

Supplementary Information:

Tracking amorphous precursor formation and transformation during induction stages of nucleation

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Information available in this document:

1. Typical pH change curve for HAP nucleation experiment with $\sigma_{\text{HAP}} = 21.06$;
2. Morphology evolution and phase transformation of ACP phase under TEM electron beam hitting for a same sample;
3. Ca/P ratio of precipitates obtained by EDX and XPS at different stages.

Supplementary information 1

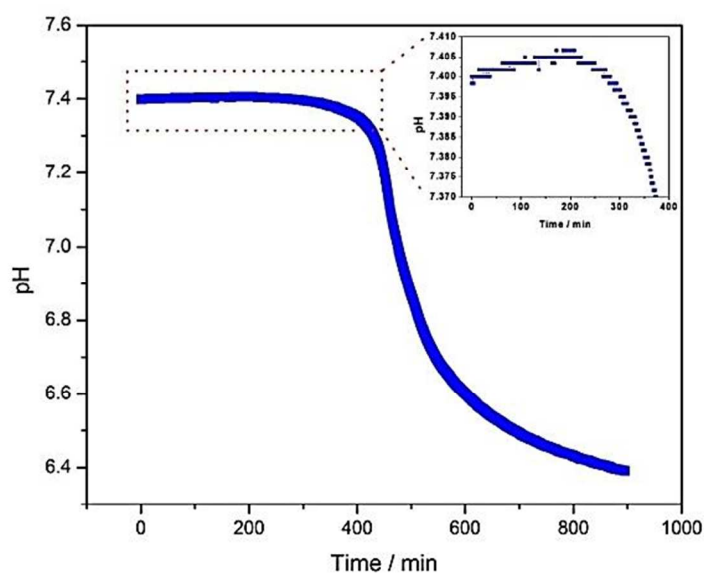


Figure S1 Typical pH change curve for HAP nucleation experiment with $\sigma_{\text{HAP}} = 21.06$, $[\text{Ca}] = 1.3 \text{ mM}$, $[\text{P}] = 0.78 \text{ mM}$, I.S. = 0.006 M and starting pH = 7.400 at 310.15 K (free drift experiments, no titrant addition). A slow pH increase at early induction time was detected.

Supplementary information 2

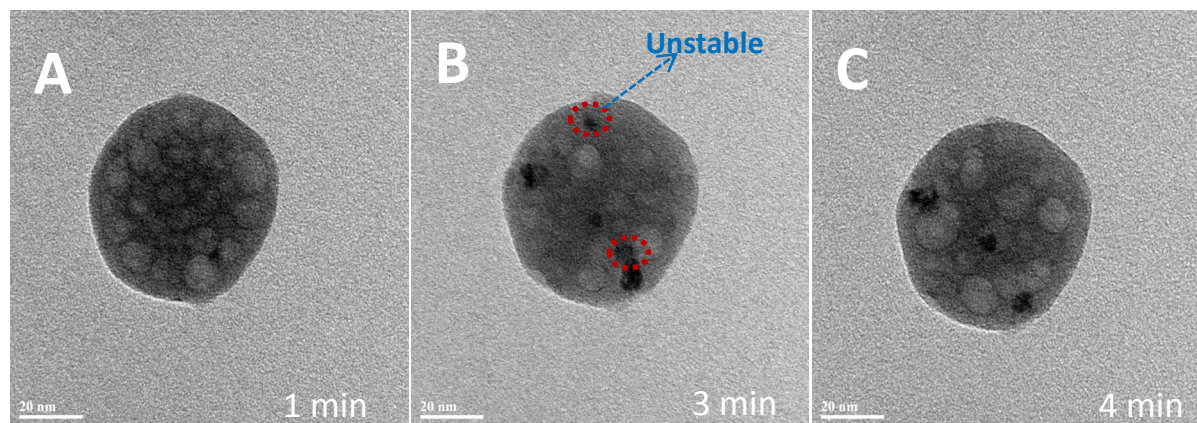


Figure S2 Morphology evolution and phase transformation of ACP phase under *in-situ* TEM electron beam hitting for a same sample. (A) Typical porous loose morphology of ACP-I phase formed after solution mixing. (B) After 3 min, the tiny pre-critical nuclei formed with the ACP phase. (B) Some of unstable pre-critical nuclei disappeared at 4 min because of the small size. Scale bar: (A-C) 20 nm.

