

Photochemical Reactions in Nanoscopic Organic Domains Generated from Oriented Crystals with Polymers: Nanocrystalline Mosaics as a New Family of Host Materials

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Oriented architectures are formed on nanocrystals with incorporation of organic polymers through a biomimetic route. The composites of potassium sulfate and potassium hydrogen phthalate/poly(acrylic acid) exhibit a mosaic structure consisting of organic polymers and ca. 20 nm nanocrystals. These nanocrystalline mosaics have organic domains originating from organic polymers in nanoscopic scale and serve as a host material for the incorporation and photochemical reaction of organic molecules. Photoisomerization of azobenzene and photodimerization of coumarin are successfully demonstrated in the composite materials, indicating that the nanocrystalline mosaic has potential as a new family of host material.

Biom mineralization and biomimetic materials chemistry have developed rapidly in the past decade.¹ Controlling the structure and morphology of crystals has been well demonstrated in various materials with the assistance of organic molecules.^{2,3} However, the properties of biomimetic materials have not been fully extracted in the field of materials science. The oriented architecture generated from nanocrystals is among the most important and interesting types of superstructures observed in real biom minerals and biomimetic materials.^{4–7} Each nanocrystal, as a building block, is organized in a common crystallographic direction. We have studied the oriented architectures formed from bridged nanocrystals with organic molecules.^{6,7} In another study, the self-assembly of primary nanoparticles also leads to an oriented architecture, which is the so-called mesocrystal and oriented attachment.^{4,5} Beyond the problems in the formation mechanisms of either assembly or growth, the functionalization of the oriented architectures is an important challenge in the next stage of materials science. We believe that these types of “nanocrystalline mosaic” are promising and have a versatile potential as a novel type of functional material.

A wide variety of host materials has been developed regardless of the inorganic and organic frameworks.^{8–14} Examples of such host materials are zeolites,⁸ clay minerals,⁹ layered compounds,^{9,10} mesoporous materials,¹¹ sol–gel derived ceramics,¹² and polymer beads.¹³ However, a new family of host materials has not been introduced since the discovery of mesoporous materials. In general, guest organic molecules are not introduced inside a large single crystalline material. A certain combination of crystals and dyes form dye-doped crystals, as reported by Kahr and co-workers.¹⁴ Since the nanocrystalline mosaics, in contrast, have interspatial organic

domain consisting of crystals and polymers, guest molecules can be introduced in the interspace. Therefore, the nanocrystalline mosaics including biomimetic nanocomposite with oriented architecture are expected to act as a new family of host materials combined with a single crystal-like framework and a flexible organic domain.

Herein, we adopted two biomimetic nanocomposites to demonstrate the inclusion of organic molecules in the interspatial organic domains: composites of potassium sulfate (K_2SO_4)/poly(acrylic acid) (PAA) and potassium hydrogen phthalate (KAP)/PAA had similarly nanocrystalline mosaics generated from oriented crystals with polymers. Photochemical reactions, including the isomerization of azobenzene (AB) and dimerization of coumarin (CM), were adopted for the model cases: AB is a typical photochromic compound and CM dimerizes with UV light irradiation. The photochemical reactions of these molecules and the derivatives have been demonstrated in various chemical environments.^{15–26} In a previous report, we suggested the potential for the introduction of dye molecules in the oriented architectures because the nanocrystals formed the interspace with the incorporation of organic polymers.⁶ However, the dye molecule was simply adopted as a probe for the nanoscopic space. The interspatial organic domains in nanocrystalline mosaics can be used more effectively for functionalization toward a broad range of application. In this report, we show a potential application as a host material for guest organic molecules. The structural analysis of the nanocrystalline mosaics is first studied, and the photochemical reaction behavior is discussed in the following sections.

Experimental

Preparation of Host Materials. The K_2SO_4 /PAA and KAP/PAA hosts were synthesized by the simple methods in our previous reports. Stock solutions containing potassium sulfate (K_2SO_4 , 100 g dm^{−3}, 0.57 M, Kanto Chemical, 99.0%) or potassium hydro-

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gen phthalate (KAP, 100 g dm^{-3} , 0.49 M, Kanto Chemical, 99.0%) were prepared in purified water at room temperature. PAA (concentration range; $C_{\text{PAA}} = 0$ and $15\text{--}30 \text{ g dm}^{-3}$, 35 wt % aqueous solution, molecular weight 250000, Aldrich Chemical) was then added to the stock solution. After these materials were dissolved, 10 cm^3 of the precursor solution was poured into a polypropylene sample bottle (30 mm in diameter and 70 mm in height) and the sample bottle was maintained at 25°C for several days without sealing. This sample was used for the subsequent introduction of organic molecules.

