Photodetectors

Nanocrystalline Perovskite Hybrid Photodetectors with High Performance in Almost Every Figure of Merit

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Conversion of photon into electron is a phenomenon of great importance in nature. Photodetectors based on this principle have immense potential applications at the frontiers of both scientific and industrial communities, thus affecting the daily life. Herein, a novel class of high-quality organic-inorganic trihalide perovskite nanoscale hybrid photodetectors is presented based on carbon electrode-molecule junctions working at mild conditions. Almost every figure of merit with high performance, such as highest responsivity, highest photogain, high detectivity, high linear dynamic range, and a broad spectral response, could be achieved simultaneously in a single device under different biases. These significant achievements benefit from rational choices of novel energy loss-prevented hybrid perovskite nanocrystals as active materials and optimized carbon electrode-molecule junctions as device architectures, which leads to a hybridization mechanism of photodiodes and photoconductors. These investigations demonstrate a useful photodetector platform that might lead to many future photoelectric conversion applications in the practical way.

1. Introduction

Photoelectric conversion is a phenomenon of great importance in nature since been initially revealed in the early 20th century.^[1] Photosensitive devices based on this principle are particularly attractive because of their potential applications at the frontiers of science and engineering, including fiber-optic communication, high-density optical information technology, chemical/biological imaging/sensing, night vision, and security.^[2,3] These applications place extreme demands on the detector performance, such as responsivity, detectivity,

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the optimization of the device architectures.^[4–8] Despite these efforts, however, it is still a formidable challenge to obtain a photodetector that exhibits the high performance in all these figures of merit, hampering its practical application. Recently, a new series of perovskite materials (chemical formula abbreviation ABX₃, where A, B, and X are organic cation, metal cation, and halide anion, respectively) have attracted worldwide

interest because they are one of the most competitive candidates as light-absorbing materials for photovoltaic applications. The highest power conversion efficiency of solar cells based on this star material

photogain, linear dynamic range (LDR),

ON/OFF current ratio, and the range

of spectral response. Previous reports proved that these figures of merit could be

improved on one or two aspects through

the choice of the active materials and/or

has been confirmed to be greater than 23%.^[9] This achievement results from the remarkable intrinsic optoelectronic properties of organic–inorganic trihalide perovskites (OITPs), such as strong optical absorption, low nonradiative recombination rate, and excellent dielectric and paraelectric/ferroelectric properties.^[10] In addition, the utilization of single crystal OITPs, because of their ultralong carrier diffusion length,^[11,12] can significantly improve the performance of OITP-based solar cells^[13] and photodetectors.^[14] In particular, photogain *G*, one of the most important figures of merit in photodetecting researches, highly relies on the photogenerated carrier lifetime τ_c

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$$G = \frac{\tau_{\rm c}}{\tau_{\rm t}} \tag{1}$$

where τ_t is the time required for the carriers moving from one electrode to the other. The longer carrier diffusion length means the longer carrier lifetime and lower recombination rate. This implies that single crystal OITP with the ultralong diffusion length is a promising active material for fabricating highperformance photodetectors.

From the point of view of device architecture, because of the better-suited contact nature between organic semiconductors and carbon electrodes,^[15,16] carbon electrode–molecule junctions (CEMJs) based transistors^[17–19] displayed the high field-effect performance with sensitive photoresponsive ability. In combination with the ease of device fabrication and good reproducibility, the unique properties of carbon electrodes render the CEMJ technology as a new-generation reliable platform for molecular optoelectronics.^[20–22] Among these investigations, we systematically revealed the intrinsic relationship between the device dimension and photogain *G* as follows^[23]

$$G = \frac{\tau_c \mu V}{l^2} \tag{2}$$

where μ , V, and l are the carrier mobility, bias voltage, and distance between electrodes (gap length), respectively. This formula proves that photogain is inversely proportional to the square of the gap length, strongly suggesting that high-performance CEMJ-based photodetectors could be fabricated when the device dimension is scaled down to the nanoscale. In this study, by integrating above-discussed two aspects (active material OITP and CEMJ nanoarchitecture) into a single device, we present a new class of nanoscale hybrid photodetectors with high performance in almost every figure of merit. It is remarkable that highest responsivity ($\approx 5.6 \times 10^8 \text{ A W}^{-1}$), highest photogain ($\approx 5.3 \times 10^9$), high detectivity ($\approx 2.8 \times 10^{16}$ Jones), high LDR (≈92 dB), and a broad spectral response (≈300-800 nm) have been achieved simultaneously in a single device by applying different biases. Benefiting from the unique device architecture used, ultrasensitive active material, and optimized contact nature of semiconductor/electrode interfaces, these significant performances were obtained at mild conditions (small bias, room temperature, and in air). These results demonstrate that OITPs and CEMJ-based devices are the key factors in the success of building such high-performance photodetectors, thus forming a model device platform with integrated operational mechanisms of both photodiode and photoconductor for photoelectric conversion applications. These investigations also offer new insights and opportunities for innovations in many other device-related fields, such as molecular electronics, logic circuits, charge-coupled device, and information technology.

