Surface Effect on 2D Hybrid Perovskite Crystals: Perovskites Using an Ethanolamine Organic Layer as an Example

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Despite the remarkable progress of optoelectronic devices based on hybrid perovskites, there are significant drawbacks, which have largely hindered their development as an alternative of silicon. For instance, hybrid perovskites are well-known to suffer from moisture instability which leads to surface degradation. Nonetheless, the dependence of the surface effect on the moisture stability and optoelectronic properties of hybrid perovskites has not been fully investigated. In this work, the influence of the surface effect of 2D layered perovskites before and after mechanical exfoliation, representing rough and smooth surfaces of perovskite crystals, are studied. It is found that the smooth 2D perovskite is less sensitive to ambient moisture and exhibits a considerably low dark current, which outperforms the rough perovskites by 23.6 times in terms of photodetectivity. The superior moisture stability of the smooth perovskites over the rough perovskites is demonstrated. Additionally, ethanolamine is employed as an organic linker of the 2D layered perovskite, which further improves the moisture stability. This work reveals the strong dependence of the surface conditions of 2D hybrid perovskite crystals on their moisture stability and optoelectronic properties, which are of utmost importance to the design of practical optoelectronic devices based on hybrid perovskite crystals.

Organic–inorganic hybrid perovskites have attracted tremendous attention in recent years and their applications on optoelectronic devices including solar cells, lasers, light-emitting diodes, and photodetectors (PDs) were widely explored.[1–17] Optoelectronic devices based on hybrid perovskites exhibit the promising performance owing to their superior optoelectronic properties such as high absorption coefficient, long carrier diffusion length, highly tunable bandgap, extraordinary diffusion lengths, and lower trap density than those based on polycrystalline perovskites. It is because the SC hybrid perovskites exhibit longer carrier diffusion lengths and lower trap density than the polycrystalline ones which expect to result in improved optoelectronic device performance.[22–24,27–32]

Despite the remarkable progress of optoelectronic devices based on hybrid perovskites, there are significant drawbacks comparing with the inorganic semiconductor counterparts such as silicon and GaAs. For example, hybrid perovskites are well-known to suffer from moisture instability and other problems such as ion migration, halide vacancies, and interstitials which has largely hindered its development as an alternative of silicon.[33–36] In the case of SC hybrid perovskites, moisture from the ambient environment can lead to hydration of perovskite crystal surface which can cause the poor contact and performance loss of optoelectronic devices.[31,32] In addition, it has been reported that the hydrated surface of SC hybrid perovskites behaves like polycrystalline perovskites and results in distinct optoelectronic properties with the bulk which have been evidenced by the time-resolved photoluminescence measurement.[32] Therefore, it is of crucial importance to understand the effect of the surface condition of hybrid perovskites on their optoelectronic properties and device performance.[37–39] Meanwhile, utilization of 2D layered perovskites is a promising approach to mitigate the moisture stability issue.[14,38,40] Since the organic layers can slow down the penetration of moisture to the perovskites, optoelectronic devices fabricated on 2D perovskites exhibit the improved stability. Moreover, due to the weak Van der Waals force between the functional organic groups at the organic layers, 2D layered perovskites can be mechanically exfoliated.
and result in extremely smooth and clean surface. Hence, it is expected the optoelectronic properties and device performance on the cleaved perovskite which has a smooth and clean surface, will be significantly differed from the perovskites with a rough surface. Nonetheless, the relationship between the surface condition of 2D layered perovskites and their optoelectronic properties has not been fully investigated.

In this letter, we study the influences of surface condition on the optoelectronic properties of 2D layered perovskites. To examine the surface effect, we fabricate the metal–semiconductor–metal (MSM) junction with the smooth and rough (HOC₂H₄NH₃)₂PbI₄ layered perovskites and characterize their optoelectronic properties in various environments including ambient with relative humidity of over 50%. It is found that the smooth 2D perovskite is less sensitive to ambient moisture which can cause the doping of perovskites. As a result, it exhibits a considerably low dark current which results in significantly improved photodetectivity as compared with the rough perovskites. Besides this, we also utilize Ethanola mine (EA, HOCH₂CH₂NH₃⁺) as the organic layer of the 2D SC perovskites which can more effectively prevent the moisture penetrating into the bulk. This work advances the understanding about the surface effect of hybrid perovskites on their optoelectronic properties.

