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Shaped inorganic, organic and inorganic-organic composite shells from surface engineering of crystal templates

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The fabrication of inorganic (silica), organic (polymer) and inorganic-organic (silica-polymer composite) shaped shells through surface coating of crystal templates is the subject of the present work. The fabrication process comprises controlled coating of cubic sodium chloride and truncated rhombohedral sugar crystallites with sol-gel derived silica and/or polymeric compounds in order to frame the crystallites surfaces with a thick enough shell such that the geometric shape persist after removal of the encapsulated crystal-templates by aqueous dissolution. The presence of inorganic and/or organic matter in the wrapped crystals was evidenced by IR spectroscopy, while, the dissolution process as well as the morphology of the derived 3D-shaped shells was observed by optical microscopy.

1. Introduction

Hollow capsules are widely used in many technological, industrial and medical applications owing to their low density, large specific area and stability, surface permeability and shell construction [1, 2]. Shaping such hollow capsules for the purpose to acquire a certain morphology has challenged several research groups that have reported the shape fabrication of hollow inorganic, organic and inorganic-organic composite objects in the nanometer to millimeter scale by mainly exploiting the spray drying/pyrolysis, emulsion, ion exchange and sacrificial core-shell techniques [2–5]. Especially, the latter technique is a generalized approach that comprises controllable surface patterning, through a combination of self-assembling, layer-by-layer deposition, sol-gel condensation and precipitation processes, of either organic templates, like liquid crystals and micelles [6, 7], polymer super-lattices [8] and bacterial superstructures [9], or inorganic templates [3, 10] with a desirable material and subsequent removal of the template by thermal or chemical treatment. The present work extends the principles of sacrificial core-shell technique for the fabrication of hollow shells to a special category of templates and, in particular, to templates possessing crystal morphology, e.g. having crystal faces and edges. Work related to this area has been reported for silica hollow fibers possessing square-shaped channels by using ammonium tartarate needles as the crystal template [11, 12], while, efforts for wrapping enzyme crystals with polymer layers, followed by dissolution of the template, have led to polymer hollow spheres and not to crystal shaped capsules, as a result of osmotic phenomena [13]. In general, shape fabrication processes of this kind would be much recommended with respect to the inherited crystal anisotropy and symmetry in the resulting hollow capsules. For instance, the impact effect of crystal symmetry on the properties of crystals, such as optical activity, pleochroism, pyro- or piezoelectricity and others is well known [14]. In the frame of such merits, we wish to demonstrate that well shaped inorganic or organic crystallites can function as effective templates that can be successfully coated with inorganic, organic or inorganic-organic matter through sol-gel condensation or deposition procedures. The core crystallites are easily removed by dissolution leaving behind hollow capsules that retain the morphology of the mother templates.

2. Experimental procedure

2.1. Materials

Tetramethyl orthosilicate (TMOS, Fluka) and tetraethyl orthosilicate (TEOS, Aldrich) were used as the silica precursors. Poly(vinyl acetate) (Aldrich, M_w: 12.800) and polystyrene (M_w: 20.000) were used for the polymer depositions. Table sugar and chemically pure sodium chloride were used. The size of sodium chloride and sugar crystallites lies in the sub-millimeter scale between 0.2 mm and 0.8 mm. Very fine crystallites of sodium chloride (2–25 μm) were obtained by the dropwise addition of a concentrated solution of the salt (0.5 g/1.5 mL) in 10 mL of ethanol under stirring.

2.2. Procedure

Hollow inorganic, organic and inorganic-organic shaped shells [silica, poly(vinyl acetate)/polystyrene and silica/polystyrene] were derived from aqueous dissolution of the corresponding sodium chloride or sugar coated crystallites. The coating procedures are described below.

