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Research Article

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Abstract

Perovskite materials have attracted extensive attention in photodetection owing to their excellent light absorption capability and high carrier generation efficiency. Among them, the lead-free perovskite Cs₃Bi₂I₉ has been widely studied due to its low

toxicity and outstanding X-ray sensitivity. However, its relatively low carrier mobility severely restricts the effective transport of photogenerated carriers, thereby limiting key device performance metrics such as responsivity, external quantum efficiency, and detectivity. To address this challenge, a $\text{Cs}_3\text{Bi}_2\text{I}_9$ /carbon nanotube (CNTs) composite photodetector is developed by introducing CNTs networks as efficient charge transport pathways into the $\text{Cs}_3\text{Bi}_2\text{I}_9$ photosensitive layer. This hybrid architecture enables a decoupled design of light absorption and carrier transport, where $\text{Cs}_3\text{Bi}_2\text{I}_9$ serves as the primary light-harvesting medium while CNTs facilitate rapid carrier extraction and transport, effectively suppressing carrier recombination. As a result, the device exhibits excellent performance under 405 nm illumination, achieving a responsivity of $1.44 \times 10^5 \text{ A/W}$ and a detectivity of $1.15 \times 10^{16} \text{ Jones}$. In addition, a high X-ray sensitivity of $2.09 \times 10^4 \mu\text{C}/(\text{Gy}_{\text{air}} \cdot \text{cm}^2)$ is achieved. These results demonstrate a new route for advancing lead-free high-performance broadband perovskite optoelectronic devices.

Introduction

Photodetectors, which convert optical signals into electrical signals[1], have been widely applied in fields such as digital imaging[2], optical communication[3], and bioinspired systems[4]. In the domain of visible light detection, key properties including strong light absorption, high carrier generation, and efficient carrier transport have attracted considerable attention. Materials such as silicon (Si)[5] and III-V semiconductors[6], owing to their excellent electrical transport properties, have

been extensively utilized in the construction of photodetectors[7], leading to significant progress in this field. In X-ray detection, photon absorption mainly occurs via the photoelectric effect and Compton scattering[8]. The photoelectric effect enables full energy deposition, signal proportional to photon energy, and a cross-section scaling with the fourth to fifth power of the average atomic number (Z). Compton scattering deposits only partial energy and distorts energy information, with cross-section scaling linearly with Z . Hence, in the 20-140 keV medical diagnostic range, the photoelectric effect dominates in high- Z materials, enabling high-quality imaging under low-dose conditions. Common materials include amorphous selenium (α -Se), Si, and cadmium telluride (CdTe)[9].

However, with the continuously increasing performance requirements for optoelectronic devices, the inherent limitations of these conventional materials—such as limited light absorption capability[10] and insufficient mechanical flexibility[11] have become increasingly prominent, making it difficult to meet the growing demands. More importantly, conventional semiconductors typically rely on high-temperature, high-purity epitaxial growth processes and are highly sensitive to crystal defects. In contrast, perovskite materials exhibit unique defect tolerance[12], enabling direct film formation via low-temperature solution processing, thereby exhibiting significant advantages for optoelectronic applications. In recent years, lead (Pb)-based halide perovskites (CsPbX_3 , $X = \text{Cl}^-, \text{Br}^-, \text{I}^-$) have witnessed rapid development. These materials have attracted considerable attention due to their tunable bandgaps[13], high optical absorption coefficients[14], and excellent carrier generation yields[15],

achieving remarkable progress in both visible light and X-ray detection. For instance, Tsarev *et al.*[16] proposed a multilayer monolithic stacked lead halide perovskite thin film (MAPbBrI₂, CsPbBr₂I, CsPbBr₂Cl), enabling selective absorption in the red, green, and blue regions of the visible spectrum, with a maximum detectivity of 1.50×10^{11} Jones. Chu *et al.*[17] developed high-quality FAPbI₃ perovskite single-crystal rods with specific orientation using a biomass-derived green solvent, and constructed X-ray detectors based on them, achieving a high sensitivity of up to 2.16×10^5 $\mu\text{C}/(\text{Gy}_{\text{air}} \cdot \text{cm}^2)$. Nevertheless, the potential biological toxicity of Pb and its associated environmental risks[18] have, to some extent, hindered its further application.

To circumvent the biological toxicity of Pb, researchers have explored substituting Pb with bismuth (Bi), an element with a high atomic number and environmental benignity[19], leading to the development of Bi-based perovskite materials that combine low toxicity with high chemical stability[20]. Benefiting from their tunable bandgaps, high optical absorption coefficients, and excellent carrier yields, together with the presence of high-Z constituent elements, Bi-based perovskites exhibit unique advantages in broadband photodetection[21-22]. In particular, the high atomic number endows them with superior X-ray absorption and detection capabilities[23], while they also demonstrate significant potential in the field of visible light detection[24]. For example, Wang *et al.*[25] constructed a p-Si/Cs₃Bi₂I₉/graphene photodetector that achieved a detectivity of 1.75×10^{13} Jones under 650 nm illumination. Chen *et al.*[26] prepared Cs₃Bi₂I₉ thin films via a two-step spray-coating method and applied them in X-ray detection, where the device exhibited

a sensitivity of $127.23 \mu\text{C}/(\text{Gy}_{\text{air}} \cdot \text{cm}^2)$. However, a relatively high density of defects is commonly present in the crystal structure of $\text{Cs}_3\text{Bi}_2\text{I}_9$ [27]. These defects act as carrier trapping centers, severely suppressing the effective separation and transport of photogenerated carriers, resulting in low electrical conductivity. Consequently, photodetectors based on $\text{Cs}_3\text{Bi}_2\text{I}_9$ often struggle to achieve desirable performance in key metrics such as responsivity and detectivity, thereby limiting their practical applications to a certain extent. Directly eliminating intrinsic defects in $\text{Cs}_3\text{Bi}_2\text{I}_9$ remains challenging. Constructing heterointerfaces with conductive materials can facilitate carrier separation and extraction, thereby reducing defect-related trapping and recombination and mitigating their impact on the optoelectronic performance of the device.

Carbon nanotubes (CNTs) possess excellent carrier mobility and a high on/off ratio, and when employed as transport channels for photogenerated carriers, they can effectively enhance the signal-to-noise ratio of photodetectors[28]. More importantly, CNTs can be fabricated into uniform thin films and integrated with perovskites to form heterojunctions[29]. Therefore, by using $\text{Cs}_3\text{Bi}_2\text{I}_9$ as the photoactive layer and CNTs as efficient charge transport pathways, it is expected to achieve high-performance detection of both visible light and X-rays. Here, we report a $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ heterointerfaces composite broadband photodetector. Benefiting from the effective integration of light absorption and carrier transport, the device exhibits outstanding detection sensitivity across both the visible and X-ray regions. Under 405 nm illumination, the device achieves a high responsivity of $1.44 \times 10^5 \text{ A/W}$, a

detectivity of 1.15×10^{16} Jones, and an external quantum efficiency of $4.41 \times 10^5\%$. Meanwhile, in X-ray detection, it delivers a high sensitivity of up to 2.09×10^4 $\mu\text{C}/(\text{Gy}_{\text{air}} \cdot \text{cm}^2)$. Compared with previously reported Bi-based perovskite photodetectors, the device developed in this work demonstrates superior detection performance along with excellent broadband response characteristics, providing a new strategy for the design of high-performance perovskite photodetectors.

