Metal Halide Perovskite and Phosphorus Doped g-C₃N₄ Bulk Heterojunctions for Air-Stable Photodetectors

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S Supporting Information

ABSTRACT: In this work, we fabricate photodetectors made of methylammonium lead trihalide perovskite (MLHP) and phosphorus-doped graphitic carbon nitride nanosheets (PCN-S). Using thermal polymerization, PCN-S with a reduced band gap, are synthesized from low-cost precursors, making it feasible to form type-II bulk heterojunctions with perovskites. Owing to the bulk heterojunctions between PCN-S and MLHP, the dark current of the photodetectors significantly decreases from $\sim 10^{-9}$ A for perovskite-only devices to $\sim 10^{-11}$ A for heterojunction devices. As a result, not only does the on/off ratio of the hybrid devices increase from 10^3 to 10^5 but also the photodetectivity is enhanced by more than 1 order of magnitude (up to 10^{13} Jones) and the responsivity reaches a value of 14 A W^{-1} . Moreover, the hybridization of MLHP with PCN-S significantly modifies the hydrophilicity and morphology of the perovskite films, which dramatically increases their stability under ambient conditions. The hybrid photodetectors, described here, present a promising new direction toward stable and efficient optoelectronic applications.

Metal halide perovskites have garnered a lot of research interest because of their impressive optical and transport properties such as tunable band gap,^{1,2} high absorption coefficient,^{3,4} long charge carrier lifetime,^{5–7} small exciton binding energies, and high ambipolar mobility.^{8–12} Together with low-temperature preparation capability, these pivotal features make perovskites excellent candidates for a variety of potential applications including solar cells,^{3,4,13} light-emitting diodes,^{14,15} photodetectors,^{16–19} lasers,^{1,4,20–22} X-ray imaging,²³ and waveguides.²⁴ Among these, light detection using perovskites stands out as a promising application, and many efforts have been dedicated to it. However, the trade-off between responsivity and detectivity is crucial in this class of materials. While large responsivity requires excellent crystals to obtain a high photocurrent, good detectivity favors defects and grain boundaries to reduce the dark current.^{25,26} Pioneering works showed that building a light-alterable energy barrier to control carrier transport with the assistance of foreign materials is one of the possible approaches to resolve this paradox.^{18,25} For example, a heterojunction formed between perovskite and WS₂ layers can either increase or decrease the Schottky barrier between electrodes and perovskites in the dark and under light illumination, respectively.¹⁸ Besides, a unique geometry

consisting of thousands of serial hopping barriers in a perovskite wire containing insulating organic blocks can remarkably suppress the dark current and conduct carriers through the edges.⁵ However, the complex fabrication processes and poor moisture stability greatly restrict their further applications. Therefore, low-cost fabrication of perovskite photodetectors with good stability in air is essential.

Recently, graphitic carbon nitride (g-C₃N₄), as a two-dimensional (2D) organic semiconductor with the Fermi level approximately in the middle of the band gap, has emerged as an attractive photocatalyst thanks to its striking features like abundance, stability, and nontoxicity.^{27–31} Compared to pristine g-C₃N₄, heteroatom-doped g-C₃N₄ has the advantages of a tunable band gap and the ability to engineer the electronic structure, leading to a wider light absorption range.^{27,31} This also underlines the feasibility of forming various junctions with other semiconductors. In addition, pristine and doped g-C₃N₄ possess advantages of easy fabrication, metal-free composition, and low cost compared to other 2D materials like MoS₂ and

Received: June 23, 2019

Accepted: August 19, 2019

Published: August 19, 2019

Figure 1. (a–c) Schematic illustration of the PCN-S synthesis process: (a) Structure of the melamine:hydroxyethylidene diphosphonic acid precursors. (b) Transformation of precursors into PCN-B through a thermal polymerization process. (c) Exfoliation of PCN-B into PCN-S in DMF. (The color code is C, gray; N, blue; P, orange; O, red; H, white.) (d) Schematic representation of the two-terminal, parallel-type PCN-S/MLHP hybrid thin-film photodetector device under visible-light illumination. The drawn PCN-S layer schematic is a simplified representation of the bulk heterojunction. The octahedral stacks represent an MLHP film. (e) The zoomed-in area of the device (dashed red frame in (d)) shows the CT between PCN-S and MLHP in the bulk heterojunctions.

