

Room-Temperature Solution-Processed $\text{NiO}_x\text{:PbI}_2$ Nanocomposite Structures for Realizing High-Performance Perovskite Photodetectors

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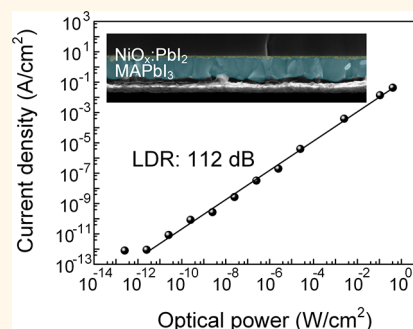
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S Supporting Information

ABSTRACT: While methylammonium lead iodide (MAPbI_3) with interesting properties, such as a direct band gap, high and well-balanced electron/hole mobilities, as well as long electron/hole diffusion length, is a potential candidate to become the light absorbers in photodetectors, the challenges for realizing efficient perovskite photodetectors are to suppress dark current, to increase linear dynamic range, and to achieve high specific detectivity and fast response speed. Here, we demonstrate $\text{NiO}_x\text{:PbI}_2$ nanocomposite structures, which can offer dual roles of functioning as an efficient hole extraction layer and favoring the formation of high-quality MAPbI_3 to address these challenges. We introduce a room-temperature solution process to form the $\text{NiO}_x\text{:PbI}_2$ nanocomposite structures. The nanocomposite structures facilitate the growth of the compact and ordered MAPbI_3 crystalline films, which is essential for efficient photodetectors. Furthermore, the nanocomposite structures work as an effective hole extraction layer, which provides a large electron injection barrier and favorable hole extraction as well as passivates the surface of the perovskite, leading to suppressed dark current and enhanced photocurrent. By optimizing the $\text{NiO}_x\text{:PbI}_2$ nanocomposite structures, a low dark current density of $2 \times 10^{-10} \text{ A/cm}^2$ at -200 mV and a large linear dynamic range of 112 dB are achieved. Meanwhile, a high responsivity in the visible spectral range of 450–750 nm, a large measured specific detectivity approaching 10^{13} Jones , and a fast fall time of 168 ns are demonstrated. The high-performance perovskite photodetectors demonstrated here offer a promising candidate for low-cost and high-performance near-ultraviolet–visible photodetection.

KEYWORDS: perovskites, photovoltaic photodetectors, nanocomposite, low dark current, high detectivity



Photodetectors (PDs) that convert incident light into electrical signals have been broadly applied in scientific measurements, industrial manufacturing, optical communications, medical/chemical sensing, and light imaging.^{1–6} In order to achieve high-performance PDs for practical applications (with low dark current density, large responsivity, high specific detectivity, and fast response time), their light-absorbing materials should meet several requirements: (i) high absorption coefficient; (ii) large carrier mobility; (iii) favorable energy-level alignment with the electrode materials. Much effort has been paid to fabricate high-performance inorganic semiconductor-based PDs,² such as silicon, gallium phosphide, and gallium arsenide phosphide, which typically require ultrahigh vacuum, high temperature, expensive substrates, and rigorous fabrication processing. In order to simplify the

fabrication and reduce the cost of PDs, low-temperature solution-processed strategies that mainly exploit organic materials and inorganic semiconductor nanomaterials, such as nanowires and quantum dots, have been explored.^{7–13} Even though some competitive figures of merit of the PDs employing these materials have been demonstrated, the majority of these PDs still have issues of large dark current,¹¹ small responsivity,^{8,9} low specific detectivity,⁹ and slow response time.¹⁰

Received: April 10, 2016

Accepted: June 24, 2016

Published: June 24, 2016

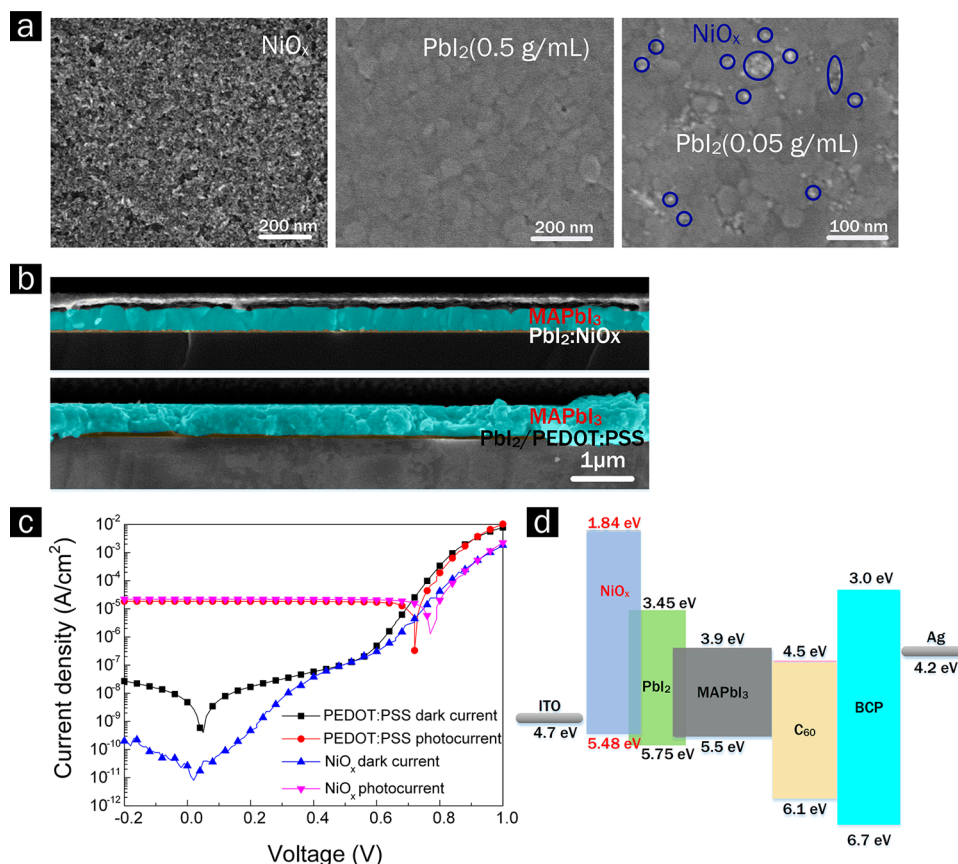


Figure 1. (a) Top view scanning electron microscopy (SEM) images of the NiO_x nanoparticle layer on ITO substrates (left), PbI₂ nanostructure grown from 0.5 g/mL PbI₂ solution on the NiO_x layer (middle), and PbI₂ nanostructure grown from 0.05 g/mL PbI₂ solution on the NiO_x layer (right). Locations of NiO_x nanoparticles are highlighted by circles in the right image. (b) Cross-sectional SEM images of MAPbI₃ polycrystalline thin films grown on the surface of NiO_x and PEDOT:PSS. (c) Current density (dark current and photocurrent) against the working bias of PEDOT:PSS and NiO_x HEL-based MAPbI₃ perovskite PDs. (d) Energy-level diagram of the NiO_x:PbI₂-based perovskite PDs.

