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# Seebeck Coefficient Measurements of Polycrystalline and Highly Ordered Metal-Organic Framework Thin Films

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In this work highly oriented Surface Anchored Metal-Organic Framework (SURMOF) films were fabricated quasi-epitaxial and were electrically characterized by Seebeck analysis and benchmarked against random polycrystalline MOF films loaded with tetracyano-quinodimethane (TCNQ) infiltration. The horizontal Seebeck coefficient of the oriented SURMOF films and the random polycrystalline MOF films parallel to the sample surface was measured and has been discussed. The isotropic random polycrystalline MOF films exhibit a high positive Seebeck coefficient of 422.32 μV/K at 350 K. However, the horizontal Seebeck coefficient of highly oriented SURMOF films fluctuates around 0 μV/K instead. Because the quasi-epitaxial oriented SURMOF films are highly anisotropic, there is no measurable horizontal carrier transport parallel to the SURMOF surface. However, in contrast to highly oriented (002) SURMOF films, the in-plane thermoelectric properties of random polycrystalline MOF films with sputtered Au contact pads could be measured due to the isotropic nature of these films. The high Seebeck coefficient of these random polycrystalline MOF films demonstrates promising application potential of MOF films in future thermoelectric and electronic devices.


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Bulk Metal-organic-framework (MOF) films are designed scaffold-like compounds that consist of metal ions connected by organic ligands, forming highly ordered porous structures. These bulk MOF frameworks were initially designed for gas storage due to high storage capacity inside the porous MOF bulk material,[1,2] but their applications for electrical devices were very limited resulting from their insulating character. Recently, it has been reported that the electrical properties of bulk host MOFs can be modulated by infiltrating guest molecules (e.g. TCNQ) inside the porous MOF framework.[3] This renders MOF materials a novel and promising material for microelectronic devices,[4] sensors,[5] and thermoelectric devices.[6] Karlsruhe Institute of Technology (KIT) recently reported a resistive switching nano-device based on SURMOF films, demonstrating a potential application of SURMOF materials for nonvolatile RRAM memories.[4] Another research group from Sandia National Laboratory reported MOF films exhibiting high Seebeck coefficients and low thermal conductivity, demonstrating that MOF films could function as novel thermoelectrical materials.[6] Semiconductor thermoelectric (TE) materials such as $Bi_2Te_3$ and PbTe have been applied for TE power generator or TE refrigerator. But it is still limited for large scale application due to its highly cost, non-eco-friendly and difficulty of large scale production. Loaded MOF film is a promising alternative for room temperature TE application because of its advantage of nontoxicity, low cost fabrication, low thermal conductivity and tunable electrical conductivity. In our work, highly oriented SURMOF films and random polycrystalline MOF films $Cu_3(BTC)_2$ (BTC: benzene tricarbonicacid), known as HKUST-1 MOF, were grown by a liquid phase epitaxy (LPE) spray method on surface functionalized gold coated silicon substrates, or on regular non-functionalized native oxide covered silicon substrates as well as on silicon substrates covered with a thick 484 nm thermal $SiO_2$ layer for dielectric isolation. The tetracyano-quinodimethane (TCNQ) guest molecules were infiltrated into the MOF films to modulate the electrical properties of the film. The horizontal Seebeck coefficient of both oriented SURMOF films and random polycrystalline MOF films were measured parallel to the sample surface. The dependence of Seebeck coefficient on the crystallographic orientation of MOF films was observed and analyzed.

