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Biomimetic assembly of calcite microtrumpets: crystal tectonics in action†

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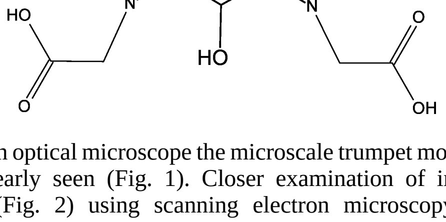
Crystallisation of calcium carbonate in the presence of the polycarboxylate 1,3-diamino-2-hydroxypropane-*N*,*N*,*N*′,*N*′-tetraacetate results in the formation of 'microtrumpets' composed of nanocrystalline calcite.

The remarkable control over crystal growth and morphology evident in biominerals is a source of wonder both at an aesthetic and a scientific level.[1] The ability to observe increasingly intricate details of such materials using electron microscopy has led to endeavours from inorganic chemists to reproduce aspects of the biomineralisation processes, motivated by the idea of being able to mimic nature and to tailor minerals for specific functions.[2] In this regard, there has been significant progress in investigating crystal formation in the presence of a variety of growth modifiers. For example, in the case of calcium carbonate, a ubiquitous biomineral with three polymorphs, addition of species containing carboxylates to reaction solutions results in modifications to crystal shape and phase arising from interaction of the carboxylate moieties at carbonate sites on the crystal surface.[3–6]

A further aspect of biomineralisation, which has been termed "crystal tectonics" by Mann, is the assembly of individual biomineral crystals into more complex structures such as shells or spines.[7–9] Given the nature of the structures produced, it is clear that achieving this in the laboratory is a considerable challenge and progress so far has been fairly limited. We were thus extremely surprised to discover during the course of experiments to gauge the effect of 1,3-diamino-2-hydroxypropane-*N*,*N*,*N*′,*N*′-tetraacetic acid (H_4hpdta) on calcium carbonate growth in aqueous media the formation after 24 h of 'microtrumpets' of calcite. They are the sole product when the molar ratio of Ca^{2+} to hpdta^{4-} is 25:1.‡ The formation of these unusual structures demonstrates that relatively simple approaches can lead to unexpected assembly processes *in vitro* that mimic the "crystal tectonics" of biomineralisation processes.



Under an optical microscope the microscale trumpet morphology can be clearly seen (Fig. 1). Closer examination of individual trumpets (Fig. 2) using scanning electron microscopy (SEM) reveals that they are constructed from ordered nanocrystals of calcite.

These trumpets are reminiscent of the calcite biomineral growths such as those seen on coccolithophores like *Discosphaera tubifera* [Fig. 2(e)]. Our findings prompted us to perform a series of crystallisation experiments to see if we could follow the formation of these remarkable structures with successive SEM snapshots [Fig. 2(a)–(d)]. On mixing the reactants under stirring, immediate precipitation of calcium carbonate is initially inhibited by the presence of hpdta^{4-} and turbidity is first observed after about 30 min. Crystals were isolated after 6, 9, 12 and 24 h, and examined using SEM. As the results show, after 6 h [Fig. 2(a)], there are plaques of calcite carrying ball-like calcite excrescences (identified by powder X-ray diffraction). After 9 h [Fig. 2(b)], longer structures that appear to grow from these 'nanobobbles', giving a 'bobble-hat' motif, start to form and after 12 h, these 'bobble hats' have begun to produce the characteristic trumpet shapes which become dominant after 24 h crystallisation [Fig. 2(c), (d)]. Further characterisation with SEM at higher magnifications indicates that on the excrescences which are seen after 6 h [Fig. 2(a)], the crystallites have rhombohedral morphology and evolve [Fig. 2(b)] into crystallites with hexagonal cross-sections of 200–400 nm which then build up the whole trumpet [Fig. 2(d)]. Experiments performed with Ca^{2+}:hpdta^{4-} ratios of 100:1, 50:1, 10:1 and 1:1 all produced fewer trumpets. In addition, as the ratio approaches 1:1, complexation by the hpdta^{4-} ligand inhibits precipitation of calcite. Thus, the 25:1 ratio must be close to the optimum for the formation of these remarkable structures.

The way in which the formation of the trumpets occurs can only be conjectured at present, but from the snapshots, it appears that the 'nanobobbles' evolving from the excrescences are the key. These are in evidence at every stage and the trumpets appear to grow from them, suggesting that the polycarboxylate is somehow involved in organising the overall structure by inhibiting crystal growth at the hexagonal faces and encouraging the elongation and divergence which leads to the trumpets.

The commercially available heptadentate ligand 1,3-diamino-2-hydroxypropane-*N*,*N*,*N*′,*N*′-tetraacetate resembles H_4edta with its four carboxylates and two nitrogen donors. However, the central alcohol function is well known to provide a bridging function between two metal sites and, with metal ions in excess, as here, effectively provides a "nucleating site" for mineral growth, as we have noted previously for Al(III) and Fe(III).[11,12] In this case, each metal ion has four coordination sites occupied by donors from the ligand (two carboxylates, one nitrogen and the central oxygen from the alcohol), with the remaining two coordination sites free for other species. It is thus possible that at the specific Ca^{2+}:hpdta^{4-}

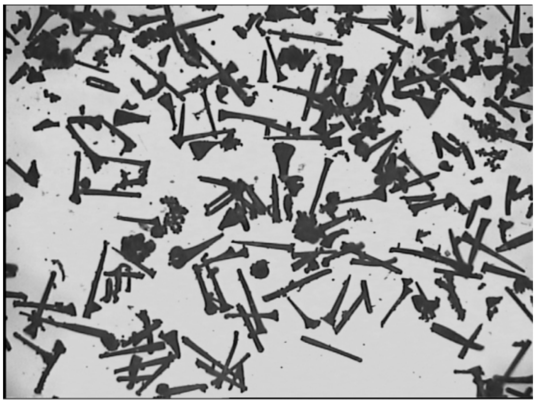


Fig. 1 Microtrumpets viewed using an optical microscope.

