Preparation of large-scale 2D zeolite crystal array structures to achieve optical functionality

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ABSTRACT

We examined a method to refine a technique to prepare close-packed monolayers of cylindrical zeolite L crystals tethered on a substrate through covalent linkages, which was developed recently for popular use. We attempted to fabricate both vertical and horizontal–unidirectional alignments of the zeolite particles. The vertical alignment for centimeter scale large areas was achieved on a flat glass substrate by using flat-based zeolite crystals with an aspect ratio (length divided by width) of 1.1 while the crystals with an aspect ratio of 1.7 failed to align vertically. Thus the parameters important for successful alignment were determined. On the other hand, the unidirectional alignment in the horizontal packing structures was achieved by employing pregrooved substrates. We found that the relationship between the sizes of zeolite crystals and grooves is a crucial factor for the preparation of a close-packed structure. In this respect, our present preparation requires further improvements because it resulted in structures with many void spaces. Furthermore, we prepared the zeolite films loaded with unidirectionally aligned dyes to achieve optical functionalities.

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1. Introduction

Two-dimensional assemblies of micrometer-sized zeolite crystals into densely-packed monolayers are currently under intense research in zeolite science since the important contributions made by Yoon's group, because they have many applications in advanced materials, such as zeolite films, surface-modified electrodes, and photofunctional materials [1]. Among various types of interactions including ionic bonding, hydrogen bonding and physical adsorption, covalent linkages using silane coupling agents have been considered promising due to their simplicity and durability. The formation of uniformly oriented and closely-packed assemblies is especially intriguing, and one key factor to achieve successful formation of strictly regular structures is the use of uniform crystal sizes with flat crystal faces, allowing the continuous movement of microcrystals. This allows the determination of the most stable position on the substrate surface by sonication in suspended solvents and utilizing hydrophilic interactions between the crystals to self-assemble in relatively hydrophobic solvents.

Among the various types of zeolite crystals used as building blocks for zeolite assemblies, cylindrically-shaped zeolite L crystals forming vertically oriented monolayers have attracted much attention. This is because the orientation of dye molecules against the surface plane of a substrate is controllable if the orientation of the dye molecules is unidirectional inside the cylindrical channels that run along the direction of the long axis (c-axis) of crystals [2–5]. Previous fluorescence microscopy studies demonstrated that the various relative orientations of incorporated dyes against the main axis of the zeolite L crystal depend on the specific shape of the molecules and on the adsorption interaction between dyes and channel walls or charge compensating cations [6]. Strictly speaking, the dye orientation in the channels is not uniform, and can instead be represented by a double-horn-type distribution model [7].

The importance of aligning dye-doped zeolite crystals is evident from the fact that fascinating optical nonlinear properties such as the second harmonic generation arising from the highly organized arrangement of p-nitroaniline in zeolites are limited to single crystals, and therefore, applications are restricted to micrometer scales [8]. The concept of aligning zeolite single crystals allows the orientation of molecules on an area that exceeds zeolite dimensions by 2–3 orders of magnitude. Thus, for practical viability, efforts should be made toward utilizing uniformly-aligned zeolite crystals instead of crystal powders as hosts for the aligned inclusion of dyes.

Although monolayered assemblies of zeolite crystals on various substrates are extremely attractive as functional materials for optical and other applications, the technique to achieve these monolayered assemblies is complex and hence not widely used. Furthermore, a reproducible preparation on centimeter scale areas...
is difficult. Preparation on large areas is especially important for applications such as photonic crystals [9]. Therefore, we examined ways to further improve the method by making the preparation of the zeolite assemblies easy thus contributing to the development of zeolite monolayer-based technologies. In this study, preparation of zeolite crystals, loading of dyes, and the formation of monolayer assemblies of zeolite crystals, both unloaded and dye-loaded, on glass and polyester substrates are performed. Each step was examined using feed back about the quality of the outcome. Here, we show the optimum conditions and parameters for improved control of the preparation.

2. Experimental

2.1. Zeolite synthesis

Large-size zeolite L crystals were synthesized by the methods described in the literature [10]. The source of Al was either Al$_2$(SO$_4$)$_3$·18H$_2$O (Aldrich) or Al metal (Wako, 99.99%), and the source of Si was 40% aqueous colloidal silica (Ludox HS-40, Aldrich). The molar ratios of the synthesis gel for various aspect ratios of the crystals are given in Table 1.

