modified silica materials under acidic conditions showed that organic chromophores can be incorporated into surfactant–silica mesophases and corresponding mesoporous replicas without extensive perturbation of the optical properties. Synthesis under alkaline conditions also produced well ordered dye-modified MCM-41 materials, which became structurally disordered after surfactant extraction. Recent work in our laboratory, however, has shown that thermal treatment prior to removal of the surfactant template produces a dye-functionalized mesoporous material with well ordered hexagonal structure.† Nevertheless, these materials are synthesized in the form of powders, excluding their use in thin film applications, such as is required for membrane and optical devices. For this reason, we have extended our previous work to the preparation of transparent thin films and monoliths of dye-functionalized MCM-41 silica. The fabrication of mesostructured silica thin films is currently under investigation by several different groups;[19–21] however, to the best of our knowledge, the work reported here is the first example to describe the processing and characterization of thin films and monoliths consisting of optically active organo-functionalized MCM-41 silica.

Direct chemical synthesis, involving the co-condensation of tetraethoxysilane (TEOS) and 3-(2,4-dinitrophenylamino)propyltriethoxysilane (DNPTES) in the presence of the surfactant, hexadecyltrimethylammonium bromide (C_{16}TMABr), was used to covalently attach the organic chromophore into the hexagonally ordered silica mesophase.[3] To produce transparent mesostructured DNPTES-modified silica thin films and monoliths, precursor solutions of the reaction mixture were prepared following the acid synthesis procedure reported by Brinker *et al.*[19,21] The C_{16}TMABr surfactant was added to an organo-silica sol which was prepared by a two step process designed to minimize the siloxane condensation rate and promote *in situ* self-assembly of the dye–silica–surfactant mesophase during film formation.‡ Yellow transparent monoliths, several millimetres in thickness, were prepared by slow solvent evaporation from the precursor solution left unstirred in an open Teflon dish (Fig. 1). Similarly, transparent yellow thin films were produced on microscope glass slides by dip-coating at 8 cm min^{-1} followed by solvent evaporation. Both as-deposited thin and thick films were aged at 150 °C for 24 h and then washed with ethanol. Analogous materials, consisting of dye-functionalized MCM-41 with increased channel size, were fabricated by addition of the micelle swelling agent, 1,3,5-trimethylbenzene (TMB),[1] to the reaction mixture.‡

Small angle XRD patterns recorded on thin films prepared from the above procedure showed two broad peaks at 28.3 and 16.3 Å that could be assigned to d_{100} and d_{110} spacings, respectively, indicating hexagonal mesocopic order in the materials (Fig. 2A). The TMB-free monolith exhibited three diffraction lines at 37.0, 21.5 and 17.7 Å assigned to d_{100}, d_{110} and d_{210} spacings, respectively, also indicative of long-range hexagonal channel packing (Fig. 2B). The lower d_{100} value observed for the thin film materials suggests that smaller C_{16}TMABr micelles are formed during the relatively rapid drying process associated with the dip-coating method. For a

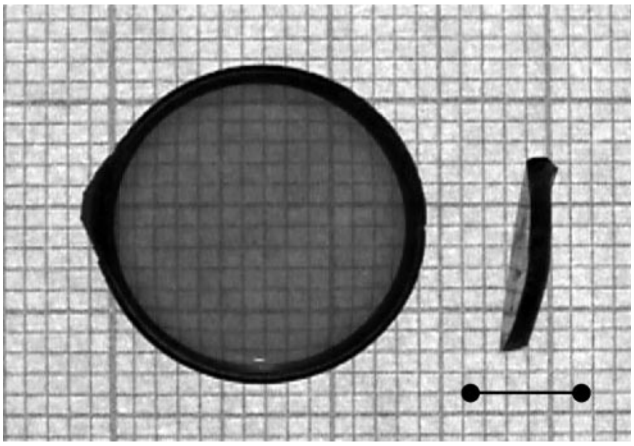


Fig. 1 Photograph of dye-functionalized MCM-41 silica monolith prepared in the absence of TMB swelling agent. Scale bar = 5 mm.

