

Supporting Information

Morphosynthesis of framboidal stable vaterite using a salicylic acid-aniline dye as an additive

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Methods for X-ray Crystallography

In each case, a crystal of suitable size was selected from the mother liquor and immersed in silicone oil, then mounted on the tip of a glass fibre and cemented using epoxy resin. Intensity data for the crystals were collected Mo-K α radiation ($\lambda = 0.71073\text{\AA}$) at 298(2) K, with increasing ω (width of 0.3° per frame) at a scan speed of 6 s/frame on a Bruker SMART APEX diffractometer equipped with CCD area detector. The data integration and reduction were processed with SAINT (SMART 1995) software. An empirical absorption correction was applied to the collected reflections with SADABS (SADABS 1999). The structures were solved by direct methods using SHELXTL (SHELXTL 1997) and were refined on F^2 by the full-matrix least-squares technique using the SHELXL-97 program package (SHELXL-97). Graphics were generated using MERCURY 2.3 (MERCURY 2.3). In all cases, non-hydrogen atoms are treated anisotropically and hydrogen atoms attached to all carbons are geometrically fixed and refined isotropically

References

Mercury 2.3, Supplied with Cambridge Structural Database; CCDC: Cambridge, U.K.,

Sheldrick, G. M. SADABS: Software for Empirical Absorption Correction; University of Gottingen, Institute fur Anorganische Chemieder Universitat: Gottingen, Germany, 1999-2003.

Sheldrick, G.M. SHELXS-97;University of Gottingen: Germany,1997.

Sheldrick, G. M. SHELXL-97: Program for Crystal Structure Refinement; University of Gottingen, Gottingen, Germany, 1997.

SMART, SAINT and XPREP; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1995.

Preparation procedure of the dye:

Aniline (5.0 g, 53.8 mmol) was added to a mixture of HCl (16 ml) and water (16 ml) and digested in a water bath for 30 min. The hydrochloride was then cooled to 5 °C and further diazotized with ice-cold aqueous NaNO₂ solution (3.7 g, 20 ml). A cold solution of salicylic acid (7.42 g, 53.8 mmol), previously dissolved in 10% NaOH solution (50 ml), was then added to the cold diazonium salt solution with vigorous stirring. A yellow color developed almost immediately and the stirring was continued for 1 h. The reaction mixture was kept overnight in a refrigerator, followed by 3 h. at room temperature, and then acidified with dilute acetic acid, where upon a yellow precipitate separated out. The precipitate was filtered, washed several times with water to remove excess acetic acid and water-soluble materials, and then dried in air. The crude product was washed with hexane to remove any tarry materials and recrystallized from methanol to yield pure dye.

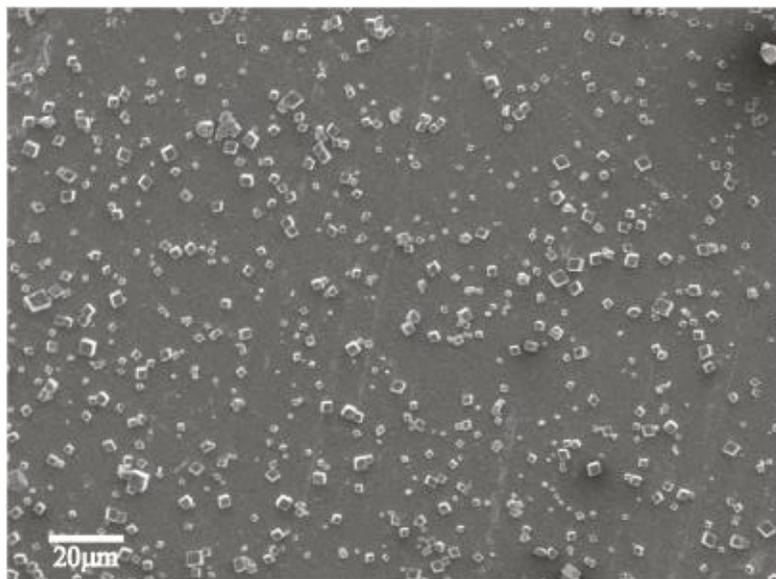


Fig S1. Predominant formation of calcite in presence of salicylic acid (taken as controlled compound for the precipitation of CaCO₃).