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## Experimental

***Sample preparation.***—The HKUST-1 MOF samples were grown by liquid phase epitaxy (LPE) spray method directly on native oxide covered silicon substrates, which then form cubic and polycrystalline 3-D pore structures. The schematic diagram for LPE spray method is shown in Figure 1. A small nozzle is used to generate aerosol from the expanding reactant solutions. During one growth cycle, the metal solution (M), the rinsing liquid (R), linker solution (L) and rinsing liquid (R) were sprayed on the silicon wafer one by one.[7,8] The thickness of the resulting MOF films can be determined by controlling the number of growth cycles. The MOF films grown directly on silicon wafers covered with either a thick thermally grown 484 nm $SiO_2$ layer or a thin ∼ 2–3 nm native oxide always resulted in randomly oriented polycrystalline films, for the case when the oxide interface was not pretreated with SAM functionalization, which was proven by their XRD characteristic signature patterns shown in Figure 2a. The resulting MOF film thickness is not strictly uniform due to the granular surface morphology, which can be clearly seen in the SEM cross-section

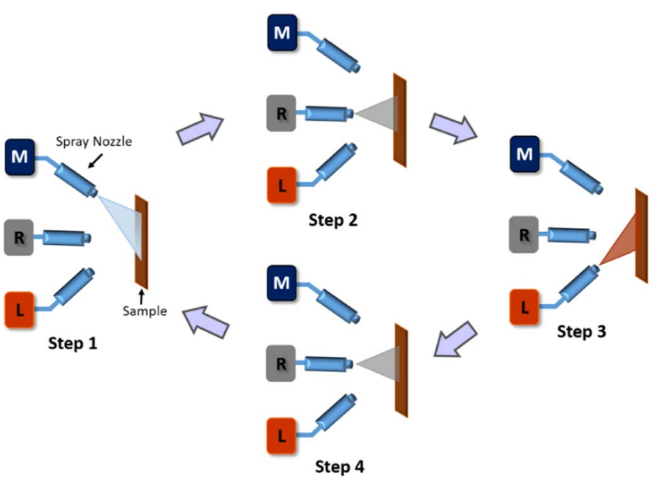


**Figure 1.** Schematic diagram of the Liquid Phase Epitaxy (LPE) spray method for the synthesis of SURMOF films.

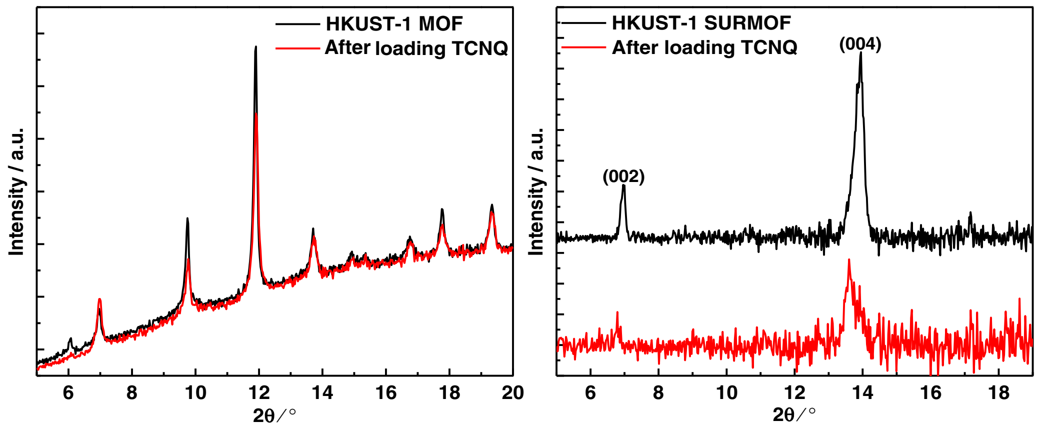


**Figure 2.** XRD results of (a) random polycrystalline HKUST-1 MOF films before (black line) and after (red line) TCNQ loading grown on thermal oxidized $SiO_2$/Si wafer, (b) highly oriented crystalline HKUST-1 SURMOF films before (black line) and after (red line) TCNQ loading grown on SAMs functionalized Au surface.

of Figure 4. The growth of MOF films on SAM terminated gold covered sample surfaces on the other hand results in a highly ordered crystal structure with a strong (002) orientation, shown as Figure 2b, which was in agreement with previously published results.[9] After the LPE spray deposition of the MOF films, the MOF pores were loaded with tetracyano-quinodimethane (TCNQ) in order to modulate the electrical properties of the host MOF film. In this paper, 100 nm thick highly oriented SURMOF films and 200 nm thick polycrystalline MOF films with TCNQ loading were studied.

