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Silica coated fullerenols: seeded growth of silica spheres under acidic conditions

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Liquid phase deposition of silica in the presence of fullerenol, $C_{60}(OH)_n$, results in the formation of uniform silica spheres, whereas the use of C_{60} gives large non-uniform agglomerates as a result of homogeneous nucleation. Raman and UV spectroscopy indicate the C_{60} is retained as the core of the silica spheres.

Liquid phase deposition (LPD) has been commonly applied to the growth of coatings on planar substrates, for example LPD of silica on silicon is well documented.[1,2] To ensure a uniform film growth with LPD, surface treatment is ordinarily required.[3] Suitable treatments may involve the formation of surface hydroxides,[4] the pre-deposition or self-assembly of an appropriate seed layer.[5,6] The growth of spherical particles has the potential for a wide range of applications. With regard to silica, Kolbe's discovery[7] (with refinement by Stober *et al.*[8]) that performing sol–gel under basic conditions and/or with the use of a capping agent resulted in the growth of uniform spheres, has led to a number of interesting developments in nanomaterials.[9,10] As an alternative approach to the formation of spherical particles, it should be possible to use appropriate nanoparticles to seed solution growth. We report herein, the use of surface functionalized fullerene as a seed for LPD of silica spheres.†

In the absence of a suitable nucleating surface, the reaction of fluorosilicic acid with water results in homogeneous nucleation.[11] This may be seen from SEM images of the resulting silica, which consists of large non-uniform agglomerates (Fig. 1a). The addition of C_{60} to the LPD growth solution does not affect the morphology of the silica (Fig. 1b). The resulting material has the appearance of silica–C_{60} hybrids prepared by sol–gel.[12] The incorporation of fullerenes into inorganic matrices has been investigated and C_{60}/SiO_2 and C_{70}/SiO_2 composites have been reported.[13,14,15,16] These prior reports incorporated the fullerene by the *in-situ* formation of a sol–gel. There is a paucity of studies for the direct coating of fullerenes with an inorganic material.

We have recently investigated the importance of creating surface hydroxide functionalization to ensure good film growth of silica by LPD. In this regard, the hydroxylated fullerene or fullerenol, $C_{60}(OH)_n$,[17] should behave in an analogous manner to that of a hydroxylated silicon surface. The addition of $C_{60}(OH)_n$ (0.02 wt%) to a LPD solution ($SiO_2 : H_2SiF_6 = 1:9$), allows for the isolation of highly uniform, spherical particles of silica coated fullerene (SiO_2–C_{60}), see Fig. 1c and d. The size and morphology of the spheres is dependent on the reaction time allowed. An initial growth rate of 1.3 nm min^{-1} is observed while the surface of the spheres has a textured appearance. Increased reaction times result in an increase of particle size up until about 180 nm (Fig. 1d). The thickness of the SiO_2 coating may be calculated by assuming a diameter for C_{60} of 0.7 nm. With extended reaction times, etching of the silica occurs due to the formation of HF in the reaction solution (*i.e.*, Eqn. (1)), at which point the particles attain an equilibrium size (100 nm) but with a smooth surface.

$$H_2SiF_6 + 2\ H_2O \rightarrow SiO_2 + 6\ HF \qquad (1)$$

The ToF MS of a sample of SiO_2–C_{60} shows only a trace peak for C_{60} as compared to samples of silica prepared using C_{60}, suggesting that the fullerene is not on the surface of the silica spheres. The XPS of the SiO_2–C_{60} spheres exhibits peaks associated with the silica as well as the presence of fluorine.[11] The C_{1s} peak associated with adventitious hydrocarbon diminishes upon Ar ion sputtering to a constant value. The shift of the C1s peak (285 eV) is close to that associated with fullerenes [284.7 ev].[18] There is no evidence for peaks attributable to covalent states of C_{60},[13] however, at the relative concentration it is difficult to prove definitively the presence of the fullerene.

The IR spectrum of SiO_2–C_{60} is dominated by bands associated with the silica, however, a weak band is observed at 576 cm^{-1} consistent with the presence of C_{60}.[19] The Raman spectrum of SiO_2–C_{60} is more informative. Shown in Fig. 2, along with band assignments, the Raman spectrum of SiO_2–C_{60} confirms the presence of fluorine in the silica. With the exception of the radial breathing mode (492 cm^{-1} in C_{60}), and two minor H_g bands (708 and 773 cm^{-1} in C_{60}) all the bands associated with C_{60} are present, albeit shifted.[20] The shift to lower wavenumber, for all but the bands at 1276 and 1598 cm^{-1}, is similar to that observed for alkali metal doped C_{60} (*i.e.*, M_nC_{60}).[20] The bands at 1598 cm^{-1} are shifted to higher frequencies than observed for C_{60}. The UV-visible spectrum of an ethanol suspension of SiO_2–C_{60} exhibits two broad bands at 228 and 270 nm. These bands are red shifted from that observed for C_{60} (216 and 264 nm), while the band at 339 nm observed for C_{60} is not seen for SiO_2–C_{60}.[21] A similar red shift in absorption bands was observed for the incorporation of C_{70} into sol–gel silica glasses.[14] The bands for SiO_2–C_{60} are closer to those associated with C_{60}, rather those observed for $C_{60}(OH)_n$ (210 and 253 nm), suggesting that the hydroxyl groups have reacted during the coating process. Based upon spectroscopic characterization, we propose that fullerenols are fullerene-like under the coating reaction conditions. It has been reported that in the absence of the LPD, fullerenes are converted to hemiketal moieties under strong acid conditions.[22]