2. Results and Discussion

2.1. OITP Nanocrystal Preparation

First, we explored how to obtain OITP single crystals with the suitable size for CEMJ technology. Through hydrophilic and hydrophobic precontrol of the substrate,^[24] we found that it

was feasible to prepare individual organolead triiodide perovskite (chemical formula:CH3NH3PbI3) nanocrystals or uniform CH₃NH₃PbI₃ polycrystalline thin films by using a two-step solution process (Figure 1a and Figure S1, Supporting Information). The experimental details can be found in the Experimental Section. Cross-sectional scanning electronic microscopy (SEM) image shows the side length of individual CH₃NH₃PbI₃ nanocrystals (about 200 nm) and high-resolution transmission electron microscopy (HRTEM) image clearly presents the lattice fringes with interplanar spacing of about 0.647 nm that corresponds to the (110) plane of β -CH₃NH₃PbI₃ phase (Figure 1b).^[25] The UV-visible spectra of CH₃NH₃PbI₃ thin film and low-coverage nanocrystals demonstrate that this OITP material has strong and broad absorption from UV-vis to near-infrared in comparison with the precursors CH₃NH₃I and PbI₂ (Figure 1c). Though the absorbance of low-coverage CH₃NH₃PbI₃ nanocrystals is lower than that of CH₃NH₃PbI₃ thin film, the absorption peaks and ranges of both are almost the same. In the X-ray diffraction (XRD) characterization, the appearance of three low angle (<35°) diffraction peaks at 20 of 14.2°, 28.5°, and 32.0°, which should be assigned to the (110), (220), and (310) planes of the typical tetragonal perovskite structure, proves that halide perovskite thin film prepared by this two-step solution process are highly crystalline (Figure 1d). All these characterizations clearly guarantee the successful preparation of high-quality OITP nanocrystals.

2.2. OITP-CEMJ Photodetector Fabrication

Nanogapped single-layer graphene (SLG) electrodes were made according to the mature procedure described in the Experimental Section. The Raman spectrum of graphene obtained by a chemical vapor deposition (CVD) process shows the G band at about 1600 cm⁻¹ without an obvious D shoulder is weaker than the 2D band ($\approx 2700 \text{ cm}^{-1}$), confirming that the graphene used in this experiment only has a single layer with high quality (Figure 1e). Then, OITP-CEMJ photodetectors were fabricated by randomly distributing the OITP nanocrystals onto SLG nanoelectrodes (Figure 2a,b, inset and Figure S1, Supporting Information). This was achieved through a drop-cast process with partially hydrophobic pretreat^[24] of the graphene nanoelectrode substrate by vapor-grown octadecyltrichlorosilane (OTS),^[26,27] whereas the control device based on gold electrodes was pretreated through an oxygen cleaning process by using reactive ion etching (RIE) to ensure the hydrophilic surface (see also Experimental Section and Figure S1, Supporting Information). SLG has a planar and inert interface with strong bonding only in two dimensions, thus the Fermi level of graphene will not be modified by the contact^[28] though OITP nanocrystals were randomly distributed onto the SLG nanoelectrodes. The inset of Figure 2b shows a pair of SLG nanoelectrodes with gap length of about 200 nm, where a single OITP nanocrystal nicely spans the gap and forms an OITP-CEMJ photodetector. The devices consist of only one individual OITP nanocrystal were selected for optoelectronic measurements (Figure S2, Supporting Information). To exclude the contribution from invisible OITP nanofilm, careful control experiments were conducted in Figure S3 (Supporting Information),

www.advancedsciencenews.com www.afm-journal.de (a) CH₃NH₃I isopropanol solution PbI, **DMF** solution Mixed PbI₂ and PbCl₂ **DMF** solution CH₃NH₃I isopropanol solution (b) 0.647 nm Platinum nanoparticle deposited by FIB CH₃NH₃PbI₃ single crystal p-doped silicon wafer 200 nm 5 nm (c) (e)₆₀₀ 0x10³ CH_NH_Pbl, thin film (110) Absorbance (a.u.) CH_NH_PH CH-NH Intensity (a.u.) 4 1.5x10³ Intensity (a.u.) low-coverage nanocrystals Pb Pbl. 1.0x10 CH.NH 2 5.0x10 314 20 0 0.0 C 300 400 500 600 700 800 10 20 30 40 50 1500 3000 2000 2500 Wavelength (nm) 2θ (degree) Raman Shift (cm⁻¹)

Figure 1. Preparation and characterization of $CH_3NH_3PbI_3$ crystals and graphene nanoelectrodes. a) Schematic illustration of the formation of halide perovskite crystals by a two-step solution process. b) Cross-sectional SEM and HRTEM images of $CH_3NH_3PbI_3$ single crystals on a p-doped silicon wafer. c) UV–vis absorption of $CH_3NH_3PbI_3$ thin films, $CH_3NH_3PbI_3$ low-coverage nanocrystals, and the precursors on quartz. d) XRD characterization of $CH_3NH_3PbI_3$ crystals. Inset: schematic diagram of the $CH_3NH_3PbI_3$ crystal structure. e) Raman spectrum of CVD-grown SLGs transferred onto a commercial Si/SiO₂ (300 nm thick) wafer. Inset: Optical micrographs of graphene nanoelectrode-based devices on a commercial Si/SiO₂ (300 nm thick) wafer before spin casting $CH_3NH_3PbI_3$.

showing that invisible OITP nanofilm does not exist. Therefore, the active device dimension was the effective area of the perovskite nanocrystal (\approx 200 nm × \approx 200 nm).