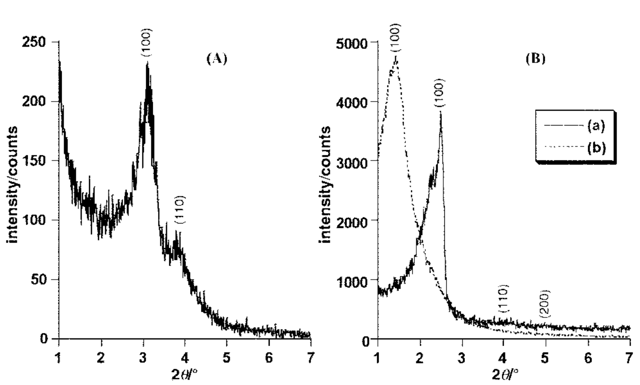


Fig. 2 XRD patterns of thin film (A) and monolithic (B) materials made in the absence (a) and presence of TMB (b).

monolith made with TMB, one broad reflection was observed at 62.2 Å (Fig. 2B), which indicated that a significant increase in the pore size, associated with swelling of the surfactant micelles, tended to produce a reduction in the long range mesoscopic order of the channel-like architecture. TEM images, which showed hexagonal sets of lattice fringes, as well as parallel fringes corresponding to side-on projections of the mesostructure (Fig. 3), were consistent with the long range order parameters determined by XRD. Thermal analysis indicated that the amount of surfactant and organic chromophore in the as-synthesized mesophases was approximately 60 wt%. Corresponding powder samples after surfactant extraction contained 26.5 wt% of the dye functionality. The calcined materials showed a broad but distinct XRD reflection at 34 Å, indicating that the hexagonal structure of the mesoporous replica was partially disordered. BET analysis gave a surface area of 1230 $m^2 g^{-1}$.

^{29}Si MAS NMR experiments were performed on self-supported thick films to determine the extent of DNPTES incorporation into the mesostructured materials and the local structure of the organically modified silica walls. Distinct resonances were observed for silica ($Q^n = Si(OSi)_n(OH)_{4-n}$, $n = 2$–4) and organosilica ($T^m = RSi(OSi)_m(OH)_{3-m}$, $m = 2$–3) species (Fig. 4). The data indicate that the amount of organo-functionalized moieties condensed into the wall structures corresponds to the synthesis composition (10 mol% DNPTES). The presence of T^2 and mainly T^3 units indicated extensive condensation of the organo-functionality in the silica network.

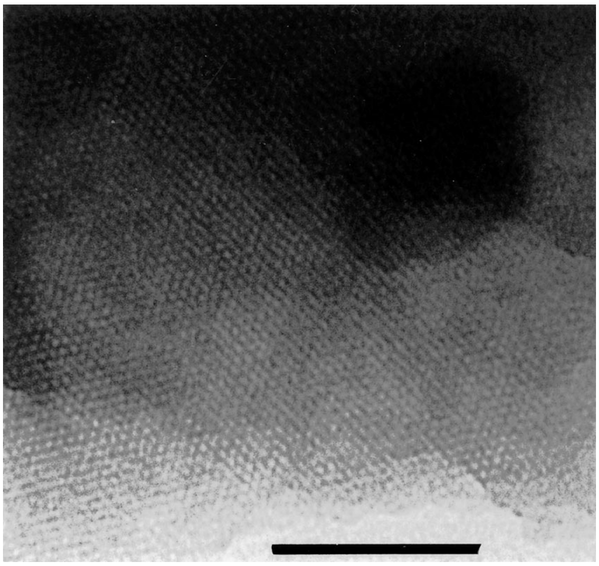
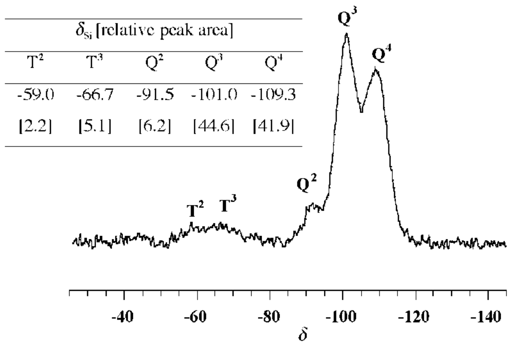


Fig. 3 TEM image of TMB-free monolith sample showing hexagonally ordered mesostructure. Scale bar = 50 nm.



T^2	T^3	Q^2	Q^3	Q^4
-59.0	-66.7	-91.5	-101.0	-109.3
[2.2]	[5.1]	[6.2]	[44.6]	[41.9]

Fig. 4 ^{29}Si NMR data and spectrum of TMB-free monolithic material.

The presence of the dye was confirmed by Fourier transform infrared (FTIR) spectroscopy.§ In addition, ^{13}C CP MAS NMR experiments on monolithic samples confirmed that the dinitrophenylaminopropyl chromophore was covalently linked into the mesostructured material as an intact unmodified moiety.¶ Optical properties of the dye-functionalized surfactant-extracted mesoporous materials were investigated by UV–vis and fluorescence spectroscopies. Transmission and diffuse reflectance were used to perform UV–vis measurements on thin films deposited on glass slides and monoliths, respectively. For all samples, two absorption bands were observed at around 350 nm and 440 nm which are characteristic of the NO_2 chromophore groups (Fig. 5A).[3] An emission spectrum recorded on a thin film with an excitation wavelength of 350 nm showed two bands at 495 and 525 nm (Fig. 5B). The data indicate that the optical activity of the dye moiety is retained when it is covalently linked to the silica network of the mesostructure.

