

Figure S1 Potentiometric titration assays in the presence of ASM with different concentrations, respectively. (a) Development of the free Ca^{2+} concentration as a function of time. The dashed black line represents the concentration of with Ca^{2+} during titration. (b) Corresponding free ion solubility products, calculated under the assumption that Ca^{2+} and CO_3^{2-} bind in equimolar ratios in both the pre- and post-nucleation stage. Dotted lines of different colors indicate the solubility of the initially precipitated phase in the presence and absence of ASM. ‘I’ depicts the prenucleation stage. ‘II’ the nucleation stage, and ‘III’ shows the CaCO_3 particle growth stage.

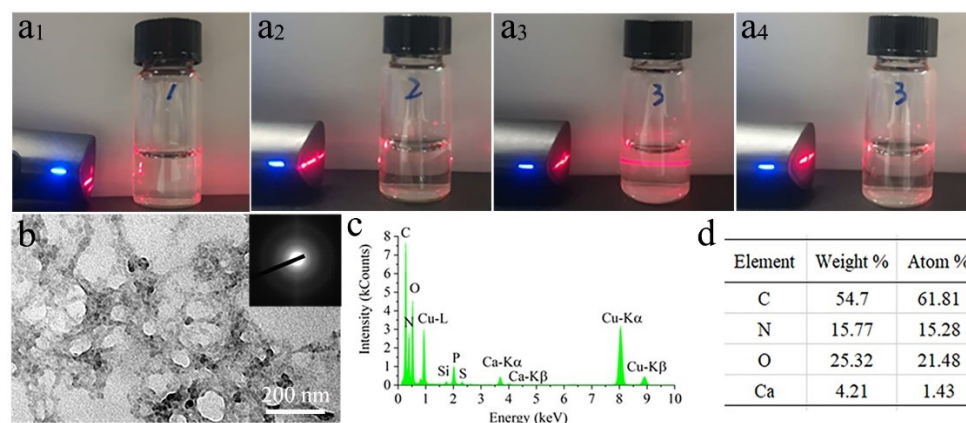


Figure S2. Characteristics of binding interaction between ASM and Ca^{2+} . (a₁-a₄) Photo showing the Tyndall effect in solutions with different compositions: (a₁) addition of the ASM at concentrations of 10 $\mu\text{g/mL}$ of 4 mL, (a₂) addition of 5 mM CaCl_2 of 4 mL, (a₃) ASM immediately mixed with CaCl_2 solution to an ultimate ASM concentration of 10 $\mu\text{g/mL}$, CaCl_2 concentration of 5 mM, (a₄) direct addition of 5 mM EDTA of 2 μl in (a₃). (b), TEM images of agglomerates with the SAED patterns

as insets. (c and d) EDS spectra and table for the elemental relative contents of the agglomerates.

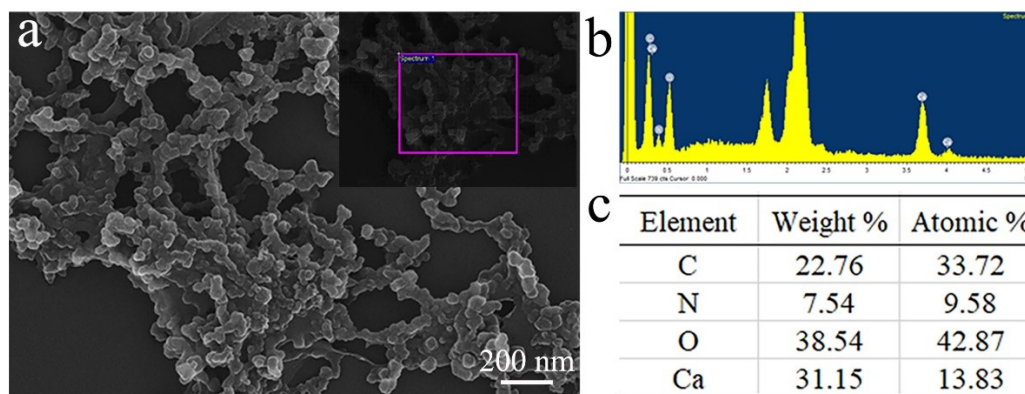


Figure S3. Characterization of the obtained nanoparticles collected from the reaction solutions after 2 hours' reaction time under otherwise standard condition. (a) SEM image. Inset shows a selected area of the nanoparticles for EDS analysis. (b and c) EDS spectra and table for the elemental relative contents of the agglomerates.