When stimulated by incandescent light with different intensities, the devices showed the responsivities *R* within the magnitude of 10³ to 10⁴ A W⁻¹ according to the formula^[4,29,30] $R = I_{\rm ph}/(P_{\rm in}(A_{\rm device}/A_{\rm spot}))$, where $I_{\rm ph}$, $P_{\rm in}$, $A_{\rm device}$, and $A_{\rm spot}$ are photoinduced current, light input power, active device area, and light spot area, respectively (Figure 2a). These values are slightly higher than those based on metal nanoelectrodes (Figure S4a, Supporting Information). Considering that perovskites themselves are good photoresponsive materials, the improved device performance sufficiently proves the effectiveness of the CEMJ platform. In addition to this, it is worth mentioning that the perovskite photodetector based on metal nanoelectrodes has not been reported previously to our best knowledge partially because of the inconvenience of metal nanoelectrode fabrication. Therefore, CEMJ nanoelectrodes show an obvious advantage due to the ease of device fabrication with tunable sizes of narrow gaps.^[23] The spectral responsivity of the devices was also shown in Figure S5a (Supporting Information). Especially, the unsaturated power intensity-dependent responsivity under rather weak illumination with $\lambda = 300$ nm implies that the perovskite photodetector could realize high-quality weak light detection (Figure S5c, Supporting Information). Another figure of merit, detectivity D^* , had the magnitude of 10^{12} to 10^{13} Jones

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Figure 2. Performance of graphene nanoelectrode based CH₃NH₃PbI₃ single crystal devices. a) Responsivity of the device illuminated by incandescent light with different intensities ($V_{DS} = 3$ V, gate voltage $V_G = 0$). Inset: schematic diagram of the device under illumination. b) Detectivity of the device illuminated by incandescent light with different intensities ($V_{DS} = 3$ V, $V_G = 0$). Inset: SEM and AFM images of a graphene nanoelectrode-based CH₃NH₃PbI₃ single crystal photodetector. c) Three representative switching cycles of the device showing good stability ($V_{DS} = 3$ V, $V_G = 0$, $I_{ill} = 25.86$ mW cm⁻²). d) The device illuminated by incandescent light with different intensities. $V_{DS} = 3$ V; $V_G = 0$. Inset shows the same plot with logarithmic coordinates. e) Photogain of the device illuminated by monochromatic light from 300 to 800 nm with different biases, $V_G = 0$. f) Photoconductor output curves under dark condition and illumination of incandescent light with different intensities. $V_G = 0$. Inset shows the same plot with logarithmic coordinates.

according to the formula^[5] $D^* = R/(2qJ_{dark})^{1/2}$ if the shot noise from dark current is the major reason limiting the detectivity (see Discussion section), where q and J_{dark} are electronic charge and dark current density, respectively (Figure 2b). As shown in the current-time (I-t) curve of Figure 2c and Figure S6 (Supporting Information), these photoresponsive behaviors were quite stable with high ON/OFF current ratio (>10³). The logarithmic coordinates were utilized to present the high ON/OFF current ratio, and the transient characteristics for the device should be discussed using the response time of photocurrent changing from 90% to 10% in Cartesian coordinates^[14,31] (see Discussion section). The LDR value of the devices was calculated to be about 54 dB according to the formula^[7,8] LDR = $20\log(I_{ph}*/I_{dark})$, where $I_{ph}*$ and I_{dark} are the photocurrent measured at light intensity of 1 mW cm⁻² and dark current, respectively (Figure 2d). The photogain G was calculated to beat the magnitude of 10^3 to 10^5 according to the formula^[23,30]

$$G = \left(\frac{I_{\rm ph} / q}{P_{\rm abs} / hv}\right) \times 100\% = \frac{I_{\rm ph}}{P_{\rm abs}\lambda} \times 124\%$$
(3)

where *h* is the Planck's constant. The absorbed power P_{abs} is calculated from the formula $P_{abs} = P_{in}(A_{device}/A_{spot}) A(v)$, where A(v) is the material absorption at the input light frequency *v*, and the input light frequency *v* can be further calculated by its wavelength λ (the unit here is micrometer). The intensity-dependent photogain with $\lambda = 300$ nm decreased when illumination became stronger (Figure S5d, Supporting Information) due to the saturation of trap states,^[32] indicating that the device

operates as a photoconductor where the secondary photocurrent provides photogain. These photogain values are higher than any other OITP photodetectors reported previously, no matter lateral structure^[33,34] or vertical structure^[14,35,36] based devices (Figure 2e and Figure S4, Supporting Information). This proves that the combination of OITP crystals with CEMJ technology can efficiently improve the device performance, which coincides with Formula (2). In addition, when measuring the current-voltage (I-V) curves of the devices stimulated by incandescent light with different intensities, we found that the intensity-dependent source-drain currents (I_{DS}) with high ON/OFF current ratio (>10³) were similar to the output curves of conventional field-effect transistors (FETs), demonstrating that this photodetector behaves as a photoconductor^[37,38] (in contrast to phototransistor^[29,30] or photodiode,^[39,40] see Figure 2f and Figure S7, Supporting Information). Different from capacitive injection of carriers at the dielectric/semiconductor interface of conventional three-terminal FET devices,[41] a photoconductor is a two-terminal device modulated by photoinduced carrier's injection without the requirement of the gate and dielectric structure. In comparison with the devices based on gold electrodes with gap length of micrometers (Figure S8, Supporting Information), IDS in the graphene-based devices had no saturation trend when the source-drain voltage (V_{DS}) increased. In contrast to the unfavorable short channel effect in conventional FET devices,^[41] the unsaturated phenomenon can efficiently enhance the device quantum efficiency.

