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Hierarchical $CaCO_3$ particles self-assembled by metastable vaterite and stable calcite during the decomposition of $Ca(HCO_3)_2$

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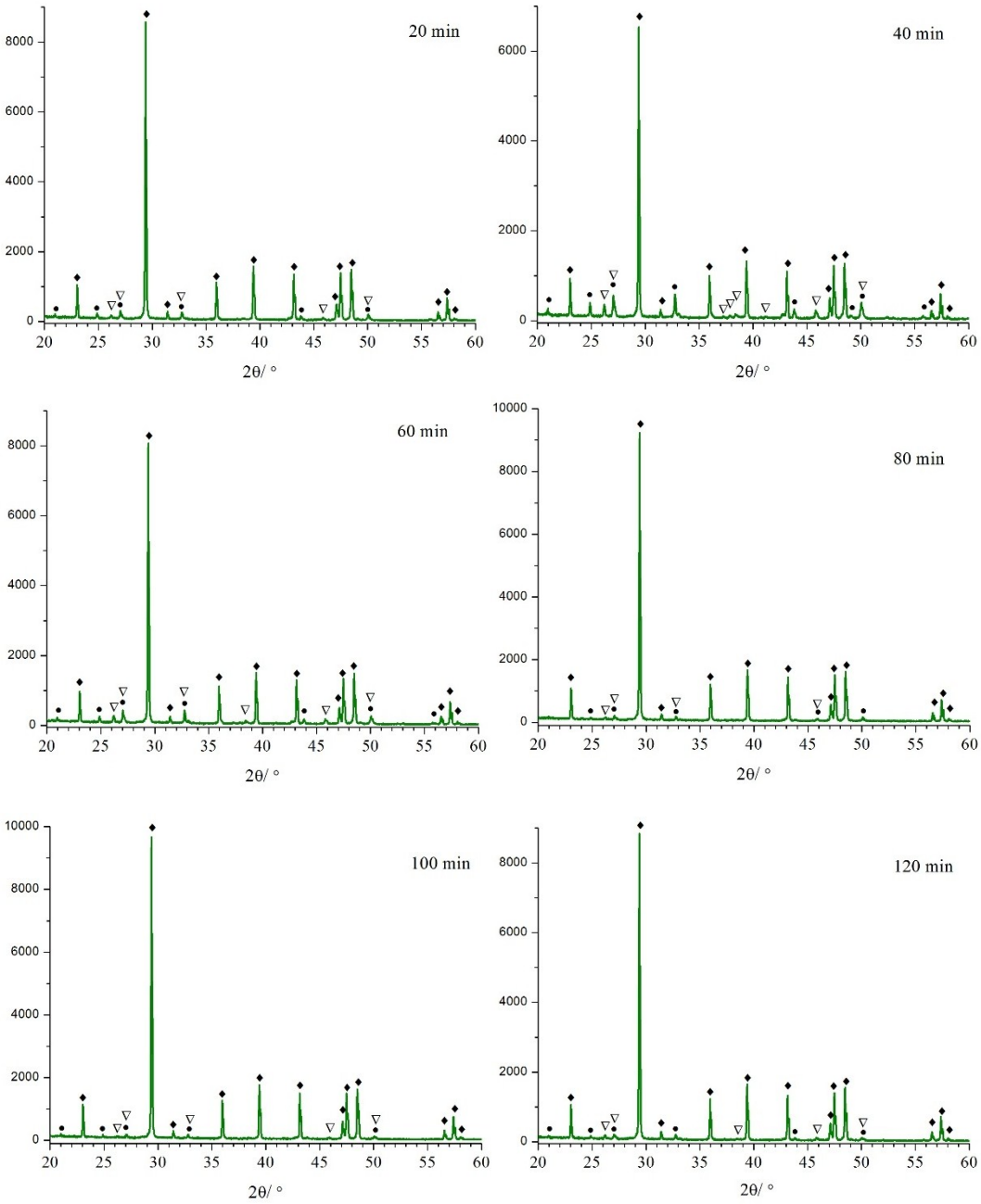

Figure S1 XRD spectrum of $CaCO_3$ at different reaction time in the presence of PEG-6000.

