Supporting Information

Implementation of *in situ* SAXS/WAXS characterization into a silicon/glass microreactor

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S1 : SAXS and WAXS images at different positions along the *z*-axis of the channel.

S2 : SAXS images at different times for a given position in the channel.

S3 : SAXS images of the calcite particles of large size cannot reveal the Kiessig fringes.

S4 : Vaterite and calcite particles are visible on a WAXS image of the channel.

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S6 : On the scattered intensity of a rhombohedron.

S1: SAXS and WAXS at different positions along the *z*-axis of the channel.

During the main study reported in the paper for the counter-injection of the two solutions $([CaCl_2] = 0.010 \text{ M} \text{ and } [Na_2CO_3] = 0.010 \text{ M})$ at flow rates of 20 µL.min⁻¹, we have controlled that the Crystal truncation rods (i.e. the streaks) observed in previous Figure 4 at z = 1 mm are present everywhere along the x = 0 axis of the main channel. For instance, in Figure S1-A, the SAXS image obtained at z = 5 mm is shown in part (a). Similar images in (b) and in (c) are recorded at z = 10 mm and z = 20 mm, respectively. The corresponding inserted zones are magnified in the right side. These magnified images reveal periodicities (i.e. Kiessig fringes) along the streaks, from which we can also deduce the micrometric size of the calcite particles encountered in the corresponding illuminated volumes by the X-ray beam of 50 µm x 50 µm cross-section. Moreover, we can note that the images are recorded few minutes from starting time of the counter-injection of the two aqueous solutions of 0.010 M reagents. However, the precise time is difficult to determine. We can precise that the image (a) is obtained 3 minutes after the image (b) which is recorded 6 minutes after the image (c).

At the same time of the SAXS analysis, the WAXS images were recorded and shown in Figure S1-B for (a) z = 5 mm, (b) z = 10 mm and (c) z = 20 mm. This reveals that the orientation of the calcite crystals has a strong influence on the diffraction peak positions and intensities.



Figure S1-A : *In situ* SAXS images obtained at x = 0, and (a) z = 5 mm, (b) z = 10 mm and (c) z = 20 mm and recorded after the mixing of the 2 reagent (0.010 M) aqueous solutions. Magnified inserted zones of (a), (b) and (c) are shown in the right side (see areas with white dashed borderline).



Figure S1-B : *In situ* WAXS images obtained at x = 0, and (a) z = 5 mm, (b) z = 10 mm and (c) z = 20 mm and recorded after the mixing of the 2 reagent (0.010 M) aqueous solutions.

S2: SAXS images at different times for a given position in the channel.

We can also note that whatever the time of reaction, similar SAXS images are obtained as shown in figure S2 at z = 20 mm. Image (a) in figure S2 is obtained ~ 1 minute after starting the injection of the two aqueous solutions at the 20 µL.min⁻¹ constant flow rate whereas the similar image (b) is obtained ~ 4 minutes after the acquisition of image (a). Zooms of the inserted profiles are displayed at the right panel, which allow to select the truncation crystal rods corresponding to the (dashed black) streak and to extract the corresponding size of the calcite crystal from its fine periodicity. In (a), we obtain a size of $4.06\pm0.02\mu$ m which is similar to the one obtained in (b) $4.05\pm0.02\mu$ m. It is clear that despite the continuous flow of the two solutions, the size of the calcite particle doesn't change. This tends to prove that calcite particles are formed very fast and, as soon as they are formed, they are certainly precipitated and attached to the wall, leading to the SAXS images obtained at a given position in the channel independent of the acquisition time.



Figure S2: In situ SAXS images recorded (a) ~ 1 minute after starting the injection of the 2 reagents and (b) ~ 4 minutes after the acquisition of image (a). The position x, z are almost similar for the 2 images, (a) x = 0.000 mm and z = 20 mm, and (b) at x = 0.005 mm and z = 20 mm. Magnified inserted zones of (a) and (b) are shown in right (see areas with white dashed borderline). Insets of the magnified zones display the profiles of the truncation rods from which we can determine the size of the calcite crystal, $4.06\pm0.02\mu$ m and $4.05\pm0.02\mu$ m for the top and the bottom profiles, respectively.