It is a clear fact that only the extremely narrow electrode gap does not guarantee a photodetector with high performance www.advancedsciencenews.com





Figure 3. Mechanism of graphene nanoelectrode-based $CH_3NH_3PbI_3$ single crystal devices. a) In *I*–In *V* plots of the device under dark condition (red) and illumination of incandescent light with different intensities (blue). b) In $I-V^{1/2}$ plot of the device under dark condition. c) Energy band diagram of graphene nanoelectrode-based $CH_3NH_3PbI_3$ single crystal device under bias and dark condition (horizontal direction), where E_C , E_V , and E_F are the conduction band energy, valence band energy, and Fermi level, respectively. d) Schematic illustration of the P-n homojunction in graphene nanoelectrode-based $CH_3NH_3PbI_3$ single crystal device under dark condition. Inset: energy band diagram of the $CH_3NH_3PbI_3$ single crystal device under dark condition (vertical direction). e) Energy band diagram of graphene nanoelectrode-based $CH_3NH_3PbI_3$ single crystal device under bias and light illumination (horizontal direction). f) Schematic illustration of the p-n homojunction in graphene nanoelectrode-based $CH_3NH_3PbI_3$ single crystal device under bias and light illumination (horizontal direction). f) Schematic illustration of the p-n homojunction in graphene nanoelectrode-based $CH_3NH_3PbI_3$ single crystal device under light illumination. Inset: energy band diagram of the $CH_3NH_3PbI_3$ single crystal device under light illumination (vertical direction).

in every figure of merit.^[23,42] Thus, to reveal the underlying physical mechanism of the above-observed interesting phenomena, the ln I-ln V plots of the I-V curves under light illumination and dark condition were compared. As shown in **Figure 3**a, the ln I-ln V plots of the devices under light illumination have a good linear relationship with a slope close to 1, indicating that the interface between graphene and OITP

crystals is an Ohmic contact dominated by the formula^[43] $I = V \exp(-c/T)$, where *c* is a positive constant and *T* is the absolute temperature. On the contrary, when the device is under dark condition, the ln $I - V^{1/2}$ plot, rather than the ln I-ln *V* plot, has a good linear relationship, indicating that the conduction is Schottky emission dominated by the formula^[44] $I = A T^2 \exp(aV^{1/2}/T - q\Phi_{\rm B}/k_{\rm b}T)$, where *A*, *a*, $\Phi_{\rm B}$, and $k_{\rm b}$ are



the prefactor, another positive constant, the barrier height, and the Boltzmann constant, respectively (Figure 3a,b). Some other conduction mechanisms, such as Frenkel-Poole emission (ln $(I/V) - V^{1/2}$ plot), Fowler-Nordheim tunneling (ln $(I/V^2) - V^{-1}$ plot), and space-charge-limited conduction $(I-V^2)$ plot), were also considered to fit the dark conduction but with poorer linear relationships than Schottky emission (Figure S9, Supporting Information). Consequently, the carriers driven by electric field under dark condition generally face a barrier between the Fermi level of graphene electrodes and the conduction band of OITPs, leading to the low current level (Figure 3c, the high resistivity of OITP single crystals under dark condition was also proved by ref. [25]). Here, graphene plays an electrode contact role where the energy structure is treated as metal electrodes for the following consideration: A) No photoresponse could be observed with the graphene in either the presence or the absence of spin-coated CH₃NH₃PbI₃ (Figure S10, Supporting Information); B) the doping level of the graphene stays constant during the measurements; and C) the Fermi level of graphene will not be modified by the contact.^[28] Although Schottky emission is a bulk related conduction mechanism (the barrier height $\Phi_{\rm B}$ should be calculated by the Schottky diode equation^[45] $I = S A T^2 \exp(\Phi_{\rm B}/k_{\rm b}T)$ $\exp(qV/nk_{\rm b}T)$ (1 - $\exp(qV/k_{\rm b}T)$), where S is the contact area), we utilize the Schottky emission equation to qualitatively present the barrier between graphene and perovskite but not quantitatively calculate the precise value of $\varPhi_{\rm B}$. Some reproducible experiments also show that the barrier is sufficiently evidenced (Figure S11, Supporting Information). Note that the perovskite is synthesized by a two-step solution process with a diffusion of CH₃NH₃I from the top of PbI₂ to the bottom, where CH₃NH₃⁺ rich/deficient perovskites are p-doped/ndoped.^[46,47] Thus, it is reasonable to find that a vertical p-n homojunction is formed (Figure 3d). Considering that SLG has a thickness of only ≈ 1 nm (Figure 2b), whereas the perovskite nanocrystal has a height of ≈200 nm (Figure 1b); SLG nanoelectrodes contact with n-type perovskite (Figure 3c. Assuming the Fermi level of perovskites and graphene are -3.9^[48] and -4.5 eV,^[28] respectively, the interface between SLG and n-type perovskite should form a Schottky barrier in theory, which coincides with the experimental results (Figure 3b and Figure S11, Supporting Information).

In contrast to the dark condition, when the device is under bias and light illumination, photoinduced Wannier-Mott excitons in halide perovskites^[49,50] could be easily separated into free electrons and holes due to the nonexcitonic nature. For the vertical direction of the device, electrons would flow from a p-type region to an n-type region due to the internal electric field established by this p-n homojunction (Figure 3f). The injection of electrons at the n-type region would further shift the Fermi level closer to the conduction band,^[51] where Ohmic contact forms at the horizontal direction in theory. Then, carriers are efficiently injected into electrodes, leading to the high current level and corresponding photogain (Figure 3e). Definitely, this is a reversible mechanism when laser switches ON and OFF (Figure S12, Supporting Information). In addition, it is interesting to observe that even rather weak light would turn the Schottky contact between graphene and perovskite into Ohmic one (Figure S13, Supporting Information), which supports the high-quality weak light detection performance of the device. The existence of the p–n homojunction also explains the prevention of carriers injection by dielectric gate (Figure S7a, Supporting Information) because the internal electric field is established by this p–n homojunction in the devices formed by a two-step solution process, whereas an ambipolar gate-dependent performance was observed in the devices formed by a one-step solution process.^[34] To further confirm this mechanism, several control experiments were carried out by using cut/uncut graphene electrodes in the absence of OITPs or uncut graphene electrodes in the presence of OITPs, where we did not observe any obvious photocurrent (Figure S10, Supporting Information).

