BINDING CRYSTALLINE SOLIDS AT LOW TEMPERATURES

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ABSTRACT

Crystalline solids are solid materials whose constituent atoms, molecules, or ions are arranged in a highly regulated fashion. Due to lack of rotational freedom in their stacking, they have been known as fragile materials. Even though some efforts have been dedicated to bind or mend defects/cracks in amorphous materials like concrete or polymers, welding or binding a crystalline solid at ambient or low temperature conditions is quite a challenging task. Mainly, low interface mobility from the atomic or ionic constituents frequently limits interface regroupings.

We recently found that one type of crystalline solid, dubbed metal-organic frameworks (MOFs), shows interfacial binding capability in their solid state. MOFs are molecularly engineered crystals that are mechanically rigid but structurally dynamic and reconfigurable. Unlike traditional studies on surface area and porous structures, our particular interest is placed on surface repairing or regrouping activities. For instance, when defects on bulk MOFs are mended using our process, the solids show a modulus leap from 4 to 12 GPa and hardness from 400 to 1000 MPa. When solids are made as polymer composite, open wounds can be healed at ambient conditions. Moreover, we found that low temperatures down to -56 ºC did not appear to restrict this solid binding process, making it outstanding for low temperature healing or binding.

If our results are utilized for many other MOFs that are adopted as catalysts or hydrogen storage/separation materials, we expect their structure integrity can be kept after multiple cycles of packing or extensive uses. Furthermore, the knowledge gained will help people design future crystalline solids or ordered structures that can be assembled, repaired or healed in various engineering applications.

1. INTRODUCTION

Supramolecules are molecularly engineered materials. Rich selections of the molecular building blocks, tunable crystalline packing, easy-to-perform one-pot synthesis, and well-defined structures make them ideal candidates in learning bonding or healing process. It is hoped that, if the bonding mechanisms from these well-defined solids are thoroughly understood, we can engineer many traditional materials as dynamic systems for a variety of important applications, such as solid adhesion, self-healing, cold welding, and polymer blend or mixing. Our work suggests that filling crystalline gaps with small molecules can drive an interfacial

binding between solids. Sufficient mobility from these fillers allows the process to happen at low temperatures.

2. MATERIALS

Cu-MOFs powders and membranes: The crystalline powders were prepared by mechanically crushing as-synthesized Cu-MOFs crystals using a mortar and pestle. The Cu-MOFs membrane (>15 μm in thickness) for nanoindentation tests was obtained by drop-casting a 2.0 wt% water suspension of Cu-MOFs powders onto a piece of Si wafer. The Cu-MOFs membrane (~ 25 μm in thickness) for three-point bending test, on the other hand, was prepared by drop-casting 5.0 wt% Cu-MOFs powder suspension on a Teflon film. After drying, a freestanding membrane was harvested directly from the Teflon substrate.
Binding Cu-MOFs membranes: The membrane for nanoindentation tests was obtained after dropping 0.2 mL of DEF (>99.0%, TCI America) over crushed MOF powders on glass and let it dry in air. The binding of membrane (freestanding) for three-point bending test was operated by soaking the freestanding piece in DEF for 12 hours.
Binding Cu-MOFs/PDMS composite: Bubble-free fresh PDMS precursor was casted atop a polycarbonate film to form a thin layer with a thickness of 1 mm. Crushed Cu-MOFs powders were then laid on this uncured PDMS surface, letting the solid sink to the bottom of the viscous liquid. Final Cu-MOFs/PDMS composite was received after annealing the mixture in the convection oven at 100 ^{o}C for 1 hour.

3. METHODS

Nanoindentation tests were performed using Hystron Bio-Ubi. Quasi-static ‘‘trapezoidal’’ load function tests were selected, with a 5-s loading, 2-s holding, and a final 5-s unloading. Maximum forces were set at 50 or 100 μN. The tip used is a Berkovich tip with a tip radius of 70 nm. In three-point bending tests, samples were placed between two glass slides with a spacing of 3 mm. Then carefully weighted small Si pieces were gradually loaded on top of each sample to investigate the maximum deflection before a failure.

4. RESULTS

Interfacial binding of MOFs is realized at both ambient and low temperature conditions. Taking Cu-MOFs ($Cu(FMA)(4,4'\text{-}Bpe)_{0.5}{\cdot}0.5H_2O$) as an example. Figure 1A demonstrates how to bind a broken elastic membrane via crushed powders of these MOFs. When the elastic membrane was cut with a blade (Figure 1A-left), the open wound was briefly treated with inert liquid, i.e., diethylformamide (DEF, $(C_2H_5)_2NCOH$). Shortly after, the membrane recovered most of its bendability in ambient conditions (Figure 1A-right). Another freestanding leaf-like structure molded from MOF powders (Figure 1B) was even capable of withholding a high temperature up to 200 ^{o}C without a major breakdown. Both microscopic (nanoindentation) and macroscopic experiments (three-point bending) were utilized to evaluate the membrane before and after the DEF treatment (Figure 1C). As the nanoindentation load increased, the physically aggregated membrane behaved rather fragile (upper inset), where failure marks on the loading curve suggest easy and permanent deformations. In contrast, the treated membrane easily deflected with a smooth

loading curve by retaining little residual strain. If we pay closer attention to the crushed pieces of these crystals, they can be loosely dispersed in water with their morphologies remaining intact for extended period of time (Figure 1D). Immediately upon the addition of DEF, dispersed solids bundled together by forming network-like, instead of dense or isolated aggregates, implying certain anisotropy of our process.