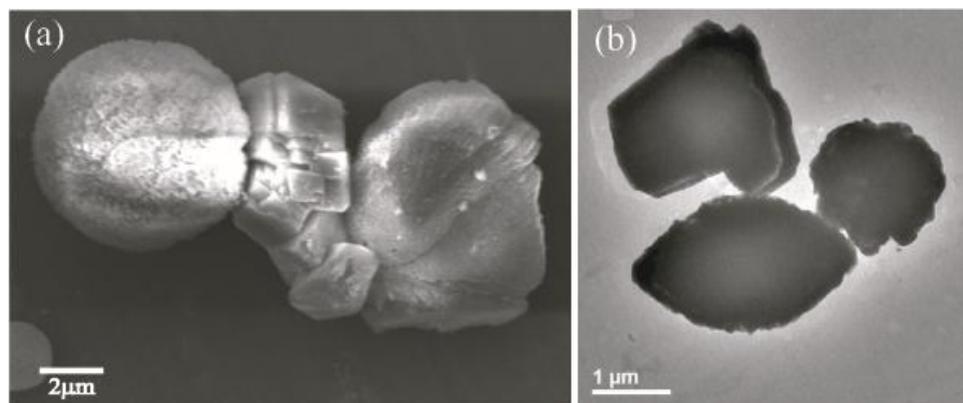


Fig S2. Dissolution of vaterite to calcite (a) SEM image and (b) TEM image.

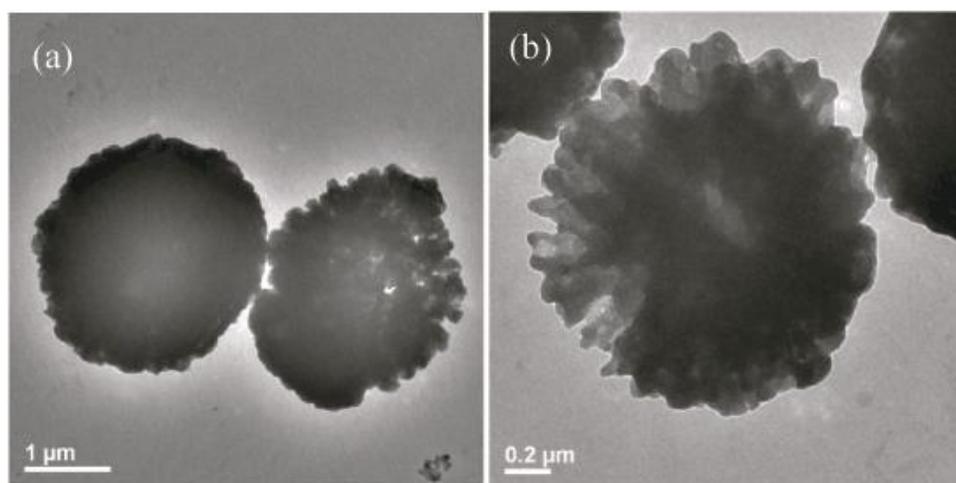


Fig S3. TEM images (a) and (b) of vaterite microspheres formed in presence of ~10 mM concentration of the dye.

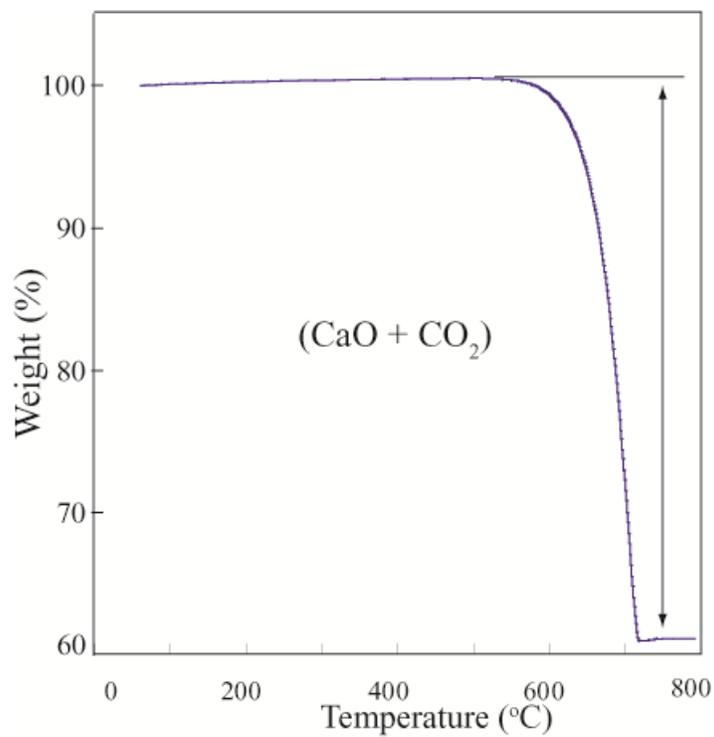


Fig S4. TGA analysis of CaCO₃ precipitates formed absence of dye.

