

Facile synthesis of hollow silica microspheres

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Hollow silica microspheres were synthesised at room temperature from a vortexed mixture of water and droplets of tetraethoxysilane (TEOS) containing 10 mol% aminopropyltriethoxysilane: droplets stabilized with the surfactant cetyltrimethylammonium bromide produced silica shells, 30.6 μm in mean diameter, whereas replacing the Br^- counterion with $[\text{Co}(\text{B}_9\text{C}_2\text{H}_{11})_2]^-$ gave an approximately hundred-fold decrease in the size of the hollow spheres. Organo-functionalized hollow microspheres containing a covalently linked dye moiety were prepared by replacing 5 mol% of TEOS with dinitrophenylaminotriethoxysilane in the reaction mixture, and encapsulation of TEOS-soluble additives within the silica shells was demonstrated by incorporating porphyrin molecules and particles into the ethoxysilane droplets.

Over the past decade, extensive research has been undertaken in the synthesis of inorganic hollow microspheres^{1–3} because shell structures are known to have potential uses as low density, mechanically and thermally stable materials in fields such as biomedicine (dental implant materials and controlled drug release agents) and engineering (thermal insulators, gas/chemical storage devices and structural low weight foams).⁴ Previous methods of preparation have involved spray drying techniques using nozzle systems to dispense individual liquid droplets of uniform size,⁵ and inorganic precipitation reactions in the presence of organic templates. The latter approach involves metal alkoxide condensation reactions, supersaturated metal salt solutions or nanoparticle-containing sols, in association with polystyrene latex spheres,^{6,7} surfactant vesicles⁸ or microemulsion droplets,^{9–11} or combinations of these.¹² In general, the use of polymer and supramolecular templates is not trivial as they need to be removed subsequently without damaging the inorganic shell. Moreover, the stability of supramolecular structures, such as vesicles and microemulsions, depends on pH, ionic strength, and the presence of

organic solvents in the reaction mixture, so they are often adversely affected by the reaction conditions.

We now report a one-step facile method for the preparation of hollow silica microspheres with diameters in the range of 0.3 to 65 μm . The procedure is based on the hydrolysis and condensation of droplets of a mixture of tetraethoxysilane (TEOS) and aminopropyltriethoxysilane (APTES) formed by vortexing the reaction mixture in water containing cetyltrimethylammonium bromide (CTA^+Br^-).[‡] The surfactant was added to improve the stability of the ethoxysilane/water interface and was critical for the production of well-defined silica shells. Although TEOS droplets have been used previously to prepare mesostructured silica shells,² the products were not well-defined and often aggregated. In contrast, the method reported here produces in high yield discrete intact shells of amorphous silica with a smooth surface texture. Moreover, because silica is deposited preferentially at the TEOS/water interface, hollow microspheres are formed *in situ*. The method therefore eliminates the need for any template extraction techniques and as the diameter of the shells depends on the droplet size, this can be controlled to some extent by varying the surfactant counterion. Our method can be easily extended to the preparation of organo-functionalized hollow silica microspheres as well as to shells with encapsulated organic species.

The as-synthesized product, which was located at the air/water interface, consisted exclusively of micron and sub-micron-sized hollow silica microspheres. SEM micrographs showed well-defined intact shells with relatively smooth surfaces (Fig. 1a). Very few shells were fractured or deformed and there was no evidence of coalescence, extensive cracking, or collapsed structures. Corresponding particle size measurements gave a mean diameter of 30.6 μm (s.d. = 12.9 μm , range 0.3–65 μm). TEM images were consistent with the SEM observations and showed hollow spheres with walls that were thin enough to be partially transparent in the electron beam (Fig. 1b). The wall thickness, which was uniform around the shells, was estimated to be *ca.* 80 nm from SEM and TEM micrographs. EDX analysis indicated that small amounts of bromide were present in the shell walls, which was presumably associated with surface-adsorbed or intercalated surfactant molecules. TEM and SEM investigations of the samples aged *in situ* for various lengths of time showed little change in the nature of the product over approximately 4 months, after which time small silica particles were observed attached to the external surface of the hollow microspheres. This was sufficient to increase the density of the shells such that they slowly sedimented in the reaction vessel.