For the preparation of the gel with the molar ratio of Al$_2$O$_3$·SiO$_2$·K$_2$O·H$_2$O = 1:20:10:1035, the following typical procedure was used: 2.80 g of Al$_2$(SO$_4$)$_3$·18H$_2$O was dissolved in an aqueous solution of 5.55 g of KOH and 45.5 g of distilled and deionized water. A diluted colloidal silica solution consisting of 12.6 g of Ludox HS-40 and 20.0 g of water was added to this transparent aqueous solution with vigorous stirring. The mixture was aged for 12 h at room temperature with continuous stirring, during which time the initial transparent gel turned turbid. The synthesis gel was then transferred into a Teflon-lined autoclave and heated to 180 °C for 4 days under static conditions. The zeolite crystals were collected by filtration and washed with a copious amount of distilled and deionized water. Finally, the zeolite crystals with similar sizes were collected after a separation based on the sedimentation of crude crystals by passing them through a 1.5 m-long water column. Syntheses following the same procedure but with different molar ratios of ingredients as given in Table 1 afforded crystals with different aspect ratios. The scanning electron microscope (SEM) images of the zeolite crystals thus prepared are shown in Fig. 1.

2.2. Zeolite assembly

Assembly of monolayered zeolite L crystals was performed according to the method proposed by Yoon’s group [1,11]. Glass substrates cleaned by immersing in a “piranha” solution (1:2 of H$_2$O$_2$·H$_2$SO$_4$) were first modified by 3-chloropropyltrimethoxysilane (CPTMS, Aldrich); typically 3–4 pieces of glass substrates (18 × 18 × 0.5 mm) supported on a comb-shaped Teflon mount were immersed in a dehydrated toluene solution (40 mL) of CPTMS

Table 1

<table>
<thead>
<tr>
<th>Label</th>
<th>Molar ratios in mother gels</th>
<th>Aspect ratio</th>
<th>Average length (nm)</th>
<th>Average width (nm)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Al$_2$O$_3$</td>
<td>SiO$_2$</td>
<td>K$_2$O</td>
<td>Na$_2$O</td>
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<td>a</td>
<td>1</td>
<td>20</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>b</td>
<td>1</td>
<td>12.5</td>
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<td>d</td>
<td>1</td>
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*a Length divided by width.

b Aluminum source is Al metal. Note that Al source in the rest of synthesis is Al$_2$(SO$_4$)$_3$·18H$_2$O.

Fig. 1. SEM images of zeolite crystals prepared in the present study. Synthetic parameters and size/shape parameters for labels from (a) to (d) are given in Table 1.
(0.1 M) and refluxed in argon for 3 h in a 100 mL cylindrical reactor (flat-bottomed separable flask with three necks). The CPTMS-modified glass substrates and dried zeolite L crystals (30 mg) were introduced into a capped 100 mL round-bottomed flask containing dehydrated toluene (40 mL) and sonicated for 5 min using a sonication bath (Branson 2510: 42 kHz, 100 W). During the sonication, a CPTMS-modified glass substrate was placed between two bare glass substrates of the same size on a Teflon mount; this method was previously used to effectively prevent the vertical accumulation of zeolite particles, resulting in a multilayered structure [1]. A similar procedure was applied for the assembly on a 76 μm thick-polyester grating film (Edmund Optics, 500 grooves/mm, depth 0.5 μm), and quartz substrates (20 × 20 mm) with rectangular grooves (surface width 2.0 μm, depth 1.5 μm, bottom width 2.0 μm, area 1.0 × 1.0 mm) supplied by AIST. SEM images of the grooved areas for both the polyester film and quartz substrate are shown in Fig. 2.

We spent three years checking the reproducibility of the zeolite assembly fabrication. Three undergraduate students were engaged in both zeolite synthesis and assembly for three consecutive years. By the end of the undergraduate research period, all three students have learned the technique to align zeolite L crystals both vertically and horizontally with a high degree of coverage and high degree of close packing of attached crystals. Considering this, the reproducibility of our experiment can be acceptable.

2.3. Dye incorporation

A cationic dye, trans-4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide (DASP+I2, Aldrich), was incorporated into the zeolite channels by ion exchange in an aqueous solution. Resorufin (7-hydroxy-3H-phenoxazin-3-one, Aldrich) was adsorbed from hot toluene solution. First, 0.5 mg of resorufin was dissolved in 50 mL of toluene by stirring for 1 h at 85 °C. Then, 0.4 g of dehydrated zeolite L crystals, were added to the solution, which was then refluxed overnight and centrifuged. Finally, the crystals were washed twice with toluene and dried in vacuum for 1 h.