Characterization. The morphology and nanoscopic structures were analyzed by using a field emission scanning electron microscope (FESEM, FEI Sirion) operated at 2.0 kV, a transmission electron microscope (TEM, FEI Tecnai G2-12) operated at 120 kV, a field emission TEM (FETEM, FEI Tecnai F20) operated at 200 kV, and powder X-ray diffraction (XRD, Bruker D8 Advance with $\text{Cu K}\alpha$ radiation). Dark-field (DF) and high-angle-annular dark-field (HAADF) detectors were used in scanning transmission electron microscopy (STEM). The powdered samples were analyzed without any conductive treatment for FESEM and FETEM analysis.

Inclusion of Guest Molecules. Azobenzene (AB, 10 mM, Tokyo Kasei Kogyo) and coumarin (CM, 10 mM, Kanto Chemical, 98.0%) were dissolved in ethanol and then 20 mL of the ethanol solution was poured into a sample bottle with the resultant composite materials. The sample bottle was sealed and put in an ultrasonic bath for 30 min. Then, the composite was immersed in AB or CM ethanol solution at 25°C for a day. The samples were adequately washed by ethanol and then dried at room temperature. The powdered samples were filled in a specimen holder to measure the absorption spectra in ultraviolet–visible region by diffuse reflectance mode (UV–vis, JASCO V-560). The irradiation part of the holder consisted of a circular quartz glass window (16 mm in diameter). The photochemical reaction was carried out by using UV lights at 365 nm (6 W) and 254 nm (6 W) and visible light (Olympus, LG-CL2). The specimen holder was placed near the light source for the reaction and then the UV–vis spectra were immediately recorded after irradiation.

Results and Discussion

Structure of the Nanocrystalline Mosaics. Figure 1 represents an overview of the mosaic architectures consisting of oriented K_2SO_4 and KAP nanocrystals with the incorporation of PAA. The aggregates of ca. 20 nm nanoparticles are observed in the FESEM images (Figures 1a and 1d). The spotted SAED pattern indicates that K_2SO_4 nanocrystals are organized with a specific crystal orientation (Figure 1b). Since peak broadening caused by the crystallite size is not observed in the XRD pattern, the nanocrystals of KAP also make up the oriented architecture (Figure 1e).²⁷ The HAADF- and DF-STEM images reveal that the nanoparticles are not isolated but are connected to each other with the bridges (Figures 1c and 1f); the white regions indicate the presence of nanoparticles and polymers. The oriented architecture is regarded as neither a random aggregate nor a perfect single crystal. Since the nanocrystals are partially bridged and fused with each other (Figures 1c and 1f), the mosaic structures would behave as a single crystalline structure in SAED and XRD patterns. The formation of these nanoscopic structures is not influenced by a change in the initial PAA concentration. The results suggest that the bridged nanocrystals direct the formation of the

oriented structures with the association of organic polymers, as represented in Figure 1g. Therefore, the nanoscopic interspace, as a host for organic molecules, is generated from the nanocrystals and polymers (Figure 1h). The formation of a mesocrystal is generally ascribed to the self-assembly of modulated particles.^{4,5} Our results suggest that the bridges lead to the similar structures through stepwise crystal growth, including inhibition and restarting.^{6,7}

Photoisomerization of Azobenzene. Figure 2 summarizes the photoisomerization behavior of AB molecules in the nanocrystalline mosaics of $\text{K}_2\text{SO}_4/\text{PAA}$ and KAP/PAA . AB molecules are never intercalated in the single crystals of K_2SO_4 and KAP without PAA. It is generally known that the absorption bands around 325 and 435 nm correspond to $\pi\text{--}\pi^*$ and $n\text{--}\pi^*$ transitions of $\text{N}=\text{N}$ in AB molecules, respectively.¹⁹ The trans-to-cis transformation results in a remarkable decrease and a slight increase in the absorption bands around 325 and 435 nm, respectively. In this study, the two peak positions are different in the $\text{K}_2\text{SO}_4/\text{PAA}$ - and KAP/PAA -nanocrystalline mosaics (Figures 2a and 2c): the absorption bands were located at 326 and 438 nm in the former composite and at 328 and 443 nm in the latter case. When commercial AB powder was mechanically mixed with fumed silica powder in a certain ratio, the absorption bands appeared at 325 and 423 nm (Figure S1 in the Supporting Information). In addition, the two bands are observed at 318 and 442 nm in an ethanol solution. These facts suggest that AB molecules are neither simply attached nor mixed with the solid surfaces but rather they are included in the interspaces of the composite structures around a certain chemical environment.