The comparison of C_{60} with $C_{60}(OH)_n$, suggests that the presence of the fullerene itself is not sufficient to seed growth. The rationale for the seed growth observed with $C_{60}(OH)_n$ is twofold. First, the fullerenols are water-soluble and hence dissolve to provide multiple seeds. The presence of surface hydroxylate groups on at least a portion of one surface of a fullerene tends to impart greater solubility to the fullerene in water, thereby discouraging aggregation and facilitating possible subsequent deposition. Second, the fullerenols may be considered reactive, rather than simply physical, seeds. It is known that addition of base to a solution of fluorosilicic acid will result in the precipitation of silica. The fullerenols may be considered to act as a carrier for the base in a similar reaction. Thus, the fullerenol initiates the liquid-phase-deposition of silica, and also acts as a seed for subsequent growth. Once a layer of silica has formed on the fullerene, subsequent SiO_2 grows on a fresh surface in a similar manner to that observed for thin film deposition.

We propose that chemical functionalization of fullerenes provides a dispersible reactive seed for growth by liquid phase

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deposition. We are presently investigating the generality of this process with other inorganic materials, as well as the effect of seeding with $C_{60}(OH)_n$ on phase and morphology of simple salts.

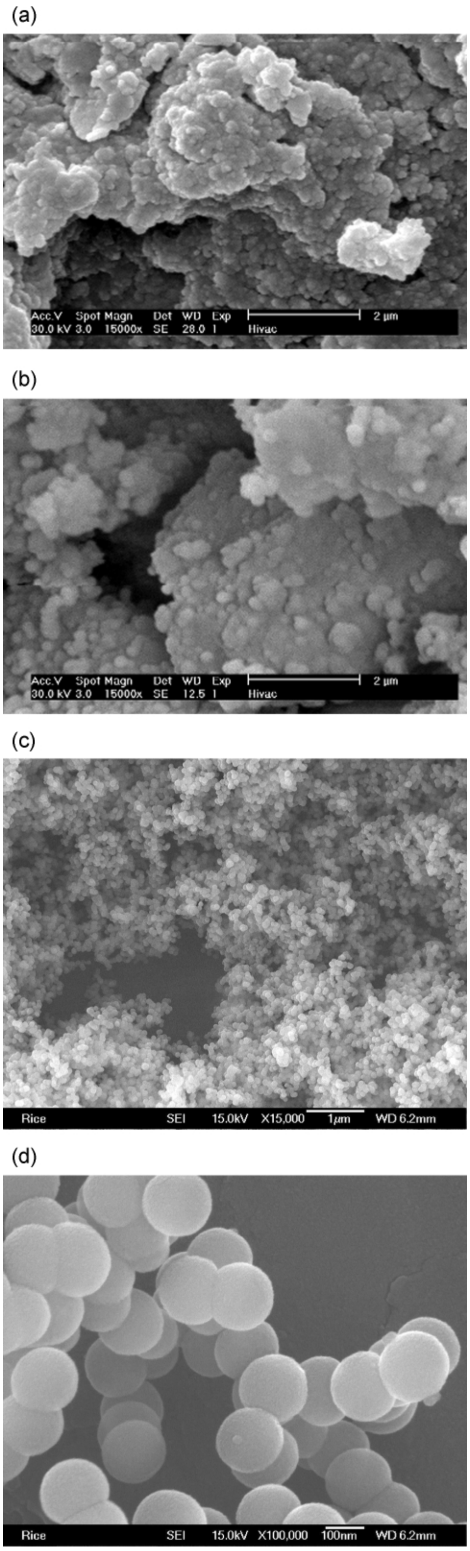

Fig. 1 SEM images of LPD silica grown (a) in the absence of fullerenes, (b) in the presence of C_{60}, and (c and d) in the presence of fullerenol, $C_{60}(OH)_n$.