Recently, hybrid organic–inorganic perovskites such as methylammonium lead iodide (MAPbI₃) became a focus of research due to the outstanding optical and electrical properties including a high absorption coefficient (10^5 cm^{-1} covering 300–750 nm),^{14,15} large carrier mobility,¹⁶ small excitonic binding energy at room temperature (meaning easy generation of free carriers following photoabsorption),¹⁷ and long electron/hole diffusion length.^{18,19} These excellent optoelectronic properties together with low-temperature and solution-processed formation of the polycrystalline films fueled attention to MAPbI₃ perovskite-based PDs.^{20–24} Further improvements in the performance of perovskite PDs is expected from (i) designing suitable hole extraction layers (HELs) with favorable energy-level alignment with MAPbI₃ for simultaneously enhancing photocurrent extraction and suppressing dark current and (ii) optimizing HELs and selecting suitable electron extraction layers (EELs) to achieve large responsivity, high specific detectivity, and fast response time of perovskite PDs.

In this work, we introduce room-temperature solution-processed NiO_x:PbI₂ nanocomposite structures to achieve highly efficient MAPbI₃ perovskite PDs. The nanocomposite structures, on one hand, facilitate the growth of high-quality MAPbI₃ crystalline films. On the other hand, the NiO_x:PbI₂ nanocomposite structures function as the effective HEL, which suppresses the dark current through the large electron injection

barrier at the interface of ITO/HEL, achieves efficient hole extraction due to the suitable energy-level alignment with the perovskite, and passivates the surface of the perovskite. Through optimizing the thicknesses of NiO_x and PbI₂ layers, the carrier recombination lifetime of MAPbI₃ is increased and the capacitance of perovskite PDs is reduced. Consequently, the perovskite PDs achieve a low dark current density of $2 \times 10^{-10} \text{ A/cm}^2$ at -200 mV and a large linear dynamic range of 112 dB. A measured specific detectivity approaching 10^{13} Jones covering the whole visible region and a fast fall time of 168 ns are achieved. With these excellent performances, the perovskite PDs offer a promising candidate for low-cost and high-performance near-ultraviolet–visible photodetection.

RESULTS AND DISCUSSION

Optimization of Device Structure and Dark Current.

The device structure of our perovskite PDs is indium tin oxide (ITO)/NiO_x:PbI₂/MAPbI₃/C₆₀/bathocuproine (BCP)/Ag. Different from the typical perovskite PDs using poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) as the HEL in the literature,^{20–22} NiO_x:PbI₂ nanocomposite structures can not only function as effective HEL but also favor the formation of high-quality perovskite films (shown in Figure 1). The nanocomposite structures are formed by a simple room-temperature solution process. We first form NiO_x nanostructures by spin-coating the NiO_x

nanoparticles²⁵ dispersed in deionized water at various speeds, followed by the vacuum processing at 10^{-2} Torr for 30 min to remove the residual deionized water. The $\text{NiO}_x\text{:PbI}_2$ nanocomposite structures are then formed by the PbI_2 nanostructure deposited from PbI_2 dissolved in dimethylsulfoxide (DMSO) and dimethylformamide (DMF) blend solution as described in the Methods.

A sub-micrometer-sized MAPbI_3 polycrystalline thin film is formed on the $\text{NiO}_x\text{:PbI}_2$ HEL via a sequential deposition as detailed in the Methods. It shows a wide absorption ranging from near-ultraviolet to all over the visible spectral range, with a photoluminescence (PL) peak at 780 nm, as shown in Figure S1. Figure 1b provides the comparison between cross-sectional images of MAPbI_3 films grown on the surface of $\text{NiO}_x\text{:PbI}_2$ and PEDOT:PSS. The perovskite layer formed on the $\text{NiO}_x\text{:PbI}_2$ nanocomposite structures exhibits more compact and ordered morphological features than the one grown on PEDOT:PSS, which is beneficial for enhancing device performances.

Suppressing the dark current density and enhancing photocurrent of PDs is of importance for achieving the large linear dynamic range (LDR) and high specific detectivity. This enables PDs to measure the low-level intensity of incident light in such applications as low-level laser therapy and fluorescence imaging.^{1,5} As shown schematically in Figure 1d, owing to the conduction band position of NiO_x being at 1.84 eV, the electron injection barrier between ITO and MAPbI_3 increases significantly from 0.8 to 2.86 eV using $\text{NiO}_x\text{:PbI}_2$ nanocomposite structures as the HEL. This considerably suppresses the electron injection in the dark from the external circuit and thus reduces the dark current. On the cathode side of perovskite PDs, BCP is introduced between C_{60} and the cathode to create a large hole injection barrier of 2.5 eV at the Ag/BCP interface (see Figure 1d) and thus contributes to suppression of the dark current, as well. As shown in Figure 1c, the dark current density of $\text{NiO}_x\text{:PbI}_2$ -based perovskite PDs is about 2 orders of magnitude lower than that of PEDOT:PSS-based devices.

Another important aspect for suppressing the dark current is the controllable formation of PbI_2 nanocrystals in the $\text{NiO}_x\text{:PbI}_2$ nanocomposite HEL. We first verify the formation of PbI_2 nanocrystals, and then its contribution on suppressing dark current will be demonstrated. As shown by X-ray diffraction (XRD) patterns in Figure 2a, by adjusting the methylammonium iodide (MAI) concentration during the sequential deposition, the PbI_2 content in the MAPbI_3 layer experiences an increase upon decreasing MAI concentration. From time-resolved PL spectra (Figure 2b) measured on the structure of $\text{NiO}_x\text{:PbI}_2/\text{MAPbI}_3$ from the front and back (close to the $\text{NiO}_x\text{:PbI}_2$) sides using a 405 nm pulse laser as an excitation source, a longer PL decay lifetime was observed at the $\text{NiO}_x\text{:PbI}_2$ side, suggesting a different carrier recombination dynamics at these two interfaces of MAPbI_3 . The longer recombination lifetime measured at the back side corresponds to the reduced carrier recombination at the interface of $\text{NiO}_x\text{:PbI}_2/\text{MAPbI}_3$, indicating that the $\text{NiO}_x\text{:PbI}_2$ nanocomposite HEL effectively passivates the surface of the perovskite. We further investigate the dark current density of perovskite PDs as a function of different concentrations of MAI (i.e., different PbI_2 thicknesses). As shown in Figure 2c, the increase of MAI concentration from 50 to 66 mg/mL induces the gradual increase of dark current density of perovskite PDs because of the reduction of PbI_2 content, as confirmed by XRD data of Figure 2a. Interestingly, the responsivity (the ratio of

