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Nanosegregated Amorphous Composites of Calcium Carbonate and an Organic Polymer

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Characterization of materials

The structural characterization was performed by using XRD (Rigaku, RINT-2400 with Cu-K α radiation), FT-IR (Jasco, FT/IR-660 Plus with KBr method), Raman spectroscopy (Jasco, NR-1800), UV/Vis spectrophotometer (Jasco, V-670), and TG-DTA (Rigaku, TG-8120). The powdered samples were used for XRD, FT-IR, and TG measurements and the bulk state materials were used for Raman and UV/Vis spectroscopy. The morphologies were observed by polarized optical microscope (Olympus, BX51), a field emission SEM (Hitachi, S-4700 operated at 2.0 kV), and a field emission TEM (FEI Tecnai F20 instrument operated at 200 kV) equipped with CCD imaging system (Gatan Imaging Filter, model 607). The dark field image of scanning TEM was obtained by a high-angle-annular dark-field detector. The powdered sample was placed on a copper grid supported by a collodion membrane. The specimens for electron microscope observations were used without any conductive treatment. For the dyes incorporating composites, the bulk objects were used for the measurements of UV/Vis and photoluminescence spectra. The photoluminescence spectra were measured by a spectrofluorometer (JASCO, FP-6300) at room temperature.

XRD pattern of the amorphous composite

No peak is observed on the profile.

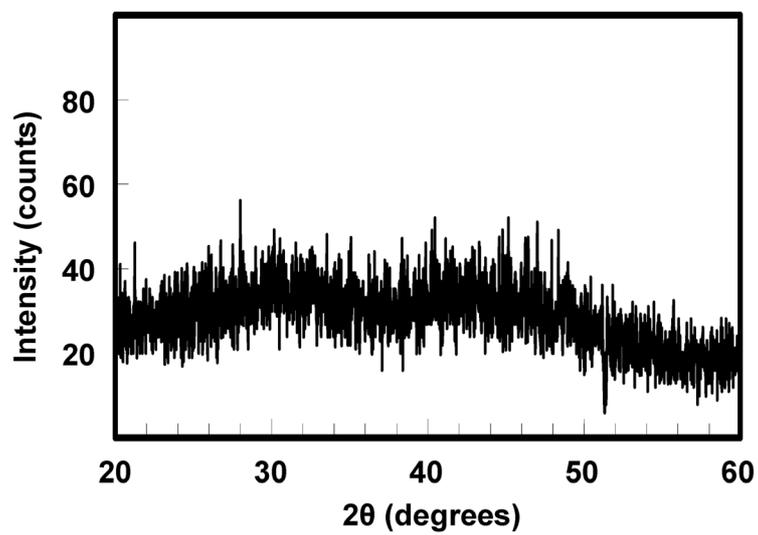


Figure S1. XRD pattern of the powdered samples.

FTIR analysis for the complexation of PAA

In the FTIR spectra, the absorptions around 2800 cm^{-1} and 1600 cm^{-1} result from the stretching vibrations of C-H bonding and carboxylate group (band Q) in PAA, respectively. In the Raman spectra, the peaks around 200 cm^{-1} and 1100 cm^{-1} are characteristic to ACC. The several broadened peaks from 400 cm^{-1} to 1000 cm^{-1} are caused by the incorporation of PAA molecules. These results support that ACC forms the composite material with PAA.

