

## Supporting Information

### Mesoporous calcite by polymer templating

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[#] Laboratoire Chimie de la Matière Condensée, UMR 7574 CNRS – Université Pierre et Marie Curie, 12 rue Cuvier, 75005 Paris, France, Tel. ++33-1-4427-6552; Fax/++49-33-1-4427-6539, E-mail: [nassif@ccr.jussieu.fr](mailto:nassif@ccr.jussieu.fr),

### Experimental Details

The synthesis of the DHBC PEO-(RGD)<sub>5</sub> was carried out as follows: a solid-phase supported peptide synthesis was applied, using a PEO preloaded PAP-resin[D. Eckhardt, M. Groenewolt, E. Krause, H. G. Börner, *Chem. Commun.* **2005**, 2814; W. Rapp, in *Combinatorial Peptide and Nonpeptide Libraries*, (Ed: G. Jung), VCH, Weinheim, Germany **1996**, pp 425-464.] ( $M_n = 3200$  and  $M_w/M_n = 1.06$ ) and following HBTU/NMP/piperidine protocols.[ W. C. Chan, P. D. White, in *Fmoc Solid Phase Peptide Synthesis (a practical approach)*, OXFORD UNIVERSITY PRESS, Oxford, UK, **2000**.]

The repetition of an adhesive unit (RGD) for about 3 to 4 times is commonly used in biology and reflects the counter balance of binding strength and binding dynamics *e.g.* transport. Polyamines used in nature to complex and compress DNA are spermidine and spermine and possess 3 and 4 amine groups respectively, thus allowing sufficiently strong but reversible binding to the DNA cargo.[ L. C. Gosule, J. A. Schellman, *Nature* **1976**, 259, 333] Larger polyamines (pentamines and hexamines) are only used if stronger binding is required i.e. in extremely thermophilic bacteria.[K. Hamana, M. Niitsu, S. Matsuzaki, K. Samejima, Y. Igarashi, T. Kodama, *Biochem. J.* **1992**, 284, 741.]

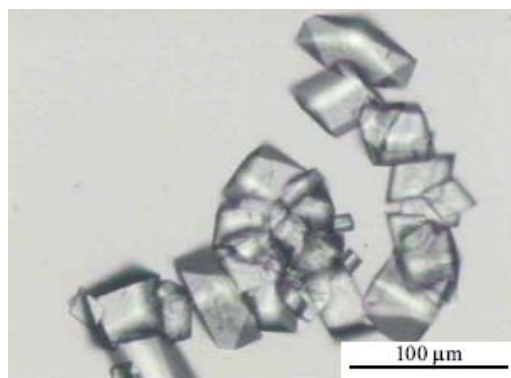
The chemical identity of the product was confirmed by mass spectrometry. Two homologous rows could be observed, assignable to the  $[(M-H)+2K]^+$  and  $[(M-2H)+2K+Na]^+$  adducts of **I** with an accuracy of about  $\pm 1$  Da. In addition to this a small amount of free dihydroxy PEO (H-PEO-OH) was detected. This results probably from an incomplete functionalization of the PAP resin. However, it can be neglected since PEO does not interfere strongly with the crystallization process.

Precipitation experiments were performed using the vapour diffusion method where the precipitation of calcium carbonate occurs *via* the diffusion of carbon dioxide vapour from the thermal decomposition of ammonium carbonate into a calcium chloride solution (0.1 M and 0.01 M). Different experiments were

carried out at room temperature ( $22^{\circ}\text{C} \pm 1$ ) with PEO-(RGD)<sub>5</sub> ( $1 \text{ g.L}^{-1}$ ) or RGD ( $10 \text{ g.L}^{-1}$ ) respectively, and stopped after 15 days. The initial pH of 5.8 rose to a stable 9.5 in the first hours of the reaction.

