Flexible Metal-Organic Framework for Mechanical sub-TByte/inch² Data Recording under Ambient Condition

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Abstract: Metal-organic frameworks (MOFs), demonstrating structural response on external stimuli, represent a promising family of crystalline materials for microelectronic and data storage devices. Herein, manipulation with MOF structure at the nanometer scales for the device miniaturization is still a challenge. Here, we report on flexible two-dimensional MOF for mechanically recording and reading the nanometer scale patterns at ambient conditions. Treatment of the MOF surface with a hot solvent decreases the roughness up to 1/7 of the layer thickness. Therefore, an atomic force microscope tip is allowed to cause patterning with the spatial resolution up to 25 nm (0.1 TByte/inch² data storage density) and the depth from 0.4 nm. Chemical etching by the solvent can further develop the pattern, while the integrity of the MOF structure maintains. The realization of the «read-only-memory» concept on flexible MOF at ambient conditions paves the way for next-generation sustainable data storage materials.

Metal-organic frameworks (MOFs) have been recently emerged as a new class of crystalline porous materials for diverse application in chemistry,[14] biology,[15] and physics.[16] Thanks to virtually unlimited structural and compositional space,[17] the design of framework compounds splits into different families depending on their specific structural (i.e., high porosity or flexibility) and functional properties (chemical versatility, rigidity, conductivity, etc.). Herein, the family of flexible MOFs[18] attracts special fundamental and commercial interest. First, an ability to control the MOF crystal structure throughout the external stimuli, underlies the application in smart sensors,[18] microelectronic and data storage devices.[18] Second, it is due to rising technologies for fabrication MOF at different scales[19] and further integration them with microelectronic devices. This seems intriguing, because recent experiments demonstrated that magnetically sensitive or redox active MOFs with cm² surface area can easily and reversibly react on applying magnetic or electric fields (Fig. 1).[6a,b] Applying the ultraviolet light to photosensitive or 2D MOFs allows the reversible/irreversible structural transformation for data storage with the limited number of cycles at the microscales.[6c-e] Intriguing, the leap from micro to nanometer scale of modifying MOF area now is possible through electron lithography by irreversible way[6f] and applying voltage to non-volatile MOF-based resistive random-access memory (ReRAM) devices.[6g,6h] However, achieving the higher density of data recording on MOF avoiding fatigue product and limited number of reading cycles at normal conditions is still a challenge.

![Figure 1. Representation of different techniques for modification of MOF structure for potential data storage application: The predicted size of modified MOF area up to one unit cell by applying pressure,[6b] AFM Lithography in our research; ReRAM technology for modification of MOF through AFM[6f,6i] and lithography[6i,j] techniques; X Ray and electron-beam Lithography for MOF patterning,[6k] Optical modification of MOF through light induced polymerization[6l] or structural conformation,[6m] as well as applying voltage and magnetic field to redox active[6n] and magnetic[6o] MOFs.](image-url)
Here we report on the nanometer scale mechanical patterning of surface of flexible 2D MOFs via atomic force microscopy (AFM) lithography under ambient condition. The family of 2D MOFs with flexible ligands has been selected due to high sensitivity to pressure and ability to clean the surface layer by layer. The latter supports the developing the surface treatment by hot solvent (dimethylformamide, DMF) to decrease the roughness up to 0.2 nm (app. 1/7 of the single layer thickness) allowing us to pattern the MOF surface with the spatial resolution up to 25 nm and the depth from 0.4 nm. Selective chemical etching by this solvent can further develop the pattern (increase of the depth by 1.5±5 times), while the integrity of the MOF structure maintains. Operating with the concept of “read-only-memory” (ROM) non-volatile device, we achieve the data storage density of 0.1 TByte per inch² on the single MOF crystal for multiple reading. Herein, two recording/reading regimes, such as “ultra-high density” and “grayscale”, have been proved allowing one to either record pixels with 0.1 TByte per inch² density, or vary the depth of patterns to achieve a multi-contrast motif with 0.01 TByte per inch² density. The stability of the pattern over time on 2D metal-organic frameworks opens up the possibilities to develop new generation of sustainable and flexible materials for ROM technology. Generally, the modification of MOF structure by physical stimuli like optical or magnetic fields, current or electron beam (Fig. 1) tends to achieve the spatial resolution from centimeter scale to tens of nanometers. Herein, there is a strong reason for achieving ~1 nm resolution which corresponds to the size of one unit cell (an elementary structural unit of MOF that can respond to external stimuli). This is potentially possible due to the flexibility of MOF structure allowing the coexistence of modified and initial unit cells in the neighborhood.[6,7] The experimental realization of this idea can be achieved using scanning probe lithography with nm resolution.[7] To demonstrate this, we firstly determined the parameters of compounds required for their use in AFM under ambient condition: MOF should possess strong adhesion to the surface and be very flat, while being highly flexible and stable when dried. In this sense, the layered MOFs based on flexible ligands, but maintaining a high elasticity perpendicular to the layers, seem suitable due to better roughness[8] compared to 3D analogues, an ability to be exfoliated layer by layer, strong van der Waals initiated adhesion to the surface, and the desired mechanical flexibility.[9]

