Transparent thin films and monoliths synthesized from fullerene doped mesoporous silica: evidence for embedded monodispersed C_{60}†

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Thin films and monoliths of mesostructured silica containing embedded monodispersed molecules of C_{60} may be prepared *via* a sol–gel route in which the C_{60} is added during the synthesis or *via* post-synthesis adsorption; evidence from diffuse reflectance spectroscopy suggests that the embedded C_{60} exist predominantly in monomeric form.

In recent years, fullerenes (C_{60}, C_{70}) and their derivatives have been subjected to intense research investigations for a wide range of potential applications in materials science.[1] In particular fullerenes show spectrally broad Reverse Saturable Absorption (RSA), covering the entire visible region, and can therefore be used as optical limiting materials.[2] Their optical limiting properties have been studied in both solid and liquid phases.[3,4] When comparing the results of C_{60} in solution and in solid form (as crystalline films), it becomes clear that the interaction between neighbouring fullerene molecules largely determines the de-excitation dynamics and consequently the optical limiting properties.[5] In other words the photophysical properties of formation of the triplet state of C_{60} are extremely dependent on the environment of the molecule.[6] It has been shown that when C_{60} molecules aggregate the yield of formation of the triplet state considerably decreases, thus compromising the optical limiting capability of such aggregate molecules.[7]

In order to avoid aggregation and undesirable interactions between C_{60} molecules, we have studied the dispersion of fullerene molecules within the pores of mesoporous molecular sieves (MMS). MMS are generally synthesized in the form of powders.[8] However, mesoporous films and monoliths are more usable, especially in membrane-based separation or novel optical/electronic applications such as in optical limiting. Here we report our attempts to disperse fullerene molecules within the pores of MMS films and monoliths *via* a surfactant mediated preparation route or *via* post-synthesis adsorption. It is hoped that once embedded, the C_{60} molecules are better protected from environmental influences that are detrimental to their optical limiting properties.[9] Previous reports on the interaction between C_{60} and silica hosts provide limited information on the nature of the incorporated C_{60};[10–14] in most cases only showing evidence for the incorporation of C_{60} in the form of *aggregates* or *clusters*. Here we show evidence for monodispersed C_{60} embedded in transparent mesoporous silica hosts.

In a typical synthesis procedure, TEOS, HCl and water were added to a round bottomed flask containing a mixture of 1.0 g of cetyltrimethylammonium bromide (CTAB, Aldrich), ethanol and a toluene solution of C_{60} (0.7 mM). The solution consisting of a single phase (with a molar ratio of CTAB/TEOS = 0.2) was refluxed at 80 °C for 2 h. The reaction mixture was then concentrated by the quick evaporation of the solvent using a rotary evaporator in a vacuum at 50 °C. The resulting high viscosity liquid was poured on a Petri dish and dried at room temperature for 12 h to yield the transparent thin films or monoliths. In order to vary the fullerene content, different volumes of toluene/C_{60} solution were added during the synthesis.

The XRD patterns of the as-synthesized C_{60} containing transparent silica mesophases shown in Fig. 1 clearly indicate that ordered materials are formed. The pattern for the as-synthesised sample shows sharp (100 and 200) peaks at $d = 3.5$ nm and 1.8 nm respectively. There is no evidence of residual CTAB surfactant peaks which are known to occur at $d = 2.6$ and 1.3 nm. The films or monoliths varied in thickness from 5 to 200 μm. After calcination at 550 °C for 6 h in air, the films/monoliths (which maintained their transparency) had XRD patterns similar to the as-synthesised materials (Fig. 1). Calcination did however cause a shift of the observed peaks to 2.9 nm and 1.5 nm (*i.e.*, a decrease of *ca*. 0.6 nm in the basal spacing). The XRD patterns of the films are consistent with the formation of a hexagonal mesoporous silica framework. The fact that only $h00$ (100, 200) low angle reflections are observed implies that the pore channels preferentially run parallel to the surface of the film.[15] The XRD pattern of the ground powder samples (not shown) had the expected (100), (110), (200), (210) peaks from diffraction planes that are typically seen in randomly oriented powder preparations of hexagonal mesoporous silica.[16] The intense peaks of pure C_{60} that normally occur at $2\theta = 10$, 17, and 21° were not detected. The absence of these peaks is an indication of the occlusion of fullerene in the pores of the MMS. Adsorption of C_{60} onto the calcined mesoporous films/monoliths had no effect on the XRD patterns.

The UV-Vis absorption spectrum of C_{60} is known to be sensitive to environmental effects (solvent, aggregation) and can be used to probe aggregation. The diffuse reflectance spectrum of C_{60} embedded in the MMS was found to be generally broader than that of solid C_{60} (*i.e.*, C_{60} in KBr) or C_{60} in solution (toluene) as shown in Fig. 2. C_{60} in toluene, which exists predominantly in *monomeric* form, has a characteristic sharp peak (spike) at 397 nm and multiple bands which appear at 537–541, 560–569, 592–598 and 621 nm.[17] It is well known that a sharp peak (spike) at *ca*. 400 nm is an indication of C_{60} in monomeric form while a band at *ca*. 450 nm is attributed to the formation of aggregates.[6,18,19] The spectra obtained for C_{60} embedded in the MMS mesophase exhibit features similar to
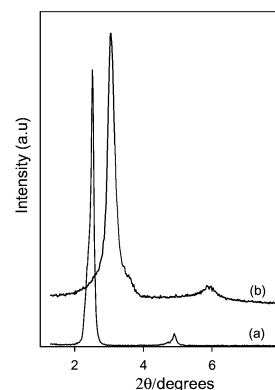

Fig. 1 XRD patterns of C_{60} containing mesoporous film before (a) and after (b) calcination.

