

Electronic Supplementary Information (ESI) for

**Microdynamic changes of moisture-induced crystallization of
amorphous calcium carbonate revealed by in-situ FTIR
spectroscopy**

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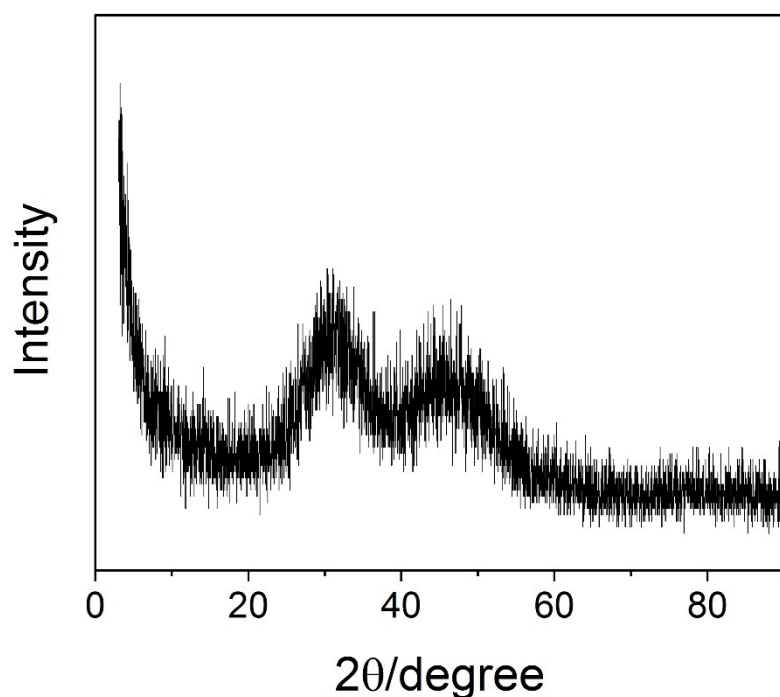


Fig. S1 Powder X-ray diffraction (XRD) profile of the prepared ACC sample.

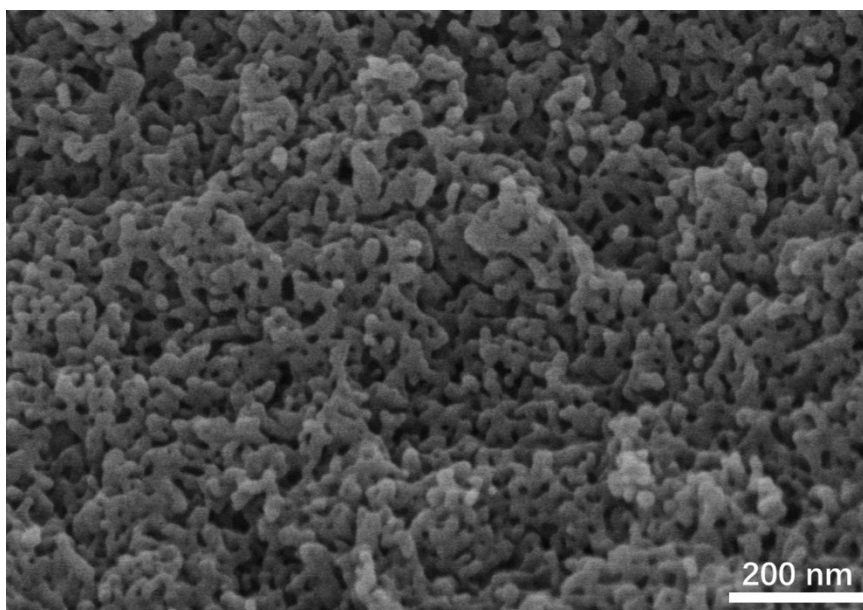


Fig. S2 SEM image of the prepared ACC sample.