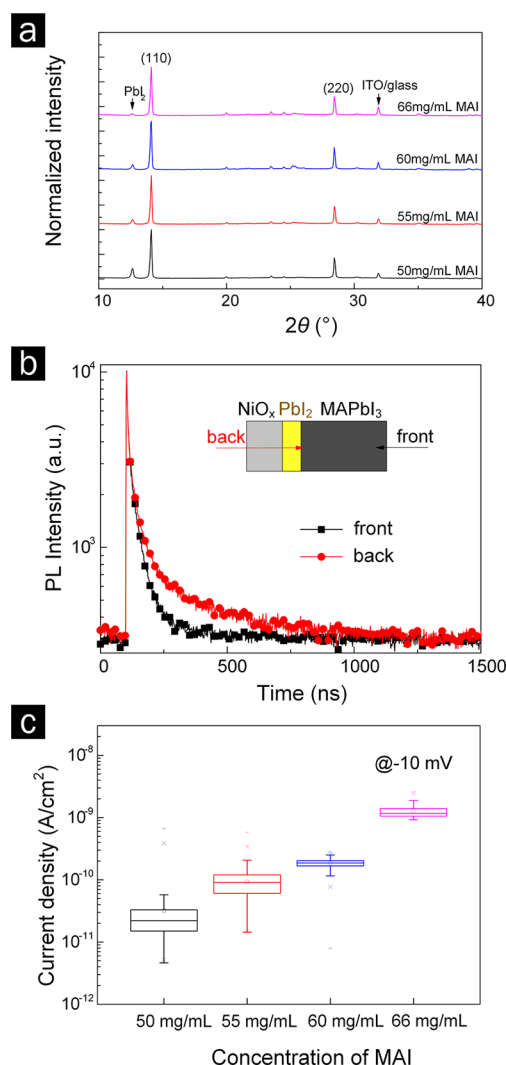


Figure 2. (a) X-ray powder diffraction patterns of MAPbI_3 films employing different (indicated) concentrations of MAI in the sequential deposition. (b) PL decay curves of MAPbI_3 films grown on NiO_x substrates measured from the front and back sides (close to the NiO_x side, as shown in the inset). (c) Dark current density of $\text{NiO}_x\text{:PbI}_2$ -based perovskite PDs operated at -10 mV as a function of different concentrations of MAI.

photocurrent density to the intensity of incident light) of the perovskite PDs improves by introducing the PbI_2 in the $\text{NiO}_x\text{:PbI}_2$ nanocomposite HEL, as shown in Figure S2, particularly when MAI concentration is reduced from 66 to 60 mg/mL because of reduced nonradiative recombination centers.²⁶ The high responsivity of 0.36 A/W can be maintained over a range of PbI_2 content (from MAI of 50–60 mg/mL). We conclude that the formation of PbI_2 can not only efficiently reduce dark current but also offer high responsivity over a wide range contents of PbI_2 in the $\text{NiO}_x\text{:PbI}_2$ -based perovskite PDs.

We optimized the thickness of NiO_x nanostructures in the nanocomposite HEL by studying performances of the devices with four different thicknesses of 18, 15, 14, and 13 nm (denoted as NiO_x -1, NiO_x -2, NiO_x -3, and NiO_x -4, respectively), as shown in Figure 3a. The dark current density at the bias of -200 mV was reduced from 1×10^{-9} to 2×10^{-10} A/ cm^2 when the NiO_x thickness decreased from 18 to 13 nm. For perovskite PDs operating at -10 mV, the measured dark

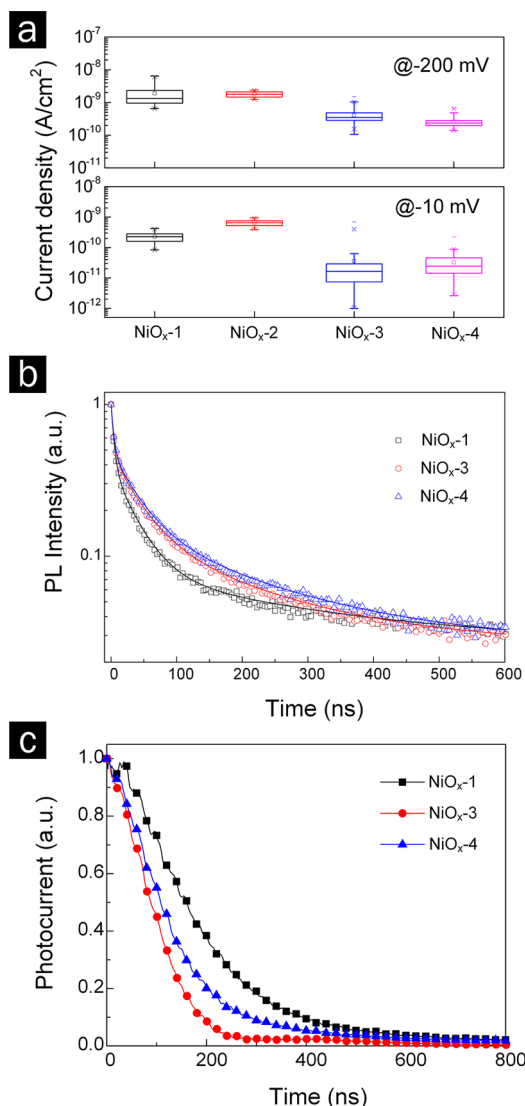


Figure 3. (a) Dark current density of NiO_x:PbI₂-based perovskite PDs as a function of four different thicknesses of NiO_x HELs. Thicknesses of NiO_x-1, NiO_x-2, NiO_x-3, and NiO_x-4 films are 18, 15, 14, and 13 nm, respectively. (b) Time-resolved PL decay curves of MAPbI₃ films formed on NiO_x-1, NiO_x-3, and NiO_x-4 films. The PL decay data were fitted with a multiexponential function. The average carrier recombination lifetimes of MAPbI₃ formed on NiO_x-1, NiO_x-3, and NiO_x-4 are 21, 25, and 25.3 ns, respectively. (c) Transient photocurrent response of NiO_x-1-, NiO_x-3-, and NiO_x-4-based perovskite PDs.

current density showed a similar tendency. Notably, its value further reduced by an order of magnitude to 2×10^{-11} A/cm².

At the same time, the photocurrent density of perovskite PDs showed negligible variation for different bias and different NiO_x thicknesses (as shown in Figure S3). Since MAPbI₃ formed on the NiO_x:PbI₂ surfaces did not display any particular morphology changes (Figure S4), there is no influence of different thickness of NiO_x on perovskite formation. Time-resolved PL spectra of MAPbI₃ formed on NiO_x-1, NiO_x-3, and NiO_x-4 are shown in Figure 3b. MAPbI₃ grown on the NiO_x:PbI₂ nanocomposite HEL with a thinner NiO_x shows a longer carrier recombination lifetime and a stronger PL intensity (Figure S5), suggesting that the nonradiative recombination rate is reduced and thus the noise is sup-

pressed.²⁷ Transient photocurrent response of perovskite PDs using NiO_x-1, NiO_x-3, and NiO_x-4 HELs are shown in Figure 3c. NiO_x-4-based perovskite PDs achieved a dark current comparable to that of NiO_x-3-based perovskite PDs, while the fall time was longer for NiO_x-4-based perovskite PDs, which can be related to their larger capacitance (16.1 nF for NiO_x-3-based PDs vs 20.1 nF for NiO_x-4-based PDs). It should be noted that since the NiO_x has a deeper valence band of 5.48 eV compared with the 5.0 eV of PEDOT:PSS, more favorable energy-level alignment of NiO_x with MAPbI₃ is realized for enhancing hole extraction and thus photocurrent, as demonstrated in Figure 1d. To demonstrate the photocurrent improvement, we measured the spectral responsivity, as shown in Figure S6. The responsivity of the optimized NiO_x:PbI₂-based perovskite PDs was better than that of the optimized PEDOT:PSS-based perovskite PDs in the whole wavelength region, except for the small region around 700 nm, probably due to different optical-field distribution in the device.²⁸ Consequently, by optimizing the thicknesses of NiO_x nanostructures and PbI₂ nanocrystals in the NiO_x:PbI₂ nanocomposite HEL, a low dark current density of 2×10^{-10} A/cm² among the vertical perovskite PDs was achieved.