† Electronic supplementary information (ESI) available: diffuse reflectance spectra of C_{60} embedded in mesoporous molecular sieve films. See http://www.rsc.org/suppdata/cc/b2/b208615h/

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that of C_{60} in toluene, *i.e.*, they both have the sharp peak (spike) at *ca.* 400 nm (*i.e.*, 397 nm for C_{60} in toluene and 405 nm for C_{60} in MMS) and very weak absorption at *ca.* 470 nm. The presence of the characteristic spike, slightly red shifted to *ca.* 405 nm, is clear evidence of the presence of C_{60} monodispersed in the silica hosts.[18,19] It is noteworthy that the spike is absent for solid C_{60} (*i.e.*, C_{60} in KBr, Fig. 2b) which is known to exist in aggregates. We note that the broad low intensity band in the 450–500 nm region (observed for both C_{60}/MMS and C_{60}/toluene) whilst indicating some limited aggregation also further illustrates the similarity between the two systems. The similarity between the C_{60}/MMS and C_{60}/toluene systems is a strong indication that, even after incorporation in the mesoporous matrix, C_{60} exists predominantly as monomeric species without significant formation of aggregates or clusters. This contrasts with what has previously been observed when C_{60} is embedded in inorganic hosts.[11–14]

The diffuse reflectance spectra of C_{60} embedded (*via* post-synthesis adsorption) in calcined MMS films are shown in Fig. 3 for various C_{60}/SiO_2 mol ratios. For typical C_{60}/SiO_2 mol ratios (up to 1.5×10^{-3}, spectrum a) the embedded C_{60} exists predominantly in monodispersed form, that is, the spectrum shows the characteristic spike near 400 nm and a low intensity band at *ca.* 440 nm. However at higher C_{60} content we observed a gradual change from monodispersion to aggregation as shown in Fig. 3. The spike near 400 nm, which is an indication of monodispersion, is just discernible at a C_{60}/SiO_2 mol ratio of 2.4×10^{-3} (spectrum b) and disappears at a C_{60}/SiO_2 mol ratio of 4.07×10^{-3} (spectrum c). This is accompanied by a more prominent band at *ca.* 440 nm. This semi-quantitative analysis of the diffuse reflectance spectra confirms that the spike near 400 nm is observed when the C_{60} is predominantly monodispersed and is consistent with previous reports.[18,19]

All the C_{60} containing thin films/monoliths also had an absorption band at *ca.* 330 nm (see ESI†) which was also present for C_{60} in toluene. This band, assigned to the transition of the 3^1T_{1u} excited state of C_{60}, has previously been used as evidence for the incorporation of C_{60} into solid hosts.[14,18] As expected, Fig. 2 and 3 show a red shift in the spectra of C_{60} in MMS films compared to C_{60} in toluene. The red shift is usually observed when C_{60} is immobilized in a polar environment.[20,21] We also note that the considerable absorption in the visible region (420 to 700 nm) suggests that the symmetry of the fullerenes is somewhat distorted as would be expected for C_{60} embedded in a solid host.[20,21] The diffuse reflectance spectra therefore point to a scenario where the MMS embedded C_{60}
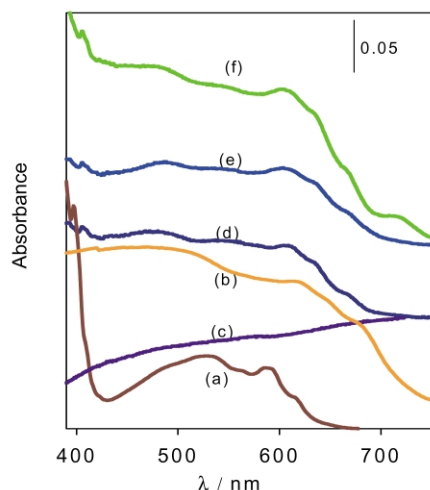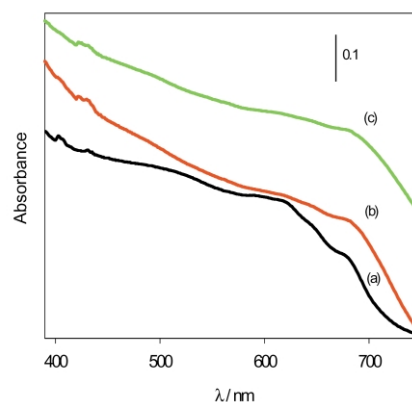
Fig. 3 Diffuse reflectance spectra of C_{60} embedded in calcined mesoporous molecular sieve (MMS) films at various C_{60}/SiO_2 mol ratios: (a) 1.22×10^{-3}, (b) 2.42×10^{-3} and (c) 4.07×10^{-3}.

exists predominantly (but perhaps not exclusively) in a *monomeric* form similar to that of C_{60} in toluene. The presence of monodispersed C_{60} in a transparent host matrix is likely to lead to solid state materials with enhanced optical limiting properties.

Notes and references

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Fig. 2 Diffuse reflectance spectra of C_{60} embedded in mesoporous molecular sieve (MMS) films. The spectra of the MMS film, C_{60} in KBr and UV-Vis spectra of C_{60} in toluene are included for comparison. (a) C_{60} in toluene, (b) C_{60} in KBr, (c) MMS in the absence of C_{60}, (d) C_{60}/SiO_2 (mol ratio = 1.5×10^{-4}), (e) C_{60}/SiO_2 (mol ratio = 2.0×10^{-4}), (f) C_{60}/SiO_2 (mol ratio = 2.0×10^{-4}, 20 h contact time).