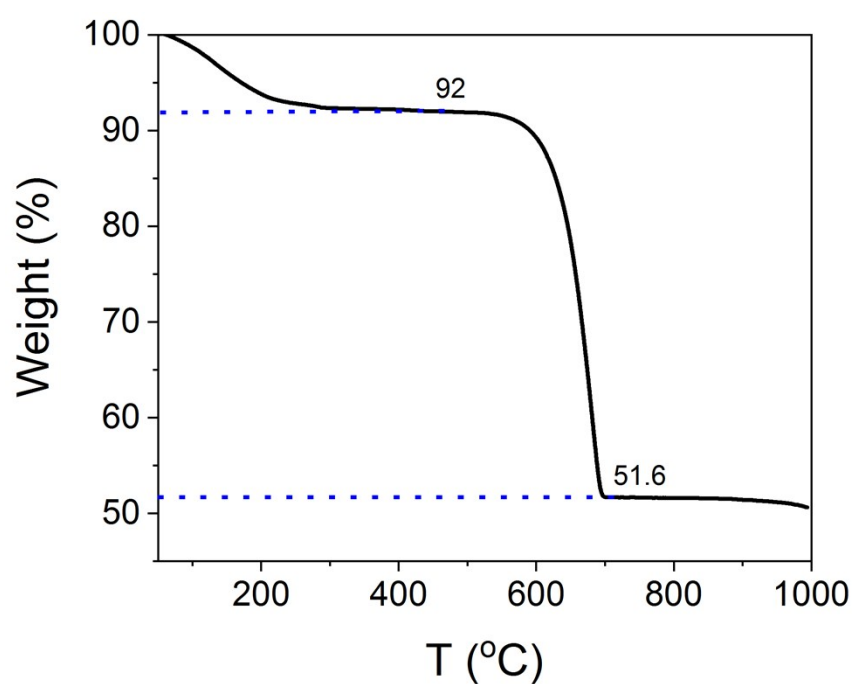


Fig. S3 Thermogravimetric analysis (TGA) of ACC. The sample shows a mass loss of 8 wt% between 50 and 300 °C due to the removal of water. CaCO_3 decomposes into CaO and CO_2 between 600 and 700 °C. Therefore, the chemical formula of the as-prepared ACC can be expressed as $\text{CaCO}_3 \cdot 0.48\text{H}_2\text{O}$.

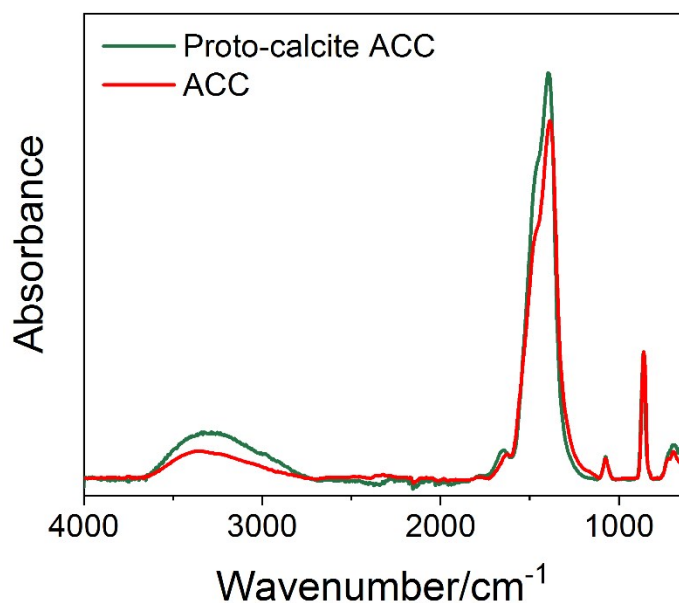


Fig. S4 Infrared spectral comparison between ACC and proto-calcite ACC. Both spectra are normalized by the integral area of ν_2 (898-815 cm^{-1}). Proto-calcite ACC is known to have a formula of $\text{CaCO}_3 \cdot \text{H}_2\text{O}^{\text{s1}}$, thus according to the integral area of ν (O-H of water) (3637-3000 cm^{-1}), the formula of the as-prepared ACC in this work can be calculated to be $\text{CaCO}_3 \cdot 0.56 \text{H}_2\text{O}$.

