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Versatile synthesis of nanometer sized hollow silica spheres†

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Using the controlled precipitation of silicic acid on functionalized polystyrene latexes, nanometer sized silica-coated spheres could be prepared and subsequently modified to allow dispersion in non-aqueous solvents; removal of the interior polymer by calcination resulted in the formation of hollow silica spheres.

The formation of hollow shell architectures with a tunable diameter is of interest for a number of purposes, *e.g.* as capsules, photonic bandgap or highly porous materials. Procedures for the generation of hollow SiO_2 spheres have been previously reported and involve layer-by-layer deposition on (sub)micrometer sized latex particles,[1] interfacial synthesis,[2] or the use of hybrid polystyrene/siloxane latex particles.[3] In the nanometer regime (*i.e.* 10 to 100 nm), however, SiO_2 coating procedures to our knowledge are limited to inorganic particles.[4] Here we report that with the correct choice of surface functionality, nanometer sized latex particles can be coated by the slow controlled precipitation of silica from a sodium silicate solution at a preset pH. A polycondensation reaction takes place at the particle surface and after the removal of the majority of the unreacted silicic acid by dialysis, a stable dispersion of latex particles with a shell of SiO_2 results. After deposition of the particles on a surface, calcination of the interior (polystyrene) matrix gives hollow spherical objects. ‡

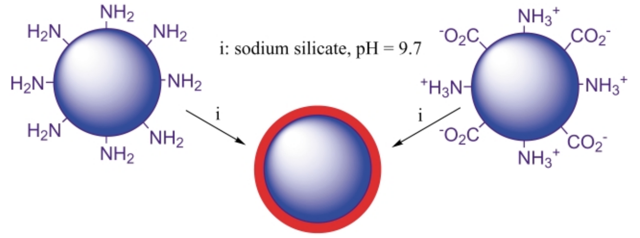
We found that using polystyrene latexes with either an amine functionalized or a zwitterionic surface, the latter consisting of amine and carboxylate groups (approx. 30 mol% of the latter), could be used to template the deposition of SiO_2 (Scheme 1). When a completely positively charged latex (*i.e.* polystyrene stabilized with hexadecyl trimethyl ammonium bromide surfactant) or a negatively charged one (*i.e.* having sulfonate surface groups) was used, no formation of coated spheres was observed (Table 1). This indicates that an attractive interaction between the surface groups and the precipitating silicate oligomers must be present.[5] Consistent with results reported for the coating of inorganic particles[4] we found that control of the pH of the sodium silicate solution is critical. For our purposes an optimum was found at pH = 9.7, giving the desired coating in 24 h with limited formation of silica particles containing no latex core formed by the non-templated precipitation of silica.

The coating of four different latexes was investigated in more detail (Table 1). Two relatively large latex spheres, 100 nm and 200 nm in diameter respectively, having amine surface functionalities, and zwitterionic particles with D = 25 and 40 nm were coated. In Fig. 1, transmission electron microscope (TEM) images of spheres having a SiO_2 shell are depicted. Untreated latex particles could not be visualized in the TEM without the use of staining reagents. Based on these TEM images, the thickness of the shells is estimated to vary between 3 and 10 nm. Dynamic light scattering (DLS) studies on the particles with diameters of 25 and 40 nm, measured before and after coating, confirmed this thickness. A larger value was found for the diameter of the particles using DLS when compared to the TEM measurements (Table 1); in addition to solvation and solvent swelling effects, this can be explained by the relatively large size distribution of the samples.[6] The thickness of the shell is mainly determined by the ratio of template to silicic acid; however, if the relative amount of silicic acid became too high, SiO_2 particles without an organic core also formed.

Table 1 Selected properties of SiO_2 coated polystyrene latexes

Diameter (nm)[a]	Surface functionality	Coating thickness (nm)[a]
100	$R–SO_3^-$	none
40	$R–N(CH_3)_3^+$	none
200	$R–NH_2$	9
108	$R–NH_2$	10
40 [61]	$R–NH_3^+/R–CO_2^-$	3 [3]
25 [46]	$R–NH_3^+/R–CO_2^-$	3 [3]

[a] As provided by manufacturer or determined by TEM. Values between brackets determined by DLS.



Scheme 1 Representation of the synthesis of SiO_2 coated latex particles.

Hollow silica spheres could be synthesised by heating the samples to 450 °C for 2 h. By IR spectroscopy no residual polystyrene could be detected after this treatment (Fig. 2).

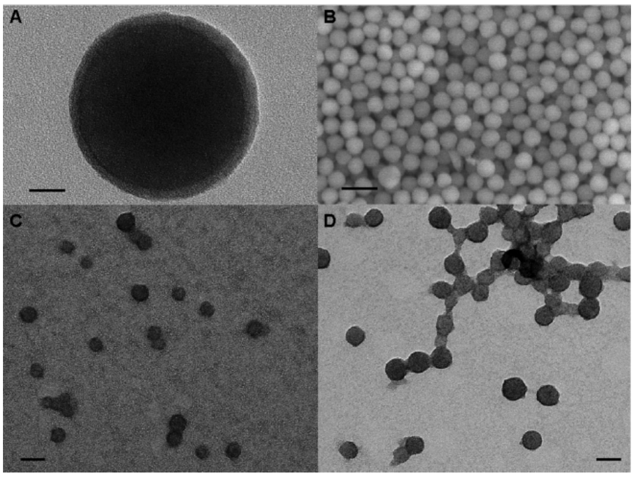


Fig. 1 EM images of SiO_2 coated latex spheres. Diameter = 100 nm: (A) TEM, scale bar = 25 nm; (B) SEM, scale bar = 300 nm. (C) TEM, diameter = 25 nm, scale bar = 50 nm. (D) TEM, diameter = 40 nm, scale bar = 50 nm.

