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COMMUNICATION

Facile Assembly of Nanocrystals by Optimizing Humidity

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5 The ambient humidity and the nature of substrates are considered coordinately in assembly of nano-sized crystals. The nanocrystal monolayers show large-area uniformity without any aggregates. Zeolite and hematite monolayers with thicknesses of 20 ~ 100 nm and excellent orientations are
10 produced.

Significant advances in nanocrystal synthesis has led to the preparation of a wide variety of high-quality nanocrystals with well-controlled sizes, shapes, compositions and frameworks.¹ The crystal shapes include spheres, cubes, plates, prisms, rods,
15 octahedrons, and etc.² The availability of these nanocrystals has provided an opportunity to systematically study the process of nanocrystal assembly,³ and the ability to assemble nanocrystals into highly ordered architectures resulting in unique and collective physical and chemical properties.⁴ The assembled
20 structures are powerful tools for designing and fabricating functional materials of interest for novel application in areas such as biomedical diagnosis, catalysis, plasmonics, high-density data storage, energy conversion and membrane separation.⁵ These promises have stimulated research efforts to study nanocrystal
25 assembly, and a number of important methods have been developed for the preparation of thin films with a variety of nanocrystals in the past decade.⁶ In particular, many reports concern the fabrication of oriented monolayers or thin films by using micro- or nano-sized zeolite and hematite crystals as
30 building blocks.⁷

Assembly of zeolite microcrystals into oriented monolayers has also attracted much attention in recent years as these materials can be applied as membranes,⁸ chemical sensors⁹ and hosts for supramolecular organization of guest molecules or
35 nanostructures.¹⁰ Methods for assembly of micro-sized zeolite have been developed, such as ultrasonic assisted assembly¹¹, manual assembly¹², and air-water interfacial assembly.¹³ Hematite (α -Fe₂O₃) has been used as photoanode,¹⁴ photocatalyst¹⁵ and ordinary catalyst.¹⁶ For many applications,
40 thin and uniform films are required. Consequently, the preparation of thin films of iron oxide nanoparticles has been reported during the past decades. These methods include electro-deposition¹⁷ and sol-gel techniques,¹⁸ oxidation of bulk iron in a surrounding gas,¹⁹ and self-assembly.²⁰

45 For assembly of nano-sized crystals, some approaches such as spin-coating,^{6a} dip-coating,²¹ slow evaporation,⁴ Langmuir-Blodgett,²² adsorption²³ etc, have been developed. They are

multi-step procedures and require a long period of time for completion of the assembly. Manual assembly has been proven to
50 be an effective and rapid method.²⁴ Former researchers reported that the lower limit for manual assembly of zeolite crystals was 500 nm,^{24a} because of the difficulty in preparing smaller crystals with flat facets in fairly uniform sizes. This limit was lowered to 100 nm by using spherical silica beads as raw material.^{24b} Nano-
55 sized zeolite MFI (Mordenite Framework Inverted) layer with crystals size of 50 nm ~ 100 nm could be produced on alumina substrate in one minute by manual assembly.^{24c} However, the random orientation of the crystal layer and the formation of unbroken aggregates are drawbacks of this method.

60 In the present study, we demonstrate the manual assembly of nano-sized crystals with different shapes (plate-like, cubic, octahedral, and spindle) into monolayers with uniform orientation on both hydrophilic and less hydrophilic surfaces. The zeolite crystal size and monolayer thickness (20 ~ 100 nm) are smaller
65 than previously reported works. The as-prepared nanocrystal monolayers show large-area uniformity without unbroken aggregates on the support. Further, we show that the humidity, substrate nature and contact pressure are important parameters that must be matched in order to arrive at well-defined
70 monolayers. The nanocrystals were synthesized according to the literature procedures,^{6a,25} experimental details were described in Supporting Information.

As shown in Fig. 1a and b, the MFI-OH and MFI-F crystals have average sizes of 40 nm and 200 × 20 nm, respectively. The
75 40 nm MFI-OH crystals have a pseudo-plate habit, it still can be used as building blocks in manual assembly to form well-defined monolayer. The flake-like MFI-F crystals have a large [010] surface resulting in a good contact with the support. However, the affinity between two [010] facets of these crystals make the
80 sparsely attached second layer hard to be removed by gentle wiping. LTA (Linde Type A) crystals with average size of 90 nm possessed rounded cube habit whereas the LTA zeolite with average size of 200 nm showed a well-developed cubic shape. Both crystals can readily be assembled into close-packed
85 monolayers with their [200] planes contact the substrates, Fig. 1c, d. Zeolite FAU (Faujasite) crystal with an average size of 80 nm has an octahedral habit. It was assembled into a monolayer with the [111] facet of each crystal parallel with the substrate, Fig. 1e. The spindle shaped hematite crystals was assembled into a
90 monolayer with its [110] face parallel to the support, Fig. 1f. XRD patterns of these crystals monolayers were shown in Fig.S1.