Spectral Responsivity Characterization. The spectral responsivity of optimized perovskite PDs with the structure of ITO/NiO_x (14 nm):PbI₂/MAPbI₃ (250 nm)/C₆₀ (50 nm)/BCP (10 nm)/Ag (120 nm) is shown in Figure 4a. Remarkably, they exhibit high responsivity in the visible spectral range of 450–750 nm, corresponding to the high EQE between 70 and 90%, which exceeds the value of commercial Si and GaAsP PDs.²⁹ The high spectral response of perovskite PDs that cover red, green, and blue regions, but does not extend its response to the near-infrared region (thus excess infrared noise will be significantly reduced), can enable their applications in visible light imaging. The comprehensive studies of other characteristics of the optimized perovskite PDs are described below.

LDR Characterization. LDR value, denoting the range where the photocurrent density of perovskite PDs is linearly proportional to the incident light intensity, is an important parameter for characterizing the detectable linear light intensity of perovskite PDs. Theoretically, the lower limit of LDR is determined by the noise current, which originates from the thermal noise (Johnson–Nyquist noise), the shot noise, and $1/f$ noise.^{7,30} Typically, shunt resistance largely contributes to the thermal noise (see details in the Supporting Information). NiO_x:PbI₂-based perovskite PDs achieve a shunt resistance of 14 GΩ, which is about 2 orders of magnitude larger than 0.16 GΩ for PEDOT:PSS-based perovskite PDs, suggesting that shunt resistance can be effectively suppressed by NiO_x:PbI₂ nanocomposite HEL. Reverse leakage current originating from the reverse-bias-induced charge injection from the external circuit makes a large contribution to the shot noise,³¹ which is efficiently suppressed in our perovskite PDs due to the large carrier injection barrier of 2.86 eV at the anode interface and 2.5 eV at the cathode interface, as shown in Figure 1d. Moreover, the introduction of C₆₀ EEL was found to efficiently passivate the surface traps of perovskites,^{22,32} which can effectively suppress $1/f$ noise that originated from the carrier trapping–detrapping process.^{33,34} In order to obtain the accurate value of the total noise, we directly measured the noise, as shown in Figure S7. The noise current was found to be ~ 20 fA Hz^{-1/2}, corresponding to a noise equivalent power of ~ 56 fW Hz^{-1/2}.

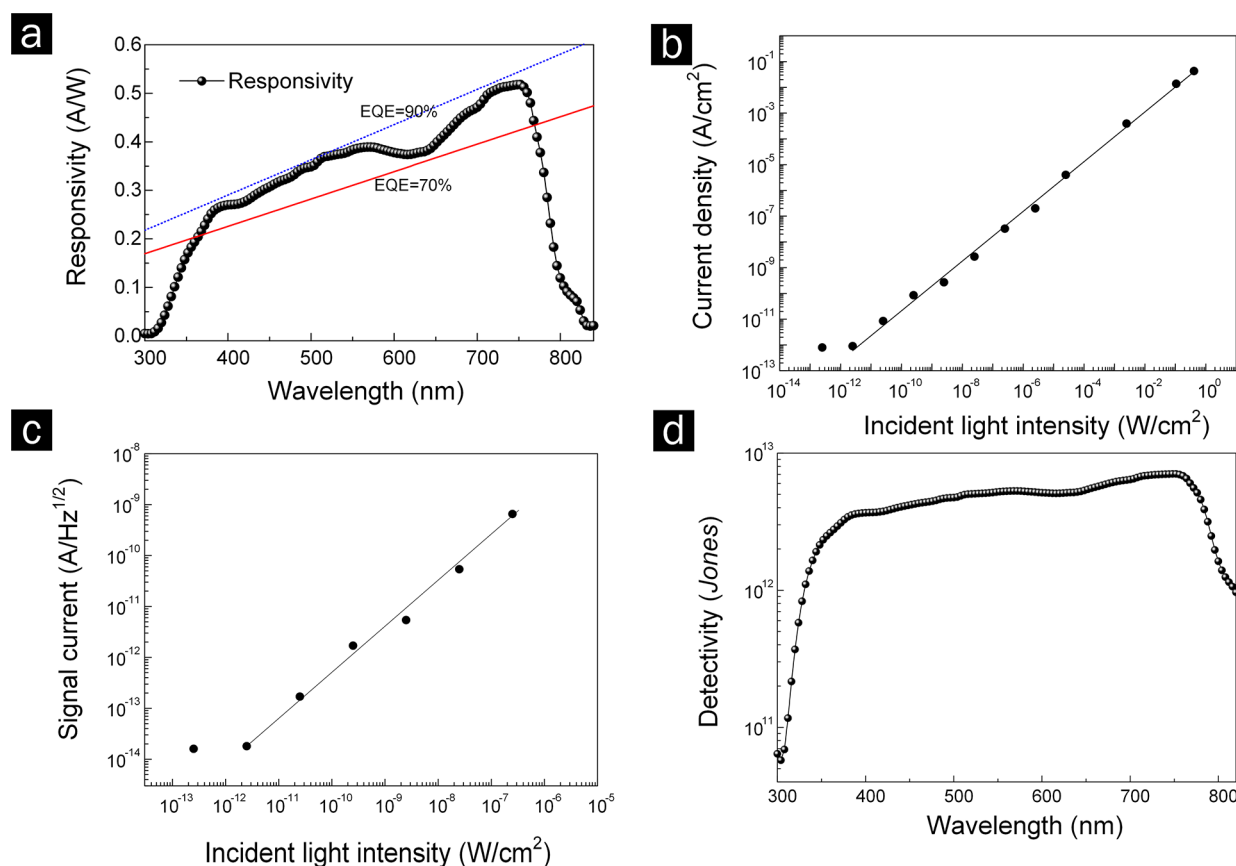


Figure 4. Performance of optimized $\text{NiO}_x\text{:PbI}_2$ -based perovskite PDs. (a) Spectral responsivity as a function of response wavelength. Theoretical EQEs of 70 and 90% are depicted for comparison. (b) Linear dynamic range plot, *i.e.*, photocurrent density vs incident light intensity. (c) Signal current against incident light intensity. (d) Measured specific detectivity vs response wavelength.

