Biomimetic growth of strontium oxalate aggregates with unusual morphologies in the presence of poly(methacrylic acid)

Paper

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Reaction of $C_2O_4^{2-}$ with Sr^{2+} ions in the presence of a polymeric additive, poly(methacrylic acid), leads to the formation of dumbbell-shaped SrC_2O_4 aggregates consisting of two dandelion-like heads composed of rod-like strontium oxalate dihydrate (SOD) crystals. The formation of the unusual aggregated structures is essentially in accord with a fractal growth mechanism.

The synthesis of inorganic materials with specific size, morphology and superstructure is a key aspect in the development of new materials in many fields.[1,2] Inspired by the exquisite control that biological systems exert over the nucleation and growth of biominerals distinguished by a complexity of form, materials chemists are trying to understand biomineralization and, thereby, to develop biomimetic or bio-inspired strategies for the controlled synthesis of advanced inorganic materials.[3] For example, a variety of polymeric additives, such as biomacromolecules,[4] polyelectrolytes,[5] dendrimers,[6,7] and double-hydrophilic block copolymers[8–11] have been used for the morphological control of inorganic particles. Moreover, various organic templates or matrices have also been employed to control the nucleation and growth of inorganic crystals; examples include Langmuir monolayers,[12] self-assembled films,[13–15] thermally evaporated films,[16] polymer surfaces,[17] and gelatin matrices.[18,19] It is noteworthy that a unique fractal growth of fluorapatite–gelatin composites from prisms through dumbbells to spheres was observed when the biomimetic growth and self-assembly of fluorapatite in denatured collagen matrices was investigated.[18,19] However, although dumbbell-shaped particles can be easily produced by immediate precipitation in the presence of suitable polymeric additives, none of the obtained aggregates showed fractal structures.[20]

In the present work, we investigated the crystallization of strontium oxalate in the presence of a typical polymeric additive, poly(methacrylic acid) (PMAA). SrC_2O_4 was chosen in this study since its dihydrate $SrC_2O_4{\cdot}2.5H_2O$ (SOD) is isomorphic with calcium oxalate dihydrate (COD), which is an important phytocrystal and showed remarkable morphological changes in the presence of polymeric additives.[11] It was found that the presence of PMAA led to the growth and self-assembly of beautiful, dumbbell-shaped SrC_2O_4 aggregates consisting of two dandelion-like heads. The formation of the unusual aggregated structures composed of rod-like SOD crystals was tentatively interpreted in terms of the fractal growth mechanism.

A commercial polymer, poly (methacrylic acid) (PMAA, $M_w = 6500$ g mol^{-1}, sodium salts), was obtained from Aldrich. The crystallization of SrC_2O_4 was conducted at room temperature (*ca.* 22 °C) using a procedure similar to the reported crystallization of CaC_2O_4.[11] In a typical synthesis, a solution of $Na_2C_2O_4$ (0.1 M, 0.4 mL) was injected into an aqueous solution of PMAA (*e.g.* 1.26 g L^{-1}, 20 mL). After the pH of the solution was adjusted to pH 10 using HCl, a solution of $SrCl_2$ (0.1 M, 0.4 mL) was added under vigorous stirring, giving a final SrC_2O_4 concentration of 2 mM. The stirring was continued for 1 min and then the solution was covered and allowed to stand under static conditions for 24 h before the product was collected for characterization. The obtained SrC_2O_4 precipitates were characterized by scanning electron microscopy (SEM) using an AMARY 1910FE microscope operated at 10 kV and transmission electron microscopy (TEM) using a JEOL JEM-200CX microscope operated at 200 kV. Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku Dmax-2000 diffractometer with Cu Kα radiation.

Fig. 1 shows the effect of the polymer concentration on the morphology of the strontium oxalate crystals. In the control system where no additive was present, the product was a mixture of the aggregated or polynucleated monohydrate phase of strontium oxalate (SOM) crystals and distorted bipyramids of the dihydrate phase of strontium oxalate (SOD) crystals (Fig. 1a). It is consistent with the corresponding XRD result shown in Fig. 2a, which shows that the obtained crystals consist predominantly of a SOD phase and a minor SOM phase.