2.4. Instrumentation

Bright-field and fluorescence microscopy images were acquired using an Olympus BX-51 microscope equipped with a 100 W mercury lamp. Emission spectra of the zeolite particles were recorded on a multichannel detector (Hamamatsu Photonics PMA-10), which was attached to the microscope. SEM images of the zeolite crystals were obtained using a Technix SEM 1710 electron microscope.

3. Results and discussion

3.1. Vertically oriented close packing of zeolite L crystals

Fig. 3a–c shows magnified images of the packing structure of zeolite L crystals with three representative shapes on a glass substrate.

The fabrication is based on a covalent linkage between OH groups on the glass surface and those on the zeolite surface through a silane coupling agent, CPTMS. Fig. 3a shows an image for zeolite L crystals with an aspect ratio (length divided by width) $A_R = 1.1 ± 0.2$ (Table 1a). In this method, random movements of the particles forced by sonication on the 2D surface created between the glass substrates placed in toluene solution facilitated the monolayer coverage of the glass surface. As shown in Fig. 3a, a vertically oriented closely-packed structure (see inset at the top-left for a magnified SEM view) of the crystals was prepared on almost the entire region of the 18 × 18 mm substrate surface. However, close inspection of Fig. 3a reveals that the observed packing structure is subject to defect sites, as typically indicated by the four boxed areas marked as 1–4.

The defects can be classified into two types: one represented by mark 1 (type A), and the rest represented by marks from 2 to 4 (type B) in Fig. 2a. Type A defects created in the monolayered crystal assemblies are small holes, in which one crystal particle failed to fill in. Previously, Yoon et al. proposed a mechanism by which a monolayer of cubic zeolite A crystals is formed on glass substrates [11]. First, randomly scattered particles are attached independently or as a small group by a covalent linkage to form seed particles. Subsequently, these seed sites grow in size by attracting surface migrating particles to form larger close-packed areas, possibly due to a self-organization mechanism stemming from inter-particle attraction forces. Mismatching arises when multiple close-packed areas meet, resulting in defect sites. The present observation for the vertical organization of cylindrical particles is consistent with the multi-nucleation mechanism, considering the large number of defects produced on the glass surface. Previously, type A defects with holes of the size of one crystal were observed to form even for the assemblies of monodispersed cubic zeolite A crystals that can be packed closely more easily [12]. Thus, type A defects are difficult to eliminate by this preparation method because the mismatching can inevitably take place at sites, where propagating assembly fronts meet.

On the other hand, type B defects generally occupy larger areas forming open spaces without particles. In addition, they contain particles that failed to align vertically, resulting in a horizontal arrangement. Type B defects are formed presumably due to the removal of small groups of particles that have a weak binding force.

**Fig. 2.** SEM images of pregrooved substrates: polyester grating film (a) and quartz substrate (b).
both with the substrate and other particles. The horizontal alignment on the substrate may weaken the binding interaction, due to smaller interaction areas, and loose packing of particles arising from distorted arrangement can result in weak interparticle interaction eventually leading to areal removal. Most importantly, the origin of type B defect is the presence of crystals defective in shape, which prevents unimpeded propagation of the close packing structure.

Factors affecting successful formation of the vertical orientation were investigated. The use of zeolite crystals with uniform size and shape is advantageous but not prerequisite. More importantly, the value of $A_R$ of the building blocks is crucial. For instance, Fig. 3b clearly shows that crystals with an aspect ratio of 1.7 ± 0.2 failed to form a vertical orientation compared with the crystals with $A_R = 1.1 ± 0.2$ (Table 1a) in Fig. 3a. Another requirement for the building block is the shape of the crystals. As shown in Fig. 3c, crystals with a round bottom by a different preparation method are not useful to form a totally vertical orientation, even though they have an $A_R$ value of 1.1 ± 0.2 (Table 1b). Here, a mixture of both vertically and horizontally oriented crystals is observed ubiquitously in Fig. 3c. Thus, the shape with a flat base is another important factor to be considered seriously. In this respect, we should pay special attention to the Al source used in crystal preparation, because the syntheses employing $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ gave superior results in terms of the crystal shape compared with those obtained employing the Al metal. Although near close-packed structures were prepared regardless of the crystal size and shape, when the orientation of the crystals is ignored, one should keep in mind that randomly oriented monolayers have many defect sites, as mentioned above, due to weaker interparticle binding interactions than those of the vertically oriented close packing.