The trans isomers of AB molecules are changed to cis after irradiation with UV light at 365 nm, and then cis-to-trans transition conversely takes place with the subsequent irradiation with visible light (Figures 2a and 2c). The photoisomerization reactions are achieved within 5 min of the irradiation of light, and further irradiation does not result in spectral changes. Furthermore, we demonstrated the reversible switching between trans and cis forms with the alternative irradiation of UV and visible lights (Figures 2b and 2d). In this way, the photoisomerization reaction is achieved in the nanoscopic interspace of $\text{K}_2\text{SO}_4/\text{PAA}$ and KAP/PAA .

Photodimerization of Coumarin. The photodimerization of CM was also performed in the $\text{K}_2\text{SO}_4/\text{PAA}$ and KAP/PAA composites (Figure 3). The absorption bands of the included CM are observed at 277 and 312 nm in the $\text{K}_2\text{SO}_4/\text{PAA}$ (Figure 3a), while the samples without PAA do not show any peaks of CM molecules. Although the KAP crystal itself shows absorption shorter than 310 nm, the shoulder resulting from CM is recognized at approximately 320 nm (Figure 3c). As a reference, the two peak positions are located at 281 and 315 nm when commercial CM powder is simply mixed with a specified amount of fumed silica (Figure S2 in the Supporting Information). In another case, CM molecules in an ethanol solution show the two absorption bands around 274 and 313 nm. The differences in the peak positions indicate that CM molecules are not simply attached but rather incorporated in the host $\text{K}_2\text{SO}_4/\text{PAA}$ and KAP/PAA . The photodimerization behavior can be monitored by the absorbance around 315 nm. When UV light at 365 nm is irradiated to the specimen, a gradual decrease