2.2.1. Silica coated crystallites

In a typical procedure, TMOS (1 g) was dissolved in ethanol (5 mL) and 2 drops of concentrated HCl aqueous solution (37%) were added. The clear solution was stirred for 30 min at ambient conditions and then passed through a glass column (length: 8 cm, diameter: 0.5 cm) containing commercially available sugar or sodium chloride crystals (250 mg) at its bottom (closed with a piece of cotton). A light stream of air was passed through the column in order to dry the crystals and remove any excess of TMOS solution retained in the inter-crystal void spaces. The procedure was repeated twice using the same mother liquid. The coated crystals were next transferred to a sealed flask containing TEOS (1 g) in ethanol (5 mL) plus 1 drop of concentrated NH_4OH aqueous solution (30%). After aging the crystals for 20 h in rest, the supernatant liquid was discarded and the crystals were rinsed with ethanol and acetone. It should be noticed that the hydrolysis of the TEOS solution leads to a concurrent precipitation of amorphous silica after ~1 h. However, the sodium chloride or sugar crystallites coated with silica can be easily separated by hand. It should be mentioned that TMOS is more preferable than TEOS during the first step because it allows the formation of denser coatings around the crystallite surfaces. On the other hand, TEOS is more preferable than TMOS during the second step because inhibits the gelation of the aging solution. Both effects result from the fact that TMOS is hydrolyzed much faster than TEOS.

2.2.2. Polymer coated crystallites

Polymer coating of crystallites was achieved by using a multistep technique. In particular, 5 mL of methanol containing 250 mg of poly(vinyl acetate) was passed through a column as above to first form a poly(vinyl acetate) layer over the sodium chloride or sugar external surfaces. Following, a second polymer layer was built by passing through the column 5 mL of cyclohexane containing 250 mg of polystyrene. This sequence was repeated twice using the same mother liquids to finally receive the sodium chloride/ and sugar/poly(vinyl acetate)/polystyrene composites.

2.2.3. Silica-polymer coated crystallites

The procedure for the preparation of hybrid silica-polymer coated crystallites was similar to that applied for the polymer coated crystallites. A hydrolyzed TMOS solution (prepared as described above) was passed through a column to first coat the crystallites surfaces with a silica layer. Then, a polystyrene solution in cyclohexane (250 mg/5 mL) was applied to form a polymer layer over the silica layer. The same procedure was repeated twice to built consecutive silica-polystyrene layers for the sodium chloride/ and sugar/silica/polystyrene composites.

2.3. Characterization

The aqueous dissolution process as well as the morphology of the derived capsules were observed using a Leica research optical microscope equipped with photographic camera. Infrared spectra were taken with a FT-IR spectrometer of Bruker, Equinox 55/S model. The samples were measured in the form of KBr pellets.

3. Results and discussion

3.1. Morphology of the crystal templates

Sodium chloride and sugar are crystalline substances belonging to the cubic and monoclinic crystal systems, respectively. The crystals of sodium chloride adopt a cubic geometry, while, those of sugar a truncated rhombohedral bipyramidal structure exhibiting tabular habit. Both morphologies are compatible with the crystal system of the crystallites [14] (Fig. 1). The optical microscopy pictures of the particular crystal templates, shown in Fig. 2, confirm the shape morphologies depicted in Fig. 1.

3.2. Silica coated crystallites

For silica coated crystallites, the sol-gel coating of the crystal surfaces comprises two steps. In the first, an acidified ethanol solution of TMOS is passed through a column (in-filtration) containing the crystal template to frame the particle surfaces with a silica film, and in the second, the silica film is further grown and reinforced by aging the coated crystals in an alkaline ethanol solution of TEOS for several hours. The presence of silica in the sodium chloride/silica composite was verified by IR spectroscopy from the presence of a strong absorption band at 1100 cm^{-1} associated with Si-O-Si stretching vibrations in the silica network [15] (Fig. 3, left). This band is significantly obscured in the sugar/silica composite by strong absorptions of the sugar molecules in the same region.