The 2D SC perovskites grown in this work are in centimeter scale as shown in Figure S1a and the experimental details of the synthesis can be found in the Supporting Information. To investigate the surface effect on the optoelectronic properties of the 2D perovskite, mechanical exfoliation is employed to obtain a smooth surface for comparing the rough surface of perovskite SC. As aforementioned, 2D layered perovskites can be mechanically exfoliated due to the weak Van der Waals force between the organic linker. Figure 1a displays the schematic diagram of the rough (as-grown) and smooth (cleaved) 2D perovskites. As illustrated in the schematic, the as-grown perovskite crystal has a rough surface containing many discontinued perovskite layers which are evidenced by the atomic force microscopy (AFM) scan in Figure S1b in the Supporting Information. This suggests that a large surface area of perovskite layer is in contact with the ambient. Figure 1b,c is the AFM images of the as-grown and cleaved perovskite respectively. It is found that the surface of the as-grown perovskite has a root mean square (RMS) roughness of 15.94 nm which is much rougher than that of the cleaved perovskite which is only 0.72 nm. The inset of Figure 1b and Figure S2a (Supporting Information) are the high- and low-magnification optical microscopy images of an as-grown 2D perovskite crystal in which many defects can be seen. After exfoliation, a fresh (100) surface of the 2D perovskite is exposed. The entire surface of cleaved perovskite is a relatively continuous single layer which is extremely clean and smooth (evidenced by the AFM and optical image of the smooth perovskites in Figure 1c and Figure S2b (Supporting Information)) and this organic layer can prevent the penetration of moisture into the inner perovskite layers. Before proceeding to the results of electrical characterization, it is worth mentioning that the X-ray diffraction (XRD) pattern in Figure S3 (Supporting Information) indicates that the as-grown and cleaved perovskites have the same bulk crystal structure, demonstrating that they have the identical intrinsic material properties so that the differences in optoelectronic properties shown in the following sections are caused by the surface condition of the perovskite crystals.
To examine the optoelectronic characteristics of the smooth and rough 2D perovskites under various gas environments, we fabricate the MSM structures with both types of perovskites (Figure 2a). The detailed MSM fabrication and characterization procedures can be found in the Supporting Information. In brief, two 60 nm thick gold electrodes with 20 μm distance in between are deposited on top of the perovskites and the images of the devices under optical microscopy can be found in Figure S4 in the Supporting Information. We first measure the dark current under 3 V bias under various gas environments by flowing gases into the chamber in the sequence of air with 57% relative humidity (RH), dry N₂, N₂ with 57% RH, dry O₂, O₂ with 57% RH, dry air, and back to air with 57% RH. Figure 2b,c are the dark current of the rough and smooth perovskites under various gases respectively. For the rough perovskite, the dark current under moisture is about 10⁻¹⁰ A which is two orders of magnitude higher than that in dry environment which is at the range of 10⁻¹² A. From the plot, it can be seen that the current is only influenced by the presence of moisture but not the type of gases, which implies that moisture is the cause of dark current increase. In addition, we have measured the dark current of both perovskites under vacuum and obtained the similar results as those dry gases. The increase of current in the presence of H₂O can be attributed to the electron donating (doping) from the water molecules to the perovskites and results in the drop of resistivity of perovskites.[31,32] Also, it is worth noting that the dark current increases with time due to the moisture chemisorption due to the exposed perovskite surfaces. To study the behavior under optical illumination, we have studied the photocurrent of the both kinds of perovskites from 400–700 nm under 3 V bias. The experimental detail of photocurrent measurement can be found in the Supporting Information. Figure 3a shows the I–V characteristics of the smooth and rough perovskites at light intensity of 0.1 mW cm⁻² and 550 nm. Although they behave very differently in term of dark current, their photocurrent are almost the same. This phenomenon can be explained by the fact that the moisture mostly affects the surface but not the bulk of perovskites. Therefore, the absorption of moisture has a significant influence on dark current but not the photocurrent which is governed by the intrinsic material properties and this is also coherent with the XRD results found in Figure S3 in the Supporting Information. Responsivity
indicating how efficient a material responds to the optical signal, and is calculated by Equation (1)

