Supplemental Materials

Efficiently Stabilized Spherical Vaterite $CaCO_3$ Crystals by Carbon Nanotubes in Biomimetic Mineralization

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S1. Preparation of SWNT-COOH

Typically, pristine SWNTs (1.0 g) were suspended in 20 mL of 60% HNO_3 and 98% H_2SO_4 solution (1:3 by vol.) in a 100 mL flask. The solution was sonicated in a bath (40 kHz) for 10 min, and then stirred for 2 h under reflux in an oil bath (130 ^oC). The solution was subsequently cooled to room temperature and diluted with deionized water (ca. 100 mL) and vacuum-filtered. The solid was redispersed in deionized water and filtered until the pH of the filtrate reached 7. After dried under vacuum for 20 h at 80 °C, carboxylic acid-functionalized SWNT (SWNT-COOH) was obtained.

S2. Mineralization of $CaCO_3$ in the Presence of SWNT-COOH

Stable uniform spherical vaterite crystals with a size of 4.5 ± 1.0 μm (about 50% of the particles with a diameter of *ca.* 4.5 μm) are also obtained, with SWNT-COOH coating on the surface of $CaCO_3$. It is noteworthy that the critical ratio of SWNT-COOH to $CaCl_2$ (1/3 wt) is higher than that (1/7 wt) of MWNT-COOH to $CaCl_2$. This is likely due to the much less defects and smaller diameter of SWNTs than those of MWNTs. The vaterite phase can also be confirmed by X-ray

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diffraction patterns. The Bragg reflection peaks for vaterite phase can be detected at the 2θ angles of *ca.* 21.0°, 24.9°, 27.0°, 32.8°, 43.8°, 50.1°, 55.8°.

Figure S1. TEM and SEM images of MWNT-g-PHEMA-COOH.

Figure S2. SEM images of mineralized $CaCO_3$ crystals in the presence of MWNT-COOH at the reaction time of 30 min.

Figure S3. SEM images (a, b), size distribution (c), and XRD patterns (d) of $CaCO_3$ crystals formed in the presence of SWNT-COOH.

Figure S4. SEM images and XRD patterns of $CaCO_3$ crystals formed in the presence of annealed MWNTs with the concentration of annealed CNTs /$CaCl_2$ 50mg/138.75mg at the reaction time of 30min (a, b) and 10 h (c, d). The scale bars in images of a, b, c and d represent 1, 1, 10 and 10 μm, respectively.

Figure S5. SEM images and XRD patterns of $CaCO_3$ crystals formed in the presence of PAA-Na with the concentration of PAA-Na/$CaCl_2$ 7 mg/138.75 mg at the reaction time of 7 h. The scale bar in the image represents 1 μm.

Figure S6. The "off line" TEM images of MWNT-COONa (a) and $CaCO_3$ crystals formed in the presence of MWNT-COONa with concentration of MWNT-COONa/$CaCl_2$ 20 mg/138.75mg at 1 min (b-d), 3 min (e), 5 min (f) and 30 min (g).