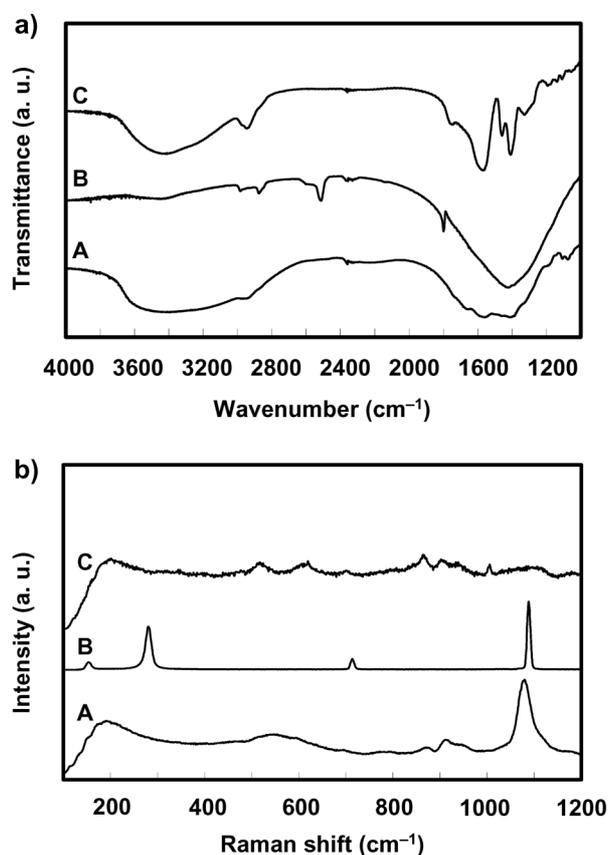


Figure S2. FTIR (a) and Raman (b) spectra of the amorphous composite (A), commercial calcite (B), and PAA sodium salt (C).

FTIR analysis for the thermal stability of the amorphous composite

Based on the FTIR spectra, the composites keep the amorphous states up to 400 °C. The crystallization of CaCO₃ takes place at 500 °C with decomposition of PAA. The broadening of the peaks around 866 cm⁻¹ and 1070 cm⁻¹ and the disappearance of the peak at 713 cm⁻¹ are characteristic to ACC. In contrast, the appearance of the sharp peaks at 713 cm⁻¹ and 880 cm⁻¹ and the disappearance of the peak around 1070 cm⁻¹ result from calcite crystal.

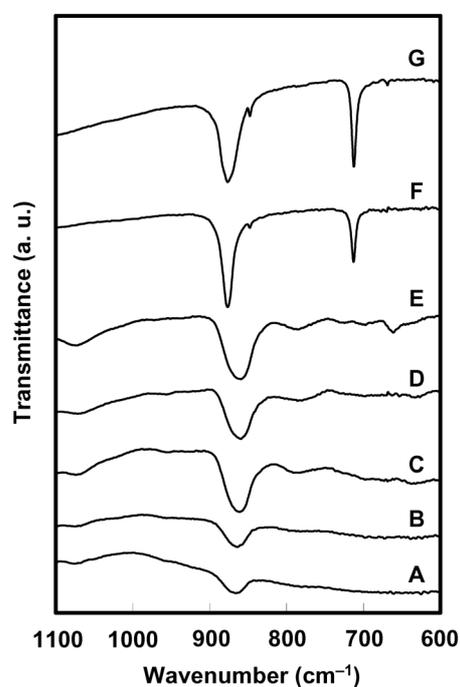


Figure S3. FTIR spectra of the amorphous composites before (A) and after heat treatments (B–F). The samples were exposed at 100°C (B), 200°C (C), 300 °C (D), 400 °C (E), 500 °C (F) for one hour. The spectrum G is obtained from commercial calcite crystals as a reference.

FTIR analysis for the long-term stability of the amorphous composite

The characteristic spectroscopic changes are not observed in FTIR and TG-DTA analysis even after 200 days. The amorphous composites keep the amorphous state and the components after 200 days.

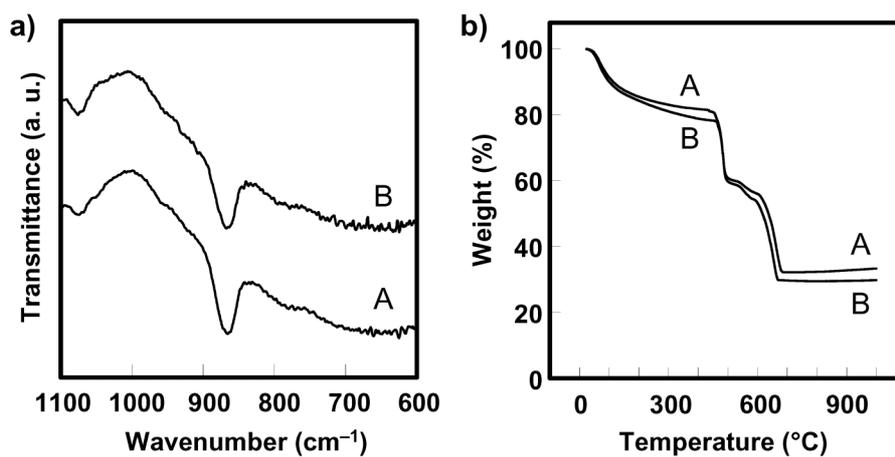


Figure S4. FTIR spectra and TG curves of the bulk materials formed after 7 (A) and 200 days (B). a) FTIR spectra. b) TG curves.