When 0.126 g L^{-1} PMAA was present, a distinct change in the morphology and crystal phase of strontium oxalate occurred. As shown in Fig. 1b, the product exhibits rods with slightly expanding ends (or peanut-like rods), which ranged from 2 to 2.5 μm in length and from 0.3 to 0.4 μm in width. The expanding ends were composed of close-packed rod-like crystals. The corresponding XRD pattern (Fig. 2b) shows that the obtained crystals were pure SOD phase. The fact that (020) and (040) peaks were significantly intensified suggested a preferential alignment of the (010) plane parallel to the specimen surface, indicating that the peanut-like rods were elongated along the *c*-axis of the tetragonal SOD crystal. It has been previously observed that tetragonal SOD prisms elongated along the *c*-axis can be obtained in the presence of poly(ethylene glycol)-block-poly(methacrylic acid) (PEG-b-PMAA).[11] The fact that rounded peanut-like rods were obtained in the present case suggested that the homopolymer PMAA with a large number of repeat units showed a partly non-specific interaction with SOD crystals, whereas the block copolymer PEG-b-PMAA with a short PMAA chain showed a specific interaction with the SOD {010} faces, which is reminiscent of the case of calcium oxalate dihydrate (COD).[11]

As the concentration of PMAA was increased to 1.26 g L^{-1}, unusual, dumbbell-shaped SrC_2O_4 aggregates consisting of two dandelion-like heads composed of radially aligned, rod-like growing crystals were obtained (Fig. 1c), which were revealed to be pure SOD crystals according to the related XRD pattern (Fig. 2c). The overall length of the dumbbell-shaped aggregate is around 7.5 μm, and the 'bar' of the dumbbell

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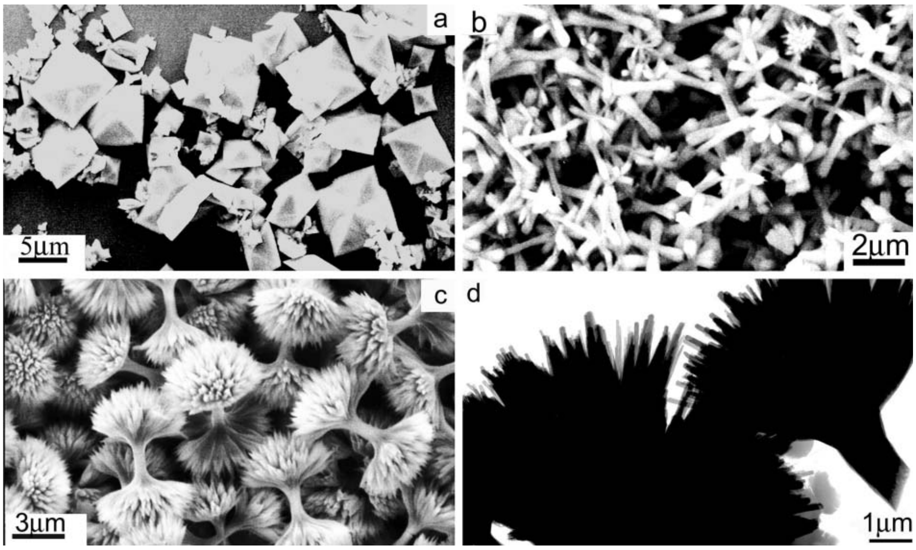

Fig. 1 SEM (a–c) and TEM (d) images of strontium oxalate crystals obtained in the absence (a) and the presence (b–d) of PMAA. [PMAA]: (a) 0, (b) 0.126, (c,d) 1.26 g L^{-1}.

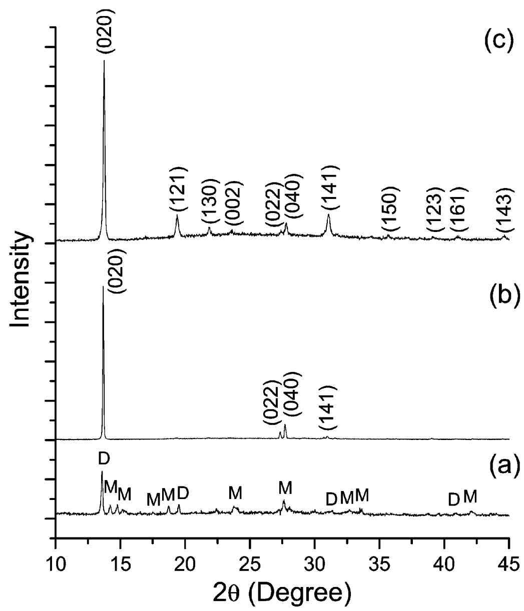

Fig. 2 XRD patterns of strontium oxalate crystals obtained in the absence (a) and the presence (b,c) of PMAA. [PMAA]: (a) 0, (b) 0.126, (c) 1.26 g L^{-1}. Peaks characteristic of SOM and SOD are labeled as 'M' and 'D', respectively. The indexed peaks are from SOD.