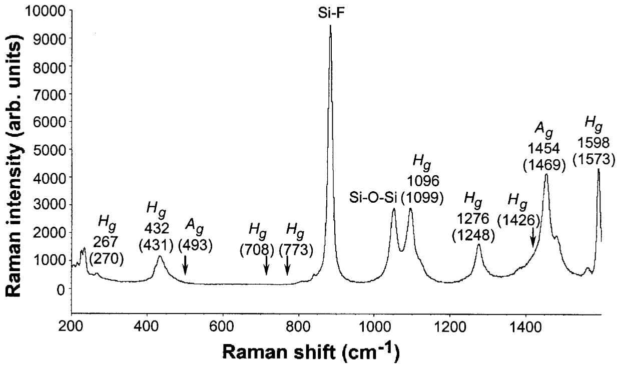

Fig. 2 The Raman spectrum of SiO_2–C_{60}. Band assignments are provided along with the appropriate values for C_{60}.

Notes and references

† Fumed silica (3.0 g) was added to 50 cm^3 of 3.20 M fluorosilicic acid solution (H_2SiF_6: Riedel de Haen, 34% wt%) and allowed to stir overnight. This solution was then filtered, by vacuum, through a 0.22 micron Millipore filter. A sample of this solution (5 cm^3) was allowed to react with a 0.05 M fullerenol solution (10 cm^3) in a plastic centrifuge tube. This mixture was stirred, at 30 °C, for 3 hours. The product was then centrifuged at 4000 rpm for 60 minutes. The supernatant liquid was discarded. The product was then redispersed in ethanol by sonification. This process was repeated six times. The product was then dried and analyzed as a powder (*ca.* yield = 1 g).

1 P. Chanthamaly, T. Arakawa and N. Haneji, *Jap. J. Appl. Phys., Part 1*, 1999, **38**, 5715.
2 C.-J. Huang, *Jap. J. Appl. Phys., Part 1*, 2002, **41**, 4622.
3 N. Ozawa, Y. Kumazawa and T. Yao, *Thin Solid Films*, 2002, **418**, 102.
4 N. F. Wang, W. J. Chang, M. P. Houng, Y. H. Wang and C. J. Huang, *J. Vac. Sci. Tech., A*, 1999, **17**, 102.
5 T. Miura, Y. Yamada, T. Suga, D. Huang, S. Kim, T. Maeda, I. Hirabayashi, H. Ikuta and U. Mizutani, *Physica C*, 2001, **357**, 983.
6 K. Koumoto, S. Seo, T. Sugiyama, W. S. Seo and W. J. Dressick, *Chem. Mater.*, 1999, **11**, 2305.
7 G. Kolbe, Thesis, Jena, 1956.
8 W. Stober, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62.
9 R. D. Averitt, S. L. Westcott and N. J. Halas, *J. Opt. Soc. Am.*, 1999, **16**, 1824; S. J. Oldenburg, J. B. Jackson, S. L. Westcott and N. J. Halas, *Appl. Phys. Lett.*, 1999, **75**, 2897.
10 P. Jiang, K. S. Hwang, D. M. Mittleman, J. F. Bertone and V. L. Colvin, *J. Am. Chem. Soc.*, 1999, **121**, 11630; R. Rengarajan, P. Jiang, V. Colvin and D. Mittleman, *Appl. Phys. Lett.*, 2000, **77**, 3517.
11 C.-F. Yeh, C.-L. Chen and G.-H. Lin, *J. Electrochem. Soc.*, 1994, **141**, 3177.
12 S. V. Patwardhan, N. Mukherjee, M. F. Durstock, L. Y. Chiang and S. J. Clarson, *J. Inorg. Organomet. Polym.*, 2001, **12**, 49.
13 L. Zhu, P. P. Ong, J. Shen and J. Wang, *J. Phys. Chem. Solids*, 1998, **59**, 819.
14 S. Dai, R. N. Compton, J. P. Young and G. Mamantov, *J. Am. Ceram. Soc.*, 1992, **75**, 2865.
15 S. Dai, R. N. Compton, J. P. Young and G. Mamantov, *J. Am. Ceram. Soc.*, 1992, **75**, 2865.
16 P. Innocenzi and G. Brusatin, *Chem. Mater.*, 2001, **13**, 3126.
17 J. Li, A. Takeuchi, M. Ozawa, X. Li, K. Saigo and K. Kitazawa, *J. Chem. Soc., Chem. Commun.*, 1993, 1784.
18 Z. Ren, Z. Ying, X. Xiong, M. He, Y. Li, F. Li and Y. Du, *J. Phys.*, 1994, **D27**, 1499.
19 K.-A. Wang, A. M. Rao, P. C. Eklund, M. S. Dresselhaus and G. Dresselhaus, *Phys. Rev. B*, 1993, **48**, 11375.
20 M. S. Dresselhaus, M. A. Pimenta, P. C. Eklund and G. Dresselhaus, in *Raman Scattering in Materials Science*, W. H. Webber, R. Merlin, Eds., Springer-Verlag, Berlin, 2000, Ch. 8.
21 W. Kratschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature*, 1990, **347**, 354.
22 L. Y. Chiang, R. B. Upasani, J. W. Swirczewski and S. Soled, *J. Am. Chem. Soc.*, 1993, **115**, 5453.