Electronic Supplementary Information

Hollow calcite rhombohedra at ionic liquid-stabilized bubbles

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Crystallization experiments

The crystallization of CaCO\textsubscript{3} was induced by mixing equally concentrated solutions of Na\textsubscript{2}CO\textsubscript{3} and CaCl\textsubscript{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\textsubscript{2}CO\textsubscript{3} and subsequently 400 µl of a 0.01 M solution of CaCl\textsubscript{2} were added. Prior to the addition of the CaCl\textsubscript{2}, the mixture (Na\textsubscript{2}CO\textsubscript{3} plus IL) was vigorously shaken in a sealed reaction vessel, until turbidity revealed the generation of air bubbles. The aqueous CaCl\textsubscript{2} solution was immediately injected into the fresh mixture. In a parallel set of experiments the IL-Na\textsubscript{2}CO\textsubscript{3} mixture was allowed to settle before adding the CaCl\textsubscript{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][C₂SO₄] + Na₂CO₃; blue - [Ch][C₆SO₄] + Na₂CO₃ + CaCl₂) and shaken systems (black - [EMIM][C₂SO₄] + Na₂CO₃; 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+ Na₂CO₃ 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, [CaCl₂]=[Na₂CO₃] = 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$_2$SO$_4$]= 60 mM and [CaCl$_2$]=[Na$_2$CO$_3$] = 2 mM). Bunches of predominantly needle-shaped crystals, corresponding to the morphology of aragonite, can be observed.