

Supporting Information

Measurement of Zeta potential for phosvitin

Zeta potential measurement of phosvitin in an aqueous solution with a concentration of 100 mgL^{-1} at pH 6 was performed on a zeta potentiometer (Zetasizer 2000, The Malvern Instruments, UK). Then, a series of solutions with phosvitin and various concentrations of CaCl_2 were also measured to study the effect of the calcium ion on the zeta potential of phosvitin. The zeta potential was -46.2 mV for the phosvitin aqueous solution without Ca^{2+} . As shown in Figure S1, it is largely negative at low Ca^{2+} concentration, while the zeta potential rapidly increases as the concentration increases. The behavior of the zeta potential indicates the strong calcium ion binding of phosvitin molecules. Since Ca^{2+} is a multivalent cation, it is easily electrostatically bound to the negatively charged surface of phosvitin. Thus, adding Ca^{2+} leads to a less negative zeta potential.

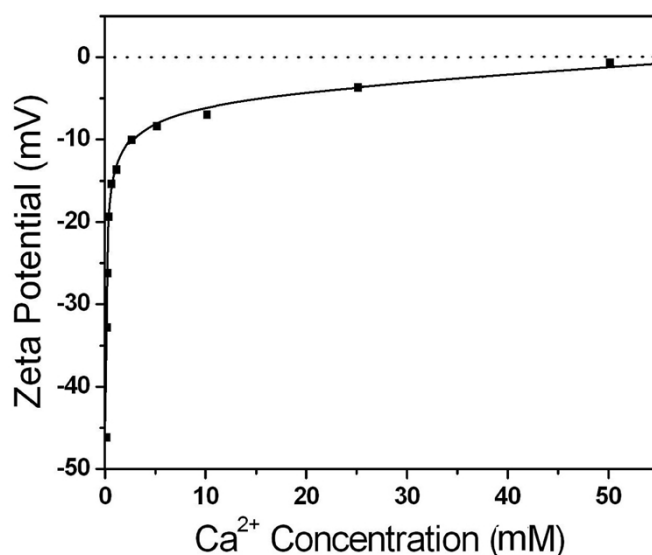


Fig. S1 Zeta potential vs. concentration of Ca^{2+} for phosvitin aqueous solution. It is largely negative at low Ca^{2+} concentration, while the zeta potential increases rapidly with increasing concentration of Ca^{2+} .

Supersaturation-driven structural mismatch

Figure S2 shows SEM images of CaCO_3 crystals grown from aqueous solutions with different supersaturations, which illustrates a self-assembly process by the effect of supersaturation-driven interfacial structural mismatch. Single CaCO_3 crystals with typical rhombohedra morphology can be grown at very low supersaturation. With the increase of supersaturation, the crystallographic structural match between the existing crystals and the nucleating phase gets worse. At relative high supersaturations, it results in loose assemblies with wide-angle branching structures due to mismatched nucleation and growth, even aggregation.

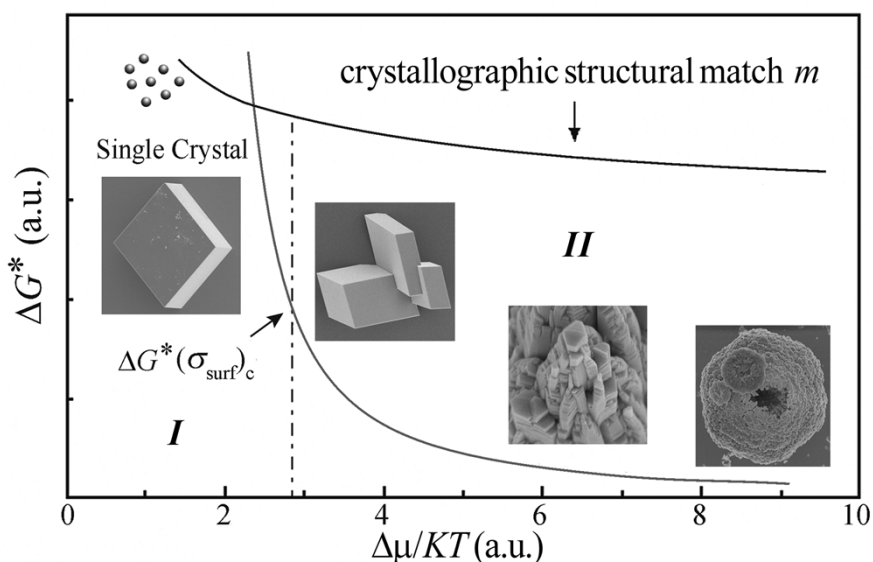


Figure S2. Illustration of crystallographic mismatch nucleation and growth of CaCO_3 from aqueous solutions. *I* regime: single crystal growth occurs at relatively low supersaturations. *II* regime: crystallographic mismatch nucleation and growth. With the increase of supersaturation, assemblies varies from crystallites with the same orientation on the surfaces of existing crystals to clusters of amorphous calcium carbonate.

Energy dispersive x-ray spectroscopy

The self-ordered meso-crystallites were observed by high-resolution transmission electron microscopy (HRTEM), HRTE-based energy dispersive x-ray (EDX) spectroscopy. The result of EDX analysis is shown in Table 1. The atomic concentration of calcium in hybrid nanocrystallites is much higher than that in controlled sample, which implies a high binding effect of phosvitin to calcium.

Table 1 EDX analysis on calcite and self-assembled CaCO₃ hybrid nanocrystallites.

Element	CaCO ₃ (controlled)		CaCO ₃ (phosvitin)	
	Atomic [%]	Number of ions	Atomic [%]	Number of ions
Ca	21.92	2.95	28.66	4.01
C	18.72	2.52	14.23	1.99
O	59.36	8.00	57.11	8.00