Hierarchically organized architecture of potassium hydrogen phthalate and poly(acrylic acid): toward a general strategy for biomimetic crystal design†

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A hierarchically organized architecture in multiple scales was generated from potassium hydrogen phthalate crystals and poly(acrylic acid) based on our novel biomimetic approach with an exquisite association of polymers on crystallization.

In biomineralization, a hierarchically organized inorganic/organic composite emerges from crystal growth with an exquisite association of organic molecules. Biomimetic crystal design has been explored in recent years.[1] Morphological control of various inorganic materials using organic molecules has been extensively investigated as a structural analogue for real biominerals.[2–7] The exquisite interaction between inorganic crystals and organic molecules plays an important role in the design of structure and morphology. However, there are challenges to the further development of the current biomimetic approach. For example, it is not easy to generate nanoscopic-to-macroscopic three-dimensional and/or hierarchical architectures. Typical polymer-mediated crystallization, as previously reported, has resulted in morphological modifications within zero- to two-dimensional nanostructures. The biomimetic approach has been adapted to a limited number of inorganic materials. We believe that various organic materials can be controlled by a similar approach with the assistance of additives as well as inorganic materials. The growth of isomorphs and single crystals has been thoroughly investigated for various organic crystals, but the crystal design of organic materials using polymers has not been extensively studied.[8–11] Designing an organic crystal and its composite with a polymer is also an important challenge in chemistry and biology.

As shown in our previous work, diffusion-controlled growth in a polymer matrix is beneficial for the macroscopic morphological design of inorganic crystals, including helical architectures.[12] We recently studied the potential of combining a specific crystal–polymer interaction and diffusion-controlled growth to induce a hierarchically organized architecture in multiple, nanometer-to-millimeter scales.[13] Hierarchically organized materials have attracted much interest because of their importance and wide range of application.[13–20] Here we describe the successful development of an approach to hierarchical composites of organic crystals and polymers. The hierarchical architecture of potassium hydrogen phthalate (KAP) and poly(acrylic acid) (PAA) was organized in four different scales, including tiers 1–4 (Fig. 1). The model cases will lead to an understanding of how to fabricate hierarchically organized materials.

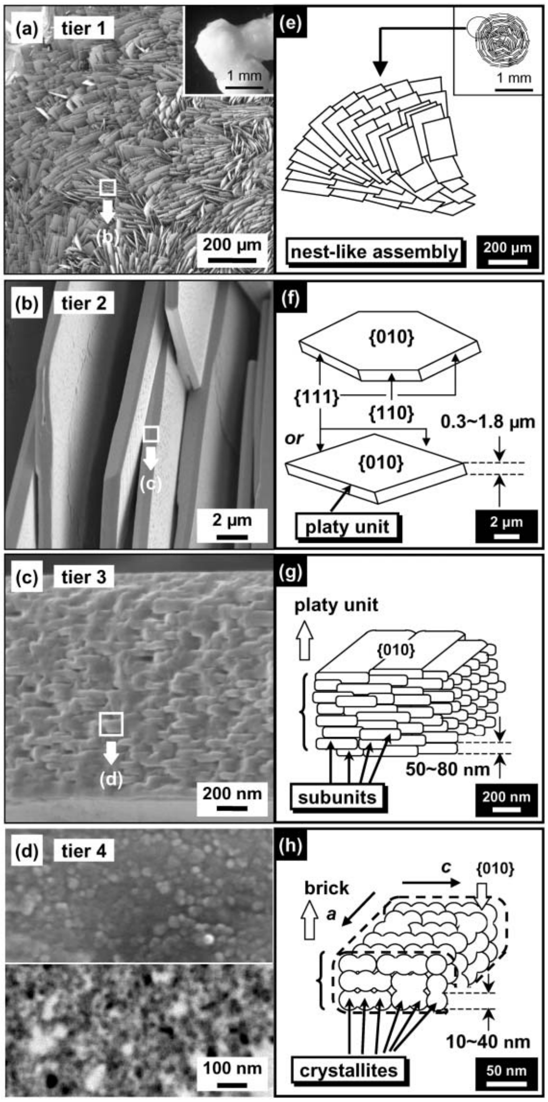

Fig. 1 Overview of the hierarchical architecture and its schematic illustration on four levels (C_{PAA} = 10–15 g dm^{-3}). (a,e) FESEM image and schematic representation of a macroscopic nest-like morphology (tier 1), (b,f) the platelike units (tier 2), (c,g) the regularly arranged brick subunits in the plate (tier 3), (d) FESEM (upper panel) and STEM-DF images (lower panel) of the crystallites, and (h) its schematic model (tier 4).

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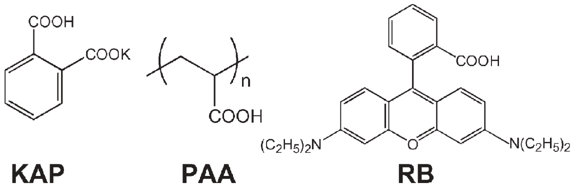

Chart 1 Structural formulae for KAP, PAA, and RB.