$$\text{R} = \frac{I_{\text{ph}}}{P_{\text{light}}} \tag{1}$$

in which $I_{\text{ph}}$ is the photocurrent and $P_{\text{light}}$ is the power of the incident light. Based on this equation, we have calculated the responsivity of the smooth perovskite which is displayed in Figure 3b. The smooth perovskite achieves the highest responsivity of 0.67 A W$^{-1}$ under light intensity of 0.1 mW cm$^{-2}$ at 550 nm. Next, we determine the detectivity ($D^*$) which is another important parameter that indicates the ability to detect weak optical signal. $D^*$ is given by Equation (2)

$$D^* = \frac{R}{\sqrt{2qI_{\text{dark}}}} \tag{2}$$

in which $R$ is the responsivity, $I_{\text{dark}}$ is the dark current, and $q$ is the elementary charge. As aforementioned, the smooth perovskite can suppress dark current significantly, thus the detectivity can be largely enhanced as compared with that on the rough perovskite. In Figure 3b, it can be seen that the smooth perovskite achieves the highest $D^*$ of $2.6 \times 10^{13}$ Jones at 550 nm (red dots) which is 23.6 times higher than that by the rough perovskite ($1.1 \times 10^{12}$ Jones, shown by blue triangles). Besides responsivity and detectivity, linear dynamic range (LDR) is an important parameter indicating the linear relationship between the photocurrent and incident light intensity and LDR is given by Equation (3)

$$\text{LDR} = 20 \log\left(\frac{I_{\text{ph}}}{I_{\text{dark}}}\right) \tag{3}$$

where $I_{\text{ph}}$ is the photocurrent at specific wavelength, and $I_{\text{dark}}$ is the dark current of device. From Figure 3c, it can be seen that the smooth perovskite has a LDR of 82 dB which is benefited by the significantly lower noise level due to the least moisture absorption. The higher LDR of the smooth perovskite suggests that it has a linear response to the optical signal over a broader range of light intensity which is essential to the practical use of hybrid perovskites on PD application. Additionally, we have also characterized the carrier lifetime in both kinds of perovskite using femtosecond transient absorption (TA) spectroscopy. Figure 3d displays the normalized TA decay kinetics probed at 535 nm after 475 nm excitation of the smooth and rough perovskites, indicating that the photoexcited carriers decay slower in the smooth perovskite, implying its longer charge carrier recombination. Particularly, in the TA measurements, the single-photon absorption can only excite the carriers within 200 nm of thickness under the surface of perovskite crystals. Therefore, the discrepancy of carrier lifetime is the result of the surface effect on the perovskite crystals. The longer carrier lifetime in the smooth perovskite can be attributed to the largely reduced surface traps on the defect-free surface after exfoliation as compared with the surface of rough perovskite. The above results regarding the surface morphology, photodetecting capability, and carrier lifetime reveal the importance of surface condition to the optoelectronic properties of 2D layered perovskite. It concludes that the clean and smooth surface of the 2D perovskites can prevent...
the absorption of ambient moisture and largely suppress the dark current which results in improved detectivity and LDR of a hybrid perovskite PD.