Results

Device design and characteristics. Figures 1a illustrate the structure of the $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ photodetector, in which the channel consists of high-purity ($> 99.9\%$) semiconducting CNTs and $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite thin film, serving as the charge transport pathway and light-absorbing layer, respectively. A CNTs solution dispersed in toluene is deposited onto a SiO_2 buried-gate transistor that has been surface-modified to tailor its wettability, thereby forming a uniform CNTs thin film. The channel is subsequently patterned via photolithography and dry etching (see Methods and Figure S1 in the Electronic Supplementary Material (ESM)). On this basis, the $\text{Cs}_3\text{Bi}_2\text{I}_9$ precursor solution is spin-coated onto the surface, followed by thermal annealing in a glovebox to form a dense thin film. Figure 1b presents an optical image of the fabricated device featuring the patterned CNTs channel and $\text{Cs}_3\text{Bi}_2\text{I}_9$ thin film. Further characterization of the device cross-section was carried out using scanning electron microscopy (SEM, Figure 1c) and energy-dispersive X-ray spectroscopy (EDS, Figure S2 in the ESM). The SEM results reveal that the $\text{Cs}_3\text{Bi}_2\text{I}_9$

thin film uniformly covers a large area and is tightly integrated with the CNTs layer, indicating an intact device structure with high-quality interfaces. The EDS elemental mapping results (Figure S2 in the ESM) show a pronounced enrichment of C elements between the $\text{Cs}_3\text{Bi}_2\text{I}_9$ film and the SiO_2 layer, confirming the presence of the CNTs channel. Meanwhile, the uniform distribution of Cs, Bi, and I elements further demonstrates the excellent film uniformity of the as-prepared $\text{Cs}_3\text{Bi}_2\text{I}_9$ layer. Figure 1d presents the typical transfer characteristics ($I_{\text{DS}}-V_{\text{GS}}$) of the phototransistor under dark conditions and at different light power densities (P). As the illumination power density increases, the transfer curves exhibit a pronounced positive shift, indicating a significant photoresponse behavior of the device. Figures 1e and Figure S3 depict the energy band alignment between $\text{Cs}_3\text{Bi}_2\text{I}_9$ and carbon nanotubes (CNTs) [30, 31]. To validate this band structure, we measured the work functions, valence band maxima (VBM), optical bandgaps, and conduction band minima (CBM) of both materials using UPS and UV-Vis absorption spectroscopy (see Table S1 for detailed parameters). The results reveal that the Fermi level of pristine $\text{Cs}_3\text{Bi}_2\text{I}_9$ rises from -4.74 eV to -4.70 eV upon compositing with CNTs, accompanied by corresponding shifts in the VBM and CBM. These energy shifts unequivocally indicate charge redistribution at the interface, which drives the system toward a new Fermi-level equilibrium and confirms electronic coupling at the $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ interface. This experimental evidence is fully consistent with the built-in electric field and interfacial band bending (due to band misalignment) shown in Figure 1e, confirming the formation of a type-I heterojunction and laying a solid foundation for subsequent photogenerated

carrier separation and transport. Figure S4 further visualizes this process via three-stage band diagrams, clearly illustrating electron transfer, energy level equilibration, and carrier behavior before and after heterojunction formation, which directly corroborates the interfacial band bending and built-in field. Upon visible light excitation, the light absorption process in $\text{Cs}_3\text{Bi}_2\text{I}_9$ is primarily governed by the I 5p orbitals that constitute the valence band maximum. Incident photon energy is absorbed by I 5p electrons, promoting them from the ground state to an excited state and thereby generating photogenerated electron-hole pairs. The photogenerated holes preferentially transfer to the CNTs channel by the built-in electrical field, while electrons remain in the $\text{Cs}_3\text{Bi}_2\text{I}_9$ thin film, enabling efficient spatial separation of photogenerated carriers[32-33]. Notably, the efficient trapping of photogenerated electrons within the $\text{Cs}_3\text{Bi}_2\text{I}_9$ layer induces a significant photogating effect. By acting as a localized negative virtual gate, this effect effectively modulates the Fermi level of the CNTs channel and triggers multiple hole circulations. The resulting high photoconductive gain, derived from the prolonged carrier lifetime, establishes the physical foundation for the device's superior photodetection performance[34]. In addition, steady-state photoluminescence (PL) measurements show that the PL intensity of the $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ composite film is significantly lower than that of pristine $\text{Cs}_3\text{Bi}_2\text{I}_9$, indicating that the introduction of CNTs introduces additional carrier transfer channels at the interface (Figure S5). Combining the PL results with the electrical measurements, it is evident that $\text{Cs}_3\text{Bi}_2\text{I}_9$ primarily serves as the light absorber and photogenerated carrier generator, whereas CNTs act as efficient transport

and collection channels for carriers, achieving functional decoupling between the two components. This synergistic effect effectively suppresses carrier recombination, promotes the separation, transport, and collection of photogenerated carriers, and ultimately endows the composite device with excellent optoelectronic response performance. This mechanism[35] is further elucidated in Figure 1f, which illustrates (I) light absorption, (II) the separation of photogenerated electron-hole pairs and subsequent electron trapping within the $\text{Cs}_3\text{Bi}_2\text{I}_9$ layer, and (III) hole conduction through the conductive CNTs channel. These synergistic processes account for the device's superior photodetection performance.

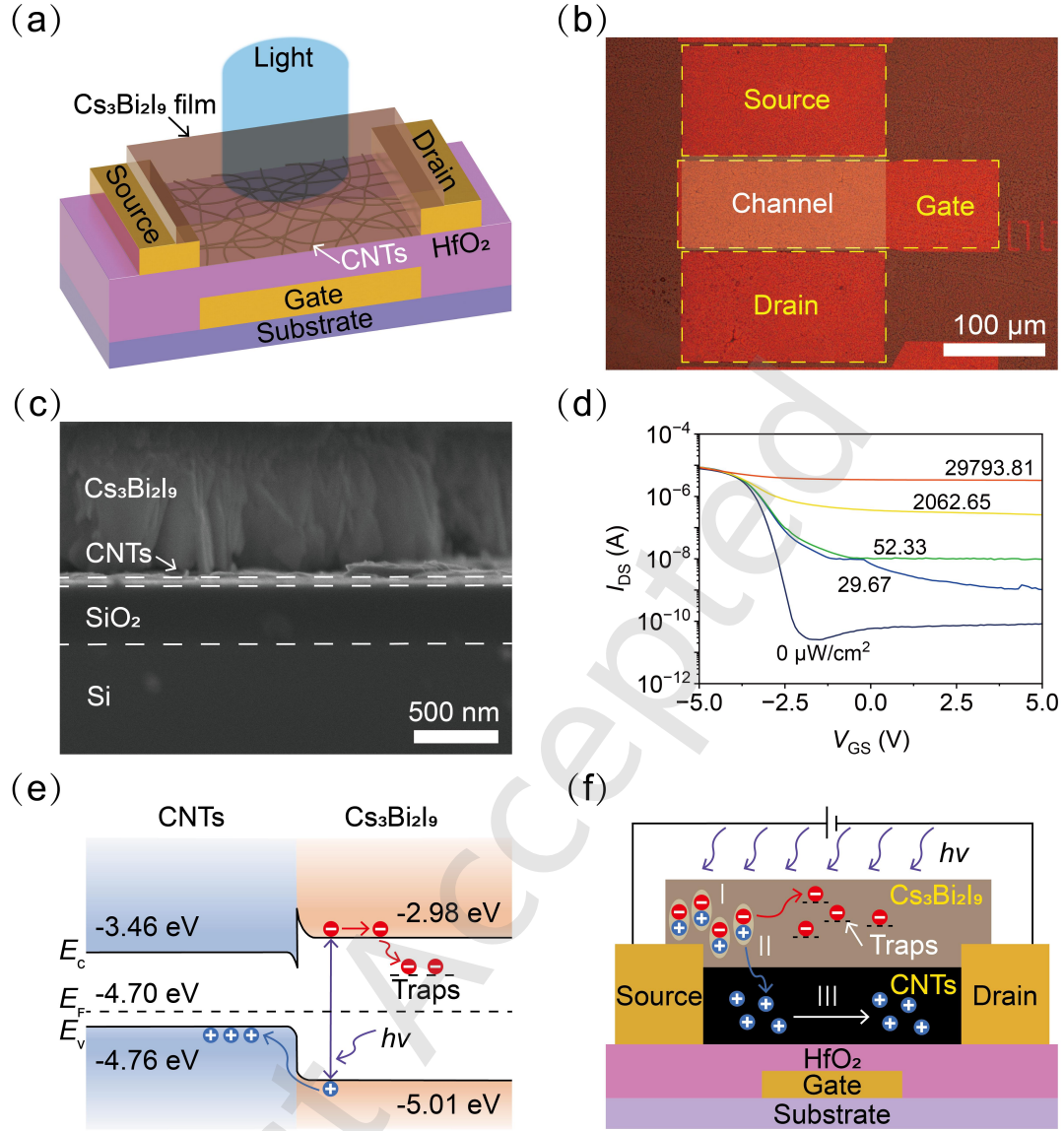


Figure 1. Structure and characterization of the $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ photodetector. (a) Three-dimensional schematic illustration of the device structure. (b) Optical microscopy image of the photodetector. (c) Cross-sectional SEM image of the device. (d) Photoresponse characteristics of the $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ photodetector under 405 nm laser illumination at different power densities. (e) Schematic energy band alignment of $\text{Cs}_3\text{Bi}_2\text{I}_9$ and CNTs films under illumination. (f) The working mechanism of the $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ photodetector.