The acidic pH of the reaction medium plays an important role in the preparation of transparent films and monoliths of organically modified MCM-41 silica. This process provides a homogeneous solution of soluble organo-silicate and silicate species in ethanol/water with an initial surfactant concentration below the critical micelle concentration (cmc). During dip-coating, or when the precursor solution is left in an open dish under ambient atmosphere, preferential evaporation of ethanol progressively enriches the concentrations of water, HCl, non-volatile solution constituents and surfactant within the forming film. The latter increases above the cmc level, resulting in micelle formation and cooperative assembly of the organically modified silica species both at the headgroup surface and within the interstitial void spaces of an organized lyotropic liquid crystalline mesophase.

In conclusion, our work shows that ordered organo-silica networks can be prepared by the above mechanism to produce self-supporting, crack-free macroscopic objects with optical properties and mesostructured architecture. The one-pot synthesis route to organo-MCM-41 materials leads to an intimate coupling of functional groups into the silica network.

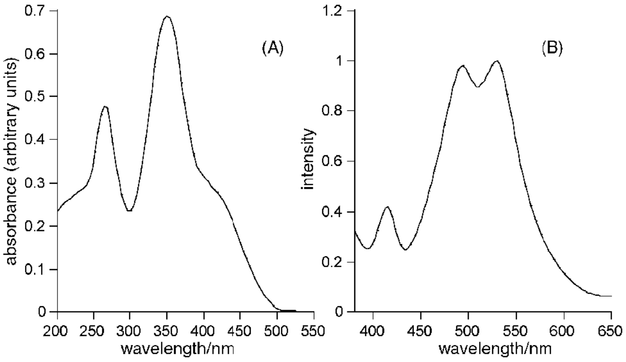


Fig. 5 UV–vis (A) and emission (B) spectra of a thin film sample.

As the organo-silane moiety is embedded in the mesostructured inorganic framework, the presence of organic groups not only contributes to enhanced physical and chemical properties but might also improve the mechanical properties and processing of silica-based materials.[22] Although further investigations are required to develop methods of *in situ* surfactant extraction from thin films and monoliths, it should be possible to prepare dye-functionalized materials with tailored pore sizes, periodic mesostructures and macroscopic shape molding by straightforward development of the methods described here. In this regard, the current investigation highlights the potential for using hybrid organic–inorganic networks in the synthetic construction of functionalized materials with higher-order structures.

Footnotes and references

†After addition of C_{16}TMABr, NaOH, TEOS and DNPTES and stirring the aqueous solution for 24 h at room temperature, as described in ref. 3, the final mixture was transferred to a closed polyethylene flask and heated at 85 °C for 24 h.

‡In a typical preparation, TEOS, DNPTES, ethanol, water and HCl were first refluxed at 60 °C for 90 min. Water and HCl were then added to give a HCl concentration of 7.34 mM. After stirring at 50 °C for 15 min, the sol was cooled to 25 °C and diluted with an ethanolic solution of C_{16}TMABr. The resulting homogeneous precursor solution was aged for 4 days at room temperature in a closed polyethylene flask prior to film deposition. The final molar compositions were 0.9TEOS : 0.1DNPTES : 22EtOH : $5H_2O$: 0.0004HCl : $0.16C_{16}$TMABr. Mesophases with increased pore size were prepared by adding TMB to the ethanolic surfactant solution (TMB : C_{16}TMABr mole ratio = 13 : 1) and stirred for 24 h at 35 °C prior to addition of the precursor organo-silica sol to give a final molar composition of 0.9TEOS : 0.1DNPTES : 22EtOH : $5H_2O$: 0.0004HCl : $0.16C_{16}$TMABr : 2.08TMB. After curing at 150 °C for 24 h, thin films and monoliths were left in a large amount of ethanol for at least 1 hour and then rinsed several times in ethanol. Samples for TEM were prepared by suspending a ground sample in water and air-drying the dispersion onto a carbon-coated copper electron microscope grid. ^{29}Si MAS NMR spectra were recorded with a recycle delay of 60 s and pulse width of 1.7 µs.

§FTIR data: Si–C band at 1140 cm^{-1}, residual surfactant at 2850–2970 cm^{-1}, and vibrations indicative of the 2,4-dinitrophenylaminopropyl group at 1341 (aromatic NO_2), 1631 (aromatic C=C), and 3370 (aromatic N–H) cm^{-1}. No evidence for a protonated NH group was observed in the FTIR spectra.

¶^{13}C CP MAS NMR data (δ): propyl (10.6, 22.8, 45.9); 2,4-dinitrophenylamine (115.2, 124.3, 130.6, 136.2, 149.0).

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