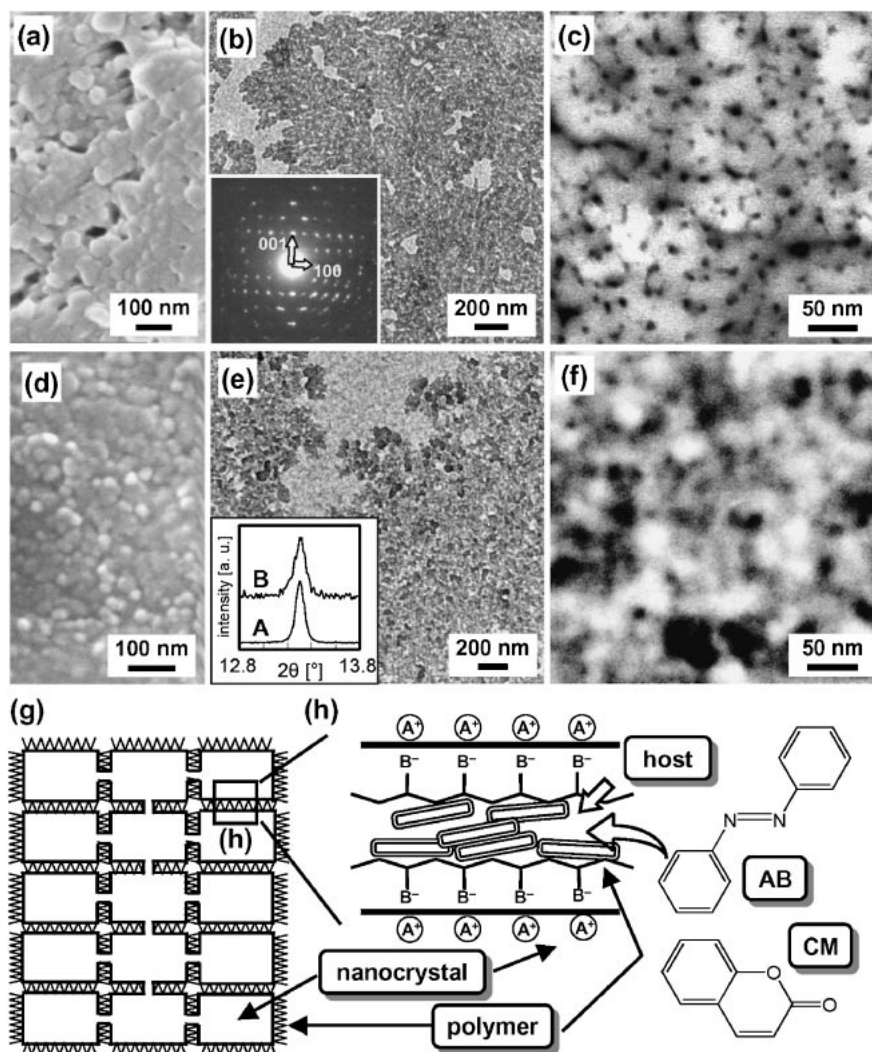


Figure 1. The oriented architectures of K_2SO_4/PAA (a–c) and KAP/PAA (d–f) and their schematic models for dye inclusion behavior (g and h): (a) FESEM image, (b) FETEM image and the corresponding SAED pattern (inset), (c) HAADF-STEM image, (d) FESEM image, (e) TEM image and the XRD pattern without peak broadening (inset), (f) DF-STEM image, (g) schematic illustration of the oriented architectures made by bridged nanocrystals, (h) the interspace formed by the nanocrystals and organic polymers and the structural formulae for AB and CM.

in the absorption band around 315 nm is observed in the spectra (Figures 3b and 3d).

The spectroscopic changes indicate that the photodimerization of CM is achieved in the nanocrystalline mosaics of K_2SO_4/PAA and KAP/PAA . Whereas we perform the photodimerization of CM in the nanocomposites in the present study, the random distribution of CM molecules did not result in the dimerization in silica–surfactant nanocomposite.²⁶ Since this [2 + 2] cyclization in the photodimerization is a key reaction in organic chemistry, designing a solid host would provide a versatile reaction field in a nanoscopic scale. After 2 h, photocleavage of the dimer is carried out with irradiation of UV light at 254 nm. The absorption band at 312 nm is rapidly restored within 2 min in the K_2SO_4/PAA , even though the absorbance does not return to the initial value (Figure 3b). Further irradiation of UV light at 254 nm causes the decomposition of CM molecules because the absorbance gradually decreased with irradiation time. Similar spectral features were

observed in various CM modified materials in previous reports.^{23,24} In the KAP/PAA composite, the recovery of absorbance around 320 nm is recorded with irradiation of UV light in 254 nm, although the shape of the spectrum varied slightly from that of the monomer before dimerization (Figures 3d and 3e). The irradiation with UV light at 254 nm influenced not only the photocleavage reaction but also the structure of KAP/PAA .

Nanocrystalline Mosaic as a Host Material. In the current study, we demonstrate that typical photochemical reactions, including isomerization and dimerization, proceed in a mosaic architecture consisting of oriented nanocrystals and polymers. The interspatial organic domains play an important role as a host for the guest organic molecules. The introduction and reaction of the guest molecules are characteristic of the nanocrystalline mosaics because a single crystalline structure never includes organic compounds, except in specific cases. The inclusion of various organic molecules suggests the

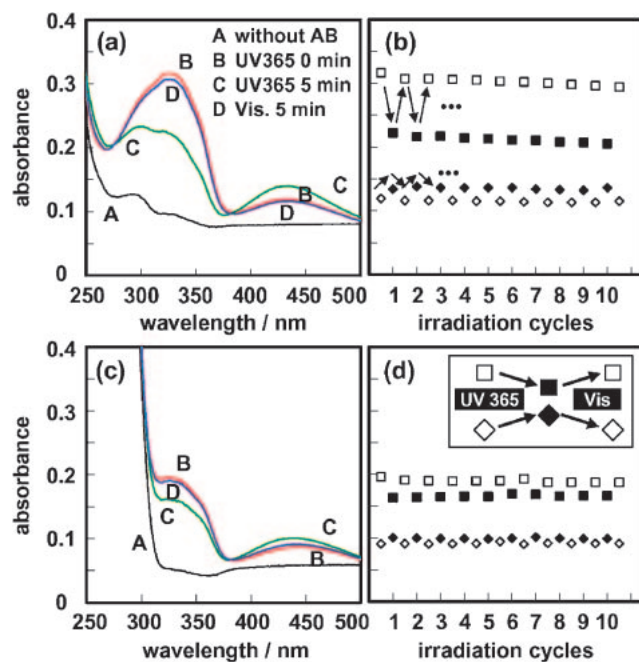


Figure 2. UV-vis spectra and the reversible changes of AB molecules incorporated in the host materials of K₂SO₄/PAA (a and b) and KAP/PAA (c and d): (a and c) UV-vis spectra without AB (black line, A), with incorporation of AB before irradiation of UV light (red line, B), after irradiation of UV light at 365 nm for 5 min (green line, C), and after the subsequent irradiation of visible light for 5 min (blue line, D), (b and d) the changes of absorbance at 325 nm (open and filled squares) and 435 nm (open and filled diamonds) with alternative irradiation of UV (filled marks) and visible (open marks) lights, as represented in the inset of panel (d). In panel (c), the absorption from 250 to 290 nm resulted from that of the host crystal, KAP itself.

formation of organic domains in the nanocrystalline mosaics. Moreover, the current study shows that the nanoscopic organic domains have the spatial flexibility for photochemical reactions.