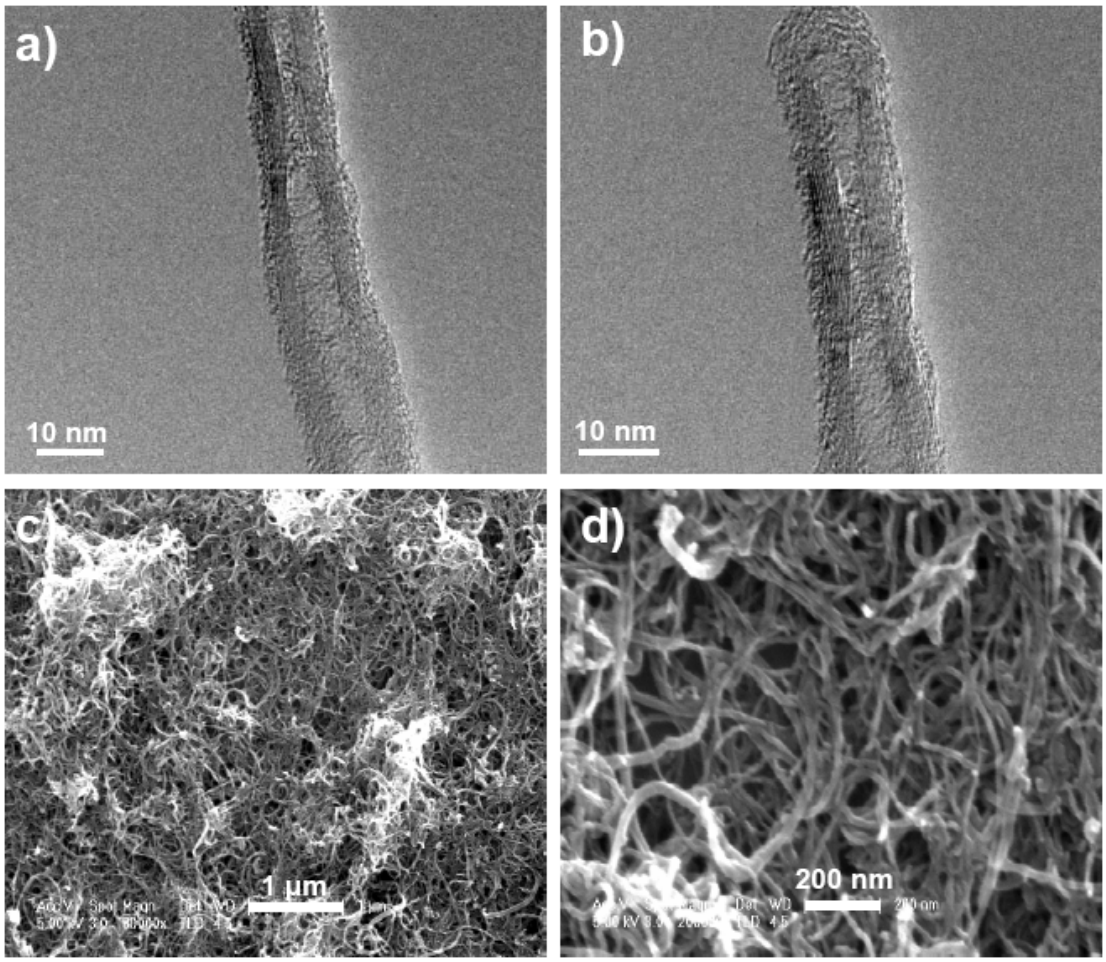

Figure S1. TEM (a, b) and SEM images (c, d) of MWNT-*g*-PHEMA-COOH.