$\text{Cs}_3\text{Bi}_2\text{I}_9$ film characteristics. The $\text{Cs}_3\text{Bi}_2\text{I}_9$ thin film in the channel region was characterized by SEM. As shown in Figure 2a, the spin-coated film exhibits good uniformity. Moreover, After the introduction of CNTs, the $\text{Cs}_3\text{Bi}_2\text{I}_9$ film overall

maintains good surface coverage and film integrity, with no obvious morphological deterioration observed, indicating that the incorporation of CNTs does not significantly compromise the basic film quality of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ film (Figure S6b). To further investigate its crystal structure, X-ray diffraction (XRD) measurements were performed, as presented in Figure 2b. The diffraction peaks located at 12.83° , 16.71° , 25.21° , 42.97° , and 51.75° can be indexed to the (101), (004), (006), (220), and (0012) crystal planes of the hexagonal phase, respectively (PDF#23-0847, $a = 8.412 \text{ \AA}$, $c = 21.182 \text{ \AA}$, space group: $P6_3/mmc$ (194)). These results are in good agreement with the previously reported crystal structure of zero-dimensional (0D) $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskites[23, 36]. As shown in Figure S6c, the XRD results show that the $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ composite film retains the main characteristic diffraction peaks of $\text{Cs}_3\text{Bi}_2\text{I}_9$, with no obvious new impurity-phase peaks observed, indicating that the incorporation of CNTs does not cause significant changes in the crystal structure of $\text{Cs}_3\text{Bi}_2\text{I}_9$. In addition, to evaluate the optical absorption properties of the film, ultraviolet-visible (UV-Vis) absorption spectroscopy was performed on the $\text{Cs}_3\text{Bi}_2\text{I}_9$ thin film (Figure 2c), where a pronounced absorption edge is observed at approximately 550 nm. Furthermore, the UV-Vis absorption spectra shown in Figure S6d indicate that the $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ composite film retains the main absorption characteristics of $\text{Cs}_3\text{Bi}_2\text{I}_9$ in the visible-light region. This result indicates that the incorporation of CNTs does not fundamentally alter the primary light absorption characteristics of $\text{Cs}_3\text{Bi}_2\text{I}_9$, which remains the main contributing component to visible-light absorption in the composite film. The corresponding Tauc plot (Figure 2d) reveals an optical bandgap of 2.05 eV,

which is consistent with previously reported results[37]. X-ray photoelectron spectroscopy (XPS) was employed to characterize the elemental composition and chemical states of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ thin film. The survey spectrum (Figure 2e) clearly confirms the presence of Cs, Bi, and I elements in the sample. High-resolution spectra of Cs 3d, Bi 4f, and I 3d are shown in Figures 2f-h, respectively. In the Cs 3d spectrum, the Cs $3d_{5/2}$ and Cs $3d_{3/2}$ peaks are located at 724.0 eV and 738.0 eV, respectively, corresponding to the characteristic binding energies of Cs^+ [38], indicating that Cs exists in the + 1 oxidation state. Figure 2g presents the spin-orbit split doublet of the Bi 4f orbital, where the Bi $4f_{5/2}$ and Bi $4f_{7/2}$ peaks exhibit symmetric intensity distribution, with an energy separation of approximately 5.3 eV, consistent with the typical splitting of Bi 4f levels. The main Bi $4f_{7/2}$ peak is located at 158.6 eV, corresponding to the characteristic binding energy of Bi^{3+} , indicating a stable and single chemical state of Bi in the film. Figure 2h shows the spin-orbit split doublet of the I 3d orbital, with the main I $3d_{5/2}$ peak located at 620 eV and an energy separation of approximately 11.5 eV between the two peaks, in agreement with the characteristic splitting of I 3d levels, confirming that iodine exists in a stable I^- state. Overall, the valence states of Cs, Bi, and I are all consistent with the stoichiometric composition of $\text{Cs}_3\text{Bi}_2\text{I}_9$. Further comparison of the high-resolution XPS spectra of Cs 3d, Bi 4f, and I 3d, as shown in Figures S6e-h, reveals slight shifts in the binding energies of the corresponding elements after the incorporation of CNTs. This change indicates the presence of interfacial electronic interactions between $\text{Cs}_3\text{Bi}_2\text{I}_9$ and CNTs, accompanied by a certain degree of interfacial charge redistribution,

demonstrating that the introduction of CNTs induces interfacial electronic interactions and charge redistribution between $\text{Cs}_3\text{Bi}_2\text{I}_9$ and CNTs. The XPS results, in agreement with the XRD and UV-Vis characterizations, collectively confirm that the as-prepared $\text{Cs}_3\text{Bi}_2\text{I}_9$ thin film possesses a pure-phase structure, providing a reliable photoactive material foundation for optoelectronic device applications.

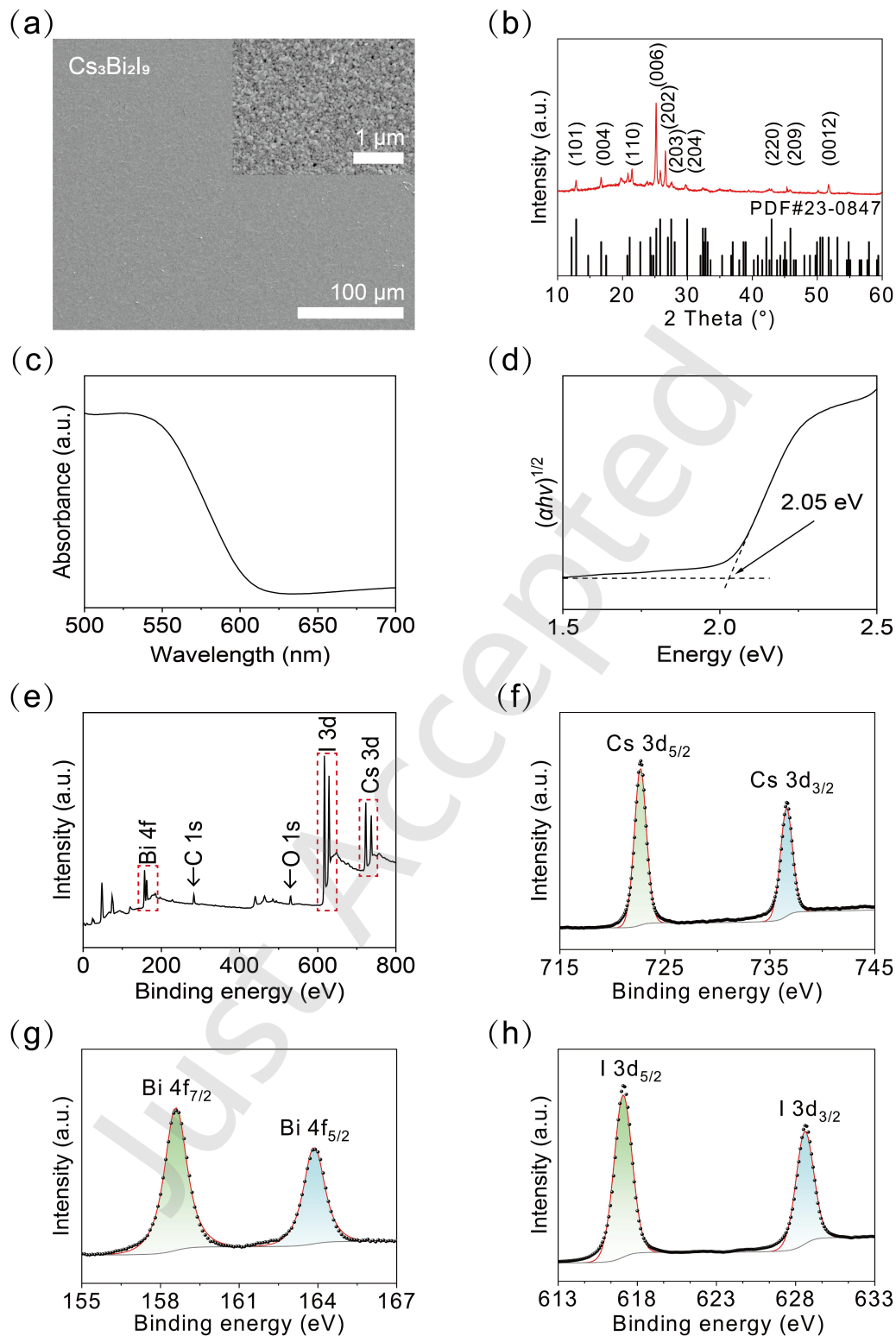


Figure 2. Characterization of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ thin film. (a) SEM image of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ thin film in the channel region (scale bar: 100 μm); inset: high-magnification SEM image of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ film in the channel region (scale bar: 1 μm). (b) XRD pattern of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ thin film. (c) UV-Vis absorption spectrum of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ thin film. (d) Tauc plot of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ thin film derived from

the absorption spectrum. (e) Full-range XPS spectra of Cs₃Bi₂I₉ film. (f)-(h). XPS high-resolution core-level spectra of Cs, Bi and I in Cs₃Bi₂I₉ film.

