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Organization of Microcrystals on Glass by Adenine−Thymine Hydrogen Bonding

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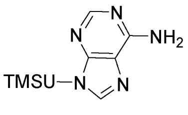
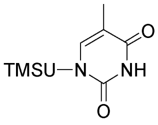
The ability to organize micrometer-sized building blocks with well-defined chemical linkages is one of the essential elements for the development of bio- and materials science.[1] Accordingly, increasing attention has been paid to acquiring the ability to organize microcrystals.[2,3] We have also been interested in developing the methods for organizing microcrystals in the form of highly oriented mono- and multilayers on glass and other substrates through well-defined covalent and ionic linkages,[4] by using zeolite crystals as model microcrystals. Knowing that multiple hydrogen bonding between the complementary oligomers of DNA strands is an effective way to organize nanoparticles tethered with the DNA strands,[5] we have been curious to know whether the comparatively very weak hydrogen bonding could also be employed for organization of even microcrystals whose external-to-internal surface ratios are much smaller than those of nanoparticles.

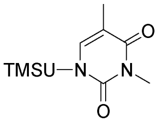
As a means to test the possibility, we prepared ZSM-5 (0.6 μm × 1.7 μm × 2.5 μm) and zeolite-A (1.7 μm × 1.7 μm × 1.7 μm) crystals and 11-trimethoxysilyl-*n*-undecyl-tethering adenine, thymine, and 3-methylthymine (designated as 9-TMSU-A, 1-TMSU-T, and 1-TMSU-3-MT, respectively) as described in the Supporting Information.



9-TMSU-A



1-TMSU-T



1-TMSU-3-MT

Adenine (A) groups were tethered to the surfaces of clean glass plates (GL, 1.8 mm × 1.8 mm × 0.2 mm) through undecyl spacers, and thymine (T) and 3-methylthymine (3-MT) groups, respectively, were similarly tethered to the surfaces of zeolite crystals through undecyl spacers as described in the Supporting Information (designated as T-zeolite-A, T-ZSM-5, 3-MT-zeolite-A, and 3-MT-ZSM5, respectively.) The evidence for the ready attachment of A, T, and 3-MT onto the corresponding substrates is also described in the Supporting Information.

As a test case, a piece of A-tethering glass plate (A-GL) was introduced into an aqueous solution (5 mL) dispersed with T-ZSM-5 (3 mg), and the heterogeneous mixture was gently shaken for 3 h. The glass plate was then washed with copious amounts of gently flowing water, dried in air, and subsequently sonicated in toluene for 5 s to remove physisorbed zeolite crystals.

Analyses of the sonicated, still opaque glass plate with scanning electron microscope (SEM) revealed that both sides were covered with very closely packed monolayers of ZSM-5 microcrystals over the entire glass plate, as typically shown in Figure 1A. However, the adhered amounts of ZSM-5 crystals were much less, even before sonication, when a bare (untreated) GL and bare ZSM-5, a bare GL and T-ZSM-5, an A-GL and bare ZSM-5, or an A-GL and 3-MT-ZSM-5 were employed (see Supporting Information for details). Furthermore, almost all of the adhered zeolite crystals fell off the corresponding GL during the 5-s period of sonication, indicating that tethering of A on GL and T (but not 3-MT) on ZSM-5, respectively, is essential for the monolayer assembly.[6] The coverage of GL with zeolite crystals was also very poor when the same type of base, either A or T, was tethered to the surfaces of both GL and zeolite crystals.

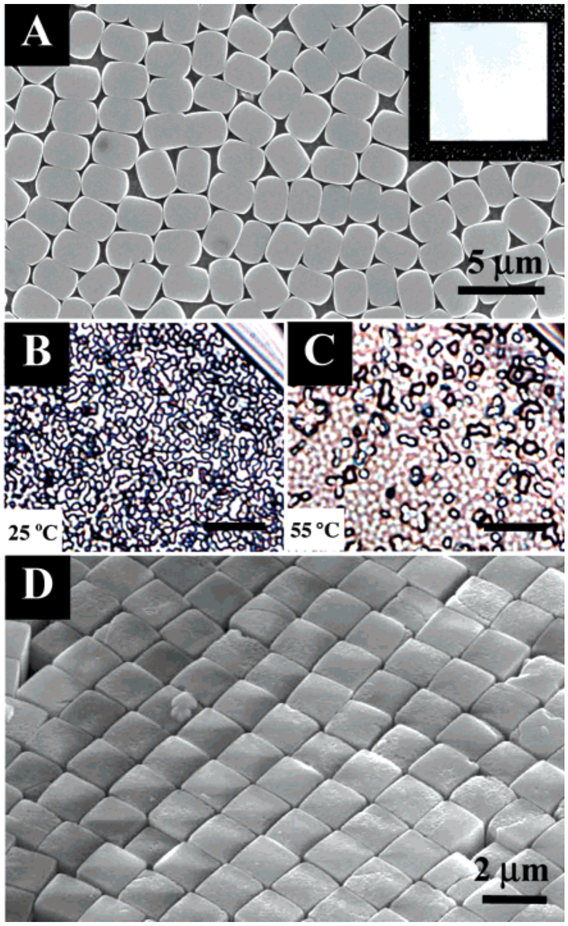


Figure 1. (A) SEM image of a monolayer of T-ZSM-5 crystals assembled on A-GL. The inset shows the digital camera image of the entire glass plate (1.8 cm × 1.8 cm) covered with the monolayer of T-ZSM-5 crystals. (B) Optical microscope image of the randomly dispersed monolayer of T-ZSM-5 crystals on A-GL obtained after 30 min at 25 °C (scale bar = 20 μm). (C) Optical microscope image of A-GL showing a closely packed monolyer of T-ZSM-5 crystals after keeping the glass plate shown in (B) still in fresh water for 20 min at 55 °C. (D) SEM image of a monolayer of cubic T-zeolite-A crystals assembled on A-GL at 50 °C.