pH evolution versus time (Article Figure 5a) was performed according to the Kitano method [Kitano Y, Park K, Hood D W, *J. Geophys. Res.* **1962**, 67, 4873.] with and without polymer (PEO-(RGD)<sub>5</sub>, 1 g/l). A supersaturated solution of CaCO<sub>3</sub> was prepared by bubbling CO<sub>2</sub> gas through a solution of 5 g of CaCO<sub>3</sub> in 4 L of pure water for 60 min to shift the CaCO<sub>3</sub>/Ca(HCO<sub>3</sub>)<sub>2</sub> equilibrium toward the more water-soluble Ca(HCO<sub>3</sub>)<sub>2</sub>. The CaCO<sub>3</sub> was subsequently filtered off. Then, to dissolve any remaining CaCO<sub>3</sub> particles, CO<sub>2</sub> was bubbled through for another 30 min. 80 ml of this Kitano solution was transformed to a beaker and the pH evolution was measured under slight but constant stirring for both samples using a Metrohm Titrino 702. The solution pH increases because CO<sub>2</sub> is constantly removed from the solution. The CaCO<sub>3</sub> nucleation is indicated by a sharp pH drop. Comparing the start of nucleation in the experiments without (54 min) and with (124 min) polymer shows that the nucleation is significantly inhibited in presence of the polymer.

Titration of Ca<sup>2+</sup> into polymer solution (article Fig 5b) was performed by addition of CaCl<sub>2</sub> at a constant rate into 80 ml of a 1 mg/ml PEO-(RGD)<sub>5</sub> solution.

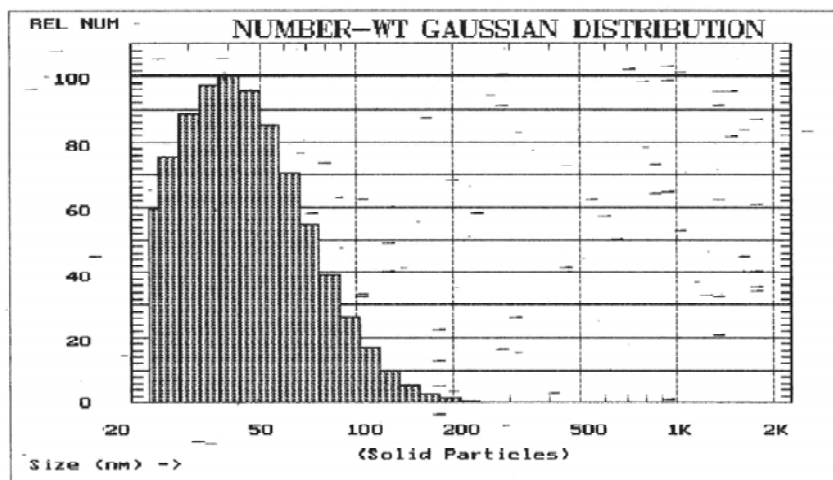


**Figure 1.** Classical rhombohedra crystals of calcite obtained under identical conditions in the presence of a PEO block.

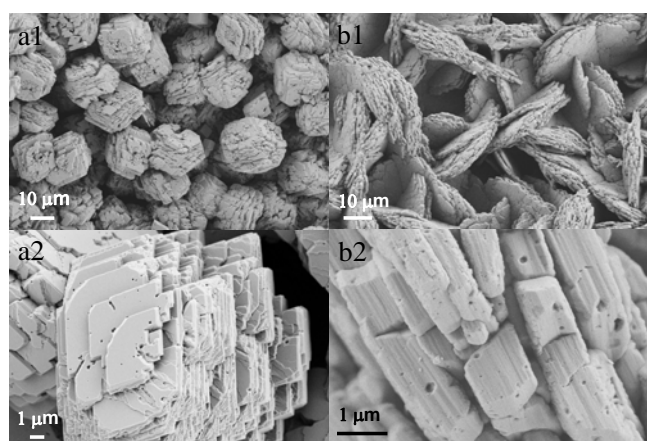
# NUMBER-Weighted GAUSSIAN Analysis (Solid Particles)