To further improve the device performance, according to Formula (2) and ref. [23], we chose single-walled carbon nanotubes (SWNTs), another allotrope of carbon nanomaterials that can be lithographically cut into nanoelectrodes with gap length of ≤10 nm, to fabricate another type of OITP-CEMJ photodetectors (see the Experimental Section) with an effective device dimension of ≈ 10 nm $\times \approx 2.0$ nm.^[52,53] Through a similar random distribution process, we combined CH₃NH₃PbI₃ nanocrystals with SWNT point contacts to fabricate the nanoscale photodetectors (Figures S14 and S15a,b, inset, Supporting Information). Remarkably, higher responsivity $(10^6-10^7 \text{ A W}^{-1})$ and higher detectivity (10¹⁴–10¹⁵ Jones) were achieved in this type of OITP-CEMJ photodetectors (Figure S15a,b, Supporting Information). Though the ON/OFF current ratio and LDR decreased a little (Figure S15c,d, Supporting Information), the photogain was ultrahigh, approaching 10⁷–10⁹ (Figure S15e, Supporting Information). Especially in the UV region, a photogain of 3.2×10^9 obtained here is higher than the best value reported so far.^[6] Once again, this result proves the predictability and validity of Formula (2), where τ_c (which further determines the carrier diffusion length) and u are the intrinsic properties of the active materials, whereas V and l can be optimized by the device architecture. In addition to the long carrier diffusion length,^[11,12] the carrier mobility of OITPs has been proved as large as dozens square centimeter per volt per second by Hall effect measurement^[25] and 0.18 (0.17) cm² V⁻¹ s⁻¹ for holes (electrons) by the FET method.^[34] Together with the architecture superiority of CEMJs, the remarkable properties of OITPs led to ultrahigh quantum efficiency in this OITP-CEMJ photodetector, which implies that the device is sensitive to small photon numbers,^[54] thus potentially endowing the OITP-CEMJ photodetector with photon number-counting capability. Similarly, this device could also provide high-quality weak light detection and work as a photoconductor (Figures S15f, S16, and S17, Supporting Information). The unsaturated trend became more obvious when compared to graphenebased devices with the longer gap length. Both the experiments (Figures S18 and S19, Supporting Information) and control experiments (Figure S20, Supporting Information) consistently demonstrated the physical mechanism similar to the case of graphene-based devices. In particular, the working device had no photoresponse under zero bias (Figure S20f, Supporting Information), proving that OITPs outside the nanogap has no contribution to the photoresponse because the electric field mainly exists in the nanogap.





Figure 4. Performance of SWNT nanoelectrode-based CH₃NH₃Pbl_{3-x}Cl_x single crystal devices. a) EDX characterization of CH₃NH₃Pbl_{3-x}Cl_x crystals, confirming that the doping level of chlorine is about 4.54%, which is also showed in Table S1 (Supporting Information). Inset: schematic diagram of the CH₃NH₃Pbl_{3-x}Cl_x crystal structure. b) Comparison of CH₃NH₃Pbl_{3-x}Cl_x and CH₃NH₃Pbl_{3-x}Cl_x and CH₃NH₃Pbl_{3-x}Cl_x crystal structure. b) Comparison of CH₃NH₃Pbl_{3-x}Cl_x and CH₃NH₃Pbl₃ thin films through steady-state photoluminescence spectrum upon excitation at 455 nm on glass substrate, proving that CH₃NH₃Pbl_{3-x}Cl_x prepared by the two-step solution process can efficiently reduce energy loss in the fluorescent form. c) Responsivity of the device illuminated by incandescent light with different intensities ($V_{DS} = 3$ V, $V_G = 0$). Inset: schematic diagram of the device under illumination. d) Detectivity of the device illuminated by incandescent light with different intensities ($V_{DS} = 3$ V, $V_G = 0$). Inset: schematic diagram of the device and provide the device between the gap length is about 10 nm. e) Three representative switching cycles of the device showing good stability ($V_{DS} = 3$ V, $V_G = 0$, $I_{iil} = 25.86$ mW cm⁻²). f) The device illuminated by incandescent light with different intensities. $V_{DS} = 3$ V, $V_G = 0$. Inset shows the same plot with logarithmic coordinates. g) Photogain of the device illuminated by monochromatic light from 300 to 800 nm with different biases, $V_G = 0$. Inset shows the same plot with logarithmic coordinates.

2.3. Energy Loss-Prevented OITP-CEMJ Photodetectors

Since chlorine doped organolead triiodide perovskite (chemical formula:CH₃NH₃PbI_{3-x}Cl_x) has even longer exciton diffusion length than CH₃NH₃PbI₃,^[55] according to Formula (2), $CH_3NH_3PbI_{3-r}Cl_r$ should be a more efficient active material than CH₃NH₃PbI₃. Therefore, we are curious to further fabricate a third type of OITP-CEMJ photodetectors using CH₃NH₃PbI_{3-x}Cl_x synthesized by two steps as active materials and SWNTs as point contacts. As shown in Figure 1a, two-step synthesis of CH₃NH₃PbI_{3-x}Cl_x is similar to that of CH₃NH₃PbI₃. Through hydrophilic and hydrophobic precontrol of the substrate, individual CH₃NH₃PbI_{3-x}Cl_x nanocrystals could be prepared (Figures S21 and S22, Supporting Information). The UV-vis spectrum and XRD characterization proved that CH₃NH₃PbI_{3-r}Cl_r synthesized by the two-step solution process was crystalline with high quality (Figures S21b,c, Supporting Information). Energy dispersive X-ray (EDX) analysis showed that the doping level of chlorine (1.55% by weight or 4.54% by mole) in CH₃NH₃PbI_{3-r}Cl_r formed by this two-step solution process was comparable to that obtained by conventional one-step method^[33-35] (Figure 4a and Table S1, Supporting Information). The chlorine content of CH₃NH₃PbI_{3-x}Cl_x nanocrystals prepared on different wafers showed little difference (Table S2, Supporting Information). In particular, it is worth mentioning that the fluorescence of CH₃NH₃PbI_{3-x}Cl_x prepared by this two-step solution process was completely quenched in contrast to that obtained by the conventional one-step method (Figure 4b), proving the depletion of defects in these OITP crystals.^[25] This implies that the two-step solution process can efficiently prevent energy loss

in the fluorescent form for the prepared $CH_3NH_3PbI_{3-x}Cl_x$ crystals, which is of crucial importance to achieve high-performance photoelectric devices.

