Supporting Information

Dipole Field Driven Morphology Evolution in Biomimetic Vaterite

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Fig. S1 SEM (a-c) and the corresponding HRTEM (d-f) images of the three different CaCO₃ polymorphs with characteristic morphologies present in the 3 h specimen. (a,d) Ellipsoidal hexagonal vaterite, (b,e) star-shaped rhombohedral calcite, and (c,f) spindle-shaped orthorhombic aragonite. The marked d-spacings, A: 3.54 Å and B: 4.14 Å in (d) can be indexed to the (100) and (002) planes of hexagonal vaterite. The d-spacings marked in (e) of A: 2.59 Å and B: 1.91 Å with an interplane angle of 66° can be indexed to the (110) and (018) planes of rhombohedral calcite. Likewise, the d-spacings marked in (f) measuring A: 5.77 Å and B: 2.41 Å with an interplane angle of 88° could be indexed to the (001) and (200) planes of orthorhombic aragonite, respectively.
Fig. S2 Low magnification SEM image of (a) 3 h, (b) 6 h, (c) 23 h and (d) 96 h specimens prepared using 5.71 M urea and 28 g/L of gelatin.
Fig. S3 PXRD patterns of 23 h specimens prepared using 5.71 M urea and varying gelatin concentrations of (a) 0 g/L, (b) 7 g/L, and (c) 28 g/L. PXRD patterns (a) and (c) are indexed to the hexagonal vaterite phase, rhombohedral calcite phase and orthorhombic aragonite (denoted V\textsubscript{h}, C and A) crystal structures, respectively. The peaks marked by * in (a) and (c) correspond to columnar peaks from the diffractometer.
Fig. S4 TGA results of 3 h, 23 h and 96 h specimens prepared using 5.71 M urea and a gelatin concentration of either 0 or 28 g/L. All specimens had a mass loss of ~40 wt% observed between 560 and 750°C corresponding to the decomposition of vaterite into CaO and CO₂. PXRD patterns (not shown) of specimens after heating to 750°C under N₂ confirmed all CaCO₃ polymorphs decomposed into a pure CaO phase with a cubic unit cell, (JCPDS 82–1691) \( a = 4.796 \) Å, space group Fm\( \overline{3} \)m. Specimens containing gelatin had an initial mass loss of approximately 2.75 wt% between 250 and 360°C caused by the elimination of organic groups (usually proline) in gelatin whilst the second mass loss of 37 wt% observed between 600 and 705°C in the 3 h specimen and 41 wt% weight loss between 600 and 730°C in the 96 h specimen occurred from the decomposition of the CaCO₃ polymorphs. The end wt% point of the gelatin containing specimens have terminal weights varying by <2 wt% between each specimen due to the thermal decomposition of the amino acid glycine in gelatin. Literature suggests this occurs between 540 and 600°C.¹ From these terminal weights it can be assumed that the 96 h specimen contains 1.7 wt% more gelatin than the 23 h specimen which in turn contains 1.8 wt% more gelatin than the 3 h specimen. The wt% embedded gelatin within the CaCO₃ particles in the 3 h, 23 h and 96 h specimen was calculated as 6.1 wt%, 7.8 wt% and 9.5 wt%, respectively. The higher temperature required to complete the decomposition of the 96 h specimen into CaO and CO₂ compared to the 3 h and 23 h specimens can be explained from the later samples containing much more densely packed structures which makes decomposition increasingly difficult.
Fig. S5 PXRD patterns of 6 h specimens prepared using 28 g/L gelatin and urea concentrations of, (a) 2.86 M, and (b) 5.71 M. PXRD pattern (a) is indexed to the hexagonal vaterite phase ($V_h$) and rhombohedral calcite (C) crystal structures, respectively. The peaks marked by * in (a) correspond to columnar peaks from the diffractometer.
**Fig. S6** TEM image of a spherulite particle found in the 6 h specimen (28 g/L gelatin, 2.86 M urea). Single crystalline-like SAED patterns recorded from the areas marked A and B, respectively. Both SAED patterns are identical confirming all nanocrystallites within a spherulite type crystal have exactly the same orientation. D-spacings measured from the spots marked A and B were 3.54 Å and 2.72 Å with an interplane angle of 67°. These could be indexed to the (100) and (012) planes of hexagonal vaterite.

**Fig. S7** (a) TEM image of a broken ellipsoid particle. (b,c) SAED pattern and HRTEM image recorded from the region located within the circle in (a). D-spacings measured from the marked diffraction spots in (b) are A: 7.99 Å and B: 3.34 Å which can be indexed to the (001) and (100) crystal planes of hexagonal vaterite. The lattice fringes in (c) measuring A: 8.54 Å can also be indexed to the (001) planes of vaterite. The indexing in (b,c) confirmed the longest dimension of the ellipsoid particle is parallel to the [001] zone axes as demonstrated by the arrow in (a).
**Fig. S8** SEM image of a broken twin cauliflower-like particle revealing a small disc in the core.

**Fig. S9** HRTEM image of the hexagonal prism particle shown in **Fig. 6f**, showing defects and an incommensurate superstructure. The arrow indicates the [001] direction.
Fig. S10 SEM image of a hollow hexagonal prism vaterite particle prepared when the 96 h specimen was treated in acidic conditions (pH 3) under hydrothermal conditions for 3 h.

Fig. S11 SEM images of vaterite particles prepared in gelatin solution (28 g/L) with the addition of KCl at concentrations of (a) 0.14 M and (b) 0.57 M, respectively. Both specimens were collected after a hydrothermal treatment time of 96 h.

REFERENCE