Supporting Information

Synthesis of CaCO$_3$/graphene composite crystals for ultra-strong structural materials

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Fig. S1 SEM images of crude composite crystals before purifications. (A) hexagonal vaterite, (B) dendritic aragonite and (C) rhombohedral calcite.
**Fig. S2** A typical SEM image of mineralization CaCO$_3$ in the system without GO. The crystals were prepared under the same condition of the VCC and reacted for 30 min.

**Fig. S3** A high magnification SEM image of the hole shown in Fig. 2a.
Fig. S4 SEM images of hexagonal VCC. The composite crystals were obtained at (A) 20 min and (B) 25 min. A small amount of rod-like crystals were also formed during the process of cooling down the reaction system from 180 °C to room temperature. Their structure was characterized by XRD to be identical to that of the rod-like crystals shown in Fig. S2.

Fig. S5 SEM images of dendritic aragonite/rGO composite crystals. These crystals were collected at (A) 1 h and (B) 3h.
Fig. S6 SEM images of rhombohedral calcite with irregular morphology. These crystals were obtained from systems with (A) 0.125 M Ca(Ac)$_2$ and 0.625 M urea, (B) 0.025 M Ca(Ac)$_2$ and 0.125 M urea. The reaction time = 20 min. The concentration of GO= 0.5 mg/mL.

Fig. S7 Typical SEM images of the fractured surfaces of PVA/45 wt% VCC composite film. The arrows indicate the places where the cracks propagated at the polymer-mineral interfaces.
**Fig. S8** A Typical stress-strain curve of PVA/VCC composite film with 32 wt% VCC.