Optoelectronic characteristics under visible light illumination. The photoresponse characteristics of the transistor device were systematically investigated, as shown in Figure 3. Figure 3a presents the typical I_{DS} - T response curves of the device under illumination with 405 nm monochromatic light at different power densities, measured at a gate voltage of + 5 V. As the illumination power density increases, I_{DS} exhibits a pronounced positive shift, indicating a clear light-intensity-dependent behavior of the device. Correspondingly, as the light power density increases from 0.13 $\mu\text{W}/\text{cm}^2$ to 300 mW/cm^2 , I_{DS} increases significantly. Meanwhile, the noise characteristics of the device were also investigated (Figure S7 in the ESM), revealing an ultralow noise power density (S_n) of $3.48 \times 10^{-26} \text{ A}^2/\text{Hz}$, which is comparable to that of pristine Cs₃Bi₂I₉ perovskite thin film transistor devices without CNTs integration. The combination of low noise power density and enhanced photoresponse is a key factor enabling the high detectivity of the device. In addition, the pristine Cs₃Bi₂I₉ device shows limited photocurrent response due to inefficient charge transport and collection (Figure S9), despite its light-absorption capability. The CNTs transistor exhibits typical electrical behavior in its I_{DS} - V_{GS} characteristics but shows negligible photoresponse under 405 nm laser illumination, even at the highest power density of 460 mW/cm^2 (Figure S10). In contrast, the Cs₃Bi₂I₉/CNTs composite device exhibits substantially enhanced photocurrent because the CNTs network provides continuous and efficient carrier pathways, as shown in Figure S5d. Under $V_{GS} = 5 \text{ V}$ and $V_{DS} = -1$

V, the dependence of responsivity and detectivity on the illumination power density of 405 nm monochromatic light was systematically investigated, as shown in Figure 3b. At the lowest light power density of $0.13 \mu\text{W}/\text{cm}^2$, the device achieves a high responsivity of $1.44 \times 10^5 \text{ A/W}$ and a high detectivity of $1.15 \times 10^{16} \text{ Jones}$, representing a leading performance among lead-free perovskite photodetectors. Figure 3c shows the dependence of the external quantum efficiency (EQE) on the light power density. As the power density increases, the EQE gradually decreases due to the absorption saturation effect; at the lowest power density of $0.13 \mu\text{W}/\text{cm}^2$, the EQE reaches a maximum value of $4.41 \times 10^7\%$. In addition, the dynamic response characteristics of the device were evaluated (Figure S8 in the ESM), yielding a rise time and decay time of 336 ms and 456 ms, respectively. Meanwhile, the effects of light power density on the responsivity and detectivity of the device under 516 nm monochromatic illumination were further investigated (Figure S11 in the ESM). The results show that, at a low light power density of $1.15 \mu\text{W}/\text{cm}^2$, the device achieves a high responsivity of $2.41 \times 10^3 \text{ A/W}$ and a detectivity of $3.07 \times 10^{13} \text{ Jones}$. After being placed in an environment of 30% humidity at 25°C for one week, the unencapsulated device exhibits a drop in its on/off ratio (under 0 V bias) to 80, indicating significant performance degradation (Figure S12 in the ESM). To achieve long-term device operation under ambient conditions in future scenarios, effective encapsulation is highly required. Additionally, the performance of the device developed in this work was systematically benchmarked against previously reported results[22-23, 25, 30-31, 39-60], as summarized in Figure 3d and Table S3. The

results demonstrate that the present device exhibits significant advantages in both responsivity and detectivity.

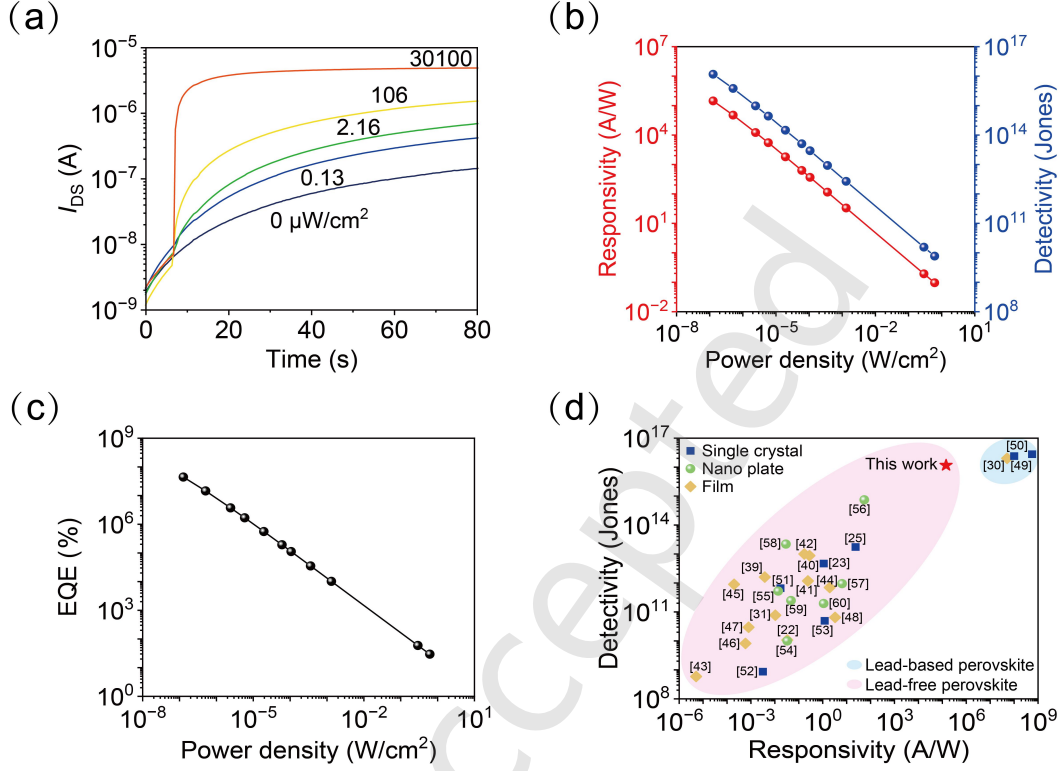


Figure 3. Optoelectronic performance of the Cs₃Bi₂I₉/CNTs photodetector. (a) I_{DS} - T curves of the device under 405 nm monochromatic illumination with different power densities at $V_{DS} = -1$ V and $V_{GS} = 5$ V. (b) Responsivity (R) and detectivity (D^*) of the Cs₃Bi₂I₉/CNTs photodetector. $R = \frac{I_{ph}}{P_{in}A} = \frac{I_{light} - I_{dark}}{P_{in}A}$, where I_{ph} is the photocurrent, which is the current generated by the PD when illuminated, minus the dark current. P_{in} is the incident optical power density, and A is the effective photosensitive area of the PD. $D^* = \frac{R(A\Delta f)^{1/2}}{I_{noise}}$, where Δf is the bandwidth, I_{noise} is the noise current, and R is the responsivity[61]. (c) External quantum efficiency (EQE) of the Cs₃Bi₂I₉/CNTs photodetector. $EQE = \frac{N_c}{N_i} = \frac{hcr}{e\lambda}$, where N_c represents the number of photogenerated charge carriers, N_i denotes the number of incident photons, r is the resistance of the PD, h is Planck's constant, c is the speed of light, e is the electronic charge, and λ is the wavelength of the incident light[30]. (d) Benchmark comparison of the performance of the present device with previously reported photodetectors.