WS₂. Furthermore, a Schottky junction between perovskites and chemically doped g-C₃N₄ may be a viable approach to suppress the dark current and facilitate the interfacial charge transfer (CT) process.

In this work, we fabricated photodetectors made of 2D phosphorus-doped graphitic carbon nitride and methylammonium lead trihalide perovskite (MLHP or CH₃NH₃PbCl_{3-x}I_x) bulk heterojunctions. Upon exfoliation of the synthesized bulk phosphorus-doped graphitic carbon nitride (PCN-B) to nanosheets (PCN-S), the band gap is reduced, and the band structure is demonstrated to match with the perovskite, facilitating the CT process at the junction interface. Owing to the light-alterable built-in barrier at the formed bulk heterojunctions, simple and robust mixing of PCN-S and MLHP presents a convenient and efficient approach to control the photoinduced interfacial carrier transfer of the junction. As a result, the photocurrent is enhanced due to the fast charge injection and charge separation, while the dark current is significantly suppressed because of the larger barrier. Consequently, the on/off ratio increases to 10⁵, and the photodetectivity reaches a value of 10¹³ Jones. In addition, the moisture stability of the hybrid film is improved due to the enhanced surface hydrophobicity. These results suggest that low-temperature-processed PCN-S/MLHP hybrids are promising to fabricate low-cost, reliable, and high-performance MLHP-based photodetectors.

In a typical experiment, bulk g-C₃N₄ (CN-B) and PCN-B were synthesized via a bottom-up method, i.e., a facile thermal polymerization process, using low-cost precursors (melamine and hydroxyethylidene diphosphonic acid). Detailed synthesis procedures are provided in the Experimental Section in the Supporting Information (SI). Figure 1a–c illustrates the facile polymerization process of the two low-cost precursors (Figure

1a) used for the synthesis of PCN-B (Figure 1b), which is subjected to further mechanical exfoliation to nanosheets (PCN-S) in *N,N*-dimethylformamide (DMF) (Figure 1c). The same procedures were followed to obtain the CN-S dispersion by using only melamine for comparison. The dispersions were further used to prepare two different hybrids with MLHP in solutions, i.e., CN-S/MLHP and PCN-S/MLHP. This was followed by spin-coating for film fabrication.

Compared to the suspension of CN-S in DMF, the color change of PCN-S dispersion as seen from the digital photographs in Figure S1 indicates successful phosphorus doping in PCN-S. Individual nanosheets can be detected by atomic force microscopy (AFM), as presented in Figure S1, where both CN-S and PCN-S have a similar thickness of ~11 nm. When blended with MLHP, both mixtures remain clean and transparent. The corresponding hybrids were then spin-coated onto glass substrates with prepatterned gold electrodes to fabricate photodetectors, as shown in Figure 1d,e. The length and width of the active area in the photodetector are 40 and 600 μm, respectively. The energy-dispersive X-ray spectroscopy (EDS) elemental mapping of phosphorus, iodine, and lead in the PCN-S/MLHP hybrid thin film, as shown in Figure S2, validates the uniform blending of MLHP with PCN-S.

The crystal structure of the as-synthesized PCN-B sample was characterized by X-ray diffraction (XRD), as shown in Figure S3, which is consistent with previous reports.²⁷ These patterns are similar to those observed for CN-B samples, indicating that the crystal structure of PCN-B is largely maintained after the phosphorus doping. Fourier transform infrared (FTIR) spectroscopy shown in Figure S4 suggests that the pristine conjugated backbone remains unchanged after doping,²⁷ which is essential for the carrier transport. The

Figure 2. Characterizations of MLHP, PCN-B/MLHP, and PCN-S/MLHP hybrids. (a) Powder XRD patterns of MLHP and hybrids. (b) SEM and (c) AFM images of a PCN-S/MLHP hybrid film. (d) UV-vis absorption spectra of MLHP and hybrids. (e) Energy band diagram of MLHP combined with CN-S and PCN-S. (f) PL spectra of MLHP, CN-S/MLHP, and PCN-S/MLHP hybrids. (g) TRPL spectra of MLHP, CN-S/MLHP, and PCN-S/MLHP hybrids. The TRPL intensities are fitted with a biexponential decay function over the range of ca. 0–200 ns.