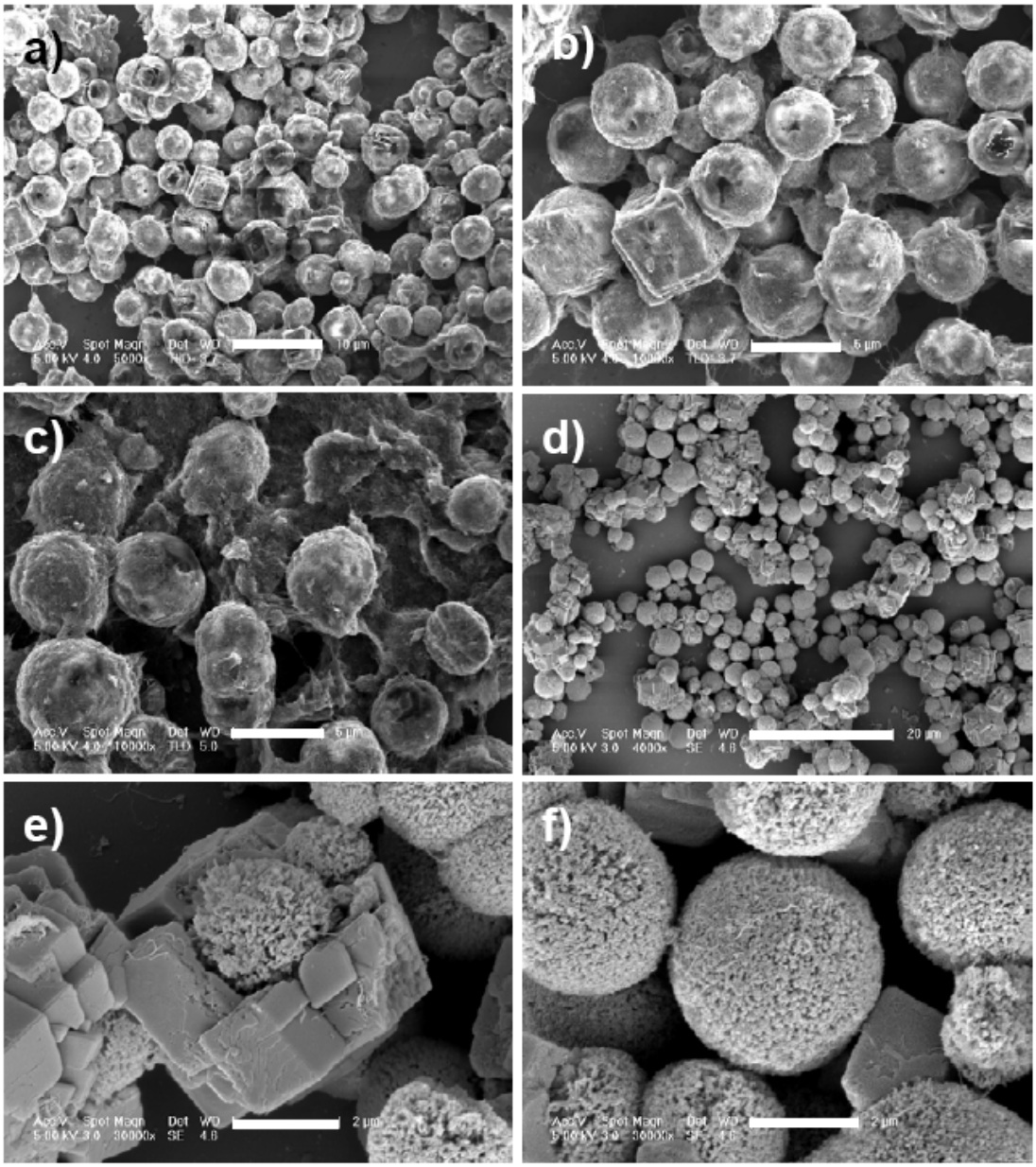

Figure S2. SEM images of mineralized $CaCO_3$ crystals in the presence of MWNT-COOH at 30 min of reaction time. The feed ratios of MWNT-COOH to $CaCl_2$ are 20 mg/69.4 mg (a, b), 20 mg/34.7 mg (c), and 4mg/138.75 mg (d-f). The scale bars in images of a, b, c, d, e and f represent 10, 5, 5, 20, 2 and 2 μm, respectively.