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After successful synthesis of $CH_3NH_3PbI_{3-x}Cl_x$ by the twostep solution process, the third type of OITP-CEMJ photodetectors was then fabricated by randomly distributing CH₃NH₃PbI_{3-x}Cl_x nanocrystals onto SWNT nanoelectrodes with gap length of about 10 nm (Figure 4c,d, inset and Figure S23b, inset, Supporting Information). Remarkably, higher responsivity (107-109 A W-1) and higher detectivity (10¹⁵-10¹⁶ Jones) were obtained in these OITP-CEMJ photodetectors (Figure 4c,d and Figure S24, Supporting Information). In addition to a slight increase of the ON/OFF current ratio and LDR (Figure 4e,f, Supporting Information), it is interesting to observe that when the V_{DS} decreased, the ON/OFF current ratio continued to increase. This phenomenon can only be observed in chlorine-doped OITP devices (Figure S25a,b, Supporting Information). As a result, when a small bias was applied, the LDR value increased to 91 dB without a substantial decrease of R and D* (Figure S25d,f, Supporting Information). It is foreseeable that the ON/OFF current ratio and LDR value would be even higher when V_{DS} becomes lower than 10 mV, and this could be proved by further experiments if the noise limit of the semiconducting parameter analyzer is below the femtoampere level. As predicted by Formula (2), the photogain of this third type of OITP-CEMJ photodetectors approached as high as 5.3×10^9 , and the photogain maintained larger than 10^9 in a broad wavelength range (Figure 4g). Similarly, these devices could behave as photoconductors with unsaturated trend (Figure 4h and Figure S26, Supporting Information) when compared to the devices formed from gold electrodes with www.advancedsciencenews.com

 $\ensuremath{\textbf{Table 1.}}$ Comparison of the device performance in this work and in the literature.

Figure of merit	Value approached here	Best value reported so far	References
Responsivity ^{a)}	$5.6 imes 10^8 \text{ A W}^{-1}$	$5 imes 10^8~A~W^{-1}$	[4]
Detectivity	$2.8 imes 10^{16}$ Jones	$3.3\times10^{17}\ Jones$	[5]
Photogain ^{a)}	5.3×10^9	$3 imes10^9$	[6]
LDR	92 dB	>120 dB	[7]
ON/OFF ratio ^{b)}	$4.0 imes 10^4$	>106	[7]
Spectral range ^{c)}	300–800 nm	300–1450 nm	[8]

 $^{a)}\mbox{Room}$ temperature; $^{b)}\mbox{Under 1 mW cm}^{-2}$ stimulation; $^{c)}\mbox{Wavelength}$ range from UV–vis to near-infrared.

gap length of micrometers (Figures S22 and S27, Supporting Information). The detection limit of the device is lower than 0.085 aW, which reaches the radiation energy level of a single photon per second (Figure S24, Supporting Information). The similar physical mechanism of this type of OITP-CEMJ photodetectors is shown in Figures S23 and S28 (Supporting Information), which is also confirmed by control experiments (Figure S29, Supporting Information).

To intuitively discuss these results, we compared them to the best values reported in the literature so far (Table 1). The responsivity and photogain of our devices are the best in comparison with previous reports at mild conditions. What is worth emphasizing here is that the values we achieved are from a single device (chlorine-doped OITP-CEMJ photodetectors or energy loss-prevented OITP-CEMJ photodetectors), while the highest values in the literature are from a variety of different devices. Definitely, it is of great significance to achieve high performance in more figure of merits in a single device. For instance, a single photon detector requires not only the high photogain to enhance the photocurrent but also the high detectivity to inhibit the dark counting. When calculating these figures of merit, the photocurrent I_{photo} and the dark current *I*_{dark} are two key factors. Therefore, we mainly divide these figures of merit into two categories: One category mainly relies on $I_{\rm ph}/I_{\rm dark} = (I_{\rm photo} - I_{\rm dark})/I_{\rm dark} = I_{\rm photo}/I_{\rm dark} - 1$ (division of photocurrent and dark current, such as ON/OFF current ratio and LDR), and the other mainly relies on $I_{\rm ph} = I_{\rm photo} - I_{\rm dark}$ (subtraction of photocurrent and dark current, such as R and G). In the literature reported so far, these two categories are hard to optimize simultaneously. For instance, the devices^[4,6,54] with a lateral structure showed ultrahigh photogain (10^8-10^9) but low ON/OFF current ratio (<10²), while the devices^[7,8,35,36] with a vertical structure showed ultrahigh LDR (>80 dB) but low responsivity (<10 A W⁻¹). According to the mechanism of OITP-CEMJ photodetectors we discussed above, to improve the first category of figures of merit, one should reduce the dark current and/or increase the photocurrent through optimizing the contact between semiconductors and electrodes. On the other hand, to improve the second category of figures of merit, active materials with high carrier diffusion length and high carrier mobility, device architecture with short gap length and ability of bias application should be optimized. These guidelines offer general insights into designing high-performance photodetectors in the future.