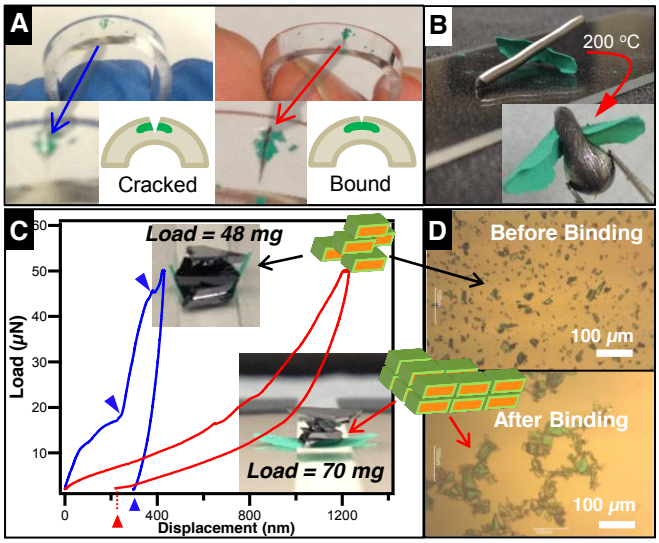

Figure 1: Binding crystalline solids as ambient conditions.

Our AFM scanning on crushed crystals revealed layered structures with individual layer thickness of 0.77 nm, closely matching 0.80 nm of lattice spacing for (200)s (Figure 2A and B). The dynamic changes on this (200) were caught after soaking the sample in water, supported by *in situ* AFM imaging at different times (Figure 2C and D). Right after water covered the crystal surface, many small holes appeared; after 17 minutes, they became deeper and larger (marked by the red ovals and yellow rectangles in Figure 2D), indicating a continuous dissolution of substances from the surfaces into the aqueous medium. When the water-soluble substance was extracted, ^{1}H-NMR confirmed the existence of fumarate (s, d = 6.7 ppm) as shown in Figure 2E. Collectively, both the AFM and NMR studies have pointed to one fact that the water-soluble fumaric acid or fumarate moieties roll off from (200) surfaces, destabilizing the Cu-MOFs crystal in a continuous manner. A brief comparison in diffraction patterns of crushed solids before and after DEF treatment suggests peak sharpening at (200)s only (Figure 2F). Since the peak intensity or sharpness is indicative to the perfectness of the inter-planar stacking, a sharper (200) peak unambiguously indicates a promoted crystal alignment and structure perfection along [200] direction.

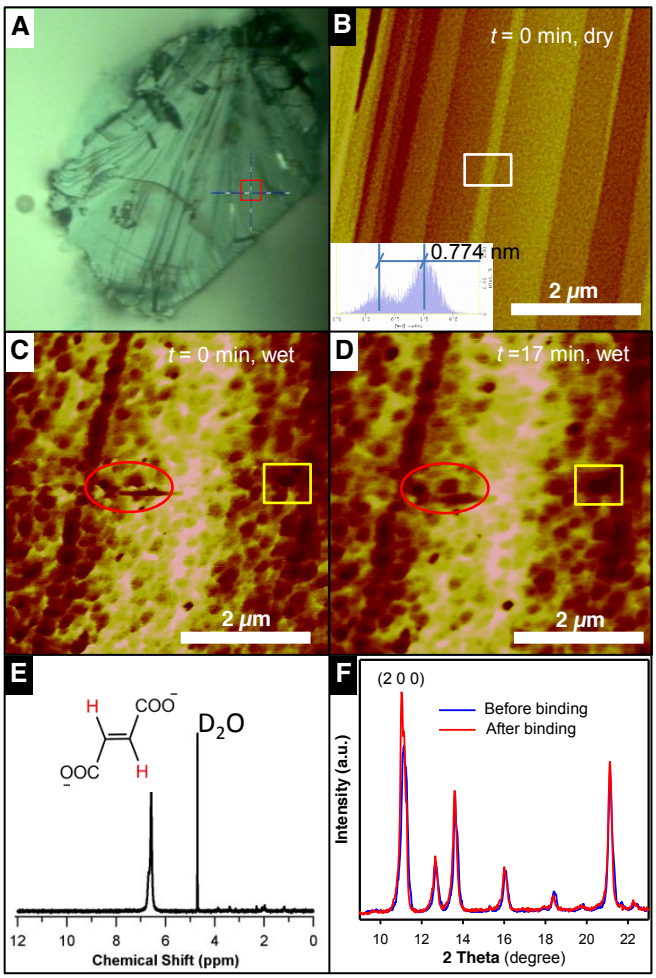

Figure 2: Dynamic properties of the crushed crystalline solids.