Optoelectronic characteristics under X-ray illumination. The absorption

coefficients of $\text{Cs}_3\text{Bi}_2\text{I}_9$, CsPbI_3 , and typical X-ray detection semiconductors (such as Si, α -Se, and CdTe) were compared over the photon energy range of 0.01-1 MeV (data sourced from the NIST XCOM: Photon Cross Sections Database), as shown in Figure 4a. Benefiting from the incorporation of high atomic number elements such as Bi and I, $\text{Cs}_3\text{Bi}_2\text{I}_9$ and CsPbI_3 exhibit absorption capabilities comparable to CdTe across the entire energy range, and significantly higher than those of Si and α -Se. The energy of X-ray photons is much higher than the binding energy of core electrons in most elements, enabling them to directly ionize the most tightly bound K-shell or L-shell electrons[23]. When X-rays illuminate $\text{Cs}_3\text{Bi}_2\text{I}_9$, the high-energy photons primarily interact with the core electrons of the high-atomic-number Bi and I atoms (the L-shell of Bi and the K-shell of I) through the primary photoelectric effect, ionizing core electrons and generating high-energy photoelectrons while leaving behind core holes. Subsequently, these core holes de-excite via Auger processes or fluorescence emission. Among these, the emission of Auger electrons further generates a large number of secondary electron-hole pairs through impact ionization, leading to carrier multiplication[62-63]. During this process, electrons are confined within $\text{Cs}_3\text{Bi}_2\text{I}_9$, whereas holes are injected into the CNTs. Finally, the photogenerated carriers are efficiently collected by the drain electrode under the source-drain bias[35]. Figure 4b presents the time-resolved response characteristics ($I_{\text{DS}}-T$ curves) of the fabricated device under X-ray irradiation at different dose rates. During the measurement, the X-ray tube voltage was increased from 0 to 80 kV, and the X-ray dose rate was gradually increased from 0 to 18.85 mGy_{air}/s, while the gate

voltage (V_{GS}) was fixed at + 5 V. The results show that the device exhibits a low current level in the off state. Upon switching on the X-ray source at 10 s, a pronounced response is observed, with the current increasing from the nanoampere level to the microampere level (corresponding to a tube voltage of 80 kV). Based on the time-dependent response curves, the sensitivity of the device was extracted and calculated, as shown in Figure 4c, the device achieves a high sensitivity of $2.09 \times 10^4 \mu\text{C}/(\text{Gy}_{\text{air}} \cdot \text{cm}^2)$. For comparison, Figure 4d and Table S4 summarize and systematically compare previously reported results[21, 23, 26, 62, 64-75]. The results demonstrate that the device developed in this work exhibits a pronounced advantage in sensitivity. The $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ photodetector presented here shows excellent X-ray detection performance, highlighting its great potential for practical applications.

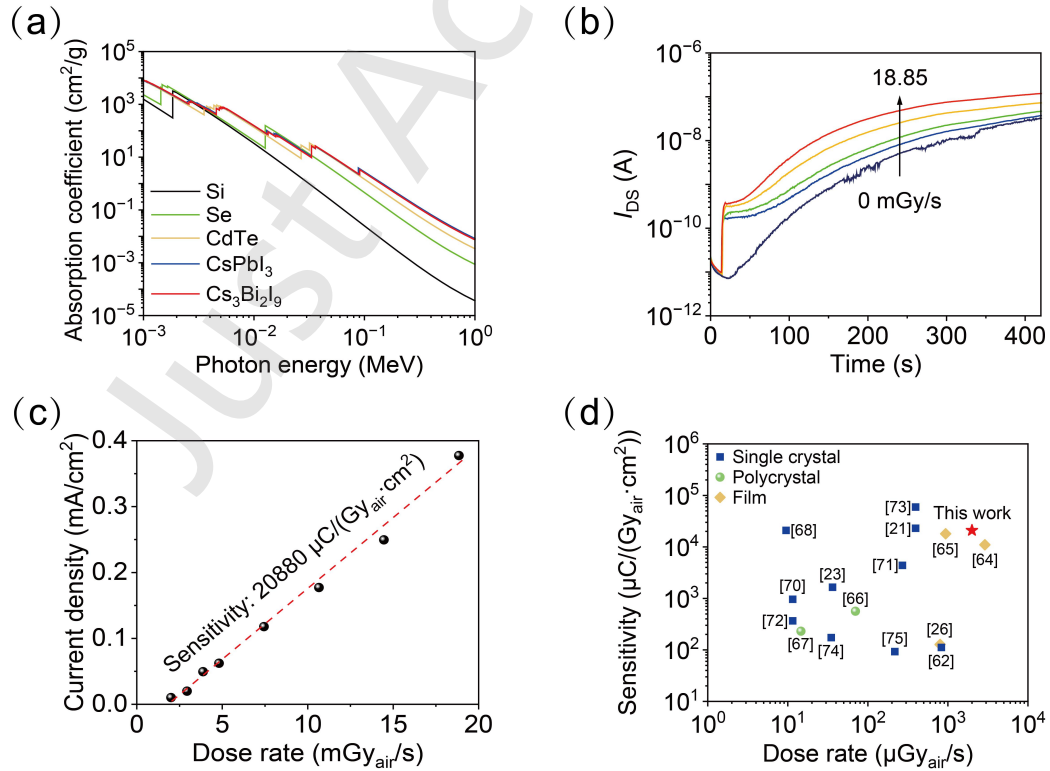


Figure 4. X-ray detection performance of the $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ photodetector. (a) Absorption coefficients of $\text{Cs}_3\text{Bi}_2\text{I}_9$, CsPbI_3 , Si, $\alpha\text{-Se}$, and CdTe as a function of photon energy. (b) I_{DS} - T

response curves of the device under X-ray irradiation at different dose rates, measured at $V_{DS} = -1$ V and $V_{GS} = 5$ V. (c) Sensitivity (S) of the $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ device as a function of dose rate. $S = \frac{I_{\text{radiation}} - I_{\text{dark}}}{DA}$, where $I_{\text{radiation}}$ and I_{dark} are the output currents with and without X-ray irradiation, respectively, D is the X-ray dose, and A is the sensor area, the channel area of the device[76-77]. (d) Benchmark comparison of the performance of the present device with previously reported X-ray detectors.

Conclusion

In this work, we report a high-performance phototransistor featuring a simple yet effective hybrid architecture that enables a decoupled design. This approach achieves efficient photoelectric conversion by integrating a CNTs conductive channel with a perovskite photosensitive layer. The composite active channel, composed of semiconducting CNTs and $\text{Cs}_3\text{Bi}_2\text{I}_9$, significantly promotes the separation and transport of photogenerated carriers, enabling the device to achieve a high responsivity of 1.44×10^5 A/W and an ultrahigh detectivity of 1.15×10^{16} Jones. Furthermore, the device also demonstrates excellent performance in X-ray detection, achieving a high sensitivity of 2.09×10^4 $\mu\text{C}/(\text{Gy}_{\text{air}} \cdot \text{cm}^2)$. These results indicate that the composite system, while maintaining low toxicity and low noise characteristics, delivers outstanding response performance in both visible light and X-ray regimes, providing a promising strategy for the development of broadband, high-sensitivity photodetectors.

Methods

Materials preparation and device fabrication. Bismuth iodide (BiI_3 , 99%), cesium iodide (CsI , 99.9%), and N,N-dimethylformamide (DMF, anhydrous, 99.8%), dimethyl sulfoxide (DMSO, anhydrous, 99.8%), and chlorobenzene (CB, anhydrous, 99.8%) were purchased from Sigma-Aldrich. High-purity (> 99.99%) semiconducting CNTs were prepared by dispersing CNTs with polycarbazole in xylene, followed by isolation via ultrasonic dispersion. The $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite thin films were prepared using a one-step spin-coating method at room temperature in a glove-box. The precursor solution, consisting of BiI_3 (1.2 M) and CsI (1.8 M) dissolved in a mixture of DMF and DMSO at a volume ratio of 3:7, was stirred at 50 °C for 12 h prior to deposition. The $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ photodetector was fabricated on a heavily doped p-type silicon substrate with a 300 nm thick SiO_2 layer. First, the silicon substrate was ultrasonically cleaned in acetone and isopropanol for 5 min, followed by rinsing with deionized water and drying with nitrogen. A 5 nm Ti layer and a 50 nm Au layer were then deposited on top of the substrate by electron-beam evaporation (EB) to serve as the gate electrode. Subsequently, a 30 nm HfO_2 dielectric layer was deposited on the gate electrode via atomic layer deposition (ALD). The source-drain Ti/Au electrodes were deposited on the substrate using EB evaporation through a designed shadow mask (channel length = 100 μm , width = 200 μm). The substrate was then treated with oxygen plasma (180 sccm O_2 , 200 W, 5 min) to improve its hydrophilicity. Afterward, the substrate was coated with a layer of hexamethyldisilazane (HMDS) and immersed in a semiconducting CNTs solution at 60 °C for 2 h. The substrate with the deposited CNTs film was subsequently rinsed in toluene and isopropanol (IPA) for 5 min each.