As another important figure of merit used to describe photodetectors, the response time of the three types of photodetector was characterized and presented in Figure S30 (Supporting Information). The device with perovskites as active materials showed rather fast response (19-91 µs for rise time and 417-481 µs for decay time) in comparison with those with polymer:fullerene materials. In particular, the rise and decay times of the CH₃NH₃PbI_{3-x}Cl_x device based on SWNT electrode are measured to be $\approx 20 \ \mu s$ and $\approx 0.445 \ ms$, respectively. These switching speeds are comparable to the perovskite photoconductors^[14,34] but slower than the perovskite photodiode.^[35,36] In addition, we also used the expression given in Formula(2)^[14,34] to estimate the photogain. The decay trace is widely proved to be an efficient way to estimate the carrier lifetime $\tau_c^{[4,6]}$ (Figure S30, Supporting Information). The mobility for iodide only and mixed halide perovskite prepared by solution process could be estimated to be 0.2 and 1.62 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively.^[34] Then, the photogain of the three types of photodetector with $V_{DS} = -5$ V in our manuscript can be estimated to be 9.4 \times 10⁵, 4.1 \times 10⁸, and 3.6 \times 10⁹ according to Formula (2), which coincides with our results calculated from expression given in Formula (3).

Furthermore, the frequency-dependent total noise current of our devices was directly measured by lock-in amplifier (Figure S31, Supporting Information). Due to the frequency-independent noise in the low frequency range, the flicker (1/f) noise could be excluded.^[56,57] Poly(3-hexylthiophene)/[6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PCBM) is a model system of polymer:fullerene photoresponsive materials where the dark current is widely proved to be the major reason for the noise limiting the detectivity.^[58,59] The noise current of both perovskite and P3HT:PCBM devices based on SWNT nanoelectrodes was at the same level and frequency independent (Figure S31c,d, Supporting Information), demonstrating that the shot noise from dark current is the major reason for the noise in our devices.^[5,60]

Considering the difficulty to measure the shift of Fermi level of such a perovskite nanocrystal by direct characterization like ultraviolet photoelectron spectrometer or other methods, some control experiments were carefully conducted to check the mechanism shown in Figure 3 (also Figures S18 and S23, Supporting Information). At first, a typical p-type semiconductor P3HT (with Fermi level of $-4.6 \text{ eV}^{[61]}$) is used as active material. In theory, it forms Schottky contact when P3HT is spin coated on graphene with a higher Fermi level (-4.5 eV) and Ohmic one when SWNT with a lower Fermi level (-5.0 eV) is used as electrode under dark condition. The conduction mechanism has no changes when illumination switches ON and OFF (Figure S32, Supporting Information). Then, a typical n-type semiconductor PCBM is introduced to form a P3HT:PCBM blend where a bulk p-n heterojunction exists. However, the conduction mechanism still has no changes when illumination switches ON and OFF (Figure S33, Supporting Information) because this p-n heterojunction is isotropic. Last but not least, the CH₃NH₃PbI_{3-x}Cl_x nanocrystal synthesized by a one-step solution process is used as active material. Due to the lack of CH₃NH₃I diffusion during the synthesis, the p-n homojunction could hardly form in a one-step synthesized CH₃NH₃PbI_{3-x}Cl_x crystal. Thus, the conduction mechanism is Ohmic when the one-step synthesized CH₃NH₃PbI_{3-x}Cl_x is spin coated on SWNT nanoelectrodes, and



no change of the conduction mechanism could be observed when illumination switches ON and OFF (Figure S34a,b, Supporting Information). The Ohmic contact in dark condition makes the dark current higher than that of the two-step synthesized $CH_3NH_3PbI_{3-x}Cl_x$ device, whereas the photocurrent level is almost the same ($\approx 10^{-7}$ A, see Figure 4e and Figure S34d, Supporting Information), leading to a lower ON/OFF current ratio. Note that the mobility of the CH₃NH₃PbI_{3-r}Cl_r is rather high; thus, the photogain of the SWNT-based one-step synthesized $CH_3NH_3PbI_{3-x}Cl_x$ device with shrunk gap length should also be very high according to Formula (3). However, it is not only lower than that of the $CH_3NH_3PbI_{3-x}Cl_x$ device by a two-step solution process but also even lower than that of the two-step synthesized CH₃NH₃PbI₃-based device (Figure 4g, Figures S15e and S34d, Supporting Information). These sufficiently prove the improvement of device performance when the vertical p-n homojunction forms in two-step synthesized perovskites. Beneficial from this vertical p-n homojunction and the lateral better-suited carbon electrodes, these devices operate with mechanistic hybridization of photodiode and photoconductor (Table S3, Supporting Information). It is worth mentioning that the integration of these two operation mechanisms would combine their own advantages into one device (Table S4, Supporting Information), leading to the achievement of high performance in almost every figure of merit (Table 1).

Temperature-dependent measurements of OITP-CEMJ devices were also carried out (Figure S35, Supporting Information). When the temperature increased, the dark currents increased because the conductance of the active materials was higher in higher temperatures. However, the photocurrents had less temperature-dependent effect. Though the figure of merits that rely on the division of photocurrent and dark current, such as ON/OFF ratio, decreased a little when temperature increased (Figure S35a–c, Supporting Information), the temperature did not obviously influence the figure of merits that rely on the subtraction of photocurrent and dark current, such as responsivity (Figure S35d,e, Supporting Information). This proves that the devices have the good tolerance to the variation of environmental temperature or the heat dissipation issue when devices work for a long time.