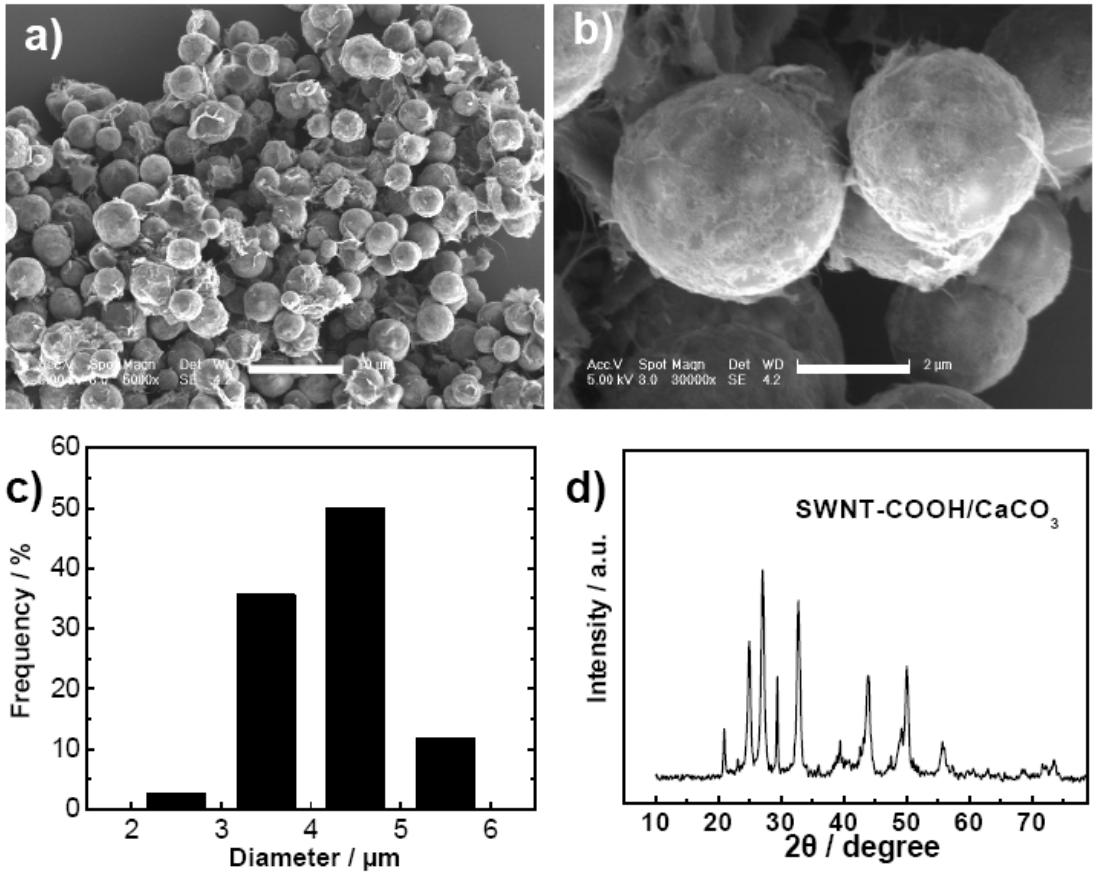

Figure S3. SEM images (a, b), size distribution (c), and XRD patterns (d) of $CaCO_3$ crystals formed in the presence of SWNT-COOH with the concentration of SWNT-COOH/$CaCl_2$ 50mg/138.75mg at 30min of reaction time. The scale bars in images of a and b represent 10 and 2 μm, respectively. It is noteworthy that more SWNT-COOH was needed to stabilize the vaterite phase than MWNT-COOH. This is likely due to the much less defects and smaller diameter of SWNTs than those of MWNTs, which means that there are less functional groups on the surfaces of SWNT-COOH. The critical ratio of SWNT-COOH to $CaCl_2$ is ca. 1/3 by mass.

