

Manual Assembly of Microcrystal Monolayers on Substrates**

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Atoms, molecules, enzymes, proteins, DNAs, RNAs, nanoparticles, microparticles, tiles, and bricks are some of the most commonly encountered building blocks in chemistry and architecture. These building blocks can be grouped into subnanometer (atoms), nanometer (molecules, enzymes, proteins, DNAs, RNAs, and nanoparticles), micrometer (microparticles), and millimeter-to-centimeter (tiles and bricks) building blocks based on their sizes.

One of the important applications of building blocks is to organize them as monolayers on various substrates. Self-assembly has been the method of choice for the monolayer assembly of nanometer^[1–5] and micrometer^[6–25] building blocks on substrates, whereas direct attachment of building blocks with the hands (referred to as “direct attachment” hereafter) on adhesive-coated substrates is the method for the monolayer assembly of millimeter-to-centimeter building blocks on substrates (floors and walls). Thus, the method for monolayer attachment of building blocks on substrates has to switch from self-assembly to direct attachment at some stage as the size of the building block increases. But what is the upper size limit for self-assembly? What is the lower size limit for direct attachment? At what size regime do both self-assembly and direct attachment work simultaneously for monolayer assembly? In the overlapping region, which method is better in terms of quality of the monolayer?

Herein, we report that the upper size limit for self-assembly is $\approx 3 \mu\text{m}$, the lower size limit for direct attachment is $\approx 0.5 \mu\text{m}$, and direct attachment is superior to self-assembly in the overlapping region ($\approx 0.5\text{--}3 \mu\text{m}$) with respect to rate, degree of close packing, uniform orientation of the assembled microcrystals, substrate area, and ecological considerations.

We used zeolite microcrystals as model system because they can be produced in fairly uniform sizes and shapes, and their monolayers can be applied as precursors for molecular sieve membranes,^[17–20] low-dielectric materials,^[24,26] supra-molecular energy-transfer systems,^[13–16,27] nonlinear optical films,^[28] anisotropic photoluminescent films,^[12] and other advanced materials.^[29]

Silicalite-1 and ETS-10 (see the Supporting Information) crystals were used in this study. In the case of silicalite-1, crystals with four different sizes were employed. The average sizes and volumes [$a \times b \times c$ (volume)] were: $0.3 \times 0.1 \times 0.6$ (0.02), $1.3 \times 0.5 \times 1.7$ (1.11), $2.5 \times 1.2 \times 4.1$ (12.3), and $4.6 \times 1.5 \times 11 \mu\text{m}^3$ ($75.9 \mu\text{m}^3$). In the case of ETS-10, only crystals with an average size of $12 \times 12 \times 7 \mu\text{m}^3$ ($1008 \mu\text{m}^3$) were used. The volume ratio for these crystals was 1:56:615:3795:50400. Glass plates with two different sizes, 18×18 and $150 \times 150 \text{ mm}^2$, were used as the substrates.

Among various tested types of bonding between microcrystals and substrates, we found that ionic bonding and hydrogen bonding (Figure 1) were most effective for the monolayer assembly of microcrystals by direct attachment. The ionic bonding was induced between trimethylpropylam-

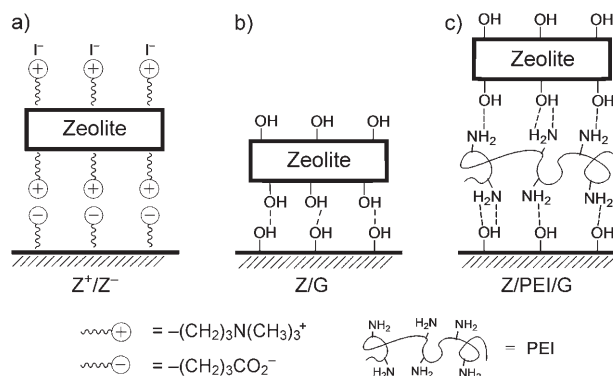


Figure 1. Types of bonding effective for the monolayer assembly of zeolite (Z) microcrystals on substrates. a) Ionic bonding between the zeolite-tethered TMP⁺ and glass (G)-tethered Bu⁻, b) hydrogen bonding between the surface hydroxy groups of zeolite and glass, and c) PEI-mediated hydrogen bonding between the surface hydroxy groups of zeolite and glass.