The two step coating procedure proved necessary in order to attain a thick enough silica film around the crystallite surfaces [16]. Neither the first process (in-filtration) nor the second (aging) by themselves were

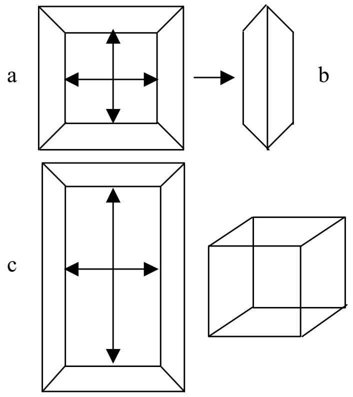

Figure 1 Crystal morphologies and habits for the sugar (a: tetragonal basis, b: side view of a, c: rectangular basis) and sodium chloride (d: cube) crystallites.

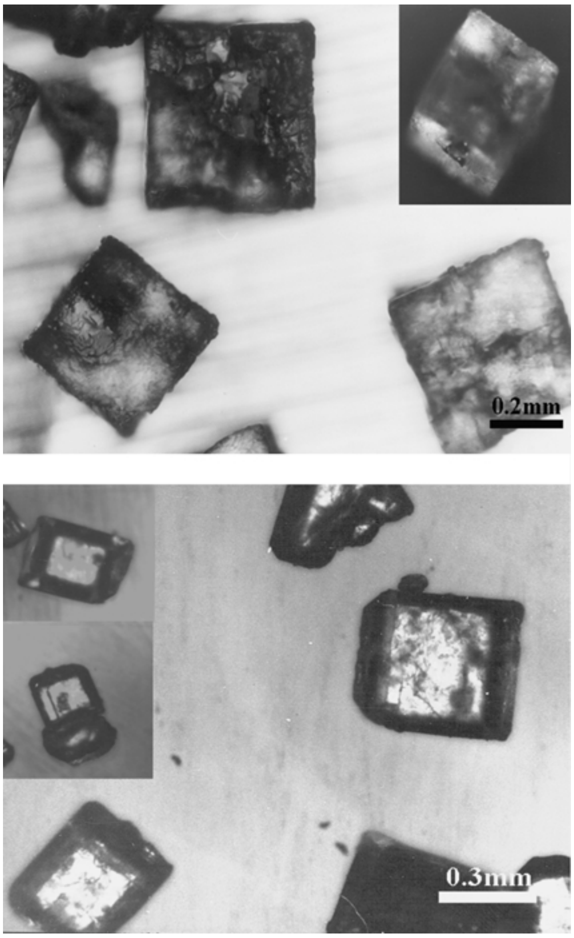

Figure 2 Optical microscopy pictures for the sodium chloride (upper) and sugar (lower) crystals.

adequate to build up crystal surfaces of a silica network with good mechanical strength against the inserted water molecules during aqueous dissolution of the template (water molecules penetrate the permeable silica membrane and etch the encapsulated crystals).

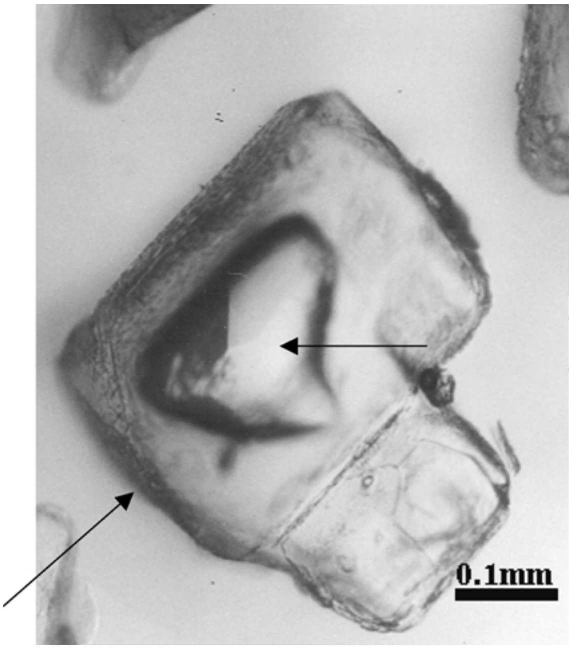

Figure 4 The photograph illustrates how the aqueous etching of the sugar crystal (central arrow) leaves behind a silica shell (side arrow), stable against osmotic pressure.

