Versatile wet-chemical synthesis of non-agglomerated CaCO₃ vaterite nanoparticles

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Supporting Information

Fig. S1. FT-IR-spectra of (i) SDS- and (ii) non-functionalized CaCO₃ nanoparticles.
Fig. S2. FT-Raman data monitoring the vaterite→calcite phase transformation.
**Fig. S3.** (a) X-Ray data monitoring the vaterite→calcite phase transformation. (b) TEM micrograph of a sample taken after the transformation.

**Fig. S4.** Pawley Fit data of Vaterite-Nanoparticles prepared by ultrasonic reaction. Crystallite size: Vaterite 25 nm.
Fig. S5. Pawley Fit data of Vaterite-Nanoparticles prepared by microwave reaction. Crystallite size: Vaterite 27 nm, Calcite 75 nm.

Fig. S6. Pawley Fit data of Vaterite-Nanoparticles prepared by conventional oilbath heating reaction. Crystallite size: Vaterite 27 nm, Calcite 58 nm.
Fig. S7. Transmission electron microscopy images of vaterite nanoparticles prepared by ultrasonic reaction.

Fig. S8. Transmission electron microscopy images of vaterite nanoparticles prepared by microwave reaction.

Fig. S9. Transmission electron microscopy images of vaterite nanoparticles prepared by conventional oilbath heating reaction.
Fig. S10. Transmission electron microscopy images of calcitic particles prepared by direct ultrasonic reaction of calcium chloride and sodium carbonate

Calculation of the particle-size with the Sauter-Formula:

\[ D = \frac{6000}{\rho \times S} \]

\((D = \text{Diameter}, \ \rho = \text{density of vaterite (2.65g/cm}^3) \text{and S = surface determined by BET-measurements)}\)
The thermal stability and the degree of crystallinity were measured by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The transformation to calcite was observed as an exothermic event at 492°C (Fig. 4) which is somewhat higher than that of ground vaterite (478°C). In contrast, the phase transition enthalpy of vaterite to calcite is smaller than that of bulk (about 11 J/g to 25 J/g). Above 520°C the sample decomposes, as indicated by a weight loss in the TGA. A comparison of the XRD patterns (Supporting Information Fig. S3a) before and after heat treatment lends further support to the phase transformation vaterite → calcite. TEM images of calcium carbonate nanoparticles before (Fig. 1) and after sintering (Supporting Information, Fig. S3b) show the change in morphology. In FT-Raman-spectra (Fig. S2, see Supporting Information), Samples taken before heating exhibit vibration bands at 740 and two single bands at 1075 and 1090 cm⁻¹, which can be assigned to vaterite, whereas the vibration bands at 173 and 1086 cm⁻¹ indicate the transformation to calcite.

Fig. S10. Thermal analysis of calcium carbonate nanoparticles upon heat treatment. Transformation to Calcite occurs at 492°C with a phase transition enthalpy of 11 J/g. The sample decomposes to Calcium oxide above 580°C.

References