monium (TMP⁺) groups tethered to silicalite-1 (TMP⁺-SL) surfaces and butyrate (Bu⁻) groups tethered to glass (Bu⁻-G) plates (Figure 1a).^[7] In the case of hydrogen bonding, two types were tested: one between the surface hydroxy groups of bare zeolite crystals and bare glass substrates (Figure 1b), and the other between the zeolite surface hydroxy groups and poly(ethyleneimine) (PEI) and between PEI and the surface hydroxy groups of bare glass substrates (Figure 1c). The effectiveness of hydrogen bonding for monolayer assembly^[8] and the phenomenon that the use of polymeric linkers increases the binding strength between microcrystals and substrates have already been demonstrated.^[9]

As a practical example of direct attachment, zeolite powders were simply rubbed onto substrates with a finger (Figure 2). To avoid contamination of the glass and microcrystals with moisture from the finger, a soft latex glove was

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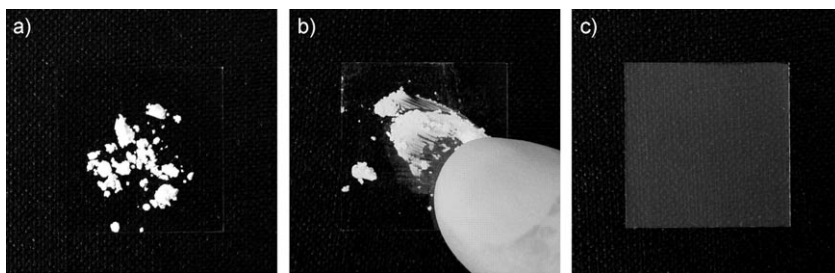


Figure 2. Photographic images showing the process (a–c) of monolayer assembly of silicalite-1 microcrystals on glass through ionic bonding by rubbing.

used. The typical rubbing period was 10–20 s for the $18 \times 18 \text{ mm}^2$ glass plates. For comparison, the sonication-with-stacking (referred to as “sonication” hereafter) method^[10] was also used for the monolayer assembly of $\text{TMP}^+\text{-SL}$ microcrystals on $\text{Bu}^-\text{-G}$. We also tested the effectiveness of rubbing for the monolayer assembly of microcrystals ($0.5\text{--}2 \mu\text{m}$ in size) through the formation of covalent linkages between the surface hydroxy (HO-) groups of silicalite-1 and the chloropropyl ($\text{Cl-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$) groups tethered to glass.^[11] Although the formation of this linkage has been highly effective for the monolayer assembly of microcrystals by sonication,^[10] it was not effective with rubbing, presumably because rubbing does not give sufficient kinetic energy to the functional groups such that they can form covalent linkages.

A typical scanning electron microscopy (SEM) image of the monolayer of $\text{TMP}^+\text{-SL}$ microcrystals ($1.3 \times 0.5 \times 1.7 \mu\text{m}^3$ in size) prepared on a $\text{Bu}^-\text{-G}$ plate by rubbing is shown in Figure 3a. For comparison, a monolayer of the same $\text{TMP}^+\text{-SL}$ microcrystals on a $\text{Bu}^-\text{-G}$ plate prepared by sonication is shown in Figure 3b. As noted, the degrees of coverage and close packing of the microcrystals on the substrates were very similar in both cases—despite the fact that rubbing is incomparably simpler than sonication and does not require solvents, reactors, or other equipment (such as a sonication bath), and that the required period for monolayer assembly