absence of the vibrational modes of phosphorus-related bonds can be attributed to the low percentage of phosphorus content in the PCN-B. X-ray photoelectron spectroscopy (XPS) measurement was further utilized to investigate the precise phosphorus content (ca. 0.3 wt %) as well as its preferred doping sites in PCN-B. The conjugated heterocycle backbone is further confirmed by the high-resolution C 1s and N 1s spectra (Figure S5). Noticeably, as displayed in Figure S5, a P 2p peak is detected at a binding energy of 133.1 eV for PCN-B, which can be assigned to P–N coordination. This indicates that P likely replaces the energy-favorable C1 site, as denoted in the inset of Figure S5, to form P–N bonds.²⁷

Furthermore, we probed the XRD patterns of MLHP and its hybrids to study the influence of CN-S or PCN-S on the crystal structure of MLHP. Similar to MLHP films,^{15–17} PCN-S/MLHP hybrid films have achieved the highest crystallinity at an annealing temperature of 100 °C (Figure S6). Thus, for comparison, all of the studied spin-coated films were first annealed at 100 °C. The corresponding XRD patterns of MLHP and the hybrid films are presented in Figure 2a, indicating that the addition of PCN-S does not affect the crystal structure of MLHP. In fact, the full width at half-maximum (fwhm) of the (110) peak for the PCN-S/MLHP hybrid film is the smallest, suggesting that the crystallinity of the MLHP is improved. Moreover, MLHP crystallizes fast with PCN-S, as illustrated in Figure S7, in which PCN-S/MLHP turned into a black MLHP phase first. Thus, the addition of PCN-S may facilitate the nucleation of MLHP on its surface. The corresponding SEM images (Figures 2b and S8) reveal that the irregular MLHP grains become connected, forming microcuboid crystals in the hybrid films. The trend is also manifested by the AFM images depicted in Figure 2c. As a

result, these better-oriented grains further increase device performances.^{32,33}

Next, to investigate the optical properties of CN-S/MLHP and PCN-S/MLHP hybrids vs the pristine MLHP, we obtained the band gaps of the CN-S, PCN-S, CN-B, and PCN-B using UV-vis diffuse reflectance measurement, as shown in Figure S9a. A red-shifted absorption edge can be seen for PCN-S, indicating a reduced band gap compared to CN-S. Most importantly, in contrast to CN-S, the PCN-S demonstrates a clear Urbach tail between 450 and 800 nm. This is attributed to the midgap states stemming from the hybridization of C 2s2p, N 2s2p, and P 3s3p, illustrating the improved light absorption and modified electronic properties.^{27,31} As a result, PCN-S/MLHP hybrids absorb more light than CN-S/MLHP and MLHP, as shown in Figure 2d. The values of band gaps are estimated from the Tauc plots in Figure S9b using the Kubelka–Munk method.^{27,34} Upon doping, the 2.92 eV band gap of the CN-S is narrowed down to 2.82 eV for PCN-S. It is also found that the band gaps of either CN-B or PCN-B are even narrower than those of CN-S or PCN-S, respectively (see Figure S9a), which is consistent with previous studies.^{27,35} The PCN-S, in particular, is found to possess a 2.19 eV transition energy from the valence band (VB) to midgap states, which is on par with previous reports.^{27,31} These midgap states are of great significance, acting as hopping centers to afford extra charge carrier transfer at the interface. Also, using the electrochemical Mott–Schottky plots displayed in Figure S10, we obtained the conduction band (CB) positions of CN-S and PCN-S. The average flat band potential is determined to be –1.35 eV for CN-S and –1.09 eV for PCN-S vs Ag/AgCl at pH = 6.6, corresponding to –3.77 and –4.02 eV of CB related to the vacuum level, respectively.

Figure 3. Photodetector performance and mechanism. (a) Semilog scale current–voltage (I – V) characteristics of (i) MLHP-only and (ii) PCN-S/MLHP hybrid photodetectors measured in the dark and under various white-light intensities from $0.5 \mu\text{W cm}^{-2}$ to 1 mW cm^{-2} with a bias voltage of $\pm 5 \text{ V}$. (b) Comparison of the photocurrent, on/off ratio, responsivity, and photodetectivity of devices based on MLHP-only and CN-S/MLHP and PCN-S/MLHP hybrids under a white-light intensity of 1 mW cm^{-2} and a bias of 5 V . (c) White-light intensity-dependent photocurrent (left) and photoresponsivity (right) of a PCN-S/MLHP hybrid photodetector under a bias of 5 V . (d) Wavelength-dependent I – V curves of PCN-S/MLHP hybrid photodetectors measured under an intensity of 1 mW cm^{-2} . (e) Calculated responsivity and detectivity under a bias of 5 V as a function of wavelength. (f) Photoswitching characteristics of PCN-S/MLHP hybrid photodetectors under a bias of 5 V with different intensities of white light under alternating on/off cycles. (g) Time response to give a rise time of 6.1 ms and a decay time of 2.2 ms . (h,i) Band diagram showing the interface between MLHP and PCN-S in dark and illuminated conditions, respectively. The width of the gray or brown arrows indicates the current magnitude, and the green line on PCN-S side denotes the position of the midgap states.