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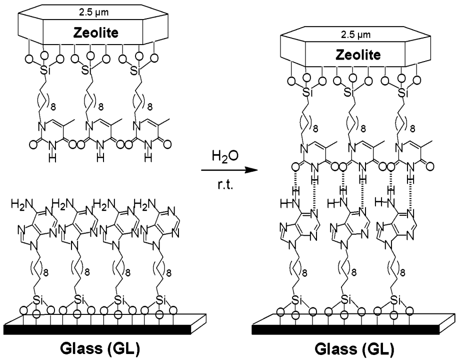
Scheme 1



On the basis of the above results, it is now clear that large microcrystals with the average size of even 2.5 μm (2500 nm) can be readily organized in the form of a monolayer on GL through A−T hydrogen-bonding interactions according to Scheme 1, although only a face of each crystal is involved in the hydrogen bonding.

The sonication-induced detachment test[4c] revealed that about half of the zeolite crystals were detached from GL after sonication for 1 min, indicating that, as expected, the average binding strength between each zeolite crystal and glass surface is much weaker than those of the zeolite crystals bound to glass plates by the previously reported covalent and ionic linkages.[4]

Interestingly, while it takes about 3 h to obtain glass plates fully covered with somewhat closely packed monolayers of ZSM-5 crystals between 25 and 50 °C, it takes only ∼1 h at 55 °C to obtain fully covered monolayers, and that with much larger closely packed domains. For instance, the optical microscope image of the A-GL which was allowed to contact with T-ZSM-5 for 30 min at room temperature showed that the glass was covered mostly with small domains of closely packed crystals consisting of less than 10 crystals as typically shown in Figure 1B. However, the small domains underwent rapid merging into much larger closely packed domains (Figure 1C)[7] when the glass plate was kept horizontal for 20 min in fresh water at 55 °C. In contrast, such a phenomenon did not occur during such a short period of time at lower temperatures ($<$50 °C). At higher temperatures ($>$55 °C), the degree of close packing sharply decreased. Interestingly, even when the glass plate was kept still vertically, the coverage of the glass plate with the zeolite crystals remained the same at temperatures equal to and below 55 °C, but it dropped sharply as the temperature exceeded 55 °C.

We believe the above phenomenon occurs due to rapid bond breaking and bond reforming (annealing)[8] between the surface-bound complementary DNA bases at 55 °C, which allows facile migration of the crystals on the glass surface leading to close packing[9] between the crystals. Indeed, analyses of the monolayers of T-ZSM-5 on A-GL and T-zeolite-A on A-GL by differential scanning calorimetry (DSC) in the dry state[10] showed endotherms at around 30 °C[11] that are ascribable to melting of the surface-bound DNA complementary bases bound to each other. (See the Supporting Information for details.) Similarly, the solid mixture of parent (unmodified) T and A powders also showed an endotherm at 25 °C.[12] In contrast, none of free T, free A, T-ZSM-5, T-zeolite-A, A-GL, and a monolayer of ZSM-5 assembled on GL by a covalent (propyl ether)[4d] linkage showed endothermic peaks in the temperature region of −10−80 °C.

T-zeolite-A crystals more readily yielded monolayers with larger domains of closely packed crystals in the same three-dimensional (3D) orientation when the assembly was carried out at 50 °C for 1 h as shown in Figure 1D, presumably due to their cubic morphologies. 3-MT-zeolite-A also did not assemble monolayers on A-GL, confirming that A−T base pairing is essential for monolayer assembly. We also found that very strong bonding results between zeolite crystals and glass plates when calcined at 400 °C for 5 h. Therefore, the methodology presented in this report could further be developed into a method for preparing glass plates covered with monolayers of zeolite-A crystals with a uniform 3D orientation.

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Supporting Information Available: Procedures for the synthesis of zeolites, 9-TMSU-A, 1-TMSU-T, and 1-TMSU-3-MT, procedures for tethering A, T, and 3-MT on solid supports, characterization of A-GL, T-ZSM-5, 3-MT-ZSM-5, camera images showing the results of control experiments, and DSC curves (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) It was reported that bare glass plates can also adsorb monolayers of bare zeolite crystals through hydrogen bonding between the surface hydroxy groups. However, the above process is highly sensitive to pH and the degree of packing between the crystals is rather poor. See ref 3.

(7) The boundary between zeolite crystals becomes dim and fuzzy in the optical microscope image when the crystals closely pack.

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(9) As for the driving force for the close packing, the weak hydrogen-bonding interaction between the surface-bound T groups, hydrophobic interaction of the modified surfaces, and capillary forces are likely to be responsible.

(10) As a means to avoid obscurity caused by the very strong DSC curve of water, the samples were loaded in the dry state.

(11) The shift of the melting temperature from 55 (in water) to 30 °C (no solvent) may arise due to change of the medium since the medium is known to sensitively affect the DSC endotherms (see. ref 8d, p 89).

(12) The endotherm from the mixture of parent A and T powders is likely to arise due to the hydrogen-bonding interaction at the interfaces between the complementary solid particles.

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