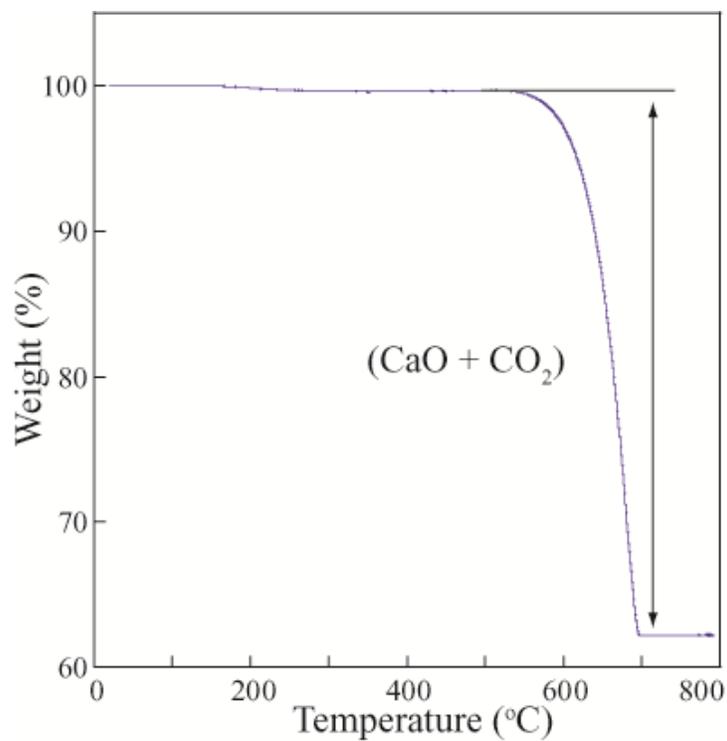


Fig S5. TGA analysis of CaCO₃ precipitates formed in presence of 10 μM dye concentration.

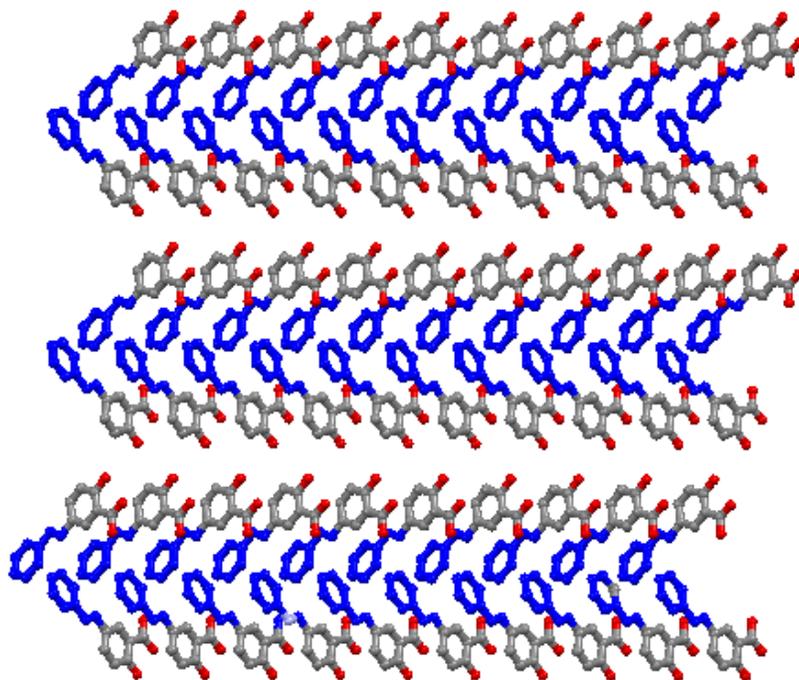


Fig S6. Crstal packingdiagram of the salicylic acid aniline dye showing the hydrophobic and hydrophilic layers.

Calculation of percentage of polymorph:

The percentage of each polymorph of calcium carbonate was calculated from their characteristic XRD peak intensities by using the following formula, as described in the literature.¹

$$X_A = \frac{3.157(I_A^{221})}{I_C^{104} + 3.157(I_A^{221}) + 7.691(I_V^{110})} \quad (1a)$$

$$X_V = 1 - X_A - X_C \text{ and } X_C = 1 - X_V \quad (1b)$$

$$X_V = \frac{7.691(I_V^{110})}{I_C^{104} + 7.691(I_V^{110})} \quad (1c)$$

X_A , X_C , and X_V are the molar fractions of aragonite, calcite, and vaterite in a mixture, respectively. I_A^{221} , I_C^{104} , and I_V^{110} are the intensities of the peaks of the 221 plane of aragonite, the 104 plane of calcite, and the 110 plane of vaterite respectively.

Reference:

1. C. G. Kontoyannis, N. V. Vagenas, *Analyst*, 2000, **125**, 251-255.