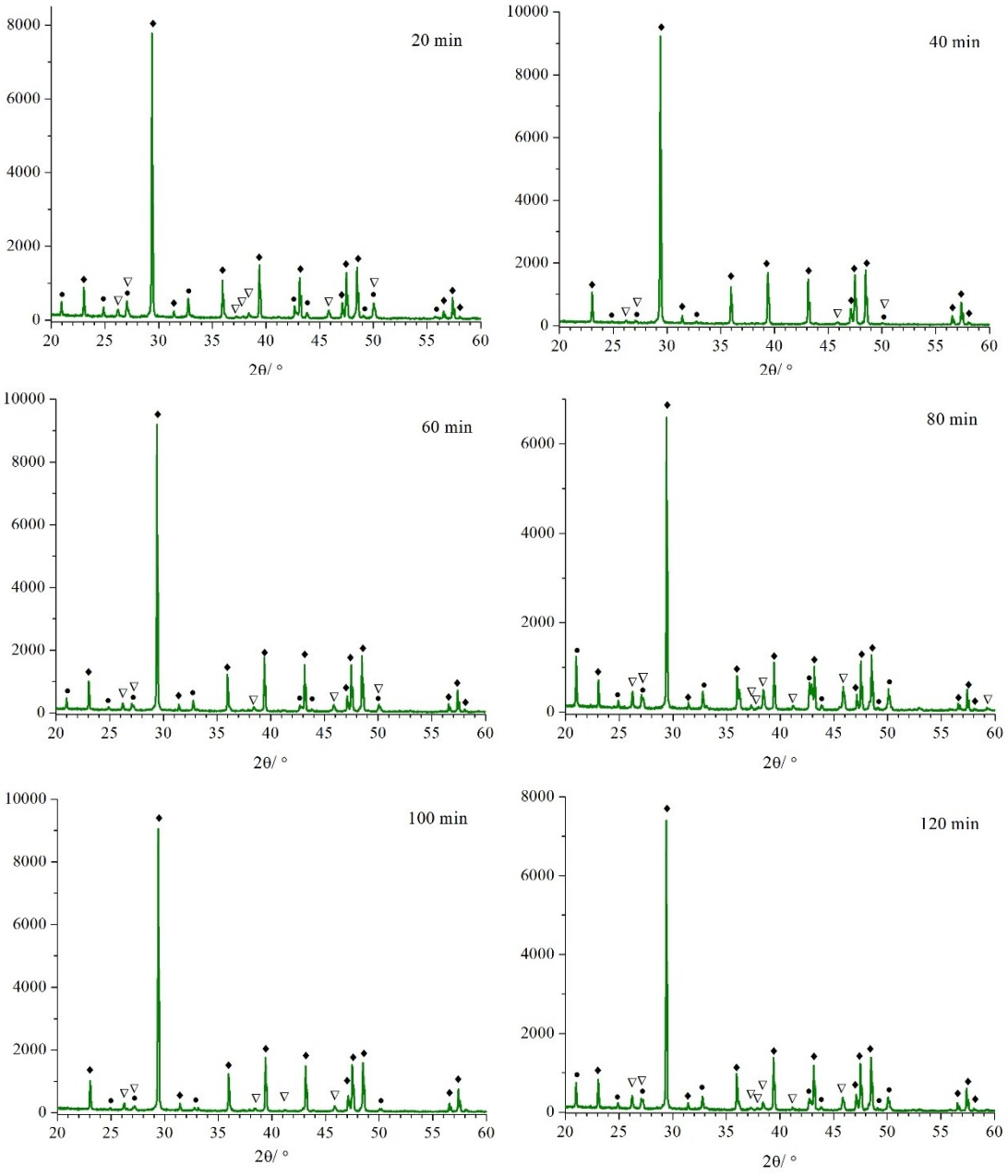

Figure S2 XRD spectrum of $CaCO_3$ at different reaction time in the presence of PEG-10000.