More specifically, we observed that as aqueous dissolution was advanced, the silica coating was gradually fallen apart, indicating that osmotic phenomena must take place during the dissolution process. On the contrary, the two step coating process leaves behind silica shells with good mechanical stability against osmotic pressure developed during template dissolution (Fig. 4).

3.3. Polymer and silica-polymer coated crystallites

For the same reasons as described above, a multistep technique was found necessary in order to develop thick

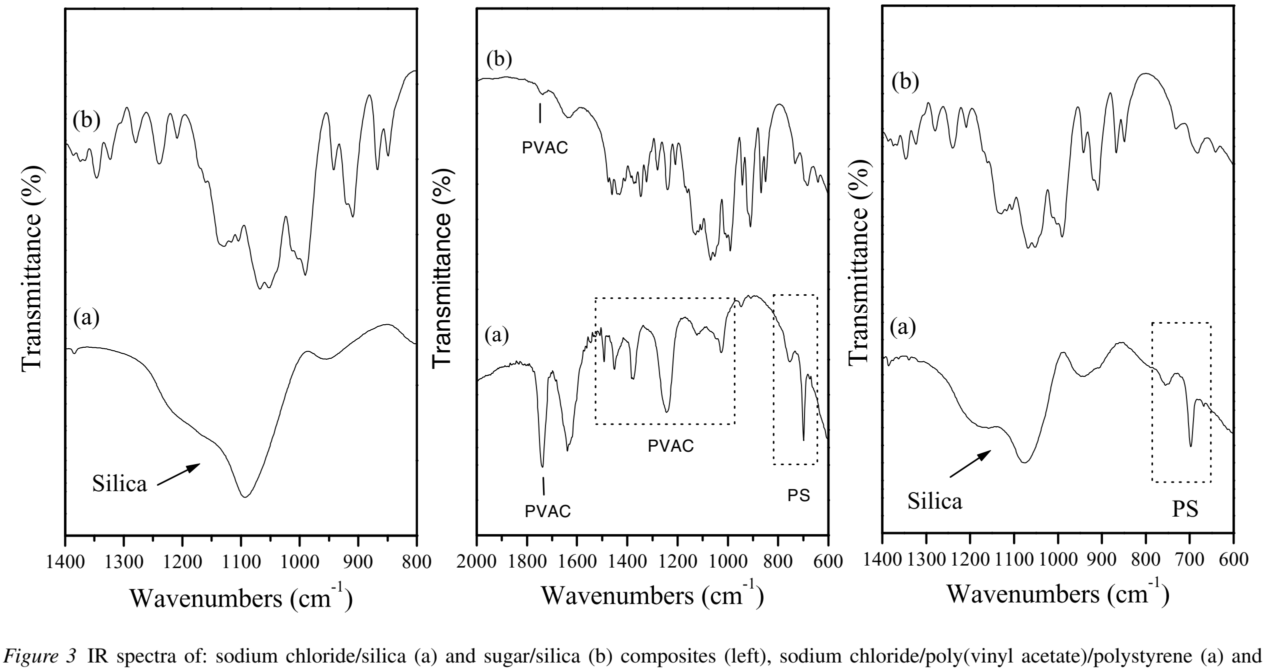

Figure 3 IR spectra of: sodium chloride/silica (a) and sugar/silica (b) composites (left), sodium chloride/poly(vinyl acetate)/polystyrene (a) and sugar/poly(vinyl acetate)/polystyrene (b) composites (center) and sodium chloride/silica/polystyrene (a) and sugar/silica/polystyrene (b) composites (right) [PVAC: poly(vinyl acetate), PS: polystyrene].

enough polymer or silica-polymer coatings around the crystallite surfaces and thus to endow the derived cells with good mechanical stability against osmosis. For polymer reinforced coatings the synergetic combination of two different polymers could fulfil this necessity. Special care was given to two factors: the sequence of the layers' depositions and the solvents in use. The oxygen containing poly(vinyl acetate), because of its large affinity towards the hydrophillic surfaces of the crystal templates, was chosen to be the first coating on top of which a second polystyrene layer could be deposited. Concerning the solvents, these must not solubilize the precedent layer in order to avoid its elution. For the poly(vinyl acetate)/polystyrene system, the methanol and cyclohexane solvents fulfill this necessity, since methanol dissolves poly(vinyl acetate) but not polystyrene and cyclohexane dissolves polystyrene but not poly(vinyl acetate). For the silica/polystyrene system, similar reasons dictate the initial covering of the crystallite surfaces with a silica layer and then the polymer follows.