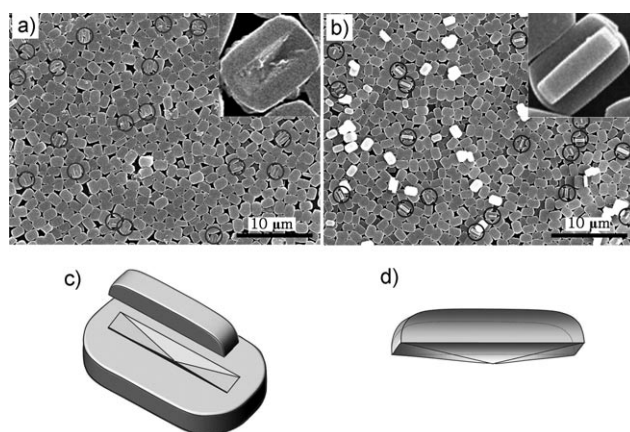


Figure 3. a,b) SEM images of the monolayers of $\text{TMP}^+\text{-SL}$ microcrystals ($1.3 \times 0.5 \times 1.7 \mu\text{m}^3$) assembled on $\text{Bu}^-\text{-G}$ plates by a) rubbing and b) the sonication-with-stacking method. c) Enlarged structures of mother and parasitic crystals that were drawn based on the inset of (a) and the twinned crystals in (b), and d) the perspective view of the parasitic crystal.

was shorter: 10–20 s in the case of rubbing versus 180 s in the case of sonication. Furthermore, there were no physically adsorbed second-layer crystals on the microcrystal monolayers prepared by rubbing, which indicates that the weakly adhered microcrystals were removed from the chemically attached crystals during rubbing.

Interestingly, in the monolayers of $\text{TMP}^+\text{-SL}$ crystals prepared by sonication, many crystals carry a 90° -intergrown parasitic crystal^[30,31] on the (010) plane of the mother crystal (see the inset and the circled crystals in Figure 3b), whereas the monolayers prepared by rubbing did not have such crystals as all the parasitic components were dislodged from the mother crystals during monolayer assembly (see the inset and the circled crystals in Figure 3a). For larger crystals ($> 20 \mu\text{m}$),^[30] it has been shown that the intergrown parasitic crystals can be removed from the mother crystals by strong sonication, and that the structures of the adjoining components look like the diagrams shown in Figure 3c and d. For smaller crystals, however, there have been no methods for dislodging the intergrown parasitic crystals from the mother crystals, and the structures of the adjoining components were not known. We now show that even in such small silicalite-1 crystals ($< 2 \mu\text{m}$), the adjoining structures are the same as those of large crystals. The above result further revealed that the binding strength between the parasitic and mother crystals at the interface is weaker than both the tensile strength of the silicalite-1 crystal along the (100) plane and the binding strength between the microcrystal and substrate.

Although the silicalite-1 crystal morphology can be controlled by structure-directing agents,^[32] it is usually difficult to prepare batches that do not have the crystals carrying 90° -intergrown crystals. Accordingly, the preparation of monolayers of silicalite-1 crystals free from the crystals carrying 90° -intergrown parasitic crystals, and of the corresponding continuous silicalite-1 films with no a -oriented spots, has been difficult. Now, the rubbing method enables the monolayer assembly of silicalite-1 crystals free from parasitic crystals.

Figure 4 shows SEM images of the monolayers of silicalite-1 (Figure 4a–d) and ETS-10 (Figure 4e,f) crystals that were formed by rubbing. These images emphasize an important fact: the rubbing (direct attachment) method, although very simple, still yields high-quality monolayers regardless of the crystal size from 0.5 to $12 \mu\text{m}$. Although we could not carry out the experiment with crystals larger than $12 \mu\text{m}$ because these were difficult to obtain with uniform sizes and shapes, we believe that rubbing would work equally well for their monolayer assembly. The above result shows that the lower limit for direct attachment is below $0.5 \mu\text{m}$. This lower size limit may decrease even further if we could conduct an experiment with smaller crystals, which was not possible at this stage because of the difficulty in preparing smaller crystals with flat facets in fairly uniform sizes.