Finally, the CNTs film was patterned by photolithography followed by oxygen plasma etching (180 sccm O₂, 200 W, 2 min) to form the channel. The precursor Cs₃Bi₂I₉ solution was then spin-coated onto the CNTs at 5000 rpm for 60 s; the CB anti-solvent was applied 20 s after the spinning commenced. Finally, the resulting films were annealed at 100 °C for 10 min.

Characterization and measurements. The materials and devices were characterized using scanning electron microscopy (SEM, HITACHI SU-70) equipped with energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD, Rigaku SmartLab), and optical microscopy (Nikon LV100ND and Olympus DSX1000). The elemental composition of the films was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). Photoluminescence spectra (PL) were measured using a confocal micro-Raman spectrometer (HORIBA LabRAM HR800) with an excitation wavelength of 532 nm. The noise measurement was performed using a semiconductor parameter analyzer (Primarius Technologies, Fs- pro) with a bandwidth of 1 - 10⁵ Hz. To minimize environmental electromagnetic interference, the device was placed in a grounded shielding box (Giga Force Electronics, Flip- top Probe Station Shielding Box) for testing. The performance of the Cs₃Bi₂I₉/CNTs photodetectors was evaluated in a dark room at room temperature using a semiconductor parameter analyzer (Agilent B1500A), a probe station (Cascade M150), and a laser diode controller (Thorlabs ITC4001) equipped with a 405 nm laser source. For X-ray detection measurements, an X-ray tube (Hamamatsu Photonics, MICROFOCUS X-RAY SOURCE L9631) was used. During testing, the X-ray tube

voltage ranges from 40 to 80 kV, and the tube current ranges from 10 to 50 μ A. The response time of the device was measured using a current amplifier (FEMTO DHPCA-100) and an oscilloscope (Tektronix MSO 2024B).

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Data availability

The data that support the findings in this study are available from the corresponding author upon reasonable request.

Conflict of interest statement. None declared.

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Electronic Supplementary Material

Decoupling light absorption and carrier transport in Cs₃Bi₂I₉ via carbon nanotube networks for high-performance visible and X-ray photodetection

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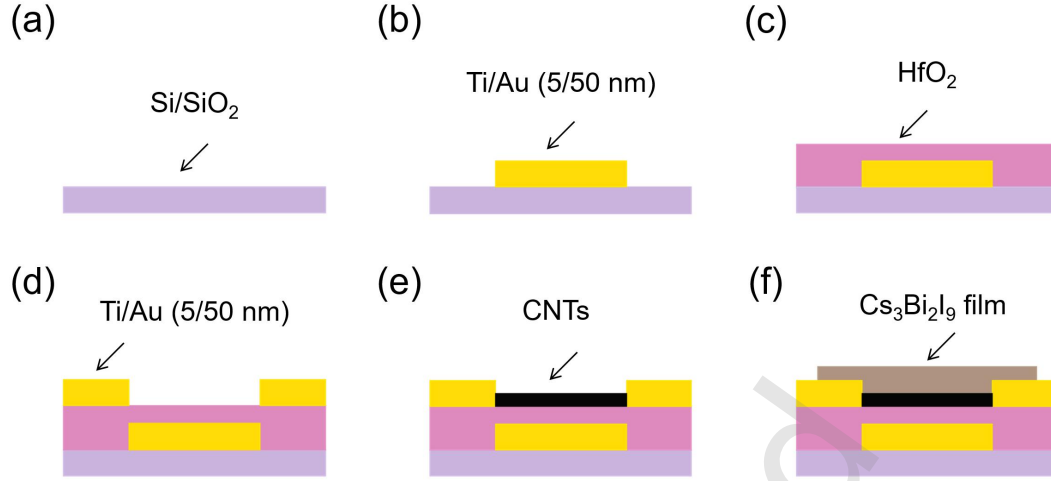


Figure S1. $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ photodetector fabrication process. (a) An initial SiO_2/Si substrate was prepared. (b) Gate electrode fabrication. The gate electrode (Ti/Au : 5/50 nm) was fabricated by standard photolithography, e-beam evaporation and lift-off. (c) Insulator layer fabrication. A 30-nm-thick HfO_2 layer was fabricated on the substrate by atomic layer deposition (ALD) technique. (d) Source/drain electrode fabrication. The source and drain electrodes were patterned on the insulator using the same method. (e) A solution-processed CNTs channel was deposited and patterned. (f) Deposition of a $\text{Cs}_3\text{Bi}_2\text{I}_9$ film layer. The $\text{Cs}_3\text{Bi}_2\text{I}_9$ film was spin-coated onto the channel.

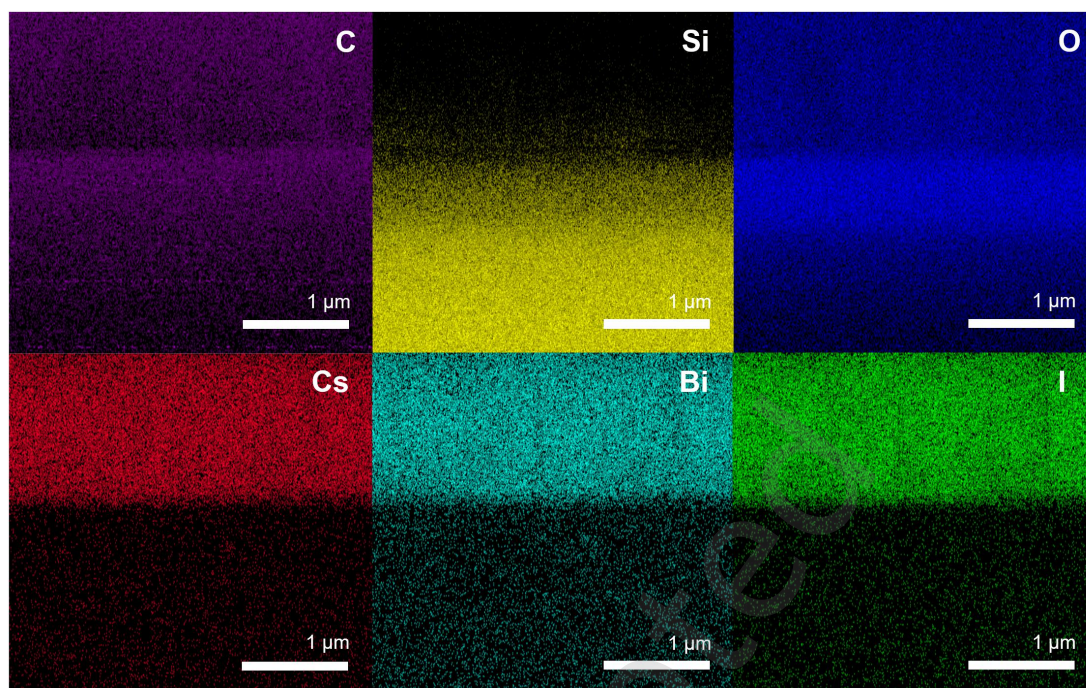


Figure S2. Cross-sectional EDS characterization of the $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ photodetector. The elemental mapping of C reveals a distinct and continuous carbon-rich region between the $\text{Cs}_3\text{Bi}_2\text{I}_9$ film and the SiO_2 layer. This region precisely corresponds to the position of the CNTs layer within the device structure, confirming the presence and integrity of the CNTs layer. The EDS elemental maps of Cs, Bi, and I exhibit uniform and continuous distributions, with stable signal intensities across the film. These distributions are in excellent agreement with the $\text{Cs}_3\text{Bi}_2\text{I}_9$ thin-film region observed in the SEM image, indicating the homogeneous chemical composition of the as-prepared $\text{Cs}_3\text{Bi}_2\text{I}_9$ film.

