Electronic Supplementary Information

Hollow calcite rhombohedra at ionic liquid-stabilized bubbles

Magdalena Kowacz[a]*, José N. Canongia Lopes[a,b], José M. S. S. Esperança[a] and Luís Paulo N. Rebelo[a]*

[a] *Instituto de Tecnologia Química e Biológica, www.itqb.unl.pt, Universidade Nova de Lisboa, Av. da República, 2780-157 Oeiras, Portugal. Fax: +351 - 21 4411 277; Tel: +351 - 21 4469 413 / 441;* * *E-mail: magda@itqb.unl.pt; luis.rebelo@itqb.unl.pt*
[b] *Centro de Química Estrutura, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal. Fax: +351 – 218464455; Tel: +351 - 218419261*

Crystallization experiments

The crystallization of $CaCO_3$ was induced by mixing equally concentrated solutions of Na_2CO_3 and $CaCl_2$ in the presence of an ionic liquid (IL): 1.0 ml of a 0.1 M solution of a given IL was mixed with 400 µl of a 0.01 M solution of Na_2CO_3 and subsequently 400 µl of a 0.01 M solution of $CaCl_2$ were added. Prior to the addition of the $CaCl_2$, the mixture (Na_2CO_3 plus IL) was vigorously shaken in a sealed reaction vessel, until turbidity revealed the generation of air bubbles. The aqueous $CaCl_2$ solution was immediately injected into the fresh mixture. In a parallel set of experiments the IL-Na_2CO_3 mixture was allowed to settle before adding the $CaCl_2$. The aliquots of the reacting mixtures were filtered by a 0.2 µm pore diameter membrane filter immediately after the reaction had been induced and, in some cases, after specific periods of time (between 7 and 30 days). The filters were washed by Milli-Q water, air-dried, gold coated and analyzed with scanning electron microscopy (SEM).

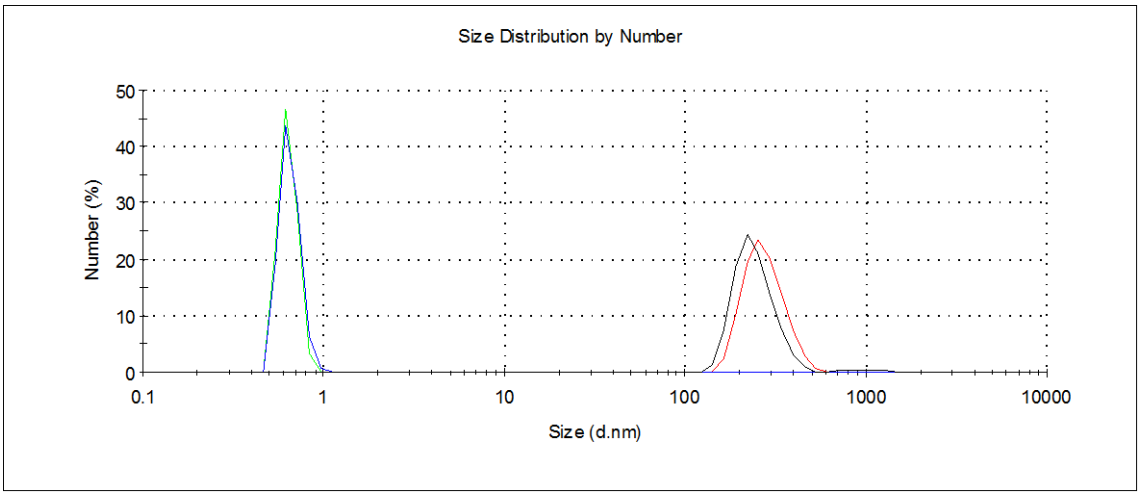

Figure S1. Representative results of dynamic light scattering (DLS) experiments showing particle size distribution in non-shaken (light green- [EMIM][C_2SO_3] + Na_2CO_3; blue - [Ch][C_1SO_3] + Na_2CO_3 + $CaCl_2$) and shaken systems (black - [EMIM][C_2SO_3] + Na_2CO_3; red – Milli-Q water). The size of the particles (0.6 nm) that could be detected in pure IL solutions and in IL+ salt(s) systems without air bubble generation corresponds approximately to the size of the bulky IL ions. Manual shaking of the pure IL or IL+ Na_2CO_3 mixture resulted in the formation of particles (air bubbles) with sizes similar to those of air bubbles generated in Milli-Q water. In all cases, [IL] = 60 mM, [$CaCl_2$]=[Na_2CO_3] = 2 mM. Results of separate measurements are superimposed on the image.

