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### **Supplementary Information**

#### Tuning of morphology and polymorphs of carbonate/polymer hybrids using photoreactive

#### polymer templates

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#### Effects of the ultraviolet (UV)-irradiation period on the matrices

The decrease in the absorption at 350 nm indicates the consumption of *trans*-4-styrylpridinium (SbQ) groups.



Figure S1. UV-Vis spectra of the (a) P1 and (b) P2 matrices during UV irradiation.

Figure S1 shows the spectral changes in the UV/Vis absorption of the PVA-SbQ films on quartz substrates during UV irradiation.

## Polymorphs of CaCO<sub>3</sub> crystals formed on theUV-irradiated PVA-SbQ matrices.

Characteristic peaks for calcite: 1085 and 280 cm<sup>-1</sup>; aragonite: 1085 and 205 cm<sup>-1</sup>; vaterite: 1090, 1075 and 300 cm<sup>-1</sup>.



Figure S2. Raman spectra of the three kinds of CaCO<sub>3</sub> films I–V.

Thickness of CaCO<sub>3</sub> crystals formed on the UV-irradiated PVA-SbQ matrices.



**Figure S3**. SEM images for cross-sections of the CaCO<sub>3</sub> crystals formed on (**a,b,c**) PVA-SbQ1 and (**d**) PVA-SbQ2 matrices.

Figure S3 shows cross-sectional SEM images of the CaCO<sub>3</sub> crystals grown on the PVA-SbQ matrices. The boundaries of the different films are presented in Figure S3(a, b, d).

### Crystallization of CaCO<sub>3</sub> on the annealed PVA-SbQ matrices

Characteristic Raman shift peaks for calcite: 1085 and 280 cm<sup>-1</sup>; aragonite: 1085 and 205 cm<sup>-1</sup>; vaterite: 1090, 1075 and 300 cm<sup>-1</sup>. Peaks at 875 cm<sup>-1</sup> and 745 cm<sup>-1</sup> of IR spectra are characteristic for vaterite.



**Figure S4**. (a) Raman spectra of the CaCO<sub>3</sub> films formed on PVA-SbQ1 matrix prepared using thermal treatment (annealed at 180 °C for 10 min). (b) FT-IR specrum of the CaCO<sub>3</sub> film formed on PVA-SbQ2 matrix prepared using thermal treatment (annealed at 180 °C for 10 min).

### Swelling behavior of the matrix





The samples in swollen states were prepared by incubation of the polymer matrices in water at 30 °C for 2 hour and subsequent freeze-drying. The PVA-SbQ matrix UV-irradiated for 10 min formed thicker and more distorted films than that irradated for 60 min.

# XRD analyses of the SrCO<sub>3</sub> crystal films



**Figure S6**. XRD patterns of the SrCO<sub>3</sub> films formed on the photoimaged (a) PVA-SbQ1 and (b) PVA-SbQ2 matrices.



## SrCO<sub>3</sub> on the annealed PVA-SbQ matrices

**Figure S7**. SEM images of SrCO<sub>3</sub> crystals formed on (a,b) PVA-SbQ1 and (c,d) PVA-SbQ2 matrices prepared by thermal treatment. Annealing temperature of the matrix: (a,c) 160 °C; (b,d) 175 °C.