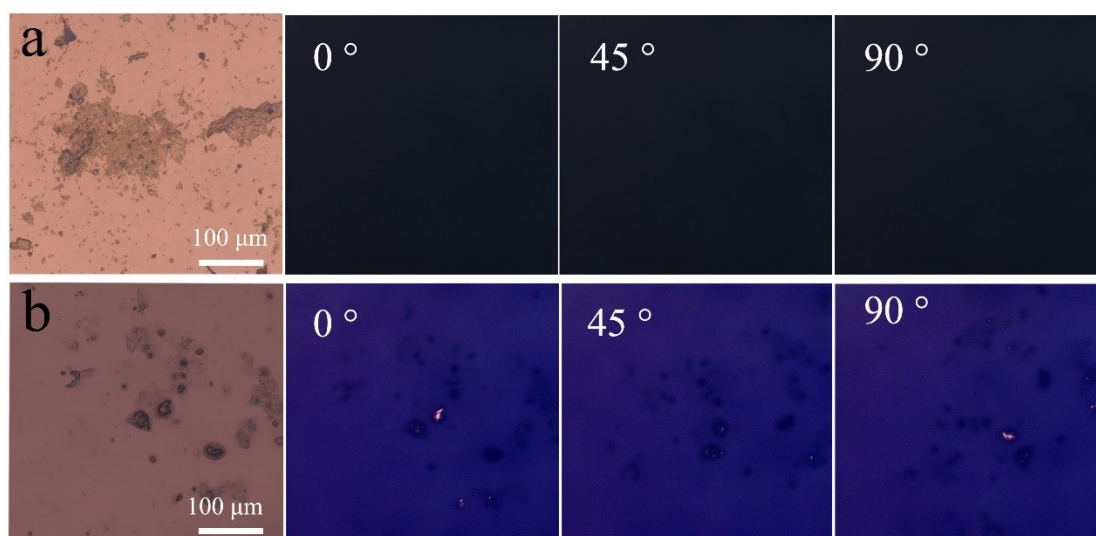


Figure S4. Polarized light microscopy images of the obtained nanoparticles collected from the reaction solution under standard conditions. (a) Image of the nanoparticles prepared for 2 h. (b) Image of the nanoparticles obtained under 100% room humidity (RH) at room temperature for 48 h.

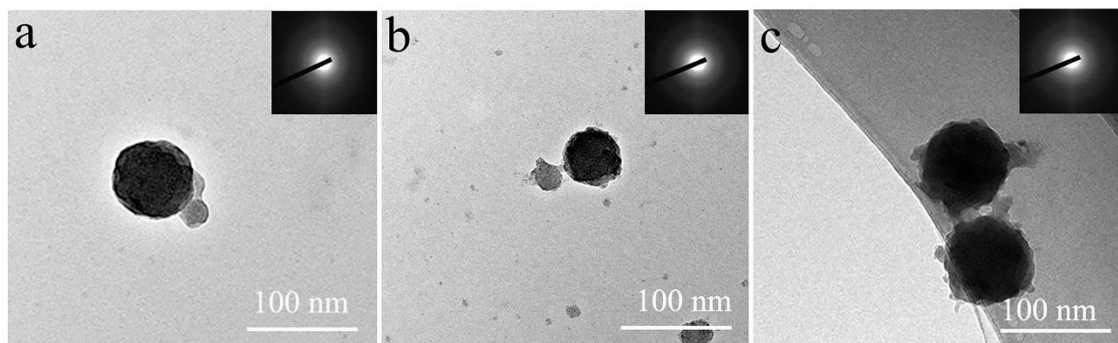


Figure S5. TEM analysis of the obtained nanoparticles from the reaction solutions after different reaction times under otherwise standard condition. (a) 4 h, (b) 6 h, (c) 8 h. Inset images in TEM micrographs are electron diffraction patterns obtained for the nanoparticles, which show an amorphous pattern.