***Seebeck coefficient measurements.***—The Seebeck coefficient measurements were performed with an MMR Seebeck coefficient measurement system. The horizontal Seebeck coefficient on polycrystalline and highly ordered HKUST-1 thin films were measured parallel to the sample surface in the temperature range from 290 K to 350 K. A small temperature gradient of ∼1 K was applied between the two ends of the sample. For the Seebeck measurements, the MOF film samples on Si substrates were cleaved into small sized rectangular stripes of 1 mm × 5 mm size. The Au contacts pads were sputtered on the two ends of the sample through use of a shadow mask. The thickness of the Au contact pads is about 40 nm. Afterwards, the MOF samples with Au contact pads were mounted on the Seebeck stage with silver paste. Figure 3 shows an actual photographic image of the sample mounted on the Seebeck stage, and lateral schematic diagram of the Seebeck stage. The sample under test plus a constantan reference sample with known Seebeck coefficient were symmetrically mounted on the Seebeck stage, so that the sample and reference sample experience the same temperature gradient. The voltage response of both the test sample side ($V_1$) and constantan reference side ($V_2$) to the temperature gradient was recorded to calculate the Seebeck coefficient of the sample under test. The I-V curve was measured to check the ohmic contact between the sample and stage, see Figure 3.

## Results and Discussion

The surface morphology of random polycrystalline MOF films with and without TCNQ loading grown directly on thermal oxidized $SiO_2$/Si substrates without the use of SAM layers is displayed in the FE-SEM micrographs of Figures 5a and 5b. These MOF films reveal a dense continuous film with full coverage of the entire substrate. The granular surface morphology shown in the cross-sectional SEM image in Figure 5d is indicative of the randomly oriented polycrystalline nature of these MOF films, which has been substantiated by XRD analysis.[10] The thicknesses of highly oriented SURMOF film and

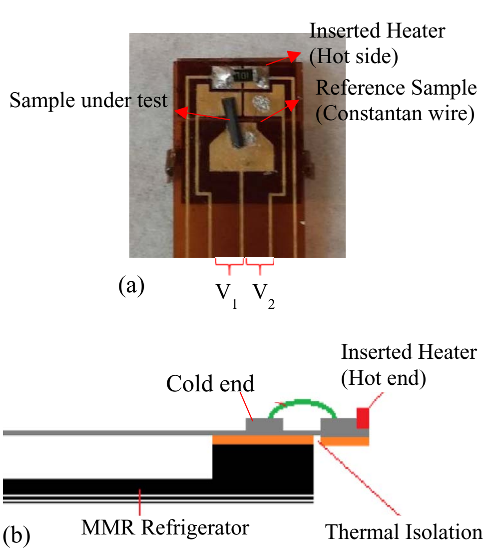


**Figure 3.** (a) Photographic image of the Seebeck stage showing the mounted test device. $V_1$ and $V_2$ are voltage response of sample side and reference sample side, respectively. (b) Lateral schematic diagram of Seebeck stage.

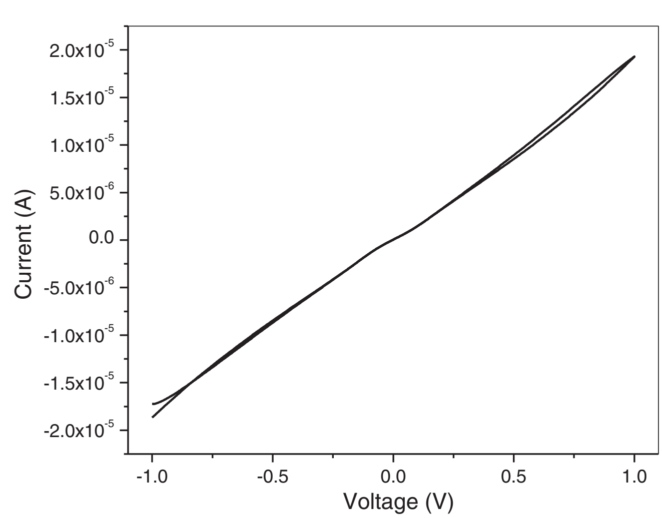


**Figure 4.** Fairly linear I-V curve of the polycrystalline HKUST-1 MOF film loaded with TCNQ and coated with Au contact pads at the two ends of the sample indicating a reasonable ohmic contact.