Using the obtained band gaps and the calculated CB edges, the band structures for CN-S and PCN-S were deduced as constructed in Figure 2e. The VB positions of CN-S and PCN-S were found to be -6.69 and -6.84 eV , respectively, with additional midgap states in PCN-S located at -4.65 eV . Accordingly, given the well-known MLHP band edges at -3.75 eV (VB) and -5.35 eV (CB),³⁶ it can be inferred that electrons would transfer from the CB of MLHP to the CB of CN-S and from the CB of MLHP to the CB and/or midgap states of PCN-S. This speculation correlates well with the photoluminescence (PL) quenching (Figure 2f) of the CN-S/MLHP and PCN-S/MLHP hybrids with respect to MLHP. This prominent electron transfer taking place in the MLHP hybrids is further confirmed by a clear reduction in the PL lifetimes of the two hybrids vs MLHP (see Figure 2g). To obtain the PL lifetimes of the three studied systems (see Table S1), time-resolved photoluminescence (TRPL) measurements were performed at an excitation wavelength of 405 nm .

The TRPL spectrum of the MLHP film shows considerably a long PL lifetime of ca. 26 ns , which has been substantially reduced to a few nanoseconds (ca. 2 – 3 ns) upon the presence of the carbon-based materials. This reduction in the PL lifetime of the perovskite film can be attributed to the CT process from the MLHP to the CN-S/PCN-S materials.^{17,18,37}

In principle, the shortened PL lifetimes in the two hybrids offer a great potential for an improved photoresponse. However, the extra midgap states located within the band gap of PCN-S/MLHP are expected to support more effortless electron transport than that in CN-S/MLHP. This will lead to efficient exciton dissociation at the interface of PCN-S and MLHP, suggesting further enhancement in the photodetection behavior of PCN-S/MLHP compared to that of CN-S/MLHP. The enhancement in the photodetection behavior of PCN-S/MLHP is also supported by the enhanced absorption cross section of the PCN-S/MLHP hybrid (higher than that of CN-S/MLHP), as depicted in Figure 2d. Hence, on the basis of all the aforementioned analysis, we believe that the cuboid-connected PCN-S/MLHP hybrid film would allow for high-performance photodetectors.^{38,39}

Accordingly, we examined the photodetection performance of MLHP-only as well as its hybrid thin films. The corresponding current–voltage (I – V) curves of devices measured in the dark and under white-light illumination with various power intensities from $0.5 \mu\text{W cm}^{-2}$ to 1 mW cm^{-2} are shown in Figures 3a(i,ii) and S11. Their performance, including the dark current (I_{off}), photocurrent (I_{on}), on/off ratio, responsivity (R), and specific detectivity (D^*), is extracted at 5 V under a light intensity of 1 mW cm^{-2} , as

Figure 4. (a) Photocurrent under a white-light intensity of 0.5 mW cm^{-2} and (b) normalized photocurrent values of MLHP and PCN-S/MLHP hybrid photodetectors recorded as a function of the number of elapsed days. Insets in (a) and (b) show digital images of MLHP and PCN-S/MLHP films, respectively, deposited on glass substrates after 1 day. The measured contact angle of water on (c) MLHP and (d) PCN-S/MLHP hybrid films as a function of time in seconds.

shown in Figure 3b. R and D^* are calculated from $R = (I_{\text{on}} - I_{\text{off}})/P_{\text{in}}$ and $D^* = R/\sqrt{2qI_{\text{off}}/A}$, where P_{in} is the incident light power, q is the electron charge, and A is the effective area of the photodetector.¹⁸ Current noise was measured as shown in Figure S12 to support the utilization of dark current in the calculation of D^* due to the domination of shot noise.¹⁸ Compared to their counterpart MLHP single-layer devices, the photocurrent of the PCN-S/MLHP devices is enhanced several times owing to the midgap states present in the PCN-S, which help in improving the interfacial CT between MLHP and PCN-S. Most importantly, the dark current of the CN-S/MLHP hybrid devices is reduced to 10^{-10} compared to 10^{-9} A for MLHP-only devices, and it continues being suppressed down to 10^{-11} A in PCN-S/MLHP devices. This could originate from a higher carrier transport barrier at the interface in the dark. Consequently, the on/off ratio of PCN-S/MLHP has reached the highest value of 10^5 , which is considered as a great increase compared to MLHP-only devices (around 10^3).