S3: SAXS images of the calcite particles of large size cannot reveal the Kiessig fringes.

After washing the channel, a similar experiment as the one shown in the main article was performed. The two reagent aqueous solutions ($[CaCl_2] = 0.010$ M and $[Na_2CO_3] = 0.010$ M) are now injected again at ambient temperature but at a constant low flow rate of 5µL.min⁻¹, i.e., a flow speed of ~1.3 mm.s⁻¹ in the main mixing channel of the microreactor. A SAXS image obtained at x = 0, z = 0.150 mm is shown in Figure S3(a). Only two main streaks are observed. This low number of streaks means that a few microparticles are located in the illuminated volume by the X-ray beam as shown in S5. Moreover, an angle of 76° can be clearly identified by the dash lines on this SAXS image. This angle is similar as the one between the faces of the rhombohedron of calcite. We can thus assume that such particle is lying down on the wall of the microreactor, either in contact with silicon wafer or in contact with the glass lid. Futhermore, in the magnified image (b) of the inserted zone of (a) (see area with white dash borderline), it is no more possible to observe the periodicity (i.e. the Kiessig fringes) with such a typical calcite particle. This leads to assume that its size is certainly too large to be measured.



Figure S3: (a) SAXS image of one (at least) calcite particle obtained at x = 0, z = 0.150 mm. (b) Zoom of the inserted zone of (a) (area with a white tireted borderline). No oscillation was observed along the streaks of this SAXS image.

Indeed, the limitation in the detection of the oscillating fringes is function of the pixel size of the detector and the distance sample to detector. The total detector size is 107.5 mm x 107.5 mm (the detector has 2150 pixels in each direction and each pixel has a size of $50\mu m \times 50\mu m$). Placed at 10 m from the sample, this corresponds to a scattering angle of

 $\theta = \operatorname{atan}(0.1075/(2*10)) = 5.35\ 10^{-4}\ rd$

Thus, the wavevector transfer defined by

$$q = \frac{4\pi\sin(\theta/2)}{\lambda}$$

covers the range -0.337 nm⁻¹ to 0.337 nm⁻¹ in each direction. The distance between two pixels in the reciprocal space is $\Delta q_{min} = 0.674 / 2150 = 0.000623$ nm⁻¹ in each direction. The maximum size Λ_{max} of the particle may be defined by $\Lambda_{max} = \pi / \Delta q_{min} = 10.0 \mu m$. We can thus easily understand that by putting the SAXS detector further than 10 m, the resolution will be increased. A recent ID02 line upgrading will allow the use of a sample-to-detector distance of 30 m (USAXS analysis) leading to $\Lambda_{max} = 30.0 \ \mu\text{m}$. Note that this simple calculation of the limit size of a particle doesn't include the limitation induced by the divergence of the beam. In figure S3, in addition to the presence of the streaks, a radial scattering is observable which originates from the presence of spherical objects like vaterite microspheres as shown in S4.

S4: Vaterite and calcite particles are visible on a WAXS image of the channel.

The WAXS image shown in Figure S4(a) was obtained at the same position and at the same time as SAXS image shown in Figure S3. First, three diffraction peaks with high intensity have been clearly identified inside the black tireted circles (with one labelled by a probable oriented-particle of calcite), which confirms the possibility that only one calcite polycrystalline particle is seen by the X-ray beam at this position. Indeed a zoom of the (-114) peak (not shown here) reveals 4 diffraction peaks. This may come from the fact that the particle is certainly made of polycrystal domains slightly tilted. Note also that, contrary to WAXS image of Figure 3 with the (-120) peak of high intensity, the present orientation of the calcite polycrystal particle is such that the (-114) peak at $q_z = 20.7$ nm⁻¹ exhibits here a high intensity.