Powder X-ray diffraction profiles showed a single broad peak centered at $2\theta = 21^\circ$ corresponding to the formation of hollow microspheres with amorphous silica walls. No low-angle reflections were observed, indicating that silica-surfactant

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‡Hollow silica shells were synthesised at room temperature from a mixture of TEOS and APTES in water containing CTABr. The molar composition was 0.044 CTABr : 0.9 TEOS : 0.1 APTES : 180 H_2O . In a typical preparation, a glass tube containing 0.02 g CTABr dissolved in 4.0 g of deionised water at pH 6.5 was placed on an Autovortex meter (Stuart Scientific, SA6) and 250 μl of a mixture of TEOS (1.70 g) and APTES (0.20 g) added slowly while vortexing at 700 rpm for 3 minutes. During this time the pH initially increased to 11.1 and then decreased to 10.2. The resulting cloudy suspension was left unstirred under ambient conditions for a further 30 minutes, after which time the pH had dropped to 9.5 and the suspension separated to produce a layer of the white product at the air/water interface and a relatively clear solution. Samples were removed by decanting the layer and collecting the particles in a glass pipette, followed by air-drying.

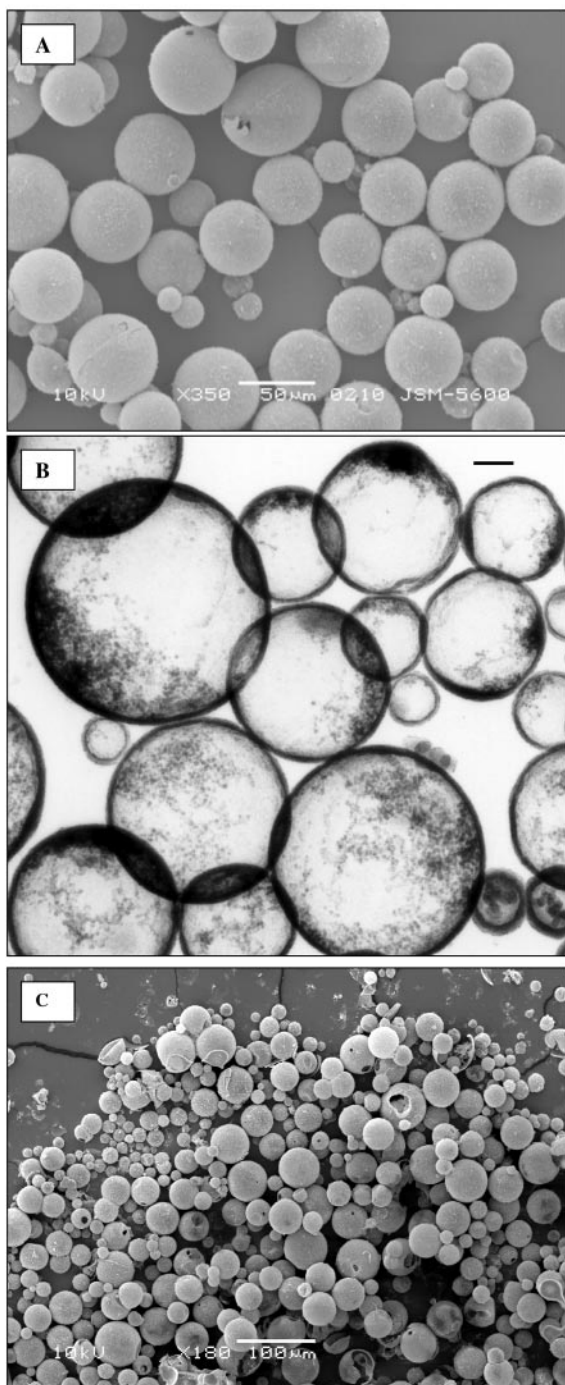


Fig. 1 (a) SEM micrograph of as-synthesized hollow silica microspheres. (b) TEM micrograph of silica shells showing high uniformity in the wall structure; scale bar = 1 μm . (c) SEM micrograph showing intact microspheres after heating to 600 $^{\circ}\text{C}$.