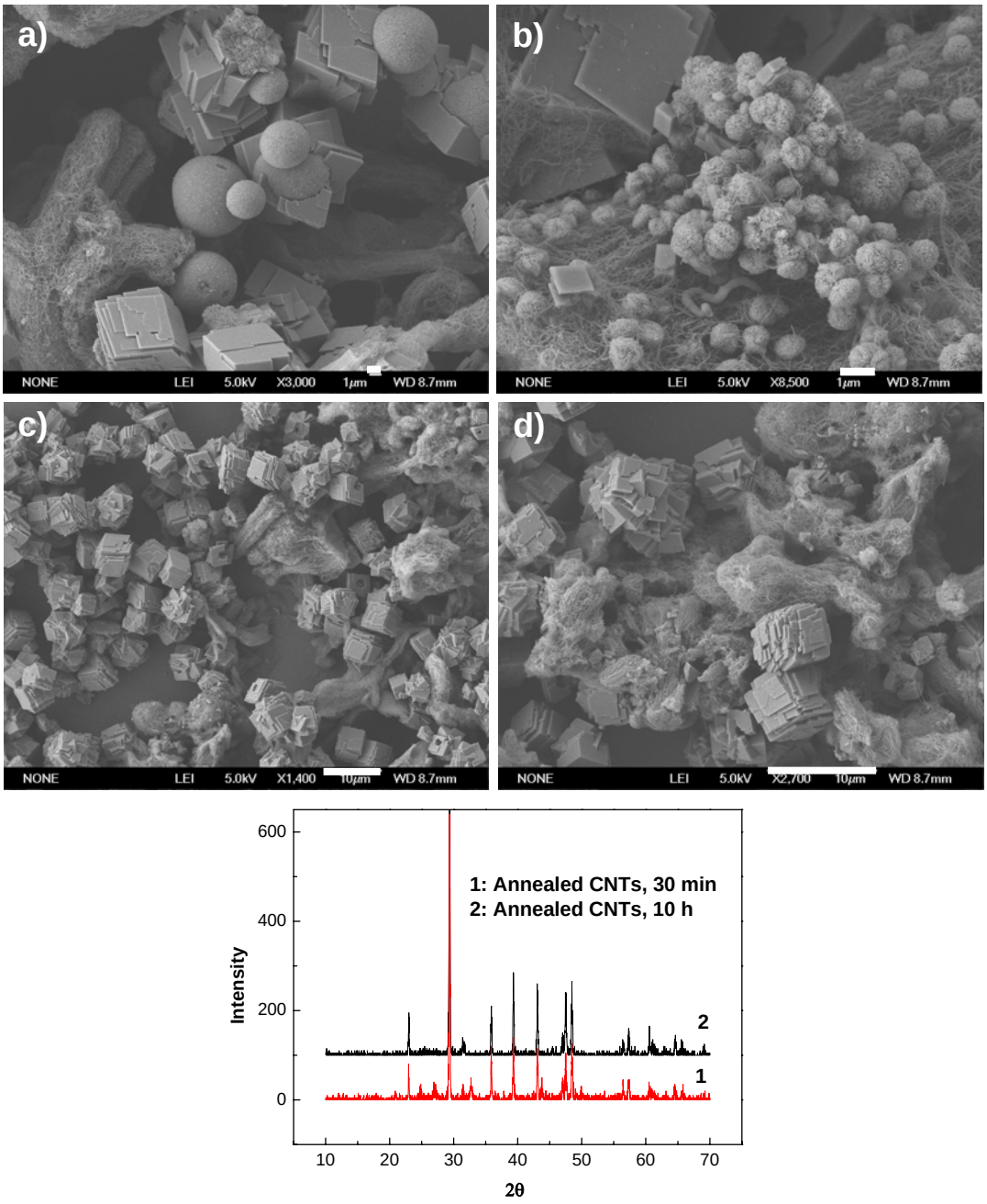

Figure S4. SEM images and XRD patterns of $CaCO_3$ crystals formed in the presence of annealed MWNTs with the concentration of annealed CNTs /$CaCl_2$ 50mg/138.75mg at the reaction time of 30 min (a, b) and 10 h (c, d). The scale bars in images of a, b, c and d represent 1, 1, 10 and 10 μm, respectively.