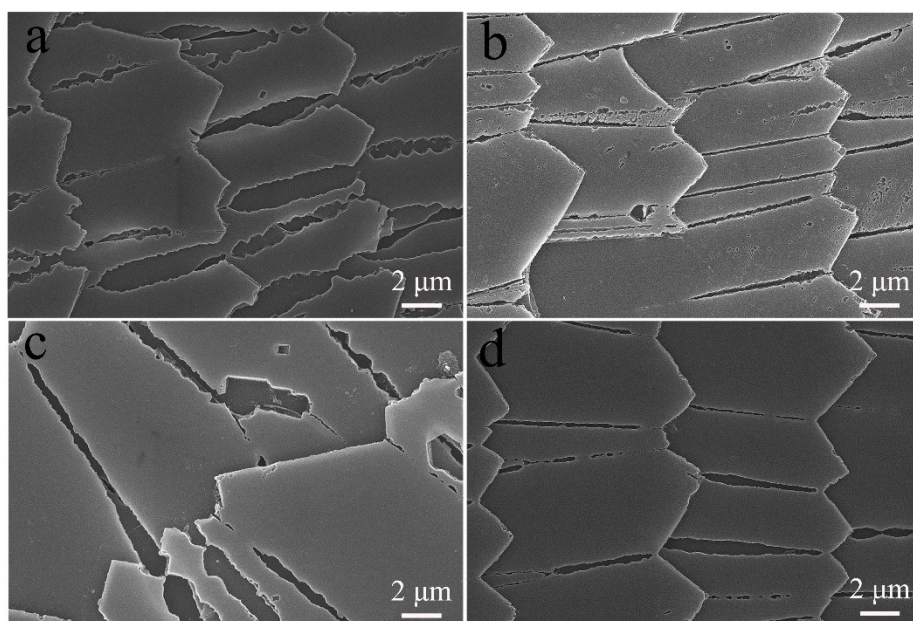


Figure S6. SEM images of CaCO_3 formed on the shell surfaces of *P. placenta* after different reaction times under otherwise standard condition. (a) 0 h, (b) 2 h, (c) 6 h, (d) 8 h.

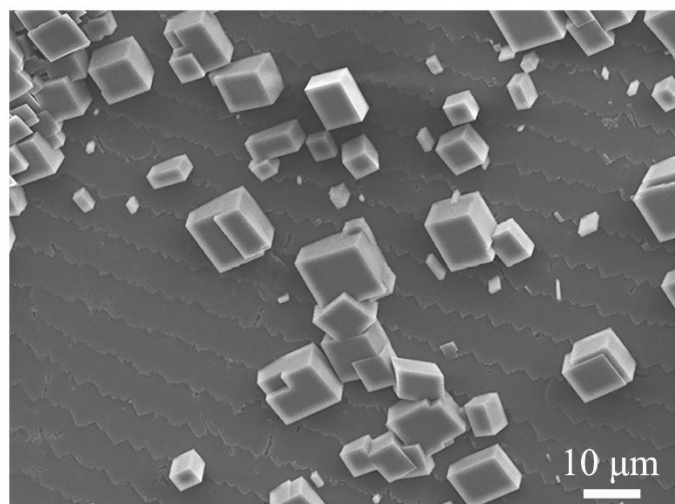


Figure S7. SEM image of the CaCO₃ formed on the shell surfaces of *P. placenta* after 30 min' reaction times in the absence of the protein.