Second, the WAXS image (a) reflects similar broad scattering contributions, in particular due to the glass lid at $q \sim 15 \text{ nm}^{-1}$ (see also Figure 3 (a)). In addition, four scattering rings can be also noticeable in (a) and labelled as vaterite (see arrows), assuming the presence of vaterite microspheres in the illuminated volume by the X-ray beam. Indeed, the intensity profile given in (b) after azimuthal averaging of the two-dimensional WAXS image, shows first the diffraction peaks due to calcite particle, while, after subtraction of background image due to the microreactor filled with water, the intensity profile displayed in (c) only reveals the difference of crystallinity of the CaCO₃ particles. The five small peaks at q = 17.6, 19.0, 22.9, 30.4, and 34.4 nm⁻¹ confirm the presence of vaterite, and the two large peaks at $q = 20.7 \text{ nm}^{-1}$ and 32.8 nm⁻¹ are due to the presence of calcite.



Figure S4: (a) WAXS image taken at the same time and the same place as the SAXS image shown in figure S3(a). (b) Intensity profile after azimuthal averaging of the two-dimensional WAXS image (where the silicon contribution is assumed negligible). (c) Scattered intensity from CaCO₃ polycrystal particles only (wavevector transfer numbers are for (rhombohedron) calcite (red) and (spherical) vaterite (blue).

S5: At low flow rate and large residence time, $CaCO_3$ particles can reach a typical size larger than 10 μ m.

After the *in situ* analysis shown in S3 and S4, the 2 flows are stopped after 140 min of flowing time, and the channel was subsequently analyzed by X-ray in transmission with a beam size of 50 μ m x 50 μ m. The X-ray radiographies of the T-junction obtained in this complementary experiment at low flow rate and large residence time are shown in Figure S5. The X-ray mapping image in transmission of the initial empty channel corresponds to (a), while the one obtained after the mixing flows stop corresponds to (b). For additional comparison, the optical microscopic image obtained in similar ending flow conditions is given in (c). Particles in the size-range of 10 μ m are clearly visible as well as by X-ray imaging as by optical microscopic imaging. The magnification of the inserted zones with white continuous borderline in (b) and (c) are shown in (d) and (e), respectively, which confirm that the particle sizes have reach values larger than 10 μ m, i. e., significantly bigger than the typical particle sizes observed in Figure 5.



Figure S5: (a) X-ray transmission image of the T-junction through the empty channel; (b) and (c) X-ray and optical microscopic transmission images, respectively, after 140 min of reagent solution mixing at a flow rate of 5 μ L.min⁻¹. (d) and (e) Zooms of the inserted zones (see areas with white continuous borderlines) of (b) and (c), respectively. The scale bar is 250 μ m.

S6: On the scattered intensity of a rhombohedron

The figure S6(a), similarly to Figure 4-c, shows the simulation of the scattered intensity of a rhombohedron of size $a = 2.0 \ \mu m$ (along <u>x</u>), $b = 1.5 \ \mu m$ and c = 1.0 (in the *xz*-plane), with $\alpha = 76^{\circ}$, in a 3 dimensional view (with an isocontour of I_{max} / 400). Futhermore, a rotation of the rhombohedron is done around the q_x axis from 10° to 80° (Figures S6 (b-f)). The simulation highlights the importance of the orientation of the rhombohedron in the scattered intensity.



Figure S6 : Simulation of the scattered intensity of a rhombohedron particle of $a = 2.0 \,\mu\text{m}$ (along \underline{x}), $b = 1.5 \,\mu\text{m}$ and c = 1.0, with $\alpha = 76^{\circ}$. Rotations of the rhombohedron at different angles around q_x ((a) 0°, (b) 10°, (c) 20°, (d) 40°, (e) 60° and (f) 80°).