Based on the structural requirements, we focus on compound recently synthesized by Barsukova et al. ([Zn(ur)(abdc)]_n·DMF·H₂O obtained by the interaction of zinc nitrate, 4,4'-diazobiphenyldicarboxylic acid (abdc), and urotropine (ur) in dimethylformamide under solvothermal conditions.[10] The structure of the resulting MOF is built on the basis of binuclear secondary building units called “paddle wheel”. These secondary building units are linked to each other by bridging 4,4'-diazobiphenyldicarboxylate anions to form the layers. While urotropine molecules coordinate zinc cations in axial positions providing extra cushioning between the layers. The resulting layers grow into each other, forming a three-dimensional supramolecular framework (Fig. 2a). The monolayer itself has a thickness of about 16 Å due to the coordinated urotropine molecules. However, when the layers are packed on top of each other, the coordinated urotropine molecules of the middle layer occupy free space in the upper and lower layers. Thus, in case of package of 2 or more layers the layer thickness becomes about 10 Å (Fig. 2a). Thermogravimetric analysis from ref.[10] also revealed respectively high thermal resistance, while we confirmed the stability of the structure for operation in air for more than a month (see below).

![Figure 2](image_url)

Figure 2. (a) Structure of 2D MOF [Zn(ur)(abdc)]_n·DMF·H₂O. (b) Schematic presentation of processing steps involving sonication, AFM lithography and bath treatment to create the desired pattern. (c,d) Optical images of sonicated MOF crystals. Scale bars, 10 um. (e) Comparison of Raman scattering spectra for bulk MOF crystal and sonicated thin crystals.

Preliminary AFM analysis of initial MOF surface, performed by silicon tip with 8 nm radius in semi-contact mode, confirmed the average roughness of ~2 nm over the large scales on different single crystals (Fig. 3a), corresponding the similar value for other 2D MOFs.[11] In contrast, we have analyzed the roughness of well-known and highly crystalline 3D compounds (HKUST-1) demonstrating 10 nm roughness in average and rising further problems to decrease this values (Fig. S1). Nevertheless, reducing the area of modification to nanometers requires the less roughness to increase the density and decrease the number of error bites. Hence, we have developed the treatment of MOFs, placed on a silicon wafer or SiO₂ substrates, by hot solvent (DMF) steams (Fig. 2b). In advance, the MOF dispersion underwent the sonication to reduce the size of crystals and roughly clean their surface. Next, the substrate with MOFs was placed in a beaker with pre-heated DMF solvent up to 90 °C and left there for 120 minutes. The sample on a silicon substrate was not in the contact with the heated solvent, while the interaction was only between steams of solvent and the MOF surface. After the treatment, the sample was dried in the oven at 70 °C for 10 minutes. Fig. 3a-c demonstrates the results of the treatment; the roughness decrease by 5 times up to 0.2 nm, which corresponds to ~1/7 of the single layer thickness (Fig. 2a), while the optical images confirm the decrease in thickness through the coloring of MOFs crystals by optical interference (Fig. 2c,d). The Raman spectra also show the similar peaks for bulk crystals with appearing additional broad peak at 1000 cm⁻¹ (Fig. 2e) corresponding to the modification of β-ring breathing mode of 2D layer attached to the surface.[11]

Intriguing, the effect of hot solvent treatment can be extended also to selective chemical etching of MOF surface[12] to achieve the controlled developing of the patterns. For this, we have created mechanically the patterns on MOF surface and then analyzed their geometric parameters before and after hot treatment (Fig.
The increase of the depth of different patterns by 1.5-5 times, depending on etching time, can be achieved in solvent bath at the same procedure’s parameters. However, in this case, used solvent bath did not provide homogeneous cleaning of the sample’s surface or etching along the crystal defects instead we observed selective chemical etching along the artificial mechanical modifications made by AFM cantilever’s tip.