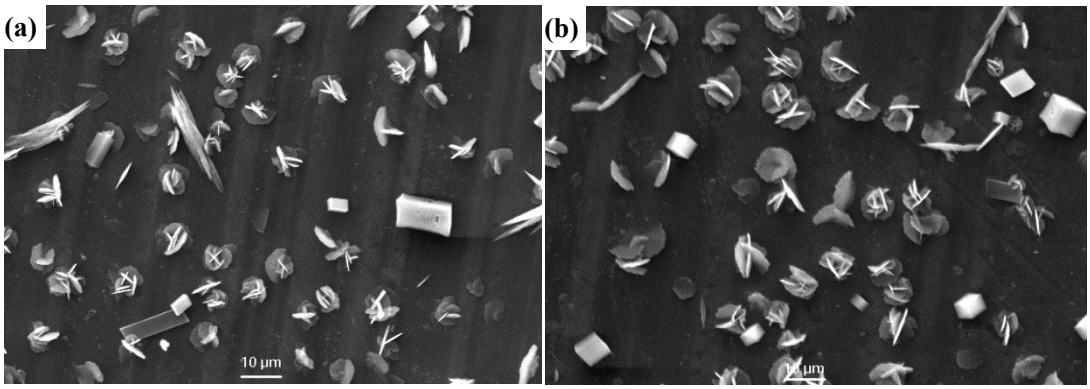

Figure S3 SEM images of laminar $CaCO_3$ observed in sample prepared at the time of 80 min (a) and 120 min (b) in the presence of PEG-10000.

Figure S1 and figure S2 are XRD spectra of $CaCO_3$ synthesized at different reaction times during the decomposition of $Ca(HCO_3)_2$ in the presence of PEG-6000 and PEG-10000, respectively. All diffraction peaks are well consistent with the JCPDS cards of No. 24-0027 (calcite), No. 24-0030 (vaterite) and No. 05-0543 (aragonite). According to the three cards, the diffraction peaks at two-theta of about 29.453°, 27.029° and 45.860° are the strongest peaks for calcite, vaterite and aragonite, respectively. From figure S1 and figure S2, the intensity of diffraction peaks for calcite is much higher than that of vaterite and aragonite. Therefore, calcite is the major crystalline phase, vaterite and aragonite are the minor phase in all samples, and reaction time has no evident influence on the polymorphs of $CaCO_3$, except for the unusually high intensity of diffraction peak at two-theta of about 21° for vaterite (discussed below).

In addition, the peak at two-theta of about 21°, corresponding to the d_{002} lattice spacing of vaterite (d_{002}=4.245, the corresponding diffraction angle is 20.908°), is a very weak peak and its relative intensity is only 5 %.

So, this peak is almost invisible when the strongest peak of vaterite at two-theta of about 27.029° is weak, e.g. $CaCO_3$ prepared in the presence of PEG-6000. However, when PEG-10000 is added in reaction system, the intensity of diffraction peak at two-theta of about 21° is unusually high, especially in the samples prepared at reaction time of 80 and 120 min, which indicates that the 002 lattice plane of vaterite phase in these two samples is dominant to a certain degree.

Figure S3 is SEM image of laminar $CaCO_3$ particles or their spherical assembly observed in sample prepared at the time of 80 and 120 min in the presence of PEG-10000. The exposed surface is considered to be the 002 lattice plane of vaterite phase, and the related research is being carried on and the result will be discussed in future work.