3.2. Horizontally-aligned close packing of zeolite L crystals

Cylindrical zeolite L crystals are forced to align horizontally rather than vertically using crystals with $A_R > 1.1$, even though they have a flat base. On flat substrates, randomly oriented zeolite L particles formed film-like pseudo-packing with absolutely horizontal
alignment, as depicted in Fig. 3b, for crystals with $A_R = 1.7$. In addition, a similar structure was formed for crystals with $A_R = 2.4$ (Table 1c). If the crystals can align in the same direction in the horizontal arrangement, macroscopic alignment can be accomplished for dye molecules adsorbed in the unidirectional channels of zeolite crystals. Such an attempt was made previously for the alignment of coffin-shaped ZSM-5 crystals on a prestructured silicon (110) wafer [13]. Note that the silicon substrate is inappropriate for applications requiring optical transparency in the visible region. Here, we used a 76 $\mu$m thick-polyester grating film with V-shaped grooves of 2 $\mu$m width and 0.5 $\mu$m depth as a substrate (see Fig. 2a for a SEM image). The film was cleaned using ethanol instead of the “piranha” solution before surface modification with CPTMS. The FTIR spectrum of the film exhibited intense absorption bands in the region of 3400–3700 cm$^{-1}$ which is ascribable to OH groups. Thus, CPTMS serves as a linker between the film and zeolite particles as in the case of the glass substrates.

Fig. 4 shows large areal optical and SEM images of the unidirectional alignment of zeolite L crystals with the $A_R = 5.4 \pm 0.4$ (Table 1d).

Generally speaking, unidirectional alignment with a monolayer coverage was achieved in a large area of 1 x 1 cm as a well-packed structure. However, close inspection of the prepared film revealed that they contain countless empty defects as typically indicated in the magnified image in the figure. At first, the unidirectional arrangement of the long cylindrical particles on a patterned surface seems feasible; but, difficulty arises during the formation of close packing because interparticle attraction impedes the formation of self-assembled continuous structures on such surfaces. In reality, the film consisted of numerous groups of small packing structures, suggesting competition between the two major interactions: self-assembly formation and alignment in the direction of the groove pattern. The polyester film has V-shaped grooves with a width of 2 $\mu$m and a depth of 0.5 $\mu$m (Fig. 2a), on which cylindrical zeolite L crystals with an average diameter of 1.7 $\mu$m are placed. Thus, in principle, the zeolite L crystals can mutually interact to form covalent bonds through a linker when they are placed in grooves. However, a wide size distribution of the building blocks is a major disadvantage in forming long-lasting monolayer structures. Because of the limitations of synthetic and separation protocols that need further improvement, the zeolite film prepared presently is far from perfect.

It is interesting to note that Bossart and Calzaferri reported the alignment of zeolite L crystals on flower petals. They found that the alignment observed on flower petals was not determined by topological forces because of the self-cleaning properties of plant surfaces, originating from the rough structure on the micro- and nanoscale [14]. From their findings, it is suggested that the hydrophobic nature of the surface of the polyester film may be responsible for the difficulty in aligning the zeolite crystals by topological forces.

3.3. Assemblies of dye-loaded zeolite crystals

Fig. 5 exhibits both bright-field and fluorescence microscopy images of trans-4-[4-(dimethylamino)styryl]-1-methylpyridinium cations (DASP$^+$) and resorufin (see the chemical structure in Chart 1) incorporated in zeolite L crystals.

Fluorescence images were acquired for vertically and horizontally polarized emission signals, as well as for an unpolarized signal. Inspection of Fig. 5 clearly indicates that resorufin molecules are mostly aligned with their long axes perpendicular to the channel direction, while the DASP$^+$ moieties are aligned with their long axes parallel to the channel direction (see the structure of the main channel of zeolite L given in Chart 2) given that both molecules have an electronic transition dipole moment in the direction of the long molecular axis.

In Fig. 5, it can be seen that the concentration distribution of DASP$^+$ is homogeneous over the entire crystallites while that of resorufin is appreciably higher at both ends and lower in the crystal centers. Clearly, dyes penetrate from both ends of the crystals, and the penetration depth of ion-exchangeable cationic dyes depends on the period of immersion in dye solution [17]. Thus, homogeneous distribution of DASP$^+$ was achieved by more than three days of immersion in $10^{-3}$ M aqueous solution of the dye with stirring at room temperature. On the other hand, the adsorption of resorufin was difficult. Resorufin is soluble in alcohols, but attempts to adsorb resorufin into zeolite L crystals from methanol,
ethanol and 1-propanol failed because these alcohols are preferentially adsorbed compared with resorufin. Therefore, we employed hot toluene for adsorption of resorufin. Because of the greater penetration depths of toluene into the zeolite L crystals compared with those of resorufin, penetration inside the crystals was not achieved for resorufin.