On the grounds of increased photocurrent and suppressed dark current, R and D^* at 5 V under 1 mW cm^{-2} of PCN-S/MLHP hybrid devices are improved to 1.7 A W^{-1} and 1.1×10^{13} Jones, respectively, as shown in Figure 3b. The 2 orders of magnitude increased D^* compared to that of MLHP-only devices makes it promising to detect light with ultralow intensity. Further analysis of light intensity-dependent R and D^* variation for a PCN-S/MLHP device measured under a voltage of 5 V is presented in Figure 3c. The photocurrent increased with increasing light intensity, while the responsivity decreased, which is consistent with previous reports.^{18,23,26} At a light intensity of $0.5 \mu\text{W cm}^{-2}$, the PCN-S/MLHP device exhibits a responsivity of 14 A W^{-1} , which then decreases to 0.86 A W^{-1} at a light intensity of 5 mW cm^{-2} .

The photoresponse of the PCN-S/MLHP hybrid is demonstrated by wavelength-dependent photocurrent measurements, as shown in Figure 3d. The corresponding R and D^*

are presented in Figure 3e. Linear I - V curves of the PCN-S/MLHP devices exhibit Ohmic-like contacts formed between the electrodes and PCN-S/MLHP hybrids, which is different from the nonlinear I - V curves obtained for MLHP-only devices (see Figure S13). Owing to the small band gap of MLHP, photodetectors made of both MLHP and PCN-S/MLHP exhibit considerably higher R and D^* compared with other reports on other photodetectors measured in the full visible range under a light intensity of 2 mW cm^{-2} . However, the striking feature of these devices is that R is nearly doubled, while D^* is improved by 1 order of magnitude; this is mostly due to the suppressed dark current and the increased photocurrent aforementioned by adding PCN-S to the MLHP. For instance, at a wavelength of 530 nm, R and D^* are increased from 1.4 A W^{-1} and 0.8×10^{12} Jones for MLHP to 2.4 A W^{-1} and 7.4×10^{12} Jones for PCN-S/MLHP, respectively.

Reliable and rapid response to light is one of the critical parameters for the performance of photodetectors, which we investigated with pulsed white-light illumination. The temporal photoresponse of the PCN-S/MLHP hybrid device is shown in Figure 3f, which demonstrates reliable photoswitching characteristics under variable light intensities. The hybrid PCN-S/MLHP films promptly respond to white light at the millisecond level, as shown in Figure 3g, resulting in rise and decay times of 6.1 and 2.2 ms, respectively. This performance is much faster than the response of MLHP-only devices with rise and decay times of 29.6 and 12.3 ms, respectively (see Figure S14), confirming the fast charge-carrier ejection and separation at the interface between PCN-S and MLHP. A comprehensive comparison of the performance of several planar MLHP-only and other materials-based photodetectors is shown in Table S2. Apparently our devices exhibit a high on/off ratio, photodetectivity, and adequate responsivity as well as a rapid response time, which lead to net performance advancements in MLHP-based photodetectors.

Our results indicate that the improved performance of the PCN-S/MLHP hybrid photodetectors is linked to the addition of PCN-S to perovskites. To further investigate the influence of PCN-S on both the dark and photocurrent, the band alignment of the MLHP and PCN-S heterojunction is plotted for both dark and illuminated situations in Figure 3h,i, respectively. The band bending directions are determined by the relative Fermi level positions of the two materials. For our perovskites, theoretical calculations and experiments show that MLHP is more n-type with a work function of around 4.0 eV.⁴⁰ CN-S is reported to be an approximately intrinsic semiconductor, and the Fermi level is further increased in PCN-S due to the phosphorus doping.^{30,31} Photoelectron spectroscopy in air (PESA) and VB XPS spectra in Figure S15 verify the increased Fermi level (−4.55 eV). From the measured band structure (Figure 2e), it is evident that there is a great barrier for electron transport from MLHP to PCN-S in the dark, which results in lower dark current. However, under illumination, free electrons and holes are simultaneously generated inside of the MLHP (due to the low exciton binding energies) to reduce the built-in field, and thus, the electrons can transfer to PCN-S due to the large kinetic energy and density. Consequently, the Fermi level of PCN-S is raised, which minimizes the barrier between the CB edges of MLHP and PCN-S. In principle, the barrier could eventually disappear, and the midgap states in PCN-S can further facilitate the carrier transfer, which enhances the photocurrent. On the other hand, the high CB, low Fermi level, and absence of midgap states in CN-S restrict the efficient carrier transfer between CN-S and MLHP, resulting in lower photocurrents.