mesophases were not present in the as-synthesized product. This was consistent with TGA studies, \S which showed only a small weight loss (<7 wt.%) at *ca.* 180 $^{\circ}\text{C}$ that was attributed to the decomposition of the aminopropyl functionality of APTES, and not imbibed surfactant or occluded solvent. Corresponding SEM and TEM studies of the hollow spheres annealed at 600 $^{\circ}\text{C}$ showed that the structural integrity of the silica shells was retained and that shrinkage, coalescence, or cracking of the structures did not take place (Fig. 1c).

\S Thermogravimetric analysis (TGA) was performed at a heating rate of 5 $^{\circ}\text{C min}^{-1}$ under flowing air. The temperature stability of the silica shells was assessed by annealing the product for 5 hours at 600 $^{\circ}\text{C}$.

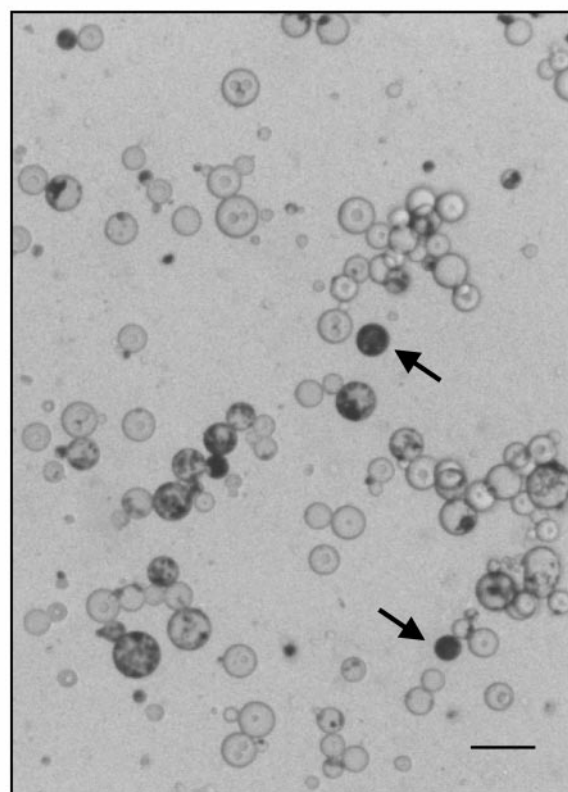


Fig. 2 Optical photograph of hollow silica microspheres containing encapsulated porphyrin particles. The particles appear dark against the low contrast of the silica shells. Some of the microspheres contain high internal loadings of the pigment (arrows) whereas others are empty. Scale bar = 50 μm .

The method was extended to the synthesis of organo-functionalized hollow silica microspheres with shell walls that contained covalently linked dinitrophenylamino groups. \P The dye moiety was chosen both as a test system and because silica matrices prepared in the presence of chromophores^{13–20} have potential applications in areas involving optical, sensor or membrane technologies. Addition of 5 mol% of dinitrophenylaminotriethoxysilane (DNPTES) to the TEOS/APTES reaction droplets resulted in a bright yellow product consisting solely of hollow spherical structures several micrometres in diameter (data not shown). FTIR and UV/Vis spectroscopic analysis confirmed that the dye functionality was co-condensed as an intact moiety within the wall structure of the silica microspheres.²¹