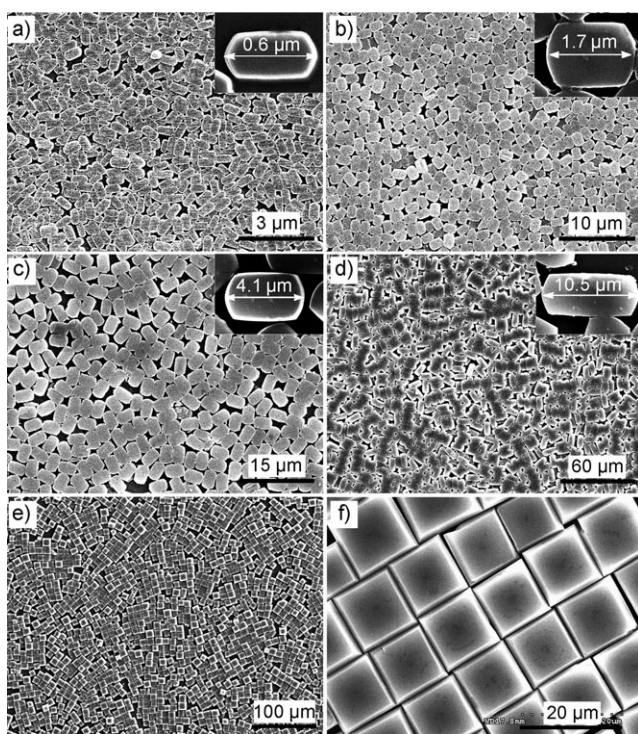


Figure 4. a–d) SEM images of TMP^+ -SL crystals of different average sizes (see insets) and e, f) TMP^+ -coated ETS-10 crystals ($12 \times 12 \times 7 \mu\text{m}^3$) at magnifications of 300 (e) and 2000 (f), respectively.

Monolayer assembly of the microcrystals was also conducted by sonication. We found that the upper size limit of the sonication method or self-assembly was about $3 \mu\text{m}$. As a result of their weight, crystals with sizes $\geq 3 \mu\text{m}$ did not disperse well into the solution even by sonication. Thus, at the present moment, the sizes of building blocks can be divided into three regimes: below $0.5 \mu\text{m}$, $0.5\text{--}3 \mu\text{m}$, and above $3 \mu\text{m}$, at which only self-assembly, both self-assembly and direct attachment, and only direct attachment, respectively, work for monolayer assembly.

Rubbing is also much more effective for the monolayer assembly of microcrystals on large-area substrates at high speed. For instance, a $150 \times 150 \text{ mm}^2$ glass plate (Figure 5) can be covered with a high-quality monolayer of silicalite-1 crystals with an average size around $2 \mu\text{m}$ within 1 min. We believe that the rate can be increased further by optimizing the procedure. This feature will enable mass production of microcrystal-coated large substrates, which will provide supported zeolite microcrystal monolayers for various applications, such as high-throughput membrane filters,^[17–20] supramolecular light-harvesting systems,^[13–16] and nonlinear optical films.^[28] Patterned monolayer assemblies can also be obtained by rubbing the zeolite microcrystals on selected areas.^[33–35]

Hydrogen bonding was also effective for monolayer assembly by rubbing. Thus, when freshly calcined silicalite powders were rubbed on clean glass plates (Figure 1 b), high-quality monolayers of silicalite crystals were formed on the substrate. However, the binding strengths between micro-