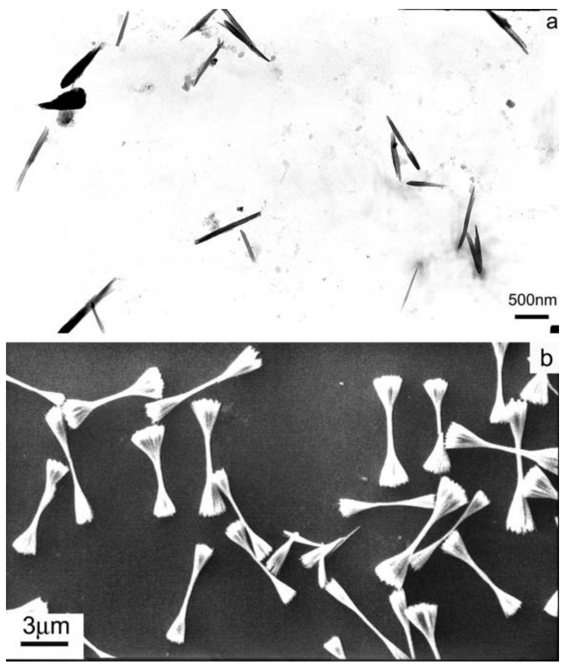

Fig. 3 TEM (a) and SEM (b) micrographs of strontium oxalate crystals obtained in the presence of PMAA. Aging time: (a) 20 min, (b) 5 h; [PMAA] = 1.26 g L^{-1}.

(rod-like seed crystal) has a length of *ca.* 2.1 μm with a diameter ranging from 0.4 to 0.6 μm. The maximum angle of divergence (between the rod axes of the growing crystals and the rod axis of the seed crystal) appears to be approximately 65–75°. The TEM micrograph presented in Fig. 1d clearly shows that the exuberant ends or dandelion-like heads are composed of uniform rod-like SOD crystals with a diameter *ca.* 150 nm. To the best of our knowledge, such dumbbell-shaped aggregates consisting of two dandelion-like heads have not been observed previously in the biomimetic growth of inorganic crystals although the structures are somewhat similar to many flower-like aragonite structures. However, the apparent dendrite morphology of the aggregated structures, which indicates a certain degree of self-similarity, suggests that they could result from a fractal growth process.

To examine the growth process of the SrC_2O_4 aggregates, the crystallization experiment was repeated at a PMAA concentration of 1.26 g L^{-1} but with different aging time. At an aging time of 20 min, the obtained product was rod-like SOD crystals with a length of 0.8–1.2 μm and an average width of *ca.* 150 nm (Fig. 3a). These rods could further evolve into rod seeds for the subsequent fractal growth. When the aging time was increased to 5 h, rod-like crystals grew radially at the ends of the rod seeds, which are *ca.* 1.7–2.1 μm in length and 0.3–0.5 μm in width, resulting in the formation of dumbbell-shaped aggregates that exhibited an overall length of about 6–7 μm and a maximum divergence angle of *ca.* 20–30° (Fig. 3b). If the aging time was long enough, perfect dumbbell-shaped aggregates consisting of dandelion-like heads as shown in Fig. 1c could be obtained (the aggregate morphology remained unchanged with further increase of the aging time).

These observations are essentially in accord with the fractal growth mechanism proposed previously for the growth and self-assembly of fluorapatite aggregates in gelatin matrices although the branches constituting the dumbbell-heads look much more separate in the present case.[18,19] In other words, progressive stages of self-assembled rod-like SOD crystals at both ends of the rod seed lead to dumbbell-shaped aggregates, which complete their morphology by successive and self-similar upgrowth processes that finally result in dumbbell-shaped aggregates consisting of dandelion-like heads. It is expected that PMAA plays an important role in the fractal growth of the SrC_2O_4 aggregates, *i.e.* it interacts non-specifically with SOD crystals leading to the formation of rod-like SOD crystals that can act as either the rod seed or the growing rods for the successive fractal growth. However, the exact reason for the observed fractal growth remains to be elucidated.

In conclusion, beautiful, dumbbell-shaped SrC_2O_4 aggregates consisting of two dandelion-like heads can grow from solution in the presence of poly(methacrylic acid). The formation of the unusual aggregated structures composed of rod-like SOD crystals is essentially in accord with a fractal growth mechanism.

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