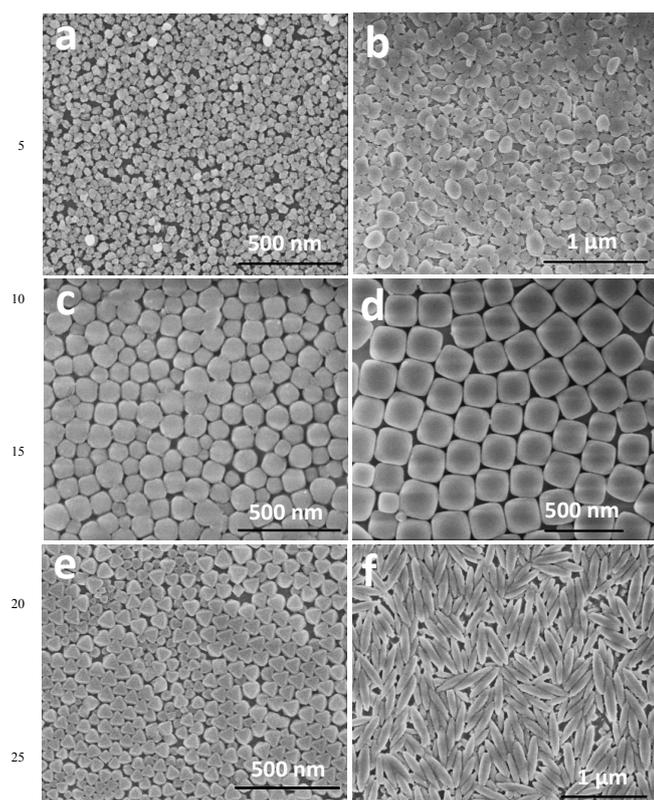


Fig. 1 SEM images of pure silica MFI monolayers with crystal size of a) 40 nm, b) 200 × 20 nm; LTA monolayers with crystal size of c) 90nm, d) 200 nm; FAU monolayer with crystal size of 80 nm e); spindle hematite monolayer with crystal size of 500 × 100 nm f).

The levels of moisture (water concentration) plays crucial role in both dry and wet assembly methods. For wet self-assembly processes, when using silane coupling agent as linker to attach zeolite micro-crystal onto silica, alumina or polymer surfaces, dry toluene reflux under dry argon atmosphere were imperative for a successful result.^{7a} While, the interfacial assembly techniques need a wet environment²⁶ or a larger volume of the water sub-phase.¹³ At a relative humidity (RH) of 60 %, zeolite and hematite nanocrystals could readily form close-packed and preferentially oriented monolayers by rubbing the corresponding dry powders on the surface of glass supported hydroxypropyl cellulose (HPC) thin film, Fig. 2a. However, at a RH of 10 %, very few particles remained on the surface after rubbing because of low affinity between crystal and substrate at this humidity, Fig. 2c. The opposite was observed when using poly(methyl methacrylate) (PMMA) instead of the HPC, i.e. the assembly process was suppressed in a high humidity atmosphere (RH = 60 %) and was facilitated when the humidity was low (RH = 10 %), Fig. 2b and d. The IR spectra of these two polymers reveal that HPC possess a large amount of hydroxyl (O-H) groups as evidenced by the broad band above ca 3000 cm⁻¹ assigned to the O-H stretching vibration, Fig. 2e, which make it a hydrophilic material with a static water contact angle of 16 ± 2°; whilst PMMA has no hydroxyl groups, the weak band at 3441 cm⁻¹ was assigned to the first overtone of the C=O stretching vibration (1732 cm⁻¹) in PMMA, and is consequently less hydrophilic with

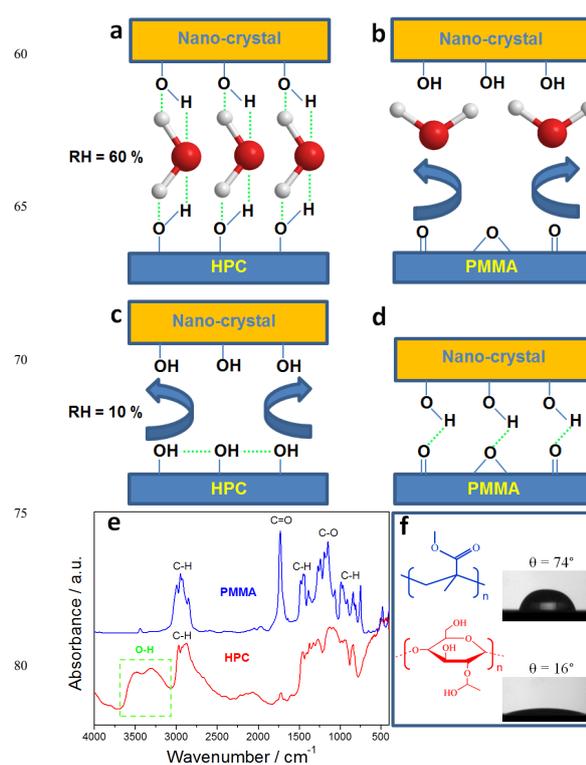


Fig. 2 Schematic drawing of the promoting effect of nanocrystals assembly onto HPC a) and inhibitive effect on PMMA b) surfaces at relative humidity of 60 %; inhibitive effect of nanocrystals assembly on HPC c) and promoting effect on PMMA d) surfaces at relative humidity of 10 %; FT-IR spectrum of PMMA and HPC e); their corresponding main molecular structures and water contact angles f).

a static water contact angle of 74 ± 2°, Fig. 2f.