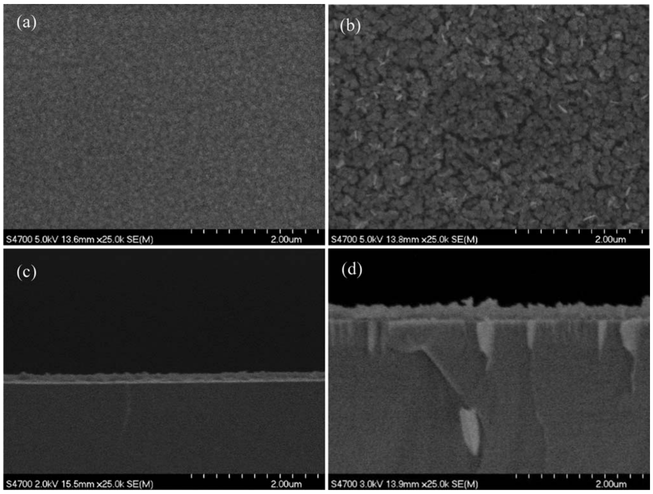


**Figure 5.** FE-SEM micrograph of (a) pristine and (b) TCNQ loaded polycrystalline MOF thin film grown on $SiO_2$/Si substrate, and cross-sectional SEM micrograph of (c) 100 nm thick highly oriented MOF film and (d) 200 nm thick random polycrystalline MOF film.

polycrystalline MOF film according to the SEM cross-section were around 100 nm and 200 nm, respectively. The Seebeck coefficient of the MOF films were measured and are discussed in the following section.

In order to obtain accurate Seebeck coefficient measurements, a good ohmic contact between sample and stage is essential.[11] Figure 4 provides the I-V curve between two ends of the polycrystalline MOF thin film on the stage. The fairly linear I-V curve in the voltage range from −1 V to 1 V reveals ohmic contact between the MOF sample and measurement stage.

The Seebeck coefficient of both 200 nm thick random polycrystalline MOF films infiltrated with TCNQ and for comparison 100 nm thick highly orientated SURMOF films with TCNQ loading were investigated in the temperature range of 290 K ∼350 K. Figure 6a exhibits the temperature dependence of the measured Seebeck coefficient of quasi-epitaxially oriented and highly anisotropic SURMOF films with and without TCNQ infiltration. In both cases, the horizontal Seebeck coefficient of oriented and anisotropic SURMOF films is hardly measurable fluctuating around 0 μV/K and in the noise level over the entire temperature testing range from 295 K to 350 K, as seen in Figure 5a. In sharp contrast, the measured horizontal Seebeck coefficient of randomly oriented TCNQ loaded and pristine polycrystalline MOF films grown on thermal oxidized Si substrates with thick 484 nm $SiO_2$ is fairly high over the temperature range between 290 K and 350 K. The maximum measured Seebeck coefficient of TCNQ loaded polycrystalline MOFs with film thickness of 200 nm and TCNQ infiltration was 422.32 μV/K at 350 K, see Figure 6b. This can be attributed to the fact that SURMOF films grown on SAM functionalized gold coated Si substrates exhibit a strong preferential orientation along the (002) direction,[9] and have demonstrated good charge carrier transport only through the vertical direction with surface top contacts and back side contacts,[4] while no carrier transport takes place in the horizontal direction parallel to the surface. However, all MOF films grown directly on thermally oxidized Si substrates without the use of SAM functionalized result in a random polycrystalline structure. The isotropic nature of these polycrystalline MOF films enabled charge carrier transport via all directions. For this reason, the measured horizontal Seebeck coefficient of highly oriented SURMOF films parallel to the surface was negligibly small around 0 μV/K, while the Seebeck coefficient of random oriented polycrystalline MOF films measured fairly high values. The measured high positive Seebeck coefficient of polycrystalline MOF films indicates the MOF films are *p*-type, so that the majority of charge carriers are holes, which is consistent with the reported work.[6]