Supplementary information 3

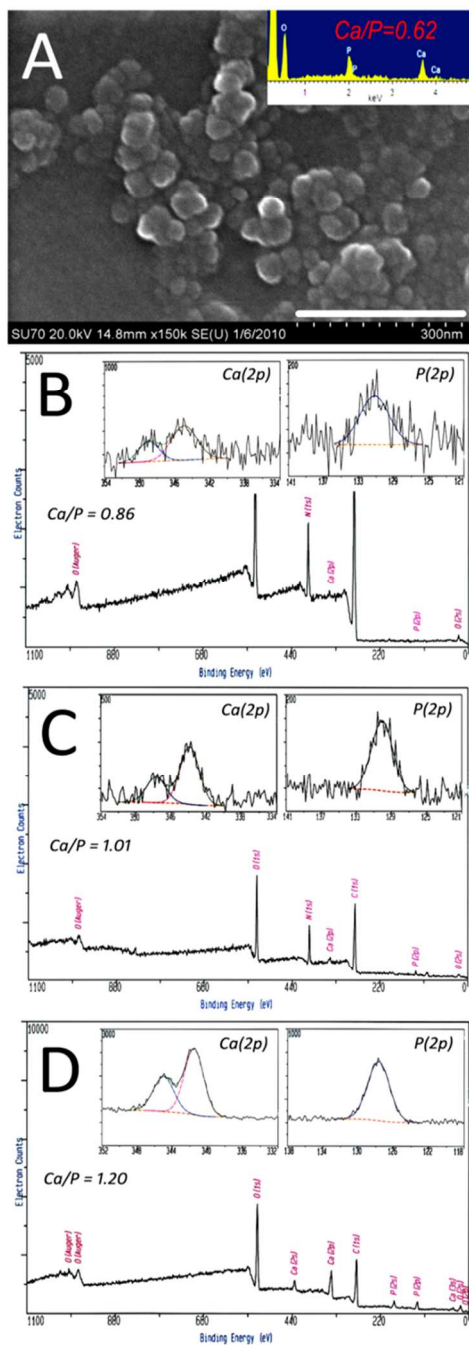


Figure S3. Ca/P ratio of precipitates at different stages. **(A)** SEM micrograph and EDX for ACP at 90 min. **(B-D)** XPS profile for the sample taken at 180 min, 400 min and 600 min, respectively.

Table S1. The estimated particle size from TEM micrographs (90 min from SEM micrograph).

Time	Particle Size (nm)
20	30
90	60
120	100
240	200
400	300
600	50

Table S2. pH, conductivity, and Ca ion activity changes during HAP nucleation experiments with $\sigma_{\text{HAP}} = 20.0$, addition rate of calcium solution was 200 $\mu\text{L}/\text{min}$. , I.S. = 0.006 M, starting pH = 7.40, at 37.0 °C. Time corresponds to Fig. 1a (manuscript).

Stage	Initial Phase	Final Phase	Change in pH (ΔpH)	Change in Ca ion activity	Change in Conductivity	Time (min)
Calcium Addition	-	ACP-1	decrease (-0.04)	increase	increase	1270-1290
Stage-1	ACP-1	ACP-2	increase (+0.01)	none	increase	1290-1480
Stage-2	ACP-2	HAP	decrease(-0.02)	none	decrease	1480-1700
Mineralization	HAP	HAP	large decrease (-1.00)	decrease	decrease	>1700