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† Electronic supplementary information (ESI) available: XRD pattern of trumpet-shaped structure. See http://www.rsc.org/suppdata/cc/b4/b401754d/

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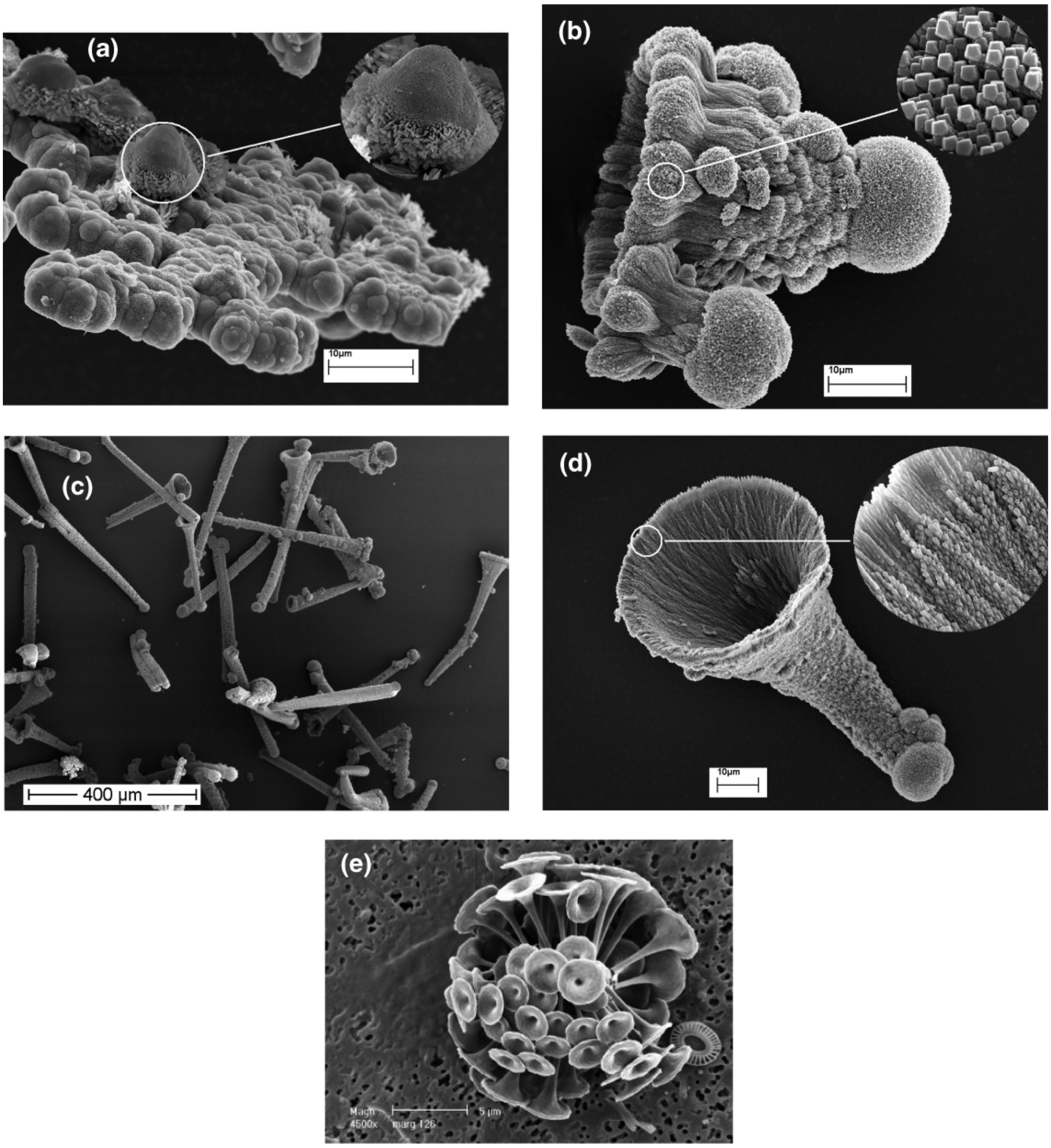

Fig. 2 (a) SEM image of calcite formation after 6 h. (b) Detail of SEM image of calcite formation after 12 h. (c) Overview SEM image of calcite formation after 24 h. (d) SEM close-up of a microtrumpet formed after 24 h. (e) The coccolithophore *Discosphaera tubifera*.[10]

ratio of 25:1, the situation is such that two calcium ions are coordinated in a similar fashion, with one surface effectively blocked by the ligand and the free coordination sites at the larger metal ion set up in a fan shape so that the situation is ideal for calcite formations organised into this trumpet morphology.

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Notes and references

‡ Calcium carbonate was crystallised by mixing 10 mL aqueous solutions containing $CaCl_2 \cdot 2H_2O$ (0.037 g, 0.25 mmol) and $NaHCO_3$ (0.043 g, 0.5 mmol) in the presence of 0.01 mmol of 1,3-diamino-2-hydroxypropane-*N*,*N*,*N*′,*N*′-tetraacetic acid solution (0.25 mL of 0.04 M solution) at pH 7.9 with stirring. On standing, precipitation is observed after 30 min, giving a 50% yield of calcite trumpets after 48 h. Experiments were conducted over different time periods (6, 9, 12 and 24 h) to observe the growth of the crystals. A STOE powder diffraction system operating with monochromated Co radiation was used for phase characterisation (see ESI†). Calcite formation was observed using a LEO Gemini 1530 scanning electron microscope.

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