The upper limit of LDR is governed by the saturation current when the incident light intensity reaches a certain level, P_{sat} , and thus photocurrent cannot be efficiently extracted due to the space charge buildup.^{35,36} The lowest charge carrier mobility within perovskite PDs determines the saturation current (*i.e.*, the maximum detectable light intensity, P_{sat}) and also is a limiting parameter for achieving high-speed response perovskite PDs that will be discussed below. In order to achieve a large P_{sat} , C_{60} that has been widely applied in perovskite PDs and solar cells is intentionally selected as the EEL of our perovskite PDs. Using the capacitance of perovskite PDs obtained from RC (resistor–capacitor) time-constant-limited transient response (discussed below) and the C_{60} electron mobility of $1.11 \times 10^{-3} \text{ cm}^2/\text{Vs}$ (extracted from the space-charge-limited current shown in Figure S8),³⁷ the calculated saturation current is 0.36 A/cm^2 and the upper limit of LDR reaches 1.067 W/cm^2 .

Consequently, LDR defined as $\text{LDR} = 10 \log(P_{\text{sat}}/P_{\text{noise}})$, where P_{noise} is the lowest detectable light intensity governed by the total noise current. Our perovskite PDs achieved a large LDR of about 120 dB when perovskite PDs were operated.

In order to experimentally characterize LDR of perovskite PDs, we measured the photocurrent density as a function of the wide-range incident light intensities, as shown in Figure 4b. The lowest light intensity of $2.5 \times 10^{-12} \text{ W/cm}^2$ and the highest light intensity of 0.41 W/cm^2 were achieved for our perovskite PDs, corresponding to the LDR of 112 dB, which is the highest value among reported perovskite PDs,^{20–22,38} comparable with the value of commercial visible Si PDs (120 dB),⁷ GaAsP PDs

(110 dB),³⁹ and state-of-the-art organic-material-based PDs (110 dB).^{29,40,41} It should be mentioned that the measured lowest light intensity approaches the value of device noise, as shown in Figure 4c, suggesting efficient trap passivation by C_{60} EEL as well as high-quality perovskites fabricated on the nanostructured $\text{NiO}_x\text{:PbI}_2$ structure. The highest light intensity of 0.41 W/cm^2 achieved in our perovskite PDs approached the theoretical value of 1.067 W/cm^2 , which probably resulted from the lower hole mobility of NiO_x and the lower electron mobility of BCP compared with that of MAPbI_3 perovskite and C_{60} .^{25,40,42}

Detectivity Characterization. Specific detectivity D^* is one of the most important figures of merit for PDs, defined as² $D^* = (A\Delta f)^{1/2}R/i_{\text{measure}}$, where A is the device area, Δf is the bandwidth, R is the responsivity, and i_{measure} is the measured noise (Figure S7). D^* normalizes variations in device working areas and bandwidth, thus enabling comparison among different PDs. Specific detectivity D^* of our optimized perovskite PDs as a function of spectral wavelength is presented in Figure 4d. Values of D^* exceeding 1.0×10^{12} Jones in the near-ultraviolet region (340–400 nm) and 4.0×10^{12} Jones covering the whole visible region (450–750 nm) are achieved, which are among the highest reported for perovskite-based PDs^{21,22,38,43–46} and organic-material-based PDs ($\sim 1 \times 10^{12}$ Jones)^{40,47,48} and comparable to the theoretical value of commercial Si ($\sim 4.5 \times 10^{13}$ Jones), GaAsP (3.0×10^{13} Jones), and GaP PDs (2.3×10^{12} Jones).^{7,29}

Transient Photocurrent Response Characterization. The photocurrent response time determines the ability of PDs

to truthfully record a high-frequency incident light signal. The upper limit of response time T_{tr} of PDs is mainly governed by the carrier transit time.³⁰ For our perovskite PDs, T_{tr} is the sum time of the carrier transit across the perovskite and the C_{60} layers; it is estimated to be 23 ns (see details in the [Supporting Information](#)). It is limited by the electron mobility of C_{60} , which is lower than that of $MAPbI_3$ perovskite.¹⁶ The transient photocurrent response of optimized perovskite PDs (under 532 nm light with the intensity of about $3 \mu W/cm^2$) is shown in [Figure 5a](#), with a rise time of 58 ns and a fall time of 168 ns. By

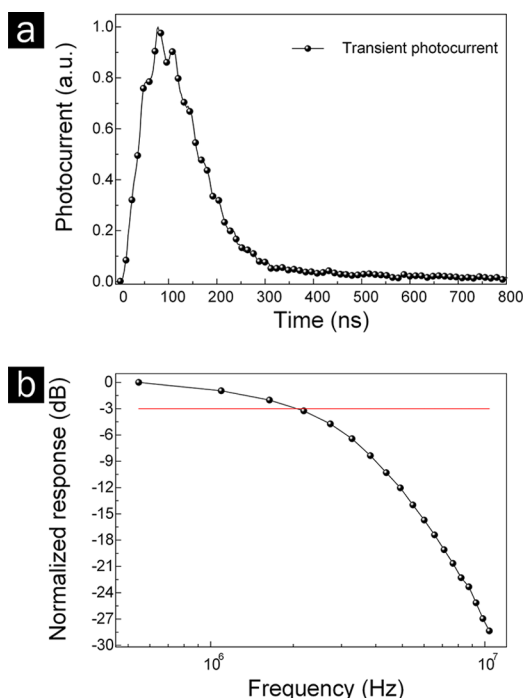


Figure 5. (a) Transient photocurrent response of $NiO_x:PbI_2$ -based perovskite PDs (under 532 nm light with the intensity of about $3 \mu W/cm^2$), with a device area of 6 mm^2 in photovoltaic mode. (b) Normalized photocurrent response vs modulation frequency of incident light through fast Fourier transform method. The line of -3 dB is depicted for reference.

reducing the size of perovskite PDs and thus the RC time constant, the photocurrent response is expected to approach the theoretical limit. In order to confirm this assumption, the RC time constant of the perovskite PD system was calculated (see details in [Figure S9](#)). Using the integrated Q of 0.9578 nC , the transient voltage V of 0.0595 V , and the load resistor R with 10Ω , RC time constant ($RC = RQ/V$) was calculated to be 161 ns, which is close to our measured fall time, suggesting that the transient photocurrent response of our perovskite PDs is governed by RC time constant. This is further confirmed in [Figure S10](#), showing that measured fall times of perovskite PDs increase with the raised resistance of load resistors. It should be noted that transient photocurrent response (rise time and fall time) is a function of the intensity of incident light. Based on the results shown in [Figure S11](#), the rise time and fall time of our perovskite PDs obeyed this trend, as they increased slowly with the increased intensity of incident light, suggesting that the capacitance of perovskite PDs increases with the increased incident light power, which is attributed to the enhanced dielectric permittivity of perovskites under illumination.⁴⁹

The photocurrent response as a function of modulation frequency of incident light is shown in [Figure 5b](#). Perovskite PDs with a working area of 6 mm^2 achieved a 3 dB cutoff frequency of 2 MHz, which is comparable to the value of 2.9 MHz for the previously reported perovskite PDs with a much smaller working area of 1 mm^2 .²⁰ It should be noted that the transient photocurrent response of our perovskite PDs is limited by the RC time constant. Through reducing the working area of perovskite PDs, our perovskite PDs achieved a 3 dB cutoff frequency of 7 MHz (see [Figure S12](#)). Consequently, the 3 dB cutoff frequency of 24 MHz can be expected if carrier transit time determines the transient photocurrent behavior. In addition to the large-bandwidth photocurrent response, our perovskite PDs are repeatable ([Figure S13](#)) and stable ([Figure S14](#)), which are beneficial for practical applications.