Precursor solutions, each containing an orthorhombic crystal of potassium hydrogen phthalate (KAP; 100 g dm^{-3}, 0.49 M, Kanto Chemical, 99.0%) and a polymer of poly(acrylic acid) (PAA; C_{PAA} = 0–50 g dm^{-3}, M_w = 250 000, 35 wt% aqueous solutions, Aldrich Chemical), were prepared using purified water at room temperature (Chart 1a,b). The corresponding content of carboxy groups of PAA molecules was estimated at 0–0.24 M. The precursor solution was maintained at 25 °C without sealing, and crystal growth proceeded as water evaporated from the precursor solution over several days. Crystal morphologies were observed by a field emission scanning electron microscope (FESEM: FEI, Sirion operating at 2.0 kV) equipped with a scanning transmission electron microscope detector (STEM, operating at 5.0 kV). The crystallographic structure of KAP and the incorporation style of PAA molecules were analyzed by powder X-ray diffraction (XRD: Rigaku RAD-C with Cu-Kα radiation) and a Fourier-transform infrared spectrometer (FT-IR: Bio-Rad FTS-60A), respectively.

Clear KAP single crystals surrounded by (010), (110), and (111) faces were observed in the absence of PAA (C_{PAA} = 0 g dm^{-3}, Fig. S1 in ESI).[11] When PAA was added in the precursor solution, the resultant KAP/PAA composite formed white hemispherical aggregates with a nest-like morphology (tier 1, Fig. 1a,e). The macroscopic architecture in tier 1 consisted of platelike units mainly exhibiting the (010) face of KAP crystals (tier 2, Fig. 1b,f), and the platelike unit contained regularly arranged brick subunits (tier 3, Fig. 1c,g). Moreover, FESEM and STEM-dark field (DF) images indicated that crystallites with a diameter of 10–40 nm made up the hierarchical architectures (tier 4, Fig. 1d,h). The peak broadening of the powder X-ray diffraction pattern, resulting from the crystallite size effect, was not clearly recognized in all the powdered samples regardless of the PAA concentration (Fig. S2 in ESI). The results indicate that the oriented assembly formed the hierarchical structure in tiers 3 and 4.

The fundamental morphologies in the hierarchical architecture were not greatly influenced by the PAA concentration. As the PAA concentration increased, the number of nest-like aggregates decreased and their diameters increased. The correlation between the thickness of a plate and the PAA concentration was not markedly recognized in tier 2. The brick subunit in tier 3 was not clearly observed in the relatively high PAA concentration (C_{PAA} = 20–50 g dm^{-3}) because an excess amount of PAA covered the structure. According to XRD analysis and STEM-DF observation, the size and the orientation of the crystallites in tier 4 were not changed by the PAA concentration.

Interestingly, rhodamine B (RB, Chart 1c) molecules were homogeneously introduced in the KAP/PAA composite with the immersion of their ethanol solutions on a nanoscopic scale. The results support the idea that the KAP/PAA composite is formed in nanoscopic scales, as is the case with the K_2SO_4/PAA system.[13] The immersed samples were washed with sufficient ethanol to remove the surface-attached dye molecules and then were dried at room temperature. The dye molecules could not be extracted from the resultant KAP/PAA/dye architecture by further immersion in ethanol over 10 days. The incorporated dye molecules exhibited the characteristic photoluminescence (PL, Fig. 2a), whereas the dye molecules were never introduced into the KAP single crystal (Fig. 2b). With an increase in the PAA concentration, the PL spectra of the RB molecules showed two important spectroscopic changes: an increase in emission intensity and a gradual red shift of the peak maximum (Fig. 2). In accordance with the previous reports,[13,21] the results indicate that the RB molecules formed a J-type aggregate in the KAP/PAA composite. Therefore, we concluded that the nanoscopic molecular storage was generated from the KAP/PAA composite under tier 4.

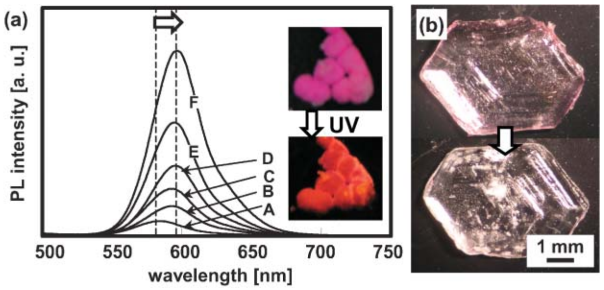

Fig. 2 KAP/PAA with incorporation of RB. (a) PL spectra at C_{PAA} = 6 (A), 12 (B), 22 (C), 30 (D), 39 (E), 48 (F), g dm^{-3}, excitation at 420 nm and its appearance with ultraviolet light excitation (inset, excitation at 254 nm). (b) The appearance of KAP single crystal (C_{PAA} = 0) with immersion of RB ethanol solution (top) and after washing away with ethanol (bottom), indicating that the dye molecules were not included but were attached on the crystal surface.