## GAUSSIAN SUMMARY:

Mean Diameter = 45.9 nm	Chi Squared = 0.876
Std. Deviation = 24.9 nm (54.3 %)	Baseline Adj. = 0.000 %
Coeff. of Var'n = 0.543	Mean Diff. Coeff. = 1.07E-07 cm <sup>2</sup> /s



**Figure 2.** DLS analysis of PEO-(RGD)<sub>5</sub> in the presence of 0.01 M CaCl<sub>2</sub>.

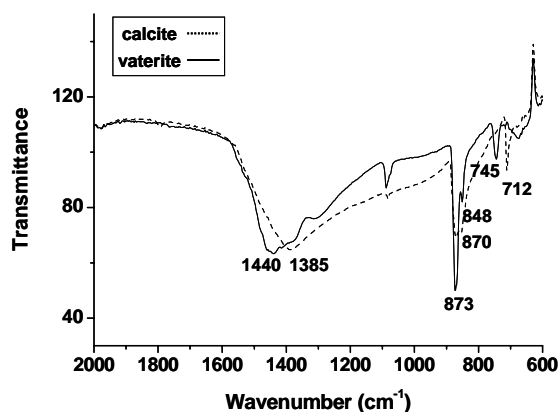


**Figure 3.** SEM images of layered calcium carbonate crystals obtained in the presence of the (RGD)<sub>5</sub>-PEO, for samples collected from the bottom (a) and the sides (b) of the flask. Low magnification images (a1, b1) show the homogeneity of the samples. At higher magnification (a2, b2), the layered texture of the crystals is evident and macropores can be observed.

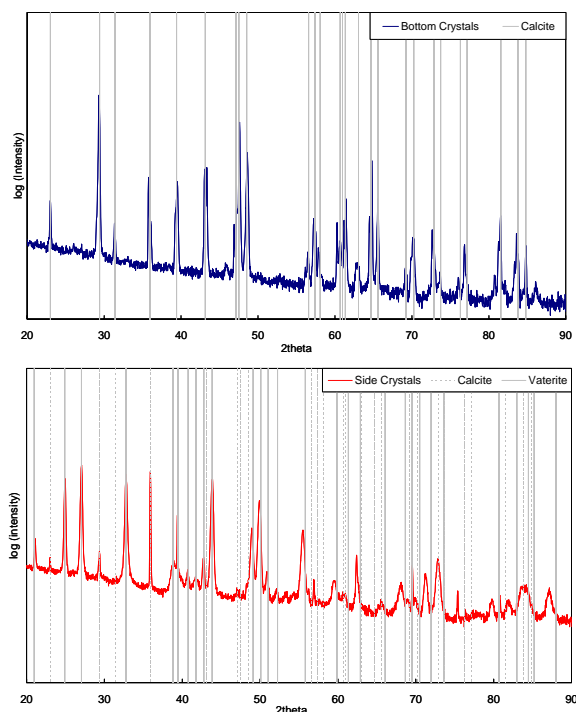
The compact, microparticulate structure of the layered rhombohedral calcite suggests homogeneous nucleation of the particles in solution, followed by three-dimensional growth and sedimentation to the bottom-glass surface (S.I. Fig. 6). On the other hand, the plate-like vaterite crystals are presumably formed by heterogeneous nucleation on the side-glass surface, as seen by the regular flat surface on one end with central 'hole' of around 4 microns (S.I. Fig. 5b) that probably results from the primary nucleation event along a polymer aggregate on the glass surface. [N. Nassif, N. Gehrke, N. Pinna, N. Shirshova, K. Tauer, M. Antonietti, H. Cölfen, *Angew. Chem. Int. Edit.* **2005**, *44*, 6004.]