CONCLUSIONS

We have introduced a room-temperature solution-processed $NiO_x:PbI_2$ nanocomposite HEL into $MAPbI_3$ perovskite-based PDs and demonstrated their excellent performance characteristics. The $NiO_x:PbI_2$ layer favors the subsequent formation of high-quality crystalline $MAPbI_3$ films and passivates the surface of the perovskite. Moreover, the $NiO_x:PbI_2$ nanocomposite structures offer a large electron injection barrier at the ITO interface for suppressing dark current and the favorable energy-level alignment with perovskite film for enhancing the hole extraction. After the thicknesses of the $NiO_x:PbI_2$ nanostructure were optimized, an ultralow dark current density of $2.0 \times 10^{-10} \text{ A/cm}^2$ at -200 mV was achieved. Besides, a high responsivity (corresponding to an EQE between 70 and 90%) covering the whole near-ultraviolet to visible spectral region, a large measured specific detectivity of approaching 10^{13} Jones , a high LDR of measured 112 dB, and a fast fall time of 168 ns limited by RC time constant were demonstrated. These excellent figures of merit of our perovskite PDs make them highly promising for a wide range of applications, such as light imaging, medical/chemical sensing, optical communications, and smoke/fire monitoring.

METHODS

$NiO_x:PbI_2$ Nanocomposite Structures. The $NiO_x:PbI_2$ nanostructured layer was produced by a simple and fast room-temperature and solution-based process on ITO/glass substrates with the square resistance of $\sim 17 \Omega/\square$. First, NiO_x nanoparticles were synthesized by a chemical precipitation method²⁵ utilizing $Ni(NO_3)_2 \cdot 6H_2O$ and NaOH. Briefly, $Ni(NO_3)_2 \cdot 6H_2O$ (0.5 mol) was dispersed in 100 mL of deionized water to obtain a dark green solution. The pH of the solution was adjusted to 10 by adding a NaOH solution (10 mol L^{-1}). After being stirred for 5 min, the colloidal precipitation was thoroughly washed with deionized water twice and dried at 80°C for 6 h. The obtained green powder was then calcined at 270°C for 2 h to obtain a dark black NiO_x nanoparticle powder. Then, the nanoparticles were dispersed in the deionized water to obtain the desired concentrations. NiO_x nanostructures were formed by spin-coating the nanoparticles at various speeds, followed by the vacuum processing at 10^{-2} Torr for 30 min to remove the residual deionized water. To form the $NiO_x:PbI_2$ nanocomposite structure, a solution of 0.5 g/mL PbI_2 (Sigma-Aldrich 99% PbI_2) in a DMSO/DMF mixture (4:6 by volume) was spin-coated on the NiO_x nanoparticle structures at 5000 rpm for 50 s.

Device Fabrication. The device structure of perovskite PDs is ITO/ $NiO_x:PbI_2$ / $MAPbI_3$ / C_{60} /BCP/Ag. The cleaning process of ITO substrates can be found elsewhere.⁴⁰ Starting from the $NiO_x:PbI_2$ nanocomposite structures, the samples were spin-coated with different concentrations of MAI (50, 55, 60, and 66 mg/mL from isopropyl

alcohol solvent). The samples were then heated in nitrogen atmosphere on a hot plate at 100 °C for 10 min to obtain the MAPbI₃ polycrystalline films. To form the EEL, 0.02 wt % C₆₀ in 1,2-dichlorobenzene was directly spin-coated on the MAPbI₃ polycrystalline film at 800 rpm for 120 s. BCP (10 nm) obtained from Nichem Fine Technology and the Ag cathode (120 nm) were evaporated in sequence onto the active layer to complete perovskite PDs. The evaporation rate was 0.4 nm/s for BCP and 2 nm/s for Ag. The final thickness was controlled by *in situ* quartz monitors. The active area of the perovskite PDs was 6 mm².

Film Characterization. The top morphology images of perovskites grown on NiO_x/PbI₂ nanocomposite structures were characterized by NT-MDT atomic force microscopy. Cross-sectional SEM images of the perovskite films grown on NiO_x and PEDOT:PSS substrates were measured by a LEO 1530 FEG SEM. The thicknesses of the NiO_x nanostructures were determined by a J.A. Woollam Co. ellipsometer. The optical transmittance of MAPbI₃ polycrystalline films was measured by the goniometer. The absorbance spectra were determined from the optical transmittance. The PL spectrum of MAPbI₃ was measured on a home-built spectrometer using an excitation source of 325 nm laser. Time-resolved PL spectra (TCSPC) of MAPbI₃ were measured on an Edinburgh Instruments FLS920 spectrofluorometer equipped with a 405 nm, 5 mW picosecond pulsed diode laser (EPL-405) as an excitation source. PL decay data were fitted using a multiexponential function. Lifetime was calculated by taking the weighted average across the exponential components.

Device Characterization. Current density as a function of working bias and of the different wavelength (responsivity) was measured on a Keithley 2635 source meter with a light source setup of 1000 W xenon arc lamp integrated with an Acton SpectraPro 2150i monochromator. Dynamic linear range measurements were performed under different intensities of monochromatic light using Thorlabs metallic-coated neutral density filters. The intensity of monochromatic light was measured by facility calibrated (Newport) Si photodetectors. The transient photocurrent measurements have been done with a 532 nm 6 ps pulse width laser (130 μJ/pulse maximum at 400 Hz) integrated with an optical chopper and a 1 GHz Agilent DSO7104B digital storage oscilloscope. Noise current of photodetectors was measured employing a Stanford Research SR830 lock-in amplifier in current measurement mode. All the measurements were carried out at room temperature in ambient conditions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.6b02425.

Additional experimental details and Figures S1–S14 (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Environment and Conservation Fund (ECF Project 33/2015), General Research Fund (Grant HKU711813), the Collaborative Research Fund (Grants C7045-14E) from the Research Grants Council of Hong Kong Special Administrative Region (HKSAR), China, Grant CAS14601 from CAS-Croucher Funding Scheme for Joint Laboratories and ECF Project 33/2015, Environment and Conservation Fund of HKSAR, and by the CityU research project 9610350.