The presence of organic and inorganic matter in the polymer and silica-polymer coated crystallites was evidenced by IR spectroscopy. For instance, the sodium chloride/poly(vinyl acetate)/polystyrene composite shows all the characteristic bands exhibited by the pure polymers themselves (Fig. 3, center). On the other hand, sodium chloride/silica/polystyrene exhibits the characteristic absorptions pertinent to the silica and polystyrene constituents (Fig. 3, right). Once again, the same bands are significantly hidden in the IR spectra of the analogue sugar composites due to strong absorptions of the sugar molecules in the same regions.

3.4. Morphology of the derived cells

Morphological features of the derived shells after immersion of the corresponding coated crystals in water are presented in Fig. 5. It is clear that the generated three-dimensional capsules inherit the shape morphology and size of the parent crystals after template dissolution. We observe the presence of slightly corrupted specimens possessing "crystal" faces and edges quite reminiscent of those of the sodium chloride and sugar crystals, e.g. having cubic or truncated rhombohedral geometry. A shell thickness of about 2–8 μm was roughly estimated for all cells. The large size of the capsules in conjunction with their thin walls could constitute a beneficial property of the cells [2]. Polarizing optical microscopy results indicate that the capsules are totally amorphous. This was evidenced by observing the coated crystals against the derived cells under polarized light in a black font throughout the dissolution process. For this purpose, a single coated crystal was orientated so as to appear black. By rotating the specimen 90°, the crystal became light over the black