Encapsulation within the hollow microspheres of guest molecules and particles confined to the TEOS droplets was demonstrated by partially dissolving 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine iron(III) acetate into the TEOS/APTES reaction mixture prior to emulsion formation. $\|$ High magnification optical micrographs of the product showed the presence of brown particles of the pigment within many of the silica shell structures (Fig. 2). Differences in the loading between microspheres were due to the heterogeneous distribution of porphyrin particles in the TEOS droplets produced by vortexing. FT-IR and UV/Vis spectroscopy of washed and

\P Dye-functionalized hollow silica microspheres were prepared as above using an ethoxysilane molar composition of TEOS: 85%, APTES: 10%, DNPTES: 5%. Typically, 2.0 g of total ethoxysilane was used.

$\|$ Hollow silica microspheres with encapsulated 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine iron(III) acetate were synthesized as above using a TEOS/APTES mixture (2.0 g) containing the partially dissolved porphyrin (0.015 g).

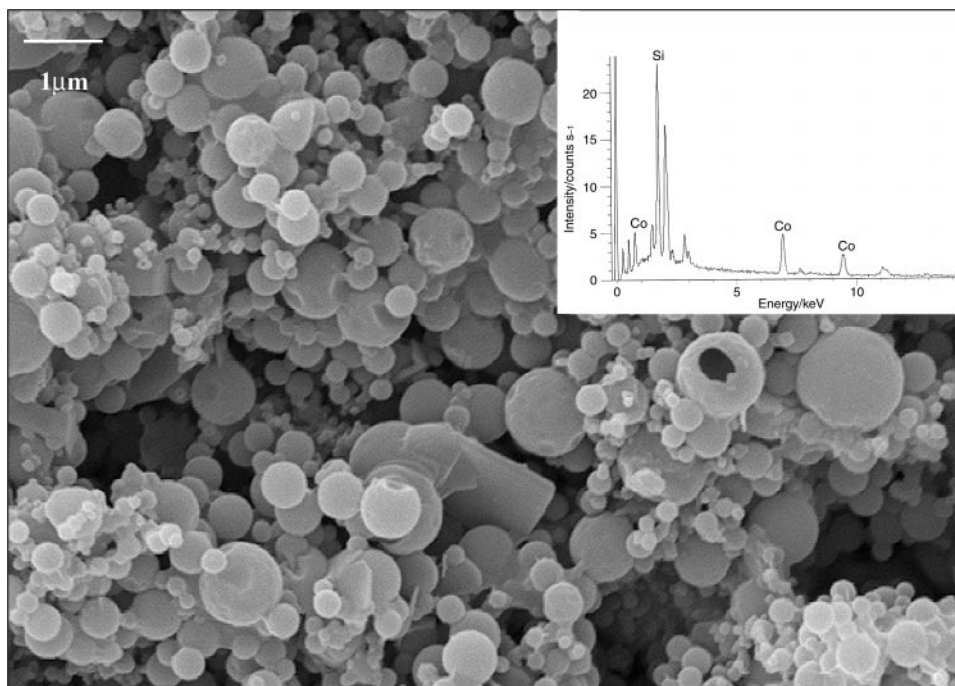


Fig. 3 SEM micrograph of as-synthesized hollow silica microspheres prepared in the presence of $\text{CTA}^+[\text{Co}(\text{B}_9\text{C}_2\text{H}_{11})_2]^-$. Note the 1 μm scale bar, and therefore the sub-micrometre diameter of most of the shell structures. Inset: Corresponding EDAX spectrum showing peaks attributed to Co and Si.

dried samples of the microspheres confirmed the presence of the intact porphyrin moiety.²²