Previous fluorescence microscopy investigations have revealed that the orientation of dyes incorporated into the channels of zeolite L depends largely on the size relationship between the host channel framework and guest species. Molecules longer than two unit cells are forced to align parallel to the channel direction while shorter molecules tend to arrange with a tilt angle or even perpendicularly. For instance, molecules such as 1, 4-bis(5-phenyl-2-oxazolyl)benzene (POPOP) and dimethylamino cyanostilbene (DCS) are examples of parallel arrangement in one-dimensional channels of zeolite L [6]. DASP⁺ has been found to align in the channel direction in silicalite-1 [15], which is consistent with the alignment observed currently in zeolite L. In contrast, in the present study, resorufin in zeolite L was found to align perpendicularly to the channel c-axis, similar to the case of N-methylacridine (MeAcr⁺) that was studied previously [5]. Interestingly, methylviologen with a size somewhere in between the above two types adopt a tilt geometry based on the Rietveld refinement of X-ray data: the angle between the main axis of a molecule and the c-axis of the zeolite is 27° [16]. Resorufin (pKₐ = 6.1) in zeolite L is deprotonated as depicted in Scheme 1 as indicated by its strongly

**Chart 1.** Structure of dye molecules.

**Chart 2.** The framework structure of the main channel of zeolite L.

Fig. 5. Optical and fluorescence microscopy images of trans-4-[4-(dimethylamino)styryl]-1-methylpyridinium cation, DASP⁺ (a–d) and resorufin (e–h) incorporated into zeolite L crystals: (a, e), bright-field image; (b, f), fluorescence image; (c, g), fluorescence image observed through a polarizer in the vertical direction; (d, h), fluorescence image through a polarizer in the horizontal direction.
emissive nature and may have a strong interaction with extra-framework K⁺ ions located in D sites (see Chart 2) [17]. According to a previous investigation on the photophysical properties of resorufin [18], the neutral form of resorufin (RH) has a broad absorption band with a peak at 500 nm and the deprotonated anionic form (R⁻) has a sharp peak at 572 nm in aqueous solution (pH 12.0). The anionic form, R⁻, is strongly luminescent with a fluorescence quantum yield of Φ_F = 0.74 and a fluorescence lifetime of τ_F = 2.9 ns while RH is only weakly fluorescent in aqueous solution. The diffuse reflectance absorption spectrum of resorufin-loaded zeolite L crystals revealed that resorufin is in neutral form in the presence of toluene and in deprotonated form upon evaporation of toluene [17]. This anionic form may be responsible for the perpendicular arrangement of zeolite in the channels, the walls of which contains cations that can interact with the anionic resorufin molecule.

The next step was to assemble zeolite L crystals incorporated with dye molecules to realize optical functionality. For this purpose, we employed two approaches: to assemble the dye-loaded zeolite crystals into a monolayer on substrates (method 1) and dye incorporation into the self-assembled monolayer of empty zeolites (method 2), using two dyes, resorufin and DASP⁺. We found that dye-incorporated zeolite crystals failed to form self-assembled structures on the substrates, leading to loose packing. This is because dye molecules adsorbed on the exterior surfaces of zeolite crystals act as obstacles to the formation of the assembly of zeolite crystals. Attempts to remove DASP⁺ residing outside the zeolite crystals by the Soxhlet extraction technique with 1-pentanol or 1-hexanol as eluent failed because a significant loss was observed for the concentration of molecules inside the channels. In this regard, Albuquerque and Calzaferri investigated a successful method to eliminate unwanted molecules from the outer surface by classifying system types describing the ability of dye-zeolite crystals to exchange matter with the environment [19]. According to their study, dyes can be washed out of the channels if the solvent is small enough to pass the dye inside. One solution might be to add stopcock molecules that can prevent dyes from going out of the channels.