Table S1 Experimental and derived electronic structure parameters of CNTs, $\text{Cs}_3\text{Bi}_2\text{I}_9$, and $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$.

Sample \ Energy	E_g (eV)	CBM (eV)	E_F (eV)	VBM (eV)
CNTs	1.30	-3.46	-4.69	-4.76
$\text{Cs}_3\text{Bi}_2\text{I}_9$	2.03	-2.98	-4.74	-5.01
$\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$	2.06	-3.00	-4.70	-5.06

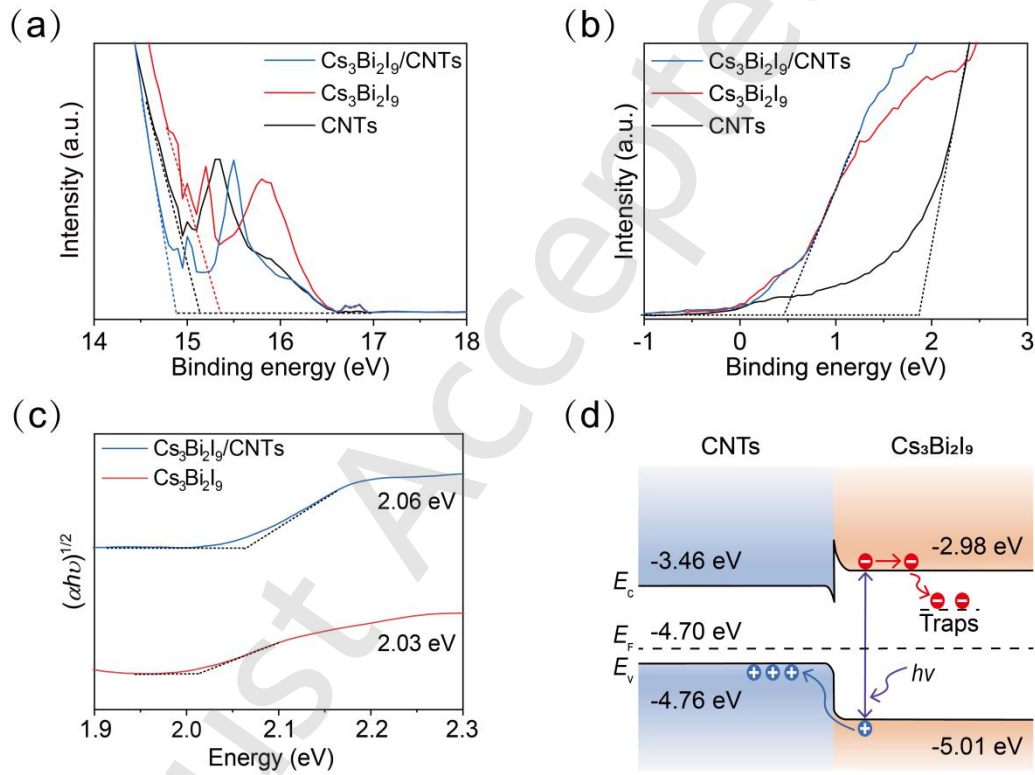


Figure S3. UPS and band alignment analysis of CNTs, $\text{Cs}_3\text{Bi}_2\text{I}_9$, and $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$. (a) UPS secondary electron cut-off spectra used to determine the work function. (b) UPS spectra near the valence-band region used to determine the valence-band onset. (c) Optical bandgaps of $\text{Cs}_3\text{Bi}_2\text{I}_9$ and $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ derived from Tauc plots. (d) Energy-level diagram constructed from UPS results and optical bandgap analysis.

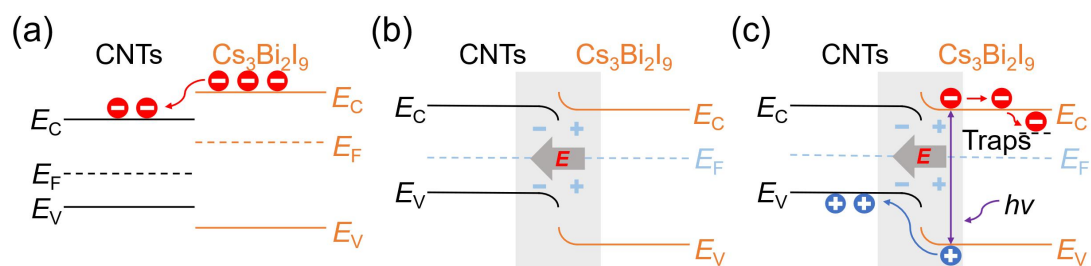


Figure S4. Alignment of the energy bands of CNTs and $\text{Cs}_3\text{Bi}_2\text{I}_9$ before and after the formation of heterojunctions. (a) Upon contact, electrons flow from $\text{Cs}_3\text{Bi}_2\text{I}_9$ to the CNTs, driven by the higher Fermi level (E_F) of $\text{Cs}_3\text{Bi}_2\text{I}_9$. (b) After electron transfer, the Fermi levels equilibrate, and a space charge region, along with a built-in electric field, forms at the $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ interface. (c) The generation, separation and transport of photogenerated excitons are described.

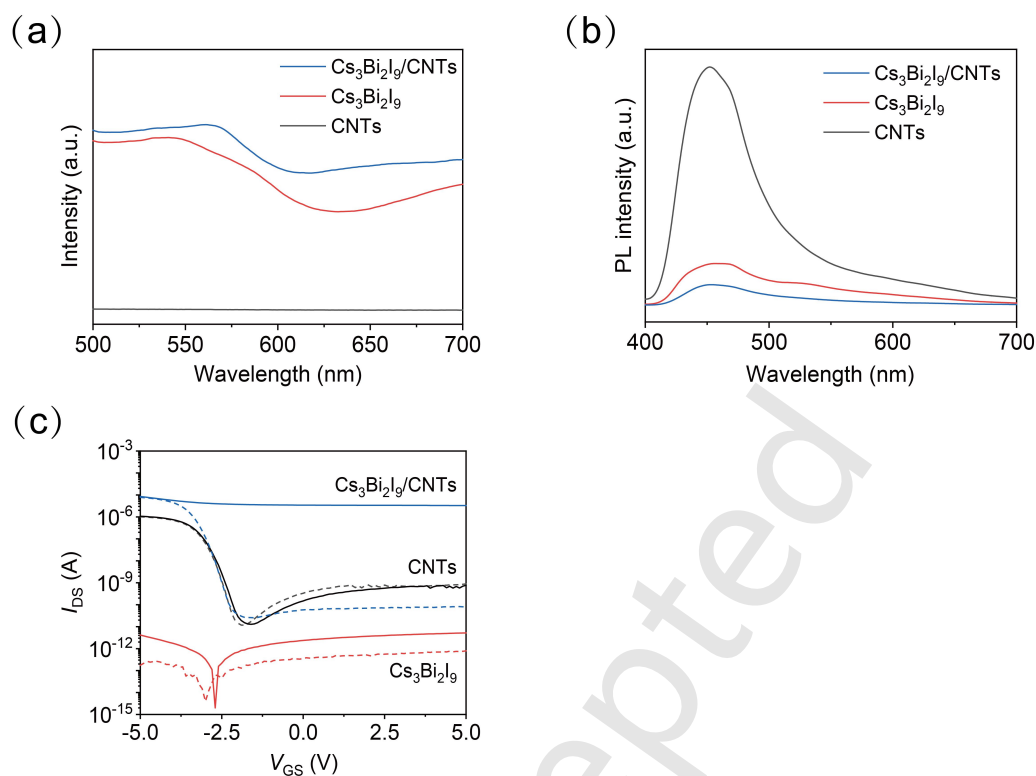


Figure S5 Characterization of optoelectronic properties of materials and devices. (a) UV-Vis absorption spectrum of the CNT、Cs₃Bi₂I₉ and Cs₃Bi₂I₉/ CNTs thin films. (b) Steady-state PL spectra of the CNT、Cs₃Bi₂I₉ and Cs₃Bi₂I₉/ CNTs thin films. (c) Comparison of dark current (dotted lines) and current under 405 nm illumination at 460 mW/cm² (solid lines) of the CNT、Cs₃Bi₂I₉ and Cs₃Bi₂I₉/ CNTs thin films.