The hierarchical structure in tiers 2–4 and the nanoscopic molecular storage were similar to those of the K_2SO_4/PAA architecture even though the macroscopic morphology in tier 1 was different in the KAP/PAA composite.[13] The PAA molecules preferentially interacted with potassium ions of KAP crystals to form tiers 2–4, and the excess PAA molecules provided the macroscopic morphology in tier 1. The roles of the interacting PAA in microscopic scales are summarized as follows: miniaturization of KAP crystals, control of growth inhibition and subsequent restart, and formation of nanoscopic molecular storage for dye molecules. Since the potassium ions are regularly arranged on the (010) face of KAP crystals, the carboxy groups of PAA molecules can electrostatically interact with the face (Fig. S3 in ESI). The miniaturized crystallites were grown under supersaturated conditions with the adsorption of PAA molecules (tier 4 in Fig. 3a). The specific adsorption of PAA on the (010) face resulted in the formation of the subunit, even though the growth was not completely inhibited (tier 3 in Fig. 3a). Thus, the next brick subunits were spontaneously produced on the original ones and were accumulated with the same orientation (tier 3 in Fig. 3b). It can be inferred that the formation of a nanoscopic mineral bridge gave the orientation to the next crystallites and subunits, as indicated by black arrows in Fig. 3. The concentration of potassium and phthalate ions declined with growth, and the strong growth inhibition by PAA on the (010) face directed the formation of a platelike unit with habit modification (tier 2 in Fig. 3b). The nanoscopic molecular storage for the organic dye

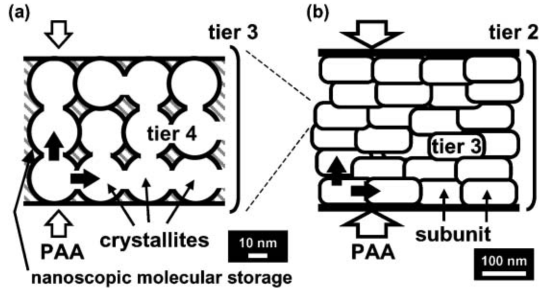

Fig. 3 Two-dimensional growth model for the emergence of a hierarchy in tiers 2–4. (a) KAP crystallites grown with the adsorption of PAA and the subsequent habit modification leading to the brick subunit. (b) Accumulated brick subunits and the resultant platelike unit resulting from incomplete and complete growth inhibition by PAA, respectively.

was eventually induced by the interaction between KAP and PAA (Fig. 3a), as was the case with the K_2SO_4/PAA system.[13] If the PAA molecules did not strongly interact with KAP crystals, the macroscopic morphology was changed only under diffusion-controlled conditions, as reported in our previous studies.‡ Considering these facts, we can conclude that the exquisite interaction between KAP and PAA plays an important role in the construction of the hierarchical composite in tiers 2–4 and the nanoscopic molecular storage. A specified crystal face exhibiting regularly arranged ions predicts the interaction between the polyelectrolytes. The potency of the interaction and the driving force for crystallization involve the inhibition and promotion, respectively, of crystal growth. A subtle balance between the inhibition and promotion of crystal growth is required for the emergence of the hierarchy. However, tailoring the balance in various combinations of crystals and polymers is the next challenge to the further development of the approach. Recently, Cölfen, Antonietti, and co-workers proposed a novel concept of mesocrystal based on aggregation-mediated crystallization.[9,22,23] The oriented assembly of nano-building blocks has been commonly observed in the presence of organic additives, although the orientation mechanisms remain unclear. We believe that hierarchical growth with polymers, as shown in Fig. 3, lies in the various oriented architectures.

The nest-like assembly of the platelike units in tier 1 is ascribed to the morphogenesis under the influence of the concentration gradient around the platelike unit. A similar morphology was found on various materials grown in a diffusion field.[24,25] In the KAP/PAA system, the presence of the excess PAA molecules promoted the diffusion-controlled growth and then included the composite material. The excess PAA molecules that did not interact with cationic species formed hydrogen bonds with each other, which resulted in the appearance of the absorption band around 1700 cm^{-1} in the FT-IR spectra (Fig. S4 in ESI). The diffusion-controlled condition resulting from the excess polymers is beneficial for macroscopic morphological design.

In summary, we successfully generated a hierarchically organized KAP/PAA composite with four different tiers and nanoscopic molecular storage. The strong interaction between crystals and polymers led to the morphogenesis with habit modification in microscopic hierarchies, and a diffusion field concurrently induced the macroscopic morphology. In accordance with our previous K_2SO_4/PAA system, these two model cases suggest that the concept for crystal growth can be applied to the generation of a hierarchically organized architecture regardless of whether organic or inorganic materials are used, even if we cannot show the general experimental technique for other materials. Our findings also shed light on the nature of hierarchical crystal growth in various biominerals, such as bone and mother-of-pearl. Furthermore, tailoring the combination of crystals and polymers could realize various hierarchically organized materials with emergent properties that are inconceivable for the individual components.

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Notes and references

‡ We could not directly detect the presence of the interacting PAA molecules by TG-DTA and FT-IR because KAP and PAA are similar organic compounds with carboxy and carboxylate groups.

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