On the other hand, method 2 allowed the formation of vertically aligned packing structures incorporating resorufin and DASP⁺ by submerging flat glass substrates assembled with a zeolite L monolayer into solutions of the dyes. A problem arises, however, as to the optical functionality of the zeolite films thus prepared given the fact that both resorufin- and DASP⁺-incorporated zeolite films strongly emit under illumination with excitation light parallel to the sample normal. The emission from resorufin-loaded film is acceptable because the excitation light is perpendicular to the direction of long molecular axis or the transition moment of the molecule; however, DASP⁺ molecules should not emit in principle when excited by a beam of light parallel to the direction of their transition moment. Thus, we have to conclude that DASP⁺ molecules are adsorbed on the outer surfaces of the zeolite L crystals with randomly oriented arrangement in addition to inside the channels.

We met another difficulty in realizing the high optical performance of horizontally aligned dye-loaded zeolite monolayers on polyester grating films because the dyes are strongly adsorbed directly on the film and emission from the base film strongly interferes with the emission signal from aligned dye molecules in the zeolite crystals. Neither surface treatment with tetraethoxysilicate (TEOS) nor vacuum deposition of SiO₂ on the polyester film helped greatly to prevent dye attachment. Thus, we switched the substrate from the polyester film to a quartz plate with rectangular

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**Scheme 1.**

**Fig. 6.** Bright-field (far left) and fluorescence microscopy images of dye-loaded zeolite L crystals aligned in the rectangular grooves on a quartz glass substrate. Dyes incorporated: (A) DASP⁺, (B) resorufin. The images in the second column are fluorescence images without a polarizer; those in the third column, fluorescence images through a polarizer in the vertical direction; and the fourth column, fluorescence images through a polarizer in the horizontal direction. Bars represent 10 μm.
grooves (see Fig. 2b for SEM image) for the horizontal alignment of dye-loaded crystals. Fig. 6 represents bright-field and fluorescence microscopy images of the same location on the quartz substrate with aligned zeolite L crystals \((A_k = 5.4 \pm 0.4 (d \text{ in Table 1}))\) along the grooves.

Resorufin and DASP\(^+\) were again loaded according to method 2 given above. Although the alignment of zeolite crystals was realized, close packing in the rectangular grooves was unsatisfactory. In addition, attachment of crystals on the surface of the grooves was not observed. This is because the rectangular grooves interfere with the formation of self-assembled crystals leading to the close packing observed on flat surfaces. Nevertheless, the fluorescence microscopy images in Fig. 6 clearly demonstrate the areal response of fluorescence intensity as an ensemble image of individual particles observed in Fig. 5. Further improvements in preparing a close packing structure by modification of groove parameters will bring about zeolite-based true optical functional materials.

4. Summary

We examined the method to prepare a close-packed monolayer of cylindrically-shaped zeolite crystal assemblies on plastic and glass substrates with both vertically and horizontally arranged array structures. Here, emphasis was placed on the preparation on large-scales. We demonstrated that the preparation of the assemblies with vertical alignment in a large area on flat surfaces can be achieved with relative ease following the procedure developed by Yoon's group, provided that zeolite L crystals of a few micrometer size with proper shapes are employed such as those with an aspect ratio of less than 1.1 \(\pm 0.2\) and with flat bases. In this respect, the separation of crystals with similar sizes from crude synthetic products is a key factor because of the large-size distribution of crude crystals. In a strict sense, however, it is difficult to avoid the formation of defects: one is a small hole in which one or two crystals failed to fill in, and the other is the formation of a relatively large empty area where a group of crystals are removed during the preparation process because of a weak binding force. The latter defects are probably triggered by the incidence of horizontally placed crystals due to ill-defined crystal shapes during the course of vertical assembly formation. On the other hand, the fabrication of horizontally aligned unidirectional array structures on grooved surfaces is difficult because of the competition between the formation of self-assemblies and alignment in the direction of grooves. As a result, in one case, small-sized crystal assemblies with scattered small empty spaces are formed on a shallow V-shaped groove structure because of a weak alignment force, while in the other case, the crystal assemblies are completely destroyed on a deep rectangular groove structure because of a much stronger alignment force. Finally, an attempt was made to load fluorescent dyes on the zeolite assemblies thus prepared to examine the optical functionality of the zeolite film for future applications. A clear response was obtained from the observation of fluorescence images of horizontally aligned films using a polarizer, suggesting the macroscopic alignment of the dyes, although no clear response was obtained for vertically aligned films due to the disturbance from the dyes attached on the outer surfaces of the crystals with random orientations. Thus, the present study showed a way to conveniently prepare two types of close-packed aligned films of zeolite L crystals for non-specially trained materials scientists. The most intriguing feature of the films is the feasibility of the preparation of macroscopically aligned dye structures, which may find many applications. Further improvements in the method may realize more sophisticated optical functionality.

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