The Seebeck coefficient of TCNQ loaded MOF film linearly increases from 342.39 μV/K to 422.32 μV/K as temperature rising from 290 K to 350 K. It may be attributed to the fact that thermal activation generates more holes contributing to the Seebeck coefficient as the temperature is increasing. A maximum Seebeck coefficient would be expected at higher temperature where intrinsic transport behavior starts to dominate. The temperature dependence of the Seebeck coefficient of the pristine MOF film exhibits the same slope and tendency over the temperature range between 290 K and 330 K, where the Seebeck graph of the pristine MOF film appears parallel shifted to higher values by approximately 50 μV/K. The measurements establish that the temperature dependent Seebeck coefficient of the pristine MOF films is higher compared to the TCNQ loaded MOF films, and this can be understood by the following explanation. The Seebeck coefficient S is inversely related to electrical conductivity σ by the relationship $S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T (\frac{\pi}{3n})^{2/3}$ and $\sigma = ne\mu$, where $n$ is carrier density, μ is the carrier mobility, $k_B$ is the Boltzmann constant, $h$ is the Planck's constant, $m^*$ is the effective mass of the charge carrier, $T$ is temperature and $e$ is carrier charge.[12] Therefore the fact that TCNQ

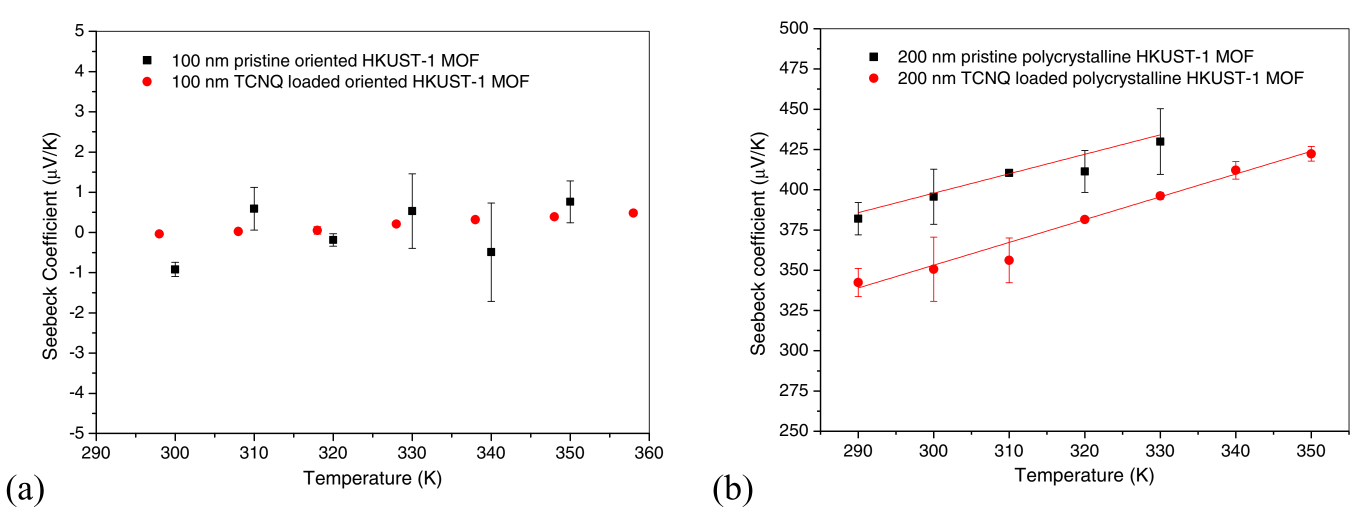


**Figure 6.** (a) Seebeck coefficient measurements as function of temperature of LPE highly oriented HKUST-1 films with a thickness of 100 nm, which were prepared with and without TCNQ loading. (b) Seebeck coefficient measurements of LPE polycrystalline HKUST-1 thin film with a thickness of 200 nm, which were prepared with and without TCNQ loading.

loading effectively enhances the electrical conductivity of isotropic polycrystalline MOF films to ∼ 0.3 S/m to result in a lower Seebeck coefficient, while at the same time the lower electrical conductivity ($\sim10^{-6}$ S/m) [3] and lower carrier density of a pristine polycrystalline MOF film has to result in higher Seebeck coefficients, which was observed in Figure 6b.