The nanocrystalline mosaics serve as a host material combined with a single crystal-like structure and an interior organic domain. These model cases suggest that other photochemical reactions, including isomerization and cyclization, can be achieved in various combinations of guest molecules and nanocrystalline mosaics. Recent reports indicate that oriented architectures, including mesocrystals, can be formed with various combinations of crystals and organic molecules.^{3–7} An appropriate integration of crystals, polymers, and guest molecules promises to form a new type of functional material. In addition, coloration in the body of biominerals, a question in biomineralization, may be relevant to the incorporation and photoresponsive features of guest organic molecules in nanocrystalline mosaics.

Conclusion

Photochemical reactions of AB and CM are demonstrated in the organic domains of the nanocrystalline mosaics. The nanocrystals ca. 20 nm in size make up the oriented architec-

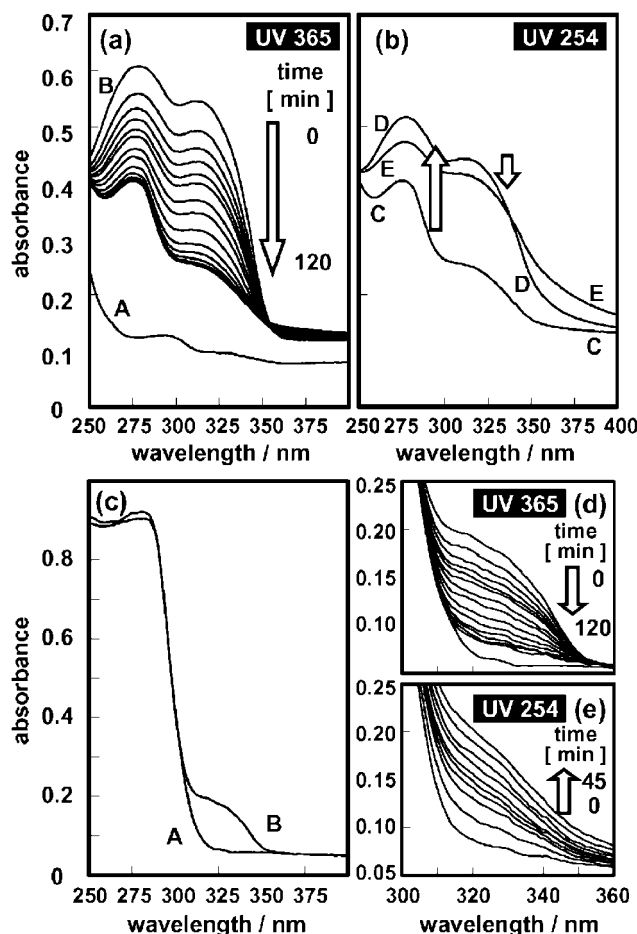


Figure 3. UV-vis spectra and their changes of CM molecules incorporated in the host materials of K₂SO₄/PAA (a and b) and KAP/PAA (c–e): (a) UV-vis spectra without CM (A) and the changes with irradiation of UV light at 365 nm recorded at 0, 2, 4, 6, 8, 10, 15, 20, 30, 45, 60, 80, 100, and 120 min (B), (b) the spectral changes with the subsequent irradiation of UV light at 254 nm recorded at 0, 2, and 20 min, (c) UV-vis spectra without CM (A) and with incorporation of CM (B), (d) the spectral changes with irradiation of UV light at 365 nm recorded at the same interval of the panel (a), (e) the spectral changes with subsequent irradiation of UV light at 254 nm monitored until 45 min with the interval of the panel (a). In panel (c), the absorption from 250 to 290 nm resulted from that of the host crystal, KAP itself.

tures with incorporation of organic polymers via the bridges. The interspatial organic domains introduce the guest molecules and afford photochemical reactions without destruction of the frameworks. Therefore, the nanocrystalline mosaic has a potential for a new family of host material combined with a single crystalline framework and a flexible organic domain.

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Supporting Information

UV-vis spectra of AB and CM molecules mixed with fumed silica as the references. This material is available free of charge on the Web at: <http://www.csj.jp/journals/bcsj/>.

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- 27 The SAED pattern for the oriented architecture of KAP/PAA could not be obtained by TEM analysis because there were many more transmission than diffraction electrons in the organic materials. If the ca. 20 nm nanocrystals randomly aggregated, the peak broadening should be observed in the XRD pattern. But in fact, the orientation of the nanocrystals led to the appearance of sharpened peaks (Figure 1e).