**Figure 3.** (a) Cross section of the surface of MOF single crystals before (b) and after (c) bath with corresponding AFM scans in magnitude mode. (d,e) AFM scan of MOF single crystal in magnitude mode with corresponding cross section demonstrating the layered structure.

Utilizing 8 nm tip, we then achieve the AFM patterning of MOF surface (Fig. 4b) with the spatial resolution up to 25 nm (Fig. S4a) and the depth of 0.4 nm (app. 1/4 of the single layer thickness) corresponding to the "ultra-high density" regime (i.e., 0.1 TByte per inch²). Such spatial modifications are in a good agreement with nanometer scale patterning of polymer films (28 to 40 nm) with different scanning probe lithography techniques. However, the depth (app. 1/4 of the single layer thickness) achieved by the presence of extra cushioning structural elements (ur) is a record for the most existing materials. Moreover, taking into account the size of MOF unit cell (1.3 x 2 x 2 nm), the region of modification we achieved corresponds to the volume of ~30 unit cells, which is a certain consequence of the predicted mechanical modification of flexible MOFs. In addition, recording at "greyscale" regime with higher depths (> 4 nm) and constant diameters of the patterns (~90 nm) possess potentially 0.01 TByte per inch² density storage.

To represent the controlled patterning of MOF surface, we also performed large-scale AFM lithography (Fig. 5). For this, we have selected MOF single crystals with an average size of 10 µm and thickness of 100 to 500 nm. The crystals were placed on monocrystalline silicon wafer and kept in DMF vapor for 15-30 minutes in order to decrease the surface roughness (Fig. 3a). The sample was then dried at a temperature of 80 °C. Using an optical microscope, we have selected single crystals through appearance of a characteristic interference pattern (Fig. 2c,d). To characterize the initial surface (i.e. roughness), we utilized atomic force microscopy with silicon probes (Fig. S2) in semi-contact mode. Next, we chose the raster force lithography for patterning the surface with simple drawing or text (in our case, "ITMO" logo). Fig. 5c-e shows the patterning performed with varied depths from 2 to 3.5 nm (Fig. S4b), while the reading have been performed by re-scanning the surface in semi-contact mode.

From a technical perspective, to simplify the process and reduce the requirements for the quality of the surface, one should apply deep mechanical deformations. However, this will lead to rapid wear of AFM tip. To address this problem, we utilized the described selective etching (Fig. 4a): Applying small deformations (app. 0.4 nm in depth) to the surface (Fig. 5f-i) was followed by keeping the sample in DMF vapor bath for 2 hours. Reading of the developed pattern (Fig. 5g,j) reveals the depth increased by about 5 times, while the structure and the rest area remain the same. Moreover, we have checked different patterns in 48 h (Fig. S3) and found that over time, this patterns not only does not disappear, but becomes more obvious.
In summary, we experimentally demonstrate the realization of “read-only-memory” concept based on MOFs. The data storage density of 0.1 TByte per inch$^2$, corresponding to ~30 modified unit cells, on the single MOF crystal for multiple reading is achieved by mechanical (AFM) lithography under ambient conditions. In details, 2D MOFs with flexible ligands and extra cushioning structural elements has been selected for following surface treatment by hot solvent to decrease MOF roughness up to 0.2 nm (app. 1/7 of the single layer thickness). This allows us to pattern the MOF surface with the spatial resolution up to 25 nm and the depth from 0.4 nm. Then, selective chemical etching by the solvent can further develop the pattern (increase of the depth by 1.5-5 times), while the integrity of the MOF structure maintains. Two recording/reading regimes, such as “ultra-high density” and “greyscale”, have been proved allowing one to either record pixels with 0.1 TByte per inch$^2$ density, or vary the depth of patterns to achieve a multi-contrast motif with 0.01 TByte per inch$^2$ density. The stability of the pattern over time at ambient conditions on 2D metal-organic frameworks opens up the possibilities to develop new generation of sustainable and flexible materials for ROM technology.

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Keywords: metal-organic frameworks, 2D materials, chemical etching, scanning probe lithography, data storage

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The concept of “read-only memory” non-volatile device is realized on 2D MOFs with flexible ligands providing 0.2 nm surface roughness for up to 0.1 TByte per inch² data recording at ambient conditions. Precise and controllable etching allows to fix the motive and operate at “ultra-high density” and “greyscale” regimes of data storage.