REFERENCES

- (1) Tafur, J.; Van Wijk, E. P. A.; Van Wijk, R.; Mills, P. J. Biophoton Detection and Low-Intensity Light Therapy: A Potential Clinical Partnership. *Photomed. Laser Surg.* **2009**, *28*, 23–30.
- (2) Sze, S. M.; Ng, K. K. *Physics of Semiconductor Devices*; John Wiley & Sons, 2006.
- (3) Ghassemloooy, Z.; Haigh, P. A.; Arca, F.; Tedde, S. F.; Hayden, O.; Papakonstantinou, I.; Rajbhandari, S. Visible Light Communications: 3.75 Mb/s Data Rate with a 160 kHz Bandwidth Organic Photodetector and Artificial Neural Network Equalization [Invited]. *Photonics Res.* **2013**, *1*, 65–68.
- (4) Steudel, S.; Myny, K.; Arkhipov, V.; Deibel, C.; De Vusser, S.; Genoe, J.; Heremans, P. 50 MHz Rectifier Based on An Organic Diode. *Nat. Mater.* **2005**, *4*, 597–600.
- (5) Davis, R. W.; Timlin, J. A.; Kaiser, J. N.; Sinclair, M. B.; Jones, H. D.; Lane, T. W. Accurate Detection of Low Levels of Fluorescence Emission in Autofluorescent Background: Francisella-Infected Macrophage Cells. *Microsc. Microanal.* **2010**, *16*, 478–487.
- (6) Ng, T. N.; Wong, W. S.; Chabinyc, M. L.; Sambandan, S.; Street, R. A. Flexible Image Sensor Array With Bulk Heterojunction Organic Photodiode. *Appl. Phys. Lett.* **2008**, *92*, 213303.
- (7) Gong, X.; Tong, M.; Xia, Y.; Cai, W.; Moon, J. S.; Cao, Y.; Yu, G.; Shieh, C.-L.; Nilsson, B.; Heeger, A. J. High-Detectivity Polymer Photodetectors with Spectral Response from 300 to 1450 nm. *Science* **2009**, *325*, 1665–1667.
- (8) Wei, W.; Bao, X.-Y.; Soci, C.; Ding, Y.; Wang, Z.-L.; Wang, D. Direct Heteroepitaxy of Vertical InAs Nanowires on Si Substrates for Broad Band Photovoltaics and Photodetection. *Nano Lett.* **2009**, *9*, 2926–2934.
- (9) Arnold, M. S.; Zimmerman, J. D.; Renshaw, C. K.; Xu, X.; Lunt, R. R.; Austin, C. M.; Forrest, S. R. Broad Spectral Response Using Carbon Nanotube/Organic Semiconductor/C60 Photodetectors. *Nano Lett.* **2009**, *9*, 3354–3358.
- (10) Clifford, J. P.; Konstantatos, G.; Johnston, K. W.; Hoogland, S.; Levina, L.; Sargent, E. H. Fast, Sensitive and Spectrally Tuneable Colloidal-Quantum-Dot Photodetectors. *Nat. Nanotechnol.* **2009**, *4*, 40–44.
- (11) Shin, D. H.; Kim, S.; Kim, J. M.; Jang, C. W.; Kim, J. H.; Lee, K. W.; Kim, J.; Oh, S. D.; Lee, D. H.; Kang, S. S.; Kim, C. O.; Choi, S.-H.; Kim, K. J. Graphene/Si-Quantum-Dot Heterojunction Diodes Showing High Photosensitivity Compatible with Quantum Confinement Effect. *Adv. Mater.* **2015**, *27*, 2614–2620.
- (12) Kim, I. K.; Pal, B. N.; Ullah, M.; Burn, P. L.; Lo, S.-C.; Meredith, P.; Namdas, E. B. High-Performance, Solution-Processed Non-Polymeric Organic Photodiodes. *Adv. Opt. Mater.* **2015**, *3*, 50–56.
- (13) Chen, M.; Yu, H.; Kershaw, S. V.; Xu, H.; Gupta, S.; Hetsch, F.; Rogach, A. L.; Zhao, N. Fast, Air-Stable Infrared Photodetectors based on Spray-Deposited Aqueous HgTe Quantum Dots. *Adv. Funct. Mater.* **2014**, *24*, 53–59.
- (14) Green, M. A.; Ho-Baillie, A.; Snaith, H. J. The Emergence of Perovskite Solar Cells. *Nat. Photonics* **2014**, *8*, S06–S14.
- (15) Barugkin, C.; Cong, J.; Duong, T.; Rahman, S.; Nguyen, H. T.; Macdonald, D.; White, T. P.; Catchpole, K. R. Ultralow Absorption Coefficient and Temperature Dependence of Radiative Recombination of CH₃NH₃PbI₃ Perovskite from Photoluminescence. *J. Phys. Chem. Lett.* **2015**, *6*, 767–772.
- (16) Wehrenfennig, C.; Eperon, G. E.; Johnston, M. B.; Snaith, H. J.; Herz, L. M. High Charge Carrier Mobilities and Lifetimes in Organolead Trihalide Perovskites. *Adv. Mater.* **2014**, *26*, 1584–1589.
- (17) Miyata, A.; Mitioglu, A.; Plochocka, P.; Portugall, O.; Wang, J. T.-W.; Stranks, S. D.; Snaith, H. J.; Nicholas, R. J. Direct Measurement of The Exciton Binding Energy and Effective Masses for Charge Carriers in Organic-Inorganic Tri-halide Perovskites. *Nat. Phys.* **2015**, *11*, 582–587.
- (18) Stranks, S.; Eperon, G.; Grancini, G.; Menelaou, C.; Alcocer, M.; Leijtens, T.; Herz, L.; Petrozza, A.; Snaith, H. Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in An Organometal Trihalide Perovskite Absorber. *Science (Washington, DC, U. S.)* **2013**, *342*, 341–344.