Control experiments indicated that the formation of well-defined, non-aggregated silica shells was dependent on the concentrations of APTES and CTABr used in the reaction mixture.²³ These components are partitioned at the TEOS droplet surface, where they markedly influenced the rate of TEOS hydrolysis specifically at the droplet/water interface under mildly alkaline conditions. Given these considerations, we were able to significantly change the mean diameter of the hollow silica microspheres by adjusting the size of the TEOS/APTES droplets whilst maintaining their interfacial stability.²⁴ This was achieved by replacing the bromide counterion of CTABr with the large cobalticborane ($[\text{Co}(\text{B}_9\text{C}_2\text{H}_{11})_2]^-$) anion.** SEM micrographs showed intact hollow spheres with a mean diameter of 0.47 μm (s.d. = 0.21 μm) (Fig. 3), which was almost two orders of magnitude less than that measured for microspheres prepared in the presence of CTABr under identical reaction conditions. The sub-micron-sized shells were thermally stable and did not coalesce upon heating to 600 °C. The product was yellow in colour and showed the presence of cobalt by EDAX (Fig. 3, inset), indicating surface adsorption on or intercalation of $\text{CTA}^+[\text{Co}(\text{B}_9\text{C}_2\text{H}_{11})_2]^-$ within the silica hollow shells.

In conclusion, hollow silica microspheres have been prepared in high yields by a one-step facile synthesis under ambient conditions. By controlling the rate of TEOS hydrolysis specifically at the droplet/water interface, intact microspheres with uniform wall thickness and thermal stability can be routinely synthesized. The procedure can be readily extended to

the synthesis of organo-functionalized silica shells, microspheres with encapsulated organic pigment, and hollow silica capsules with sub-micrometre dimensions. Such materials could have a wide range of uses in diverse materials applications.

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**[CTA][cobalticborane] was synthesised by aqueous ion-exchange of CTABr with $\text{Na}^+[\text{Co}(\text{B}_9\text{C}_2\text{H}_{11})_2]^-$. Recrystallization using a mixture of ethanol and acetonitrile afforded yellow crystals of $\text{CTA}^+[\text{Co}(\text{B}_9\text{C}_2\text{H}_{11})_2]^-$. The composition and structure were confirmed by ¹H NMR and FT-IR spectroscopies. Qualitative analysis using AgNO_3 indicated no residual bromide ions in the product. Hollow silica microspheres were prepared using the standard reaction mixture but containing 3 mL of an ethanolic solution of $\text{CTA}^+[\text{Co}(\text{B}_9\text{C}_2\text{H}_{11})_2]^-$ in place of CTABr. The molar composition of the mixture was unchanged.

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- 21 FTIR bands: 3369 cm^{-1} (ArN-H), 1627 cm^{-1} (C=C), 1338 cm^{-1} (ArNO₂). UV/Vis bands: 351, 415 nm (*o*- and *p*-nitro groups).
- 22 FTIR bands: 2850, 2120 cm^{-1} (C-H), 1627 cm^{-1} (conjugated C=C), 1488 and 1473 cm^{-1} (C=N). UV/Vis bands: 394 nm (Soret band), 487 and 600 nm. For reference spectra, see: K. M. Smith, *Porphyrins and Metalloporphyrins*, Elsevier Science, London, 1975.
- 23 If the percentage of APTES was increased to 15 mol% of the total ethoxysilane used, or the molar composition of CTABr increased to 0.055, the sol-gel reaction rate was significantly increased and bulk amorphous silica was produced along with intact shells. Very high rates of ethoxysilane hydrolysis, produced by adding NaOH to increase the pH of the reaction mixture to 12.5, resulted in coalesced shells due to large amounts of extraneous silica. On the other hand, if the amount of APTES was decreased to 5 mol%, or the molar composition of CTABr decreased to 0.033, the rate of silica formation was not fast enough to produce an intact shell around the TEOS/APTES droplets and deflated or depressed silica capsules were observed.
- 24 The size of a surfactant-stabilized oil droplet in water is strongly influenced by the critical packing parameter of the amphiphile, V/a_0l_c , where V is the effective molecular volume of surfactant, a_0 the cross-sectional area of the headgroup, and l_c the alkyl chain length: J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, London, 1991. Smaller oil droplets have a higher interfacial curvature and are stabilized by surfactant molecules with large headgroup areas.