3. Conclusion

In summary, we have demonstrated that OITP is an efficient active material and CEMJ is a mature device platform for highperformance photodetector fabrication. By incorporating OITP material and CEMJ technology into a single electrical circuit, highest responsivity, highest photogain, high detectivity, high LDR, and a broad detection wavelength range were achieved simultaneously through synergistic mechanisms of both photodiode and photoconductor. In particular, the ultrahigh quantum efficiency implies that OITP-CEMJ photodetectors are sensitive to small photon numbers, providing a promising potential to achieve single-photon detectors operating at room temperature and low driving voltage. Furthermore, these OITP-CEMJ photodetectors with high performance in almost every figure of merit are compatible with conventional complementary metal oxide semiconductor technologies. This compatibility might open exciting opportunities for a wide variety of immediate practical applications, such as logic circuits, charge-coupled devices, collimation, telecommunications, biomedical imaging, information security, and optical quantum computation.

4. Experimental Section

Graphene and SWNT Transistor Fabrication: High-quality SLG was grown through a CVD process on copper foils (purchased from Alfa Aesar) with methane as carbon precursor^[62] and transferred onto silicon wafers with 300 nm SiO₂ on the surface.^[63] Gas-flow oriented SWNTs with diameter of about 2 nm were grown from bimetallic CoModoped mesoporous silica (SBA16) catalysts with ethanol as carbon precursor on silicon wafers through a controlled CVD procedure.^[64,65] 8 nm Cr followed with 60 nm Au was thermally evaporated onto the graphene samples (preprocessed into 36 μ m wide ribbons) through photolithographically patterned photoresist masks (Figure 1e, inset) and onto the SWNT samples through copper shadow masks (Figure S14a, Supporting Information). To guarantee the device quality, only high-performance graphene and metallic SWNT samples in electrical properties were selected for the next step (Figures S10a, S20a, and S29a, Supporting Information).

Graphene and SWNT Electrode Formation: Carbon nanoelectrodes were fabricated by cutting graphene and SWNT transistors as follows.^[15-19] A layer of PMMA (950, A5, purchased from MicroChem) was spin cast (4000 r min⁻¹ for 45 s) onto the graphene and SWNT transistors as sacrificial resist followed by baking it at 180 °C for 2 min. Then, we opened windows on the polymethyl methacrylate (PMMA) resist at specific positions through an optimized electron beam lithography process. The transistors were locally cut by RIE through the opened windows (30 W RF power, 15 Pa of oxygen, cutting 90 s for the graphene samples, and 50 W RF power, 35 Pa oxygen, cutting 60 s for the SWNT samples). The samples were soaked and washed by copious amounts of acetone followed by electrical measurement. The completely cut graphene and SWNT samples were selected for the next step (Figures S10a, S20a, and S29a, Supporting Information). The cutting yield of graphene nanoelectrodes was close to 100%, but only about a half of the SWNTs were completely cut to obtain nanoelectrodes with gaps less than 10 nm. The wafers containing preformed graphene and SWNTs nanoelectrodes were then placed in a Petri dish with 1-2 drops of an OTS solution in a vacuum oven. The oven was immediately heated to 120 °C to evacuate the OTS and kept for 2 h under vacuum. After rinsed by hexane, ethanol, and chloroform, respectively, the devices were dried with nitrogen.

Photodetector Fabrication: CH₃NH₃PbI₃ was prepared similar to a previously reported two-step solution process.^[46,66] PbI₂ (purchased from Aldrich without further purification) and CH₃NH₃I were dissolved into dimethylformamide (DMF) and 2-propanol with concentrations of 450 mg mL⁻¹ for PbI₂ and 55 mg mL⁻¹ for CH₃NH₃I, respectively. After that, PbI₂ solution was heated at 65 °C for about 0.5 h to make sure it was fully dissolved and then spin cast (5000 r min⁻¹ for 30 s) onto the graphene or/and SWNT nanoelectrodes fabricated above. The CH₂NH₂I solution was subsequently spin cast onto the top of PbI₂ at 5000 r min⁻¹ for 20 s. These PbI₂/CH₃NH₃I stacking composites were thermally annealed at 100 °C for 30 min and kept overnight at ambient temperature in argon atmosphere before photoresponsive characterization. The $CH_3NH_3PbI_{3-x}Cl_x$ based photodetector was fabricated similarly except that a mixed lead halide solution (427.5 mg PbI2and 13.5 mg PbCl2, molar ratio 19:1, dissolved in 1 mL DMF) was used to substitute the pure 450 mg mL⁻¹ PbI_2 solution.^[33,35]

Material Characterization: Perovskite materials synthesized in our experiments were characterized by X-ray diffraction spectrums on a Bruker D8-Advance X-ray powder diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å) and a step size of 0.02° to ensure the material quality. The UV-vis spectroscopy was carried out by an Agilent Cary 5000 spectrometer. HRTEM images were taken using Hitachi H9000 TEM.





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Photodetector Characterization: Atomic force microscopy (AFM) characterizations were performed by a tapping mode on a Bruker Dimension EDGE. SEM images were taken by a Hitachi S4800. A Karl Suss PM5 probe station equipped with an Agilent 4155C semiconductor parameter analyzer was used to measure the photoresponsive performance of the devices. Incandescent and monochromatic light were obtained by a 150 W Halogen lamp and a 150 W Xe lamp (TLS1509-150A, Beijing Zolix Instruments Co., Ltd), respectively, with power intensity measured by a laser power energy meter (LPE-1A, Beijing Physcience Opto-Electronics Co., Ltd). All the samples were measured at ambient temperature and in air with humidity lower than 50%. Transient photocurrent and frequency-dependent dark current were measured on a Zurich HF2LI lock-in amplifier.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

carbon nanotubes, graphene, hybrid perovskites, photodetectors

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