- (19) Xing, G.; Mathews, N.; Sun, S.; Lim, S. S.; Lam, Y. M.; Grätzel, M.; Mhaisalkar, S.; Sum, T. C. Long-Range Balanced Electron- and Hole-Transport Lengths in Organic-Inorganic CH₃NH₃PbI₃. *Science* **2013**, *342*, 344–347.
- (20) Dou, L.; Yang, Y.; You, J.; Hong, Z.; Chang, W.-H.; Li, G.; Yang, Y. Solution-Processed Hybrid Perovskite Photodetectors with High Detectivity. *Nat. Commun.* **2014**, *5*, 5404.
- (21) Lin, Q.; Armin, A.; Lyons, D. M.; Burn, P. L.; Meredith, P. Low Noise, IR-Blind Organohalide Perovskite Photodiodes for Visible Light Detection and Imaging. *Adv. Mater.* **2015**, *27*, 2060–2064.
- (22) Fang, Y.; Huang, J. Resolving Weak Light of Sub-picowatt per Square Centimeter by Hybrid Perovskite Photodetectors Enabled by Noise Reduction. *Adv. Mater.* **2015**, *27*, 2804–2810.
- (23) Dong, R.; Fang, Y.; Chae, J.; Dai, J.; Xiao, Z.; Dong, Q.; Yuan, Y.; Centrone, A.; Zeng, X. C.; Huang, J. High-Gain and Low-Driving-Voltage Photodetectors Based on Organolead Triiodide Perovskites. *Adv. Mater.* **2015**, *27*, 1912–1918.
- (24) Song, J.; Xu, L.; Li, J.; Xue, J.; Dong, Y.; Li, X.; Zeng, H. Monolayer and Few-Layer Inorganic Perovskite as New Two-Dimensional Semiconductors for Printable Photodetectors. *Adv. Mater.* **2016**, *28*, 4861–4869.
- (25) Jiang, F.; Choy, W. C. H.; Li, X.; Zhang, D.; Cheng, J. Post-Treatment-Free Solution-Processed Non-Stoichiometric NiOx Nanoparticles for Efficient Hole-Transport Layers of Organic Optoelectronic Devices. *Adv. Mater.* **2015**, *27*, 2930–2937.
- (26) Roldan-Carmona, C.; Gratia, P.; Zimmermann, I.; Grancini, G.; Gao, P.; Graetzel, M.; Nazeeruddin, M. K. High Efficiency Methylammonium Lead Triiodide Perovskite Solar Cells: The Relevance of Non-Stoichiometric Precursors. *Energy Environ. Sci.* **2015**, *8*, 3550–3556.
- (27) Yoon, W.; Boercker, J. E.; Lumb, M. P.; Placencia, D.; Foos, E. E.; Tischler, J. G. Enhanced Open-Circuit Voltage of PbS Nanocrystal Quantum Dot Solar Cells. *Sci. Rep.* **2013**, *3*, 2225.
- (28) Lin, Q.; Armin, A.; Nagiri, R. C. R.; Burn, P. L.; Meredith, P. Electro-Optics of Perovskite Solar Cells. *Nat. Photonics* **2015**, *9*, 106–112.
- (29) Armin, A.; Hambsch, M.; Kim, I. K.; Burn, P. L.; Meredith, P.; Nardas, E. B. Thick Junction Broadband Organic Photodiodes. *Laser Photonics Rev.* **2014**, *8*, 924–932.
- (30) Liu, J.-M. *Photonic Devices*; Cambridge University Press, 2009.
- (31) Baeg, K.-J.; Binda, M.; Natali, D.; Caironi, M.; Noh, Y.-Y. Organic Light Detectors: Photodiodes and Phototransistors. *Adv. Mater.* **2013**, *25*, 4267–4295.
- (32) Xu, J.; Buin, A.; Ip, A. H.; Li, W.; Voznyy, O.; Comin, R.; Yuan, M.; Jeon, S.; Ning, Z.; McDowell, J. J.; Kanjanaboos, P.; Sun, J.-P.; Lan, X.; Quan, L. N.; Kim, D. H.; Hill, I. G.; Maksymovych, P.; Sargent, E. H. Perovskite-Fullerene Hybrid Materials Suppress Hysteresis in Planar Diodes. *Nat. Commun.* **2015**, *6*, 7081.
- (33) Hooge, F. N. 1/f Noise Sources. *IEEE Trans. Electron Devices* **1994**, *41*, 1926–1935.
- (34) Carbone, A.; Mazzetti, P. Grain-Boundary Effects on Photo-current Fluctuations in Polycrystalline Photoconductors. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1998**, *57*, 2454–2460.
- (35) Goodman, A. M.; Rose, A. Double Extraction of Uniformly Generated Electron-Hole Pairs from Insulators with Noninjecting Contacts. *J. Appl. Phys.* **1971**, *42*, 2823–2830.
- (36) Mihailetschi, V. D.; Wildeman, J.; Blom, P. W. M. Space-Charge Limited Photocurrent. *Phys. Rev. Lett.* **2005**, *94*, 126602.
- (37) Sha, W. E. I.; Zhu, H. L.; Chen, L.; Chew, W. C.; Choy, W. C. H. A General Design Rule to Manipulate Photocarrier Transport Path in Solar Cells and Its Realization by the Plasmonic-Electrical Effect. *Sci. Rep.* **2015**, *5*, 8525.
- (38) Sutherland, B. R.; Johnston, A. K.; Ip, A. H.; Xu, J.; Adinolfi, V.; Kanjanaboos, P.; Sargent, E. H. Sensitive, Fast, and Stable Perovskite Photodetectors Exploiting Interface Engineering. *ACS Photonics* **2015**, *2*, 1117–1123.
- (39) Hamamatsu; <http://www.hamamatsu.com/jp/en/G1117.html> (accessed October 2, 2015).
- (40) Zhu, H. L.; Choy, W. C. H.; Sha, W. E. I.; Ren, X. Photovoltaic Mode Ultraviolet Organic Photodetectors with High On/Off Ratio and Fast Response. *Adv. Opt. Mater.* **2014**, *2*, 1082–1089.
- (41) Fang, Y.; Guo, F.; Xiao, Z.; Huang, J. Large Gain, Low Noise Nanocomposite Ultraviolet Photodetectors with a Linear Dynamic Range of 120 dB. *Adv. Opt. Mater.* **2014**, *2*, 348–353.
- (42) Yasuda, T.; Yamaguchi, Y.; Zou, D. C.; Tsutsui, T. Carrier Mobilities in Organic Electron Transport Materials Determined from Space Charge Limited Current. *Jpn. J. Appl. Phys.* **2002**, *41*, 5626–5629.
- (43) Hu, X.; Zhang, X.; Liang, L.; Bao, J.; Li, S.; Yang, W.; Xie, Y. High-Performance Flexible Broadband Photodetector Based on Organolead Halide Perovskite. *Adv. Funct. Mater.* **2014**, *24*, 7373–7380.
- (44) Liu, C.; Wang, K.; Yi, C.; Shi, X.; Du, P.; Smith, A. W.; Karim, A.; Gong, X. Ultrasensitive Solution-Processed Perovskite Hybrid Photodetectors. *J. Mater. Chem. C* **2015**, *3*, 6600–6606.
- (45) Guo, Y.; Liu, C.; Tanaka, H.; Nakamura, E. Air-Stable and Solution-Processable Perovskite Photodetectors for Solar-Blind UV and Visible Light. *J. Phys. Chem. Lett.* **2015**, *6*, 535–539.
- (46) Lee, Y.; Kwon, J.; Hwang, E.; Ra, C.-H.; Yoo, W. J.; Ahn, J.-H.; Park, J. H.; Cho, J. H. High-Performance Perovskite–Graphene Hybrid Photodetector. *Adv. Mater.* **2015**, *27*, 41–46.
- (47) Zhu, L.; Wang, W. S.; Yao, Z. G.; Zhang, X. Q.; Wang, Y. S. Ultraviolet Photodetectors With Narrow-Band Spectral Response Using TAPC Donor. *IEEE Trans. Electron Devices* **2012**, *59*, 3583–3586.
- (48) Azzellino, G.; Grimoldi, A.; Binda, M.; Caironi, M.; Natali, D.; Sampietro, M. Fully Inkjet-Printed Organic Photodetectors with High Quantum Yield. *Adv. Mater.* **2013**, *25*, 6829–6833.
- (49) Juarez-Perez, E. J.; Sanchez, R. S.; Badia, L.; Garcia-Belmonte, G.; Kang, Y. S.; Mora-Sero, I.; Bisquert, J. Photoinduced Giant Dielectric Constant in Lead Halide Perovskite Solar Cells. *J. Phys. Chem. Lett.* **2014**, *5*, 2390–2394.