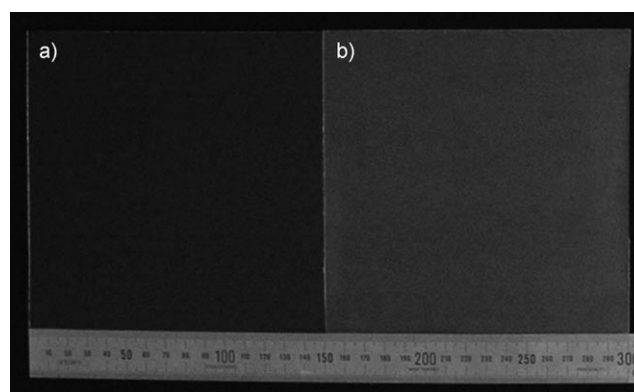


Figure 5. Photographic images of large glass plates ($150 \times 150 \text{ mm}^2$) a) before and b) after monolayer assembly of silicalite-1 microcrystals ($1.3 \times 0.5 \times 1.7 \mu\text{m}^3$) using PEI as the interfacial hydrogen-bonding mediator.

crystals and substrates were weak, and this method was only effective with very clean substrates. The use of PEI as the interlayer hydrogen-bonding mediator (Figure 1 c) was highly advantageous for the assembly of high-quality monolayers of large silicalite-1 and ETS-10 microcrystals. This method seems to be the most appropriate for the monolayer assembly of microcrystals on large substrates at high speed, as PEI can be conveniently coated on glass plates by either spin- or dip-coating, which are highly suitable for the high-speed coating of large-area substrates with polymers. The microcrystals can be almost permanently attached to the substrate by calcination.

We believe that “pressing” of the microcrystals against the substrate and the forced surface migration of the crystals during rubbing are the two most important factors that led to the facile attachment of crystals on substrates with high degrees of close packing. The use of a folded flexible rubber sheet or a folded piece of ultrafine-threaded cloth (see the Supporting Information) proved as effective as the use of fingers. This result will be helpful for mass production of microcrystal monolayers on large substrates, including those that were coated with mesoporous silica films.

In summary, we have reported that monolayers of submicro- and microcrystals can be readily assembled on substrates not only by self-assembly as if they were molecules and nanoparticles, but also by direct attachment by hand (rubbing), without using solvents, reactors, or equipment, as if they were tiles or bricks. The upper size limit of the self-assembly method (sonication-with-stacking method)^[10] was around $3 \mu\text{m}$, whereas rubbing worked well for microcrystals with sizes between 0.5 and $12 \mu\text{m}$. Ionic and hydrogen bonding gave the best results for the monolayer assembly of microcrystals by rubbing. The rate of monolayer assembly by rubbing was much faster than that by sonication-induced self-assembly. The degrees of close packing and uniform orientation of the crystals in the monolayer were also better. This method was highly suitable for the monolayer assembly of microcrystals on large substrates at high speeds. The use of PEI as the hydrogen-bonding mediator is highly desirable. In the case of silicalite-1 crystals, the 90° -intergrown parasitic

crystals were removed from the mother crystals during rubbing, resulting in monolayers of all-*b*-oriented silicalite crystals.

Experimental Section

Procedures for monolayer assembly: The materials used are described in the Supporting Information. A sodium butyrate tethered glass (Bu⁻Na⁺-G) plate was placed on a clean weighing paper. Subsequently, crystals of trimethylpropylammonium iodide tethered zeolite (TMP⁺I⁻-Z; 10 mg) were placed on the plate and were gently rubbed by a finger. To avoid contamination of substrates and zeolite microparticles, a clean soft latex glove was placed tightly on the finger. Other devices, such as a soft rubber sheet or folded ultrafine fabric, were also employed. PEI was coated on the glass plates by spin- or dip-coating. The above procedure for the monolayer assembly of microcrystals on glass was repeated by replacing the TMP⁺I⁻-Z crystals with bare zeolite crystals and the Bu⁻Na⁺-G plates with PEI-coated glass plates.

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