The hydrophilic HPC surface interacts well with water molecules present in a high humid atmosphere. In addition, the zeolite nanocrystals are known to be hydrophilic and interact with water molecules, even if no condensation occurs. During rubbing the H₂O molecules may mediate hydrogen bonding interaction between nanocrystals and the hydrophilic substrate, Fig. 2a. In an atmosphere of low humidity, a substantial fraction of the hydroxyl groups on the HPC surface may instead form intramolecular hydrogen bonds with nearest neighbors, Fig. 2c, implying that the number of free hydroxyl groups on the substrate surface available to form hydrogen bonds with the nanocrystals will be reduced. This is supported by the infrared spectrum of HPC recorded at an ambient pressure of 2 hPa. The broadness and wavenumber position of the OH-band clearly indicates hydrogen bonding interaction between OH entities, Figure 2e.

The less hydrophilic PMMA surface has a tendency to increasingly repel (less affinity) H₂O molecules, and a larger concentration of H₂O in humid environment would inhibit the hydrogen bond formation between the crystals and substrate, Fig. 2b. A hydrophobic surface (contact angle > 90°) would rather prohibit water to attach. On the contrary, in a dry atmosphere where the concentration of water molecules is much lower, the contact between the nanocrystals and the less hydrophilic surface is improved, facilitating hydrogen bonding interaction, Fig. 2d.

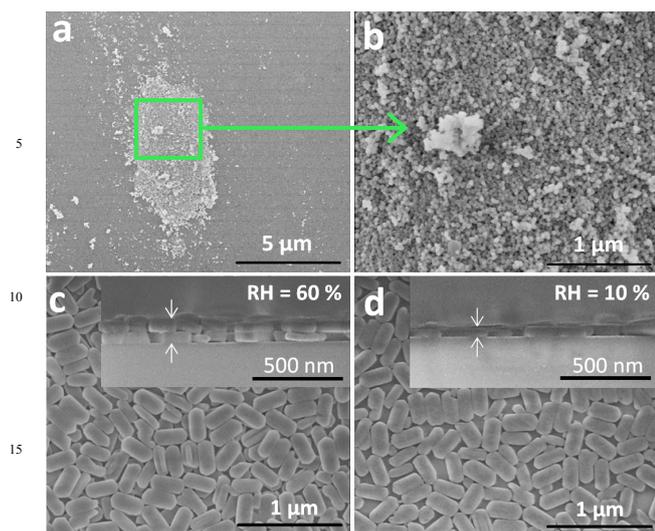


Fig. 3 SEM images of 40 nm MFI-OH aggregate formed on glass supported HPC surface a) and enlarged view b); SEM images of uniformly *b*-oriented dual-layer c) and monolayer d) of sheet-like pure-silica MFI crystals.

In manual assembly, nanocrystals tend to aggregate into unbroken blocks on the surfaces when it was applied relatively high contact pressure (ca 0.3 kg/cm²), Fig. 3a, b. Similar observations have been reported for manual assembly 50 ~ 100 nm MFI crystals and 5 μm × 1.5 μm SAPO-5 crystals.^{24c,27} These aggregates do not form easily during assembly of micro-sized MFI crystal but form readily during assembly of nanocrystals. A possible explanation is that nano-sized crystals possess higher surface area per unit of mass (m²/kg), and consequently higher concentration of hydroxyl groups per unit of mass, which result in aggregation by formation of hydrogen bonds. In the present work, it was found that the formation of these unbroken aggregates can be avoided by lowering the applied contact pressure (ca 0.03 kg/cm²), which produce only close-packed monolayers throughout the entire supports.

Using sheet-like pure-silica MFI crystal (340 nm × 170 nm × 60 nm) as building block, uniformly *b*-oriented dual-layer with thickness of 120 nm could be produced on the surface of HPC modified substrate by rubbing the powder at RH = 60 %, Fig. 3c. The humid atmosphere facilitates formation of hydrogen bonds between zeolite crystal and HPC surface, as well as between the flat [010] facets of two MFI crystals. While, uniformly *b*-oriented monolayer with thickness of 60 nm was formed on the PMMA modified surface by rubbing the crystals at RH = 10 %, Fig. 3d. It indicates that dry atmosphere promote formation of hydrogen bonds between zeolite crystal and PMMA surface, but inhibit bond formation between crystals.

Conclusions

In summary, manual assembly of nano-sized crystals into monolayers was performed in this study. Several types of zeolite and hematite nanocrystals with different sizes and habits were organized into uniform layers with high-degree of close-packing. Factors that are critical for a successful monolayer formation

were identified in present work. The surrounding humidity, substrate nature and the contact pressure are imperative conditions for the formation of high-quality monolayers in large-area surfaces. We anticipate the findings in this communication will contribute to the organization of other types of nano-sized crystals²⁸ and promote the fabrication of advanced devices with increased performance in the future.

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