The stability of metal halide perovskite photodetectors is a critical issue that must be improved for these materials to realize their full potential. A stability comparison between MLHP and PCN-S/MLHP photodetectors is shown in Figure 4a,b, where the photocurrent is recorded for a few days, with the samples stored in a Petri dish under ambient conditions. It is clear from these data that PCN-S/MLHP hybrid photodetectors have better stability compared to MLHP-only devices. After 2 days, the photocurrent is slightly reduced from 757 to 725 nA, corresponding to a 4.2% drop. In contrast, for the MLHP-only photodetector, the photocurrent decreased from 531 to 253 nA, corresponding to a 52.3% drop. After 7 days, the PCN-S/MLHP hybrid photodetector maintained a relatively high photocurrent of 497 nA, while the MLHP-only device showed almost no photoresponse. This increased stability is evident from the digital image (insets of Figure 4a,b). Besides, the PCN-S/MLHP hybrid photodetectors exhibit higher stability compared to most solution-processed MLHP photodetectors, whose photocurrents degraded more than 50% in the time frame of 10 min to a few days.^{41–44}

It is generally believed that the poor stability of metal halide perovskites stems from reactions with water that start at the amorphous grain edges.^{43,45} Thus, a reasonable approach to improve their stability involves modifying the surface wetting behavior (making it more hydrophobic to minimize water absorption on the surface of the MLHP films). Interestingly, the introduction of PCN-S into MLHP seems to achieve this desired result. Contact angle measurements performed on MLHP-only and PCN-S/MLHP hybrid films are shown in Figure 4c,d, respectively. The measured contact angle of water on MLHP-only films is 22.1°, indicating a very hydrophilic surface. However, this angle becomes significantly smaller due to reaction with water, finally reaching a value of 10.4° after 90

s.^{45,46} In sharp contrast, the PCN-S/MLHP hybrid film has exhibited an initial contact angle of 45.6°, which is significantly larger than that of MLHP, suggesting that the hybrid films are more hydrophobic. Moreover, the contact angle decays much slower compared with MLHP-only films, reaching half of its initial value after 240 s. Therefore, the addition of PCN-S minimizes the moisture diffusion into MLHP grains by modifying the surface wetting behavior and significantly increases the stability of the devices in ambient conditions.

In summary, high-performance and air-stable planar photodetectors based on 2D phosphorus-doped g-C₃N₄ nanosheets (PCN-S) and methylammonium lead trihalide perovskite (MLHP) bulk heterojunctions have been fabricated using a simple and low-temperature solution-processing approach. The hybrid photodetectors demonstrate a high on/off ratio of 10⁵, photodetectivity of 10¹³ Jones, and responsivity of 14 A W^{−1} with reliable and fast photoswitching characteristics. This performance can be ascribed to suppression of the dark current of MLHP in the presence of PCN-S and the efficient charge transfer processes at the interfaces between PCN-S and MLHP. Furthermore, the PCN-S/MLHP hybrid photodetectors exhibit increased moisture resistance thanks to their improved surface hydrophobicity. Our results show a new approach to fabricate air-stable efficient perovskite photodetectors by creating bulk heterojunctions with 2D materials. The low-cost fabrication process and high detector performance open a novel window for practical devices.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.9b01339.

Experimental and characterization section, additional experimental results, including photographs, AFM, EDS, FTIR, XPS, UV–vis, Schottky–Mott plots, and PESA of the CN-B, CN-S, PCN-B, and PCN-S samples, average lifetime extracted from the TRPL measurements, XRD, photographs, SEM, AFM, UV–vis, photoresponse, noise measurement, wavelength-dependent photoresponse, and time response of the hybrid films or photodetectors, and table of performance comparison with previous reports (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Research reported in this publication was funded by King Abdullah University of Science and Technology (KAUST).

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