Similar morphologies were found previously by precipitating calcium carbonate on the otolith (ear bone of teleost fish) surface asteriscus.[G. Falini, S. Fermani, S. Vanzo, M. Miletic, G. Zaffino, *Eur. J. Inorg. Chem.* **2005**, *1*, 162.] The vaterite crystals remained unchanged in aqueous solution for more than a month, whereas pure inorganic vaterite would transform into calcite within hours[A. Richter, D. Petzold,

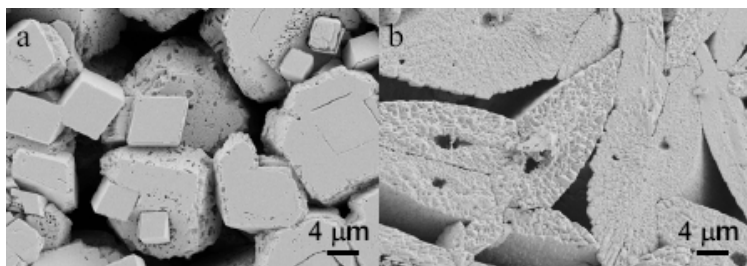
H. Hofmann, B. Ullrich, *Chem. Tech-Leipzig*, **1996**, 48, 271.] indicating that the conjugate also plays an important role in stabilizing the vaterite polymorph.[F. Lippman, in *Sedimentary Carbonate Minerals* (Eds: W. von Engelhardt, T. Hahn, R. Roy, P. J. Wyllie), SPRINGER, Berlin, Germany **1973**; W. D. Carlson, in *Reviews in Mineralogy*, Vol 11 (Ed: R. J. Reeder), MINERALOGICAL SOCIETY OF AMERICA, Blacksburg, USA, **1983**, p 191.]



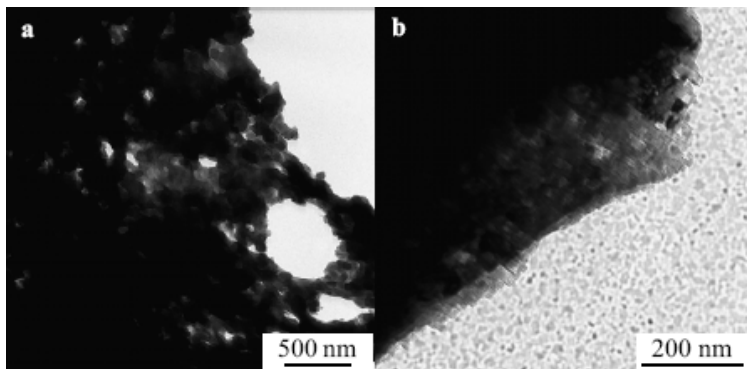
**Figure 4.** IR spectra showing characteristic vibrational bands at 745, 848 and 873 cm⁻¹ from vaterite (side crystals, solid line) and the singlet at 712 cm⁻¹ from calcite (bottom crystals, dashed line).



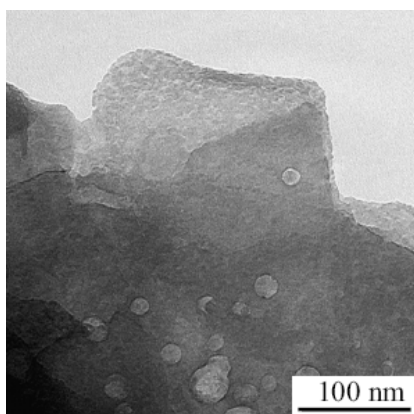
**Figure 5.** WAXS characterization of bottom-crystals showing pure calcite and side-crystals showing mixed vaterite/calcite.



**Figure 6.** (a) calcite, bottom-crystals and (b) vaterite, side-crystals, inverted to show the morphology of the underside of the crystals at the interface with the reaction container.



**Figure 7.** TEM of raw crystals showing (a) aggregated nanoparticles of vaterite (side) and (b) surface pores in calcite (bottom) crystals.



**Figure 8.** TEM of calcite grown in 10 g. L<sup>-1</sup> RGD (without the PEO block). Though these pores appeared occasionally, in the same 10-50 nm size range as for the polymer-peptide conjugate, they were not widespread as in the crystals grown with PEO-RGD<sub>5</sub>.