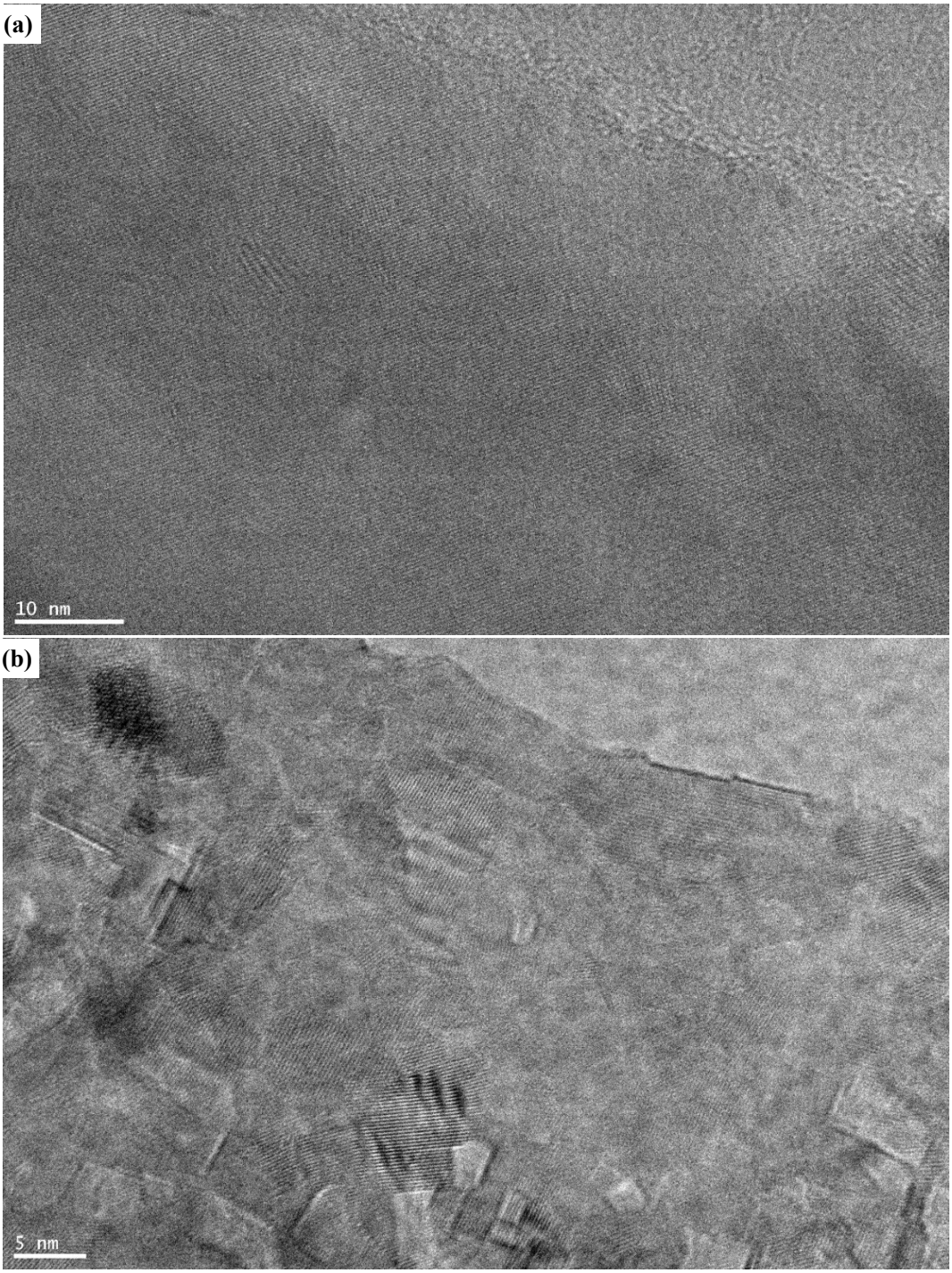

Figure S4 HRTEM images of snow-like $CaCO_3$ particles of truck (a) and filling (b).

During the morphology observation on a TEM, accelerated electrons can only penetrate the fillings and the edge of trunk because of the thickness of snow-shaped particles, so we can only obtain the lattice fringe images of the filling and the edge of the trunk of snow- shaped particles, which is shown in figure S4. From figure S4 *a*, a uniform lattice fringe can be found in almost the entire visual field although few discordance in some small areas, which indicates that the crystals of the trunk of snow-shaped particles well crystallized and grown, and their size is large. In contrast, from figure 4 S*b*, the filling consists of many small $CaCO_3$ crystals with different orientations.