In addition to enhancing the moisture stability by improving the surface condition of hybrid perovskites, the layered perovskites in this work utilize EA as the organic layer which can improve the resistance to ambient moisture as compared to the commonly used organic linker PEA. Figure S5 (Supporting Information) shows the photoresponsivities against wavelength of the MSM junctions based on EA and PEA perovskites. It can be seen that the photoresponsivity of EA perovskite is significantly higher than that of PEA perovskite over the entire range of wavelength. We attribute this to the higher carrier mobility of the EA perovskites due to the enhanced screening effect for charge impurities resulting from the high dielectric constant of the EA organic linker. Figure 4a displays the normalized photoresponsivities against time of the MSM junctions fabricated on EA and PEA perovskites respectively. The responsivity of the PEA perovskite drops about 50% after 7 days, while that of EA perovskite remains over 70% of photoresponsivity after the same period of time. We attribute the reduction of photoresponsivity in both types of perovskites to the drop of photocurrent. It is because the hydrated surface of the perovskite with increased roughness degrades the contact with the gold electrode and results in current loss by the higher resistance. In our previous work, it has been shown that the aged surface of 2D PEA layered perovskites becomes very rough and even porous, which can explain the degradation of electrical contact and the reduction of photocurrent over time. The moisture resistance of EA perovskite is found to be much better than that of PEA perovskites as indicated in Figure 4a. In the AFM of EA perovskite surface scanned on day 0, 1, 2, and 4 (shown in Figure S6a–c (Supporting Information) and Figure 4b respectively), despite the fact that the roughness of EA perovskite increases with time, it still remains 23.44 nm. In case of PEA perovskite, the RMS roughness increase from 1.68 nm on day 0 to 52.89 nm on day 4 which are evidenced by AFM topologies shown in Figure S6d (Supporting Information) and Figure 4c respectively. The improved moisture stability can be explained by the stronger Coulomb interactions between the organic layers (dipole–dipole interaction as illustrated in Figure 4d) in EA perovskite comparing with the weak Van der Waals force in PEA perovskites. As a result, the hydrophilic organic groups can prevent the penetration of water and oxygen more effectively. The moisture stability of EA perovskites can be further evidenced by the TA spectroscopy which can measure the carrier lifetime of a material. Figure S7a (Supporting Information) displays the TA results of the EA and PEA perovskites which showing the longer carrier lifetime of the EA perovskites. It has been reported that when the surface of a perovskite SC is being hydrated, it will transform into polycrystallines and the carrier lifetime is shortened due to the increase of recombination site. We measured the carrier lifetime of EA perovskite by TA on day 0, 2, 6, and 21 and the results is shown in Figure S7b (Supporting Information). It is found that the carrier lifetime has little difference from day 0 to day 21. This implies the good stability of the crystallinity and chemical composition of EA perovskite under the ambient. The above time-dependent studies including photoresponsivity, surface topology by AFM, and carrier lifetime measurements by TA unveil the improved moisture stability of the EA perovskite over the 2D perovskite with the common PEA organic layer.

In conclusion, we have demonstrated the dependence of surface condition to the moisture stability and optoelectronic properties of 2D perovskites. We have prepared MSM junctions based on both smooth and rough perovskites and studied their photodetecting properties. The dark current of the smooth perovskite with a relatively clean and defect-free surface is...
substantially suppressed in the ambient environment. As a result, smooth 2D perovskite achieves the highest $D^*$ of $2.6 \times 10^{13}$ Jones which is 23.6 times higher than that on the rough perovskite containing numerous of defects and discontinued 2D perovskite layers. In addition, the time-dependent dark current in the smooth perovskite is found to be more stable than that in the rough perovskite due to the better moisture resistance of relatively continuous organic linker in the smooth perovskite. Furthermore, we have utilized EA as the organic linker in the 2D perovskites which has demonstrated the better moisture stability than the 2D perovskite based on the commonly used PEA. This work reveals the strong dependence of the surface condition of 2D hybrid perovskite crystals on their moisture stability and optoelectronic properties which are of paramount importance to the design of practical optoelectronic devices based on hybrid perovskite crystals.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
K.T.H. and S.F.L. contributed equally to this work. This work was financially supported by the Office of Sponsored Research of King Abdullah University of Science and Technology (KAUST), KAUST Sensor Initiative, KAUST Solar Center, and KAUST baseline funding.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
2D materials, moisture stability, optoelectronics, perovskites, surface effect

References