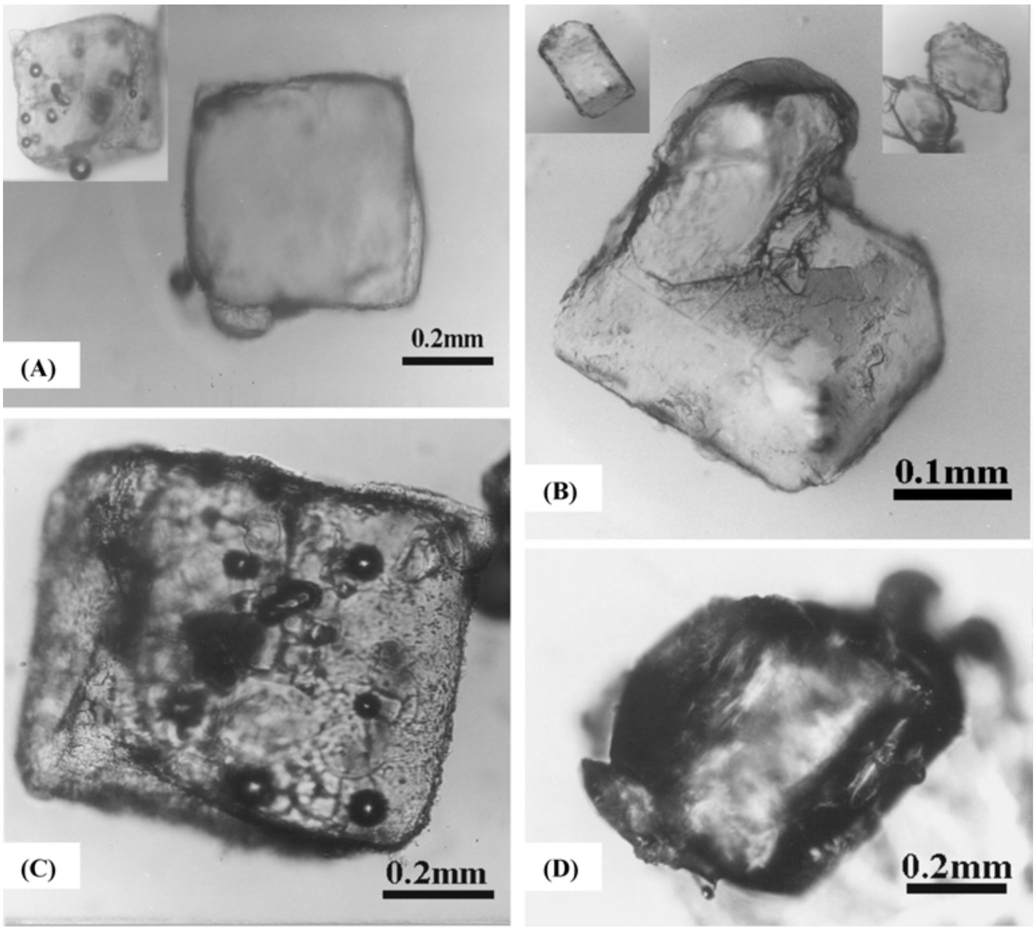

Figure 5 Optical microscopy pictures of: (A) a cubic silica shell (inset photo depicts a slightly tilted cubic specimen), (B) silica shells possessing a truncated rhombohedral geometry, (C) a slightly tilted poly(vinyl acetate)/polystyrene cubic shell and (D) a poly(vinyl acetate)/polystyrene shell derived from the corresponding sugar composite. Similar pictures emerge also for the silica/polystyrene shells.

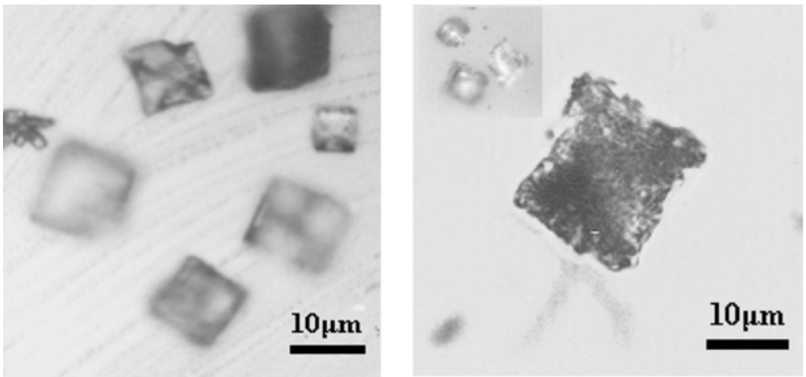

Figure 6 Optical microscopy pictures of sodium chloride microcrystallites (left) and of the derived hollow silica microcubes (right).

font. This is a typical behavior of crystalline material observed under polarized light and is attributed to the encapsulated crystals [17]. When this specimen was wetted with water, its lightness gradually disappeared and eventually became black irrespective of its orientation. This behavior characterizing amorphous substances, indicates the presence of amorphous silica or/and amorphous polymer in the present cases.

It should be pointed out that, the hollow capsules retain their fine architecture as long as they are kept in their aqueous environment. Water evaporation leads to cracked specimens probably as a result of surface tension phenomena, mechanical stresses near the edges and of the large size to shell thickness ratio of the capsules. However, the use of smaller in size crystallites could enable the isolation of the resulting hollow capsules intact in shape. Framing of very fine crystallites, obtained as described in the experimental section, with silica in the same manner as above, led to microcomposite sodium chloride/silica structures that upon template removal and drying yielded almost intact hollow silica microcubes (Fig. 6).

4. Conclusions

In conclusion, crystal-shaped inorganic, organic and inorganic-organic membranes of the sub-millimeter scale were fabricated by the sol-gel and polymer surface moulding of cores exhibiting certain crystal morphologies. We consider that this template approach is of particular interest since it makes it possible to transcribe some of the characteristic properties of a crystal (symmetry and anisotropy) to the resulting shell-type structure, thus endowing the latter with additional properties as well as those that could be possessed by the constituents of the shell (magnetic, semiconducting or others). Shape fabrication of other sol-gel derived coatings (Al_2O_3, TiO_2) and also of polymeric, composite and carbonaceous materials by the same strategy will appear soon.

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