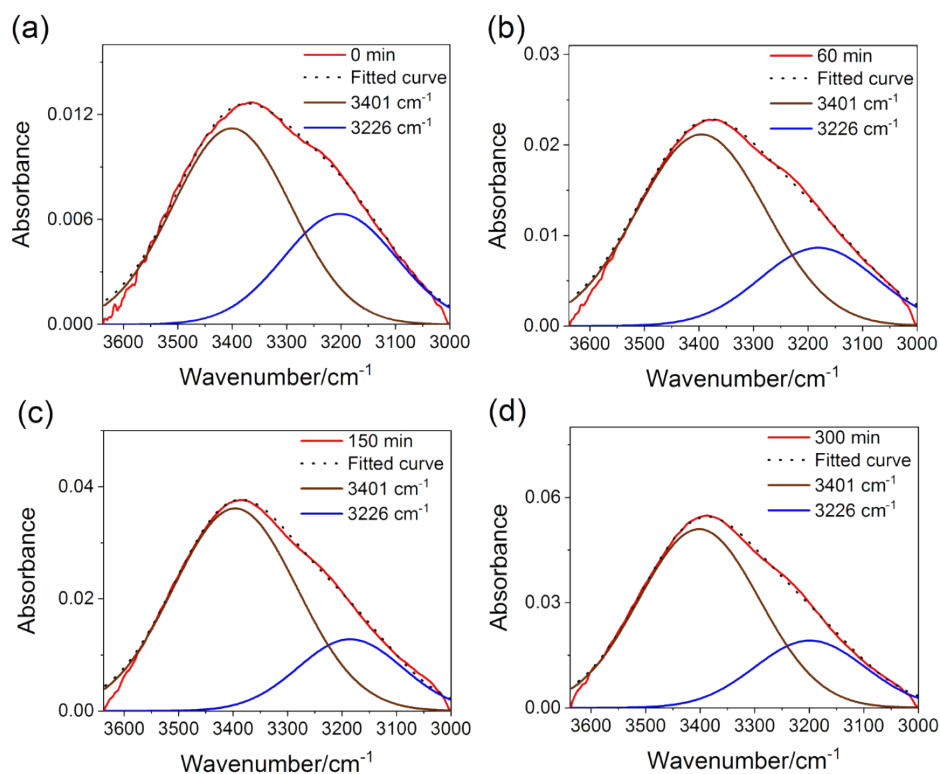


Fig. S5 Four representative fitted spectra of the O-H stretching region of ACC at (a) 0, (b) 60, (c) 150 and (d) 300 min.

Operation Details of Sequence Order Determination from 2DCOS Results

Noda's rule can be summarized as follows: if the cross-peaks (ν_1 , ν_2 , and assume $\nu_1 > \nu_2$) in synchronous and asynchronous spectra have the same sign, the change at ν_1 may occur prior to that of ν_2 , and vice versa. Thus, we firstly listed all the signs of cross-peaks in asynchronous spectra, then turned back to list the corresponding signs in synchronous spectra. Multiplication was performed in succession on these two signs of each cross-peak. To each final sign of cross-peaks, two corresponding wavenumbers can be found on the left and bottom respectively. Because all the signs are above the diagonal line ($\nu_1 = \nu_2$) in accordance with our spectra-reading habits, the wavenumber on the bottom is larger than the one on the left. Therefore, according to Noda's rule, if the sign is positive (+), the larger wavenumber or the bottom wavenumber will respond to external perturbation earlier than the smaller wavenumber or the left wavenumber. Similarly, if the sign is negative (-), the left wavenumber will respond earlier than the bottom one. If the sign is zero (or blank), we cannot make an exact judgment.

The following are the final results of multiplication on the signs of each cross-peak in synchronous and asynchronous spectra in Fig. 9.

698	-	+	-	-	-	-	-	-	-	-	-
744	+	+	-	-	-	+	-	-	+		
856	-	+	-	-	-	-	-	-			
874	+	+	+	-	-	+	+				
876	+	+	-	-	-	+					
1064	-	+	-	-	-						
1086	+	+	+	-							
1402	+	+	+								
1485	+	+									
3130	-										
3410											
	3410	3130	1485	1402	1086	1064	876	874	856	744	698

Thus, we have the sequence order as follows:

$3130\text{ cm}^{-1} \rightarrow 698\text{ cm}^{-1} \rightarrow 856\text{ cm}^{-1} \rightarrow 1064\text{ cm}^{-1} \rightarrow 3410\text{ cm}^{-1} \rightarrow 744\text{ cm}^{-1} \rightarrow 876\text{ cm}^{-1}$
 $\rightarrow 1485\text{ cm}^{-1} \rightarrow 874\text{ cm}^{-1} \rightarrow 1086\text{ cm}^{-1} \rightarrow 1402\text{ cm}^{-1}$

References

- S1. S. Sun, D. M. Chevrier, P. Zhang, D. Gebauer and H. Cölfen, *Angew. Chem. Int. Ed.*, 2016, **55**, 12206-12209.