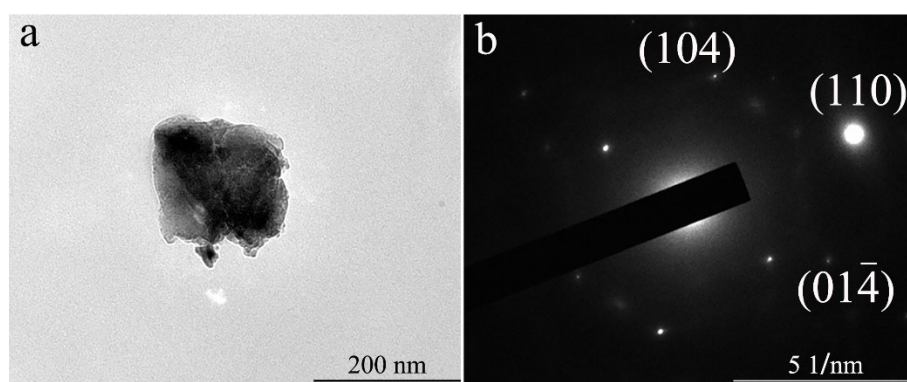


Figure S8. TEM image and SEAD pattern of an CaCO₃ single crystals collected from the shell surface of *P. placenta* after 11 hours' reaction time under otherwise standard condition. (a) TEM image. (b) SAED pattern of individual CaCO₃ shown in (a).

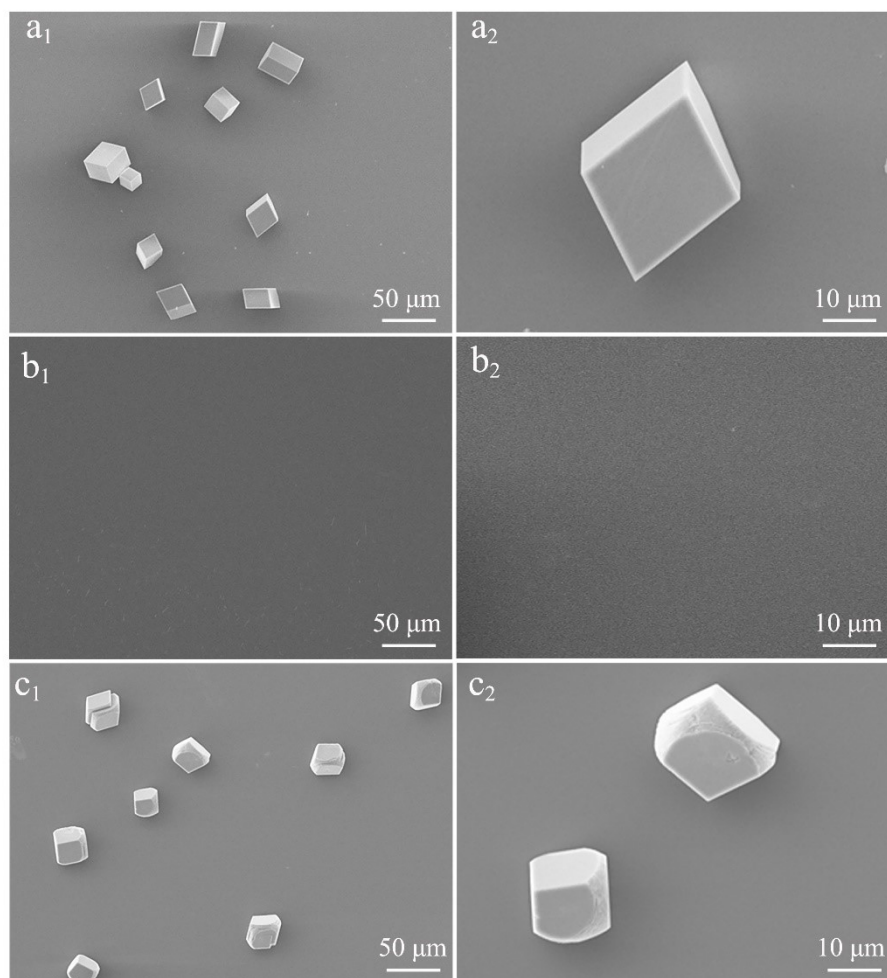


Figure S9. SEM images of CaCO_3 formed on glass substrates in the solution in the absence of ASM (a) in the presence of $10 \mu\text{g/mL}$ of ASM (b-c) via gas diffusion process after different reaction times. (a_1 - a_2) 6 h; (b_1 - b_2) 18 h; (c_1 - c_2) 24 h.