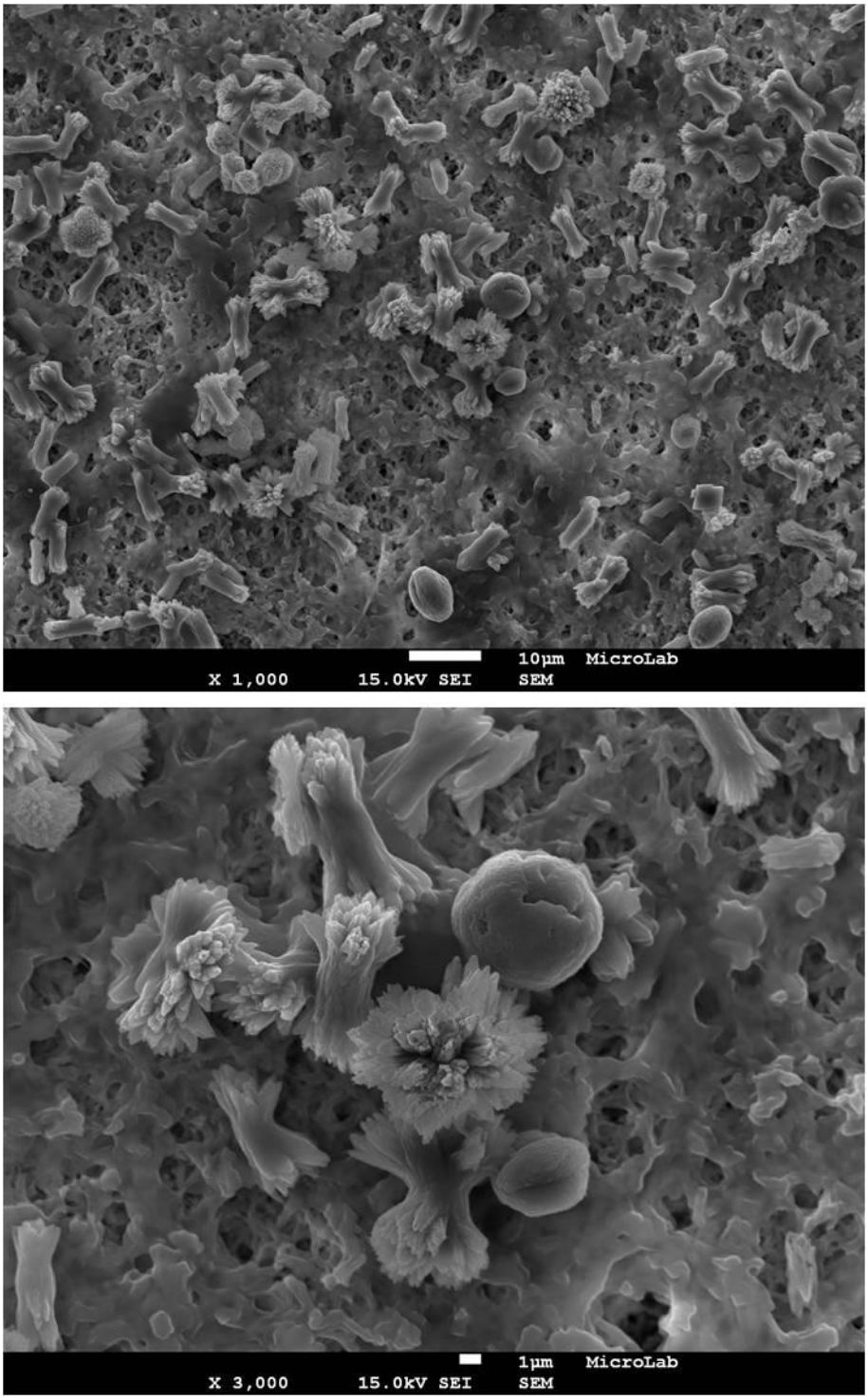

Figure S2. SEM image presenting $CaCO_3$ particles generated in solution shaken for 3 minutes in the course of the crystallization process (after mixing [EMIM] $[C_2SO_3]$= 60 mM and $[CaCl_2]$=$[Na_2CO_3]$ = 2 mM) . Bunches of predominantly needle-shaped crystals, corresponding to the morphology of aragonite, can be observed.