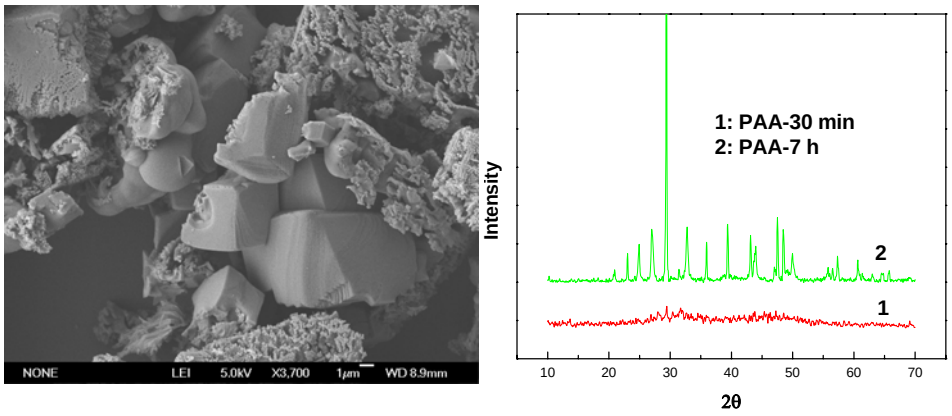

Figure S5. SEM images and XRD patterns of $CaCO_3$ crystals formed in the presence of neat PAA-Na with the concentration of PAA-Na/$CaCl_2$ 7 mg/138.75 mg at the reaction time of 7h. The scale bar in the SEM image represents 1 μm.

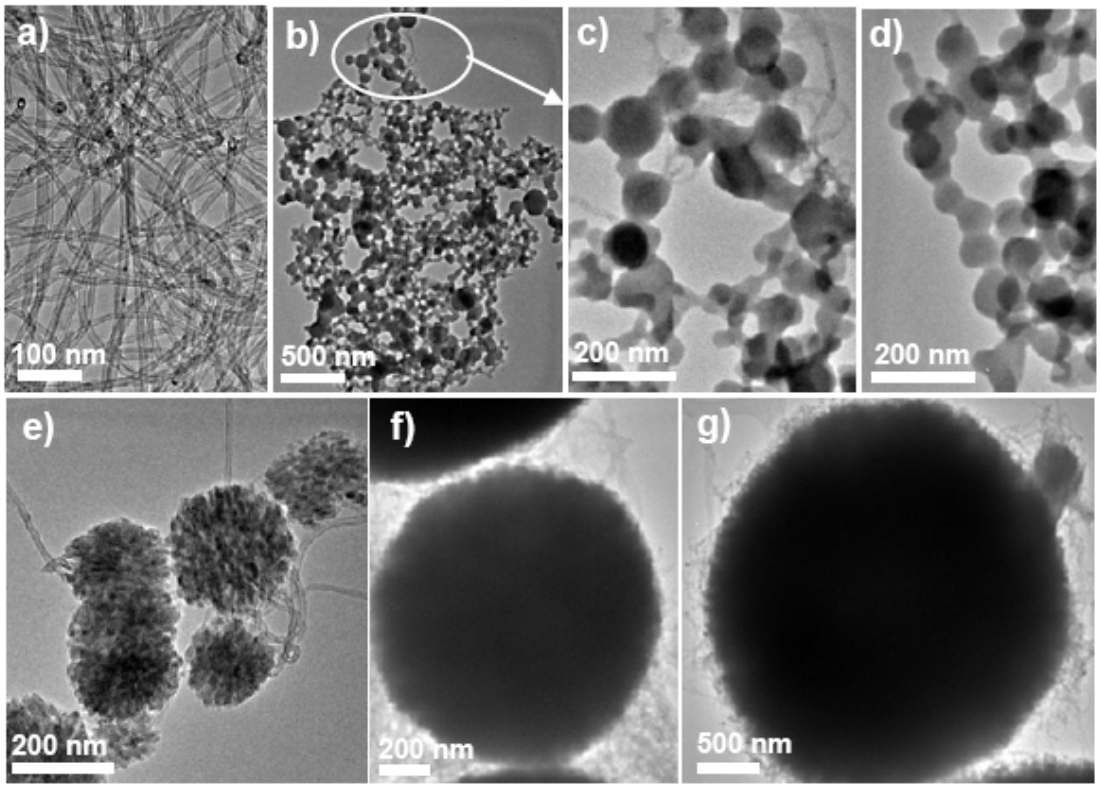

Figure S6. The "off line" TEM images of MWNT-COONa (a) and $CaCO_3$ crystals formed in the presence of MWNT-COONa with concentration of MWNT-COONa/$CaCl_2$ 20 mg/138.75 mg at 1 min (b-d), 3 min (e), 5 min (f) and 30 min (g).