Optical properties of the amorphous composite with organic dyes

Based on the UV/Vis and photoluminescence spectra, the peak positions of the dye aqueous solutions are almost the same as those of the bulk amorphous nanocomposite with incorporation of RB and RU.

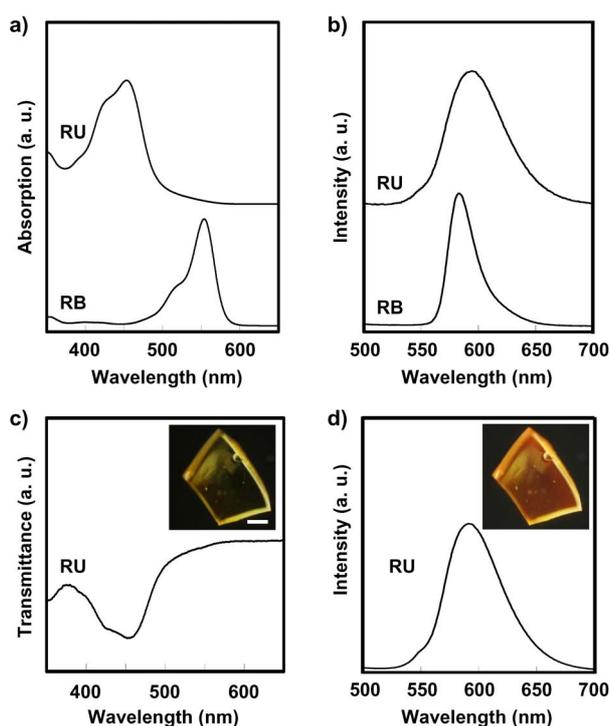


Figure S5. UV/Vis and photoluminescence spectra of the dye aqueous solutions (a and b) and the amorphous composite with dispersion of RU (c and d). a) the UV/Vis absorption spectra of 0.2 mM RB and RU aqueous solutions. b) photoluminescence spectra of 0.2 mM RB and RU aqueous solutions excited at 420 nm. c) UV/Vis transmittance spectrum and its macroscopic appearance (inset) of the amorphous nanocomposite with incorporation of RU (scale bar = 0.2 mm). d) photoluminescence spectrum and its macroscopic appearance (inset) with introduction of RU.

FTIR analysis of the incorporation of PY with the surfactant molecules

The absorption due to the surfactant is observed on the amorphous composite after introduction of PY with C₁₈TAC. Therefore, PY molecules are dispersed with C₁₈TAC molecules in the amorphous nanocomposite.

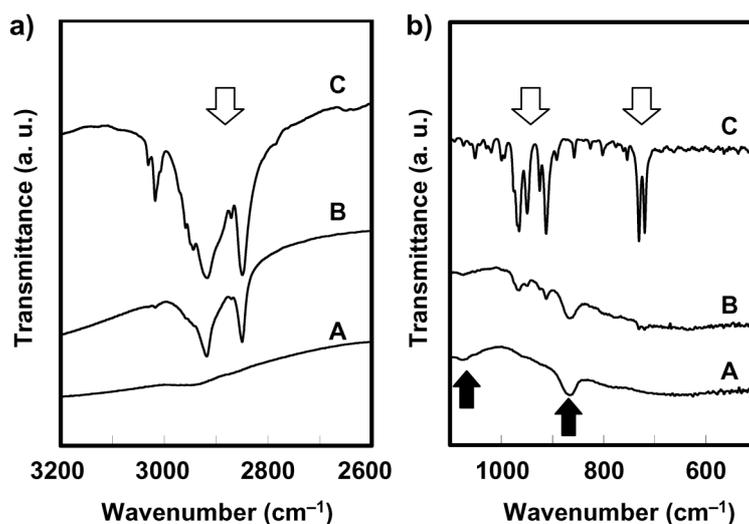


Figure S6. FTIR spectra of the amorphous nanocomposite (A), the composite after introduction of PY with a surfactant [CH₃(CH₂)₁₇N(CH₃)₃]Cl (C₁₈TAC) (B), and C₁₈TAC (C). a) C–H stretching vibration around 2900 cm⁻¹ (white arrow). b) the characteristic absorptions of ACC (black arrows) and C₁₈TAC (white arrows).