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† Electronic supplementary information (ESI) available: experimental; IR and XPS; AFM, SEM and TEM images. See http://www.rsc.org/suppdata/cc/b2/b212811j/

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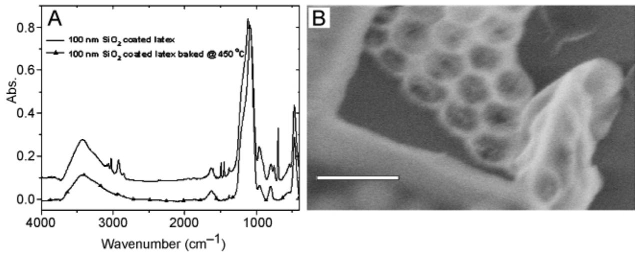

Fig. 2 (A) IR spectra of 100 nm SiO_2 coated spheres before and after calcination (see also ESI†). (B) SEM image of the same spheres after calcination, scale bar = 250 nm.

Electron microscopy indicated that the samples still exhibit the spherical morphology and especially in the case of the larger SiO_2 coated particles, scanning electron microscopy (SEM) also revealed holes in the shells (Fig. 2).[7] These are probably caused by exhausting the volatile products of the calcination step through the SiO_2 shells. X-Ray photoelectron spectroscopy (XPS) confirmed the removal of the interior organic polymer[8] and from the shift in the silicon 2p and oxygen 1s binding energies it was concluded that the incomplete polycondensation of the SiO_2 shell present on the latex particles was driven to completion during this calcination step. These changes in the Si–O–Si chemical environment were confirmed by shifts in the corresponding signals in the IR spectra of the coated particles before and after calcination; an absorption at $\nu = 1120\ \text{cm}^{-1}$ with a shoulder at $\nu = 1090\ \text{cm}^{-1}$ was observed for the coated latex spheres, the major absorption after heating the sample was found at $\nu = 1090\ \text{cm}^{-1}$ with some tailing to higher energies (Fig. 2).[9]

Deposition of the coated particles on a surface from aqueous solution by slow evaporation of the solvent led to highly organised hexagonal lattices, visualised by SEM. As an example the organisation of the coated spheres having a diameter of 200 nm is shown (Fig. 3A). The voids between adjacent spheres are still open, indicating that the organised array is indeed formed by the stacking of SiO_2 coated spheres. Zhong *et al*. reported that using a silica sol and a crystalline array of polystyrene beads as a template, led to a three dimensional structure with arrays of interconnecting spherical pores.[10] The size of the ordered domains in our case ranged up to several tens of micrometers (see ESI†).

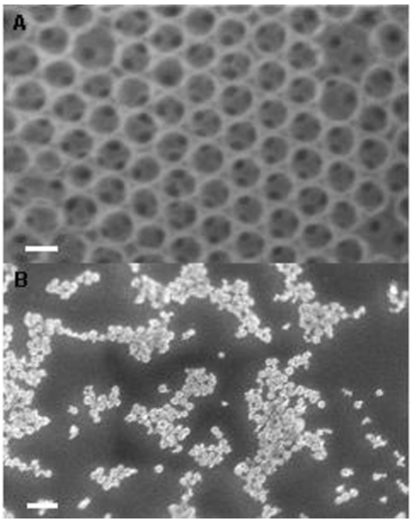

Fig. 3 (A) SEM images of an organized multilayer of 200 nm sized coated spheres after calcination, scale bar = 200 nm. With the chosen acceleration voltage the complete coating is not visible in this case. (B) SEM image of 40 nm coated spheres after surface modification (see text), scale bar = 200 nm.

In a preliminary experiment we studied the coating of a core-shell star-shaped polymer, having a highly cross-linked polynorbornene interior and a polyethyleneglycol (PEG) rich shell with SiO_2. Consistent with results reported by Anonietti and coworkers,[5] we also found a postive interaction between the PEG part and the silica precursor, resulting in the formation of coated polymer particles with diameters as small as 20 nm (see ESI†).

To be able to modify the surface of the SiO_2 coated spheres, we transferred the particles from water to acetonitrile by azeotropic destillation. After complete removal of the water a slightly cloudy dispersion was obtained. In acetonitrile the peripheral R_3SiOH groups on the particles could be capped. We chose hexamethyldisilazane to modify the SiO_2 surface in such a way that the particles could be transferred to organic solvents to form stable dispersions, enabling their processing or to perform subsequent reaction steps. After reaction overnight, a precipitate was formed from which excess reagents could be removed by dispersion/centrifugation cycles in MeOH. Microscopic investigation of the product revealed spherical particles with similar diameters to the starting latexes and the corresponding unreacted silica coated particles (Fig. 3B).

We have shown that by the correct choice of surface functionality, small polystyrene latexes can be coated with a silica shell and that this concept can be extended to different types of polymer architectures, e.g. star-shaped macromolecules. Complementary to known procedures this approach allows the fabrication of hollow SiO_2 capsules with sizes in the nanometer regime, which after straightforward modification can be suspended in non-aqueous solvents.

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Notes and references

‡ Both amine (Polysciences Inc.) and zwitterionic (Interfacial Dynamics Corporation, Portland, OR) functionalized nanosized latexes were commercial products.

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