## Conclusions

In conclusion, liquid-phase epitaxially oriented and largely anisotropic HKUST-1 SURMOF thin films were fabricated, electrically characterized and compared for benchmarking with random polycrystalline MOF films infiltrated with TCNQ guest molecules. The cross-sectional FE-SEM micrographs plus XRD of MOF films grown on thermal oxide covered silicon substrates with granular surface morphology reveal their randomly oriented polycrystalline nature. The horizontal Seebeck coefficient yielded a high value of 422.32 μV/K at 350 K only for the polycrystalline HKUST-1 thin films. Our measured Seebeck coefficient at room temperature (RT = 294.15 K) is consistent with previously reported work. In contrast the horizontal Seebeck coefficient of LPE oriented SURMOF films parallel to the sample surface is practically at zero μV/K. This can be interpreted that these highly oriented SURMOF films exhibit a large anisotropy with no charge carrier transport in horizontal direction parallel to the sample surface, but only carrier transport in vertical direction, where resistive switching effects have been reported recently.[4]

In summary, only isotropic randomly oriented polycrystalline MOF films grown by the LPE spray method on thermal oxide covered silicon substrates exhibit a fairly high horizontal Seebeck coefficient, rendering these films as competitive novel thermoelectric materials for potential future thermoelectric applications in the near RT range.

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## References

1. H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. Ö. Yazaydin, R. Q. Snurr, M. O'Keeffe, and J. Kim, *Science*, **329**(5990), 424 (2010).
2. U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, and J. Pastre, *Journal of Materials Chemistry*, **16**(7), 626 (2006).
3. A. A. Talin, A. Centrone, A. C. Ford, M. E. Foster, V. Stavila, P. Haney, R. A. Kinney, V. Szalai, F. El Gabaly, and H. P. Yoon, *Science*, **343**(6166), 66 (2014).
4. Z. Wang, D. Nminibapiel, P. Shrestha, J. Liu, W. Guo, P. G. Weidler, H. Baumgart, C. Wöll, and E. Redel, *ChemNanoMat*, **2**(1), 67 (2016).
5. L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, and J. T. Hupp, *Chemical reviews*, **112**(2), 1105 (2011).
6. K. J. Erickson, F. Léonard, V. Stavila, M. E. Foster, C. D. Spataru, R. E. Jones, B. M. Foley, P. E. Hopkins, M. D. Allendorf, and A. A. Talin, *Advanced Materials*, **27**(22), 3453 (2015).
7. O. Shekhah, H. Wang, S. Kowarik, F. Schreiber, M. Paulus, M. Tolan, C. Sternemann, F. Evers, D. Zacher, and R. A. Fischer, *Journal of the American Chemical Society*, **129**(49), 15118 (2007).
8. H. K. Arslan, O. Shekhah, J. Wohlgemuth, M. Franzreb, R. A. Fischer, and C. Wöll, *Advanced functional materials*, **21**(22), 4228 (2011).
9. O. Shekhah, J. Liu, R. Fischer, and C. Wöll, *Chemical Society Reviews*, **40**(2), 1081 (2011).
10. H. Gliemann and C. Wöll, *Materials today*, **15**(3), 110 (2012).
11. S. van Reenen and M. Kemerink, *Organic electronics*, **15**(10), 2250 (2014).
12. Z.-G. Chen, G. Han, L. Yang, L. Cheng, and J. Zou, *Progress in Natural Science: Materials International*, **22**(6), 535 (2012).