If crushed solids or powders can bind, this process might even repair defects on as-synthesized bulk crystals (Figure 3). Unlike mechanical tests for crushed membranes in Figure 1C, neither of our samples here showed permanent deformation. Rather smooth curves were observed in both loading and unloading regions, where the modulus jumped from 4 to 12 GPa and hardness from 400 to 1000 MPa. Since the statistical plot in Figure 3B suggests this as a general trend, we tend to believe this binding process once again is closely resulted from structure transition on surfaces. As revealed in Figure 3C, before the interfacial binding, the Cu-MOFs surface was composed of many small grains with an average size of 10 nm, after the binding the average diameter increased drastically to 30 nm. The XRD patterns (Figure 3D) before and after this transition suggest these growths occur mostly in (200) and (002) planes, where the peak sharpening follow a similar trend as that in the powder case. When crystal grain size increases, the surface area and the surface defect density decrease, rendering less scattering in measurement (Figure 3B, upper corner) and a much-enhanced mechanical performance. We also soaked freshly-made bulk crystals of Cu-MOFs in cold-baths of DEF at various low temperatures (-20, -41, and -56 ºC). Average grain size has increased from 15 to 25 nm, accompanied by nearly doubled mechanical properties (Figure 3E). In comparison, soaking at a slight higher temperature of either -20 or -41 ^{o}C has tripled the hardness and modulus. While the latter ones are not hugely different from those obtained in the ambient temperature, substantial viscosity increase in DEF at -56 ºC

has limited the diffusion of fumarate for reattachment of surface dangling bonds. Nonetheless, these experiments suggest that low temperatures do not restrict the binding between crystalline gaps.

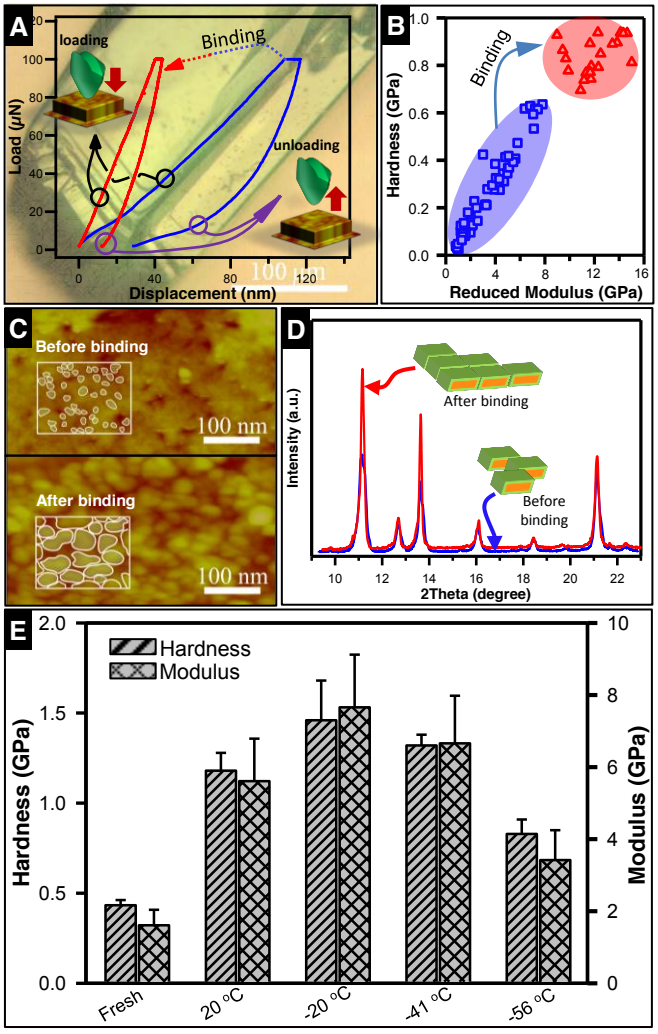

Figure 3: Bulk crystals can heal at ambient and low temperatures.

5. CONCLUSIONS

Crystals of metal-organic frameworks (MOFs) can be mechanically cleaved to reveal defects or dangling bonds, which can be further utilized towards binding at ambient and low temperature conditions. After DEF treatment, solid membranes exhibit greater mechanical resistance, which can potentially be molded into freestanding 3D objects or mend a broken elastic membrane.

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