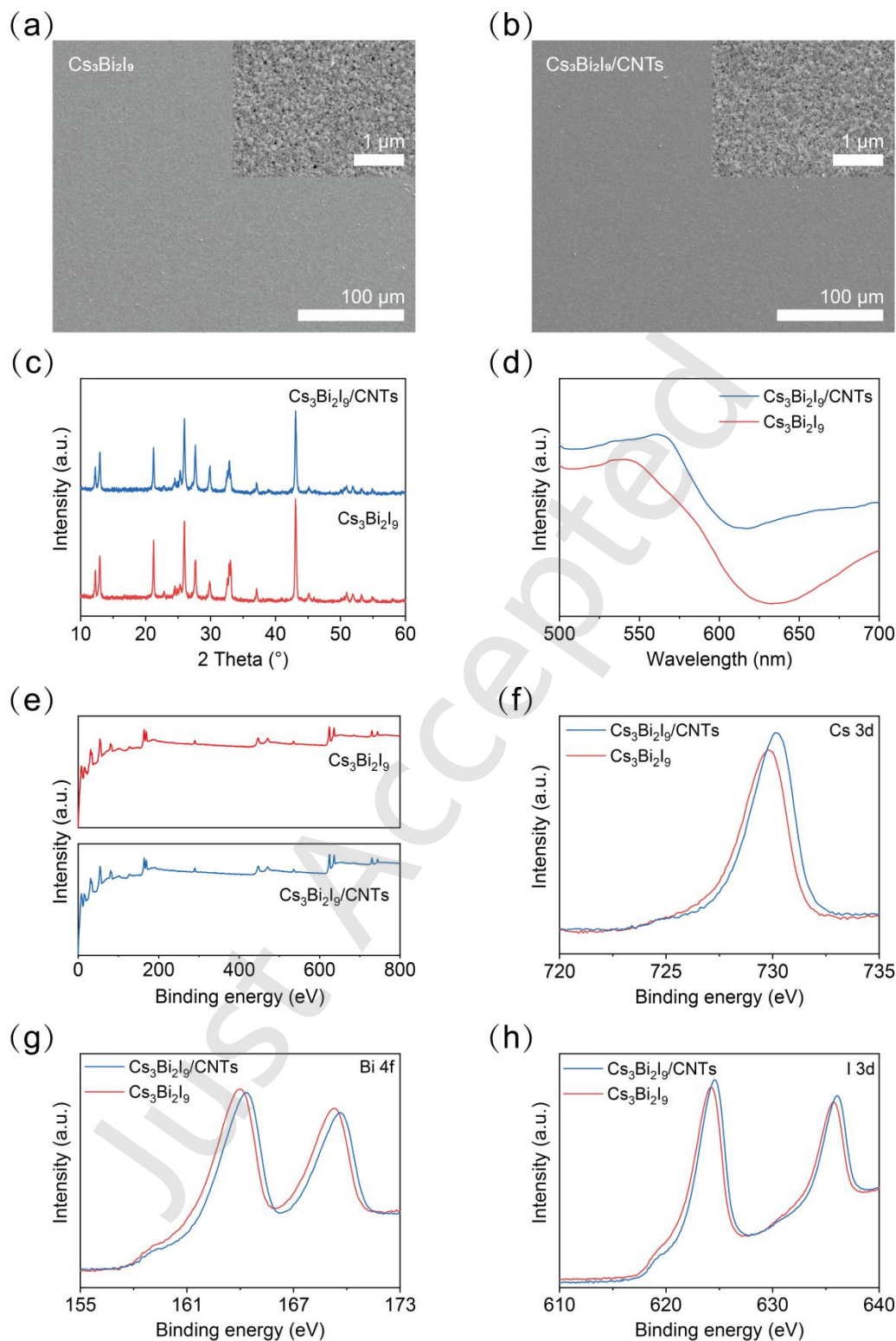


Figure S6 Characterization of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ and $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ thin films. (a) SEM images of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ and (b) $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ thin films in the channel region (scale bar: 100 μm); insets show high-magnification SEM image of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ film in the channel region (scale bar: 1 μm). (c)

XRD patterns of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ and $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ thin films. (d) UV-Vis absorption spectra of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ and $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ thin films. (e) Full-range XPS spectra of $\text{Cs}_3\text{Bi}_2\text{I}_9$ and $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ thin films. (f)-(h). XPS high-resolution core-level spectra of Cs, Bi and I in $\text{Cs}_3\text{Bi}_2\text{I}_9$ and $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ thin films.

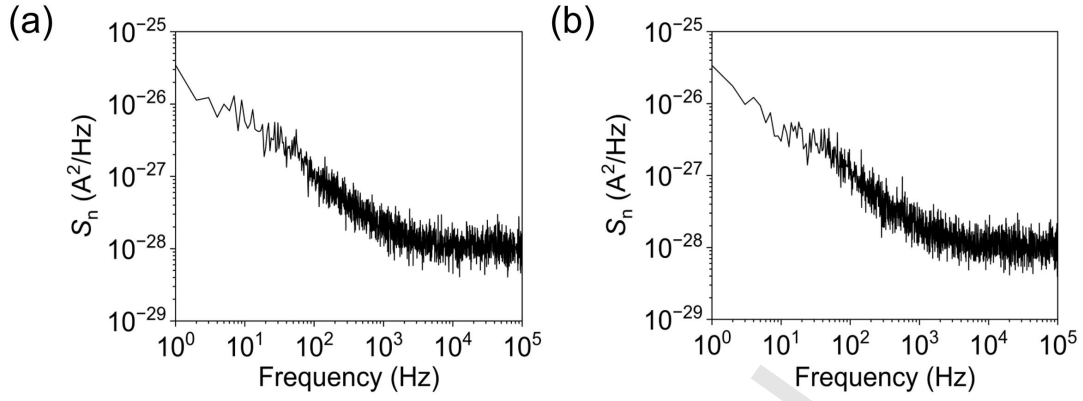


Figure S7. Noise power density spectra of $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ and $\text{Cs}_3\text{Bi}_2\text{I}_9$ photodetectors. **a.** $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ and **b.** $\text{Cs}_3\text{Bi}_2\text{I}_9$ photodetectors. To characterize the actual performance of the $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ hybrid, the spectral noise power of the phototransistor has to be recorded. The measured noise in the dark current shows a strong $1/f$ component. Measured at a frequency of 1 Hz, this leads to a S_n of $3.48 \times 10^{-26} \text{ A}^2/\text{Hz}$. $V_{\text{DS}} = -1 \text{ V}$, $V_{\text{GS}} = 5 \text{ V}$. The noise level of the $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ photodetector is comparable to that of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ photodetector, indicating good interfacial bonding quality at the $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ interface.

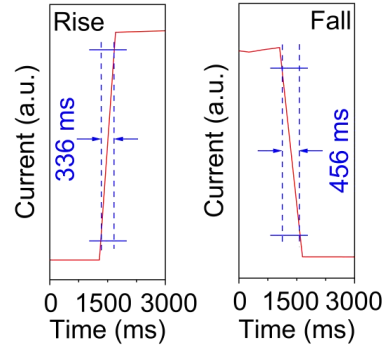


Figure S8. Time-resolved photoresponse of the $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ photodetector. The rise time (τ_r) and fall time (τ_f) are defined as the time required to switch between 10% and 90% of the maximum photocurrent.

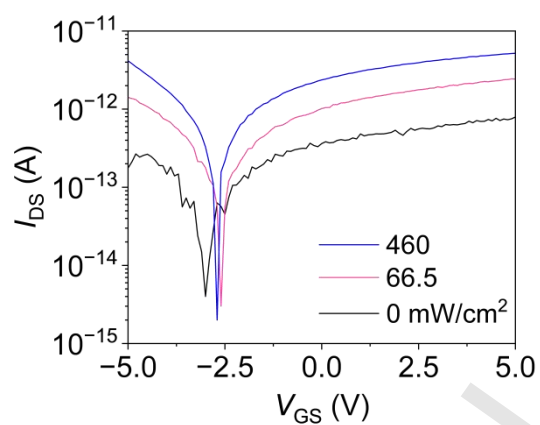


Figure S9. Photoresponse of the $\text{Cs}_3\text{Bi}_2\text{I}_9$ transistor under 405 nm laser illumination at various power densities. Due to the intrinsically low carrier mobility of $\text{Cs}_3\text{Bi}_2\text{I}_9$, the $\text{Cs}_3\text{Bi}_2\text{I}_9$ thin film exhibits non-conductive behavior. Measurements were carried out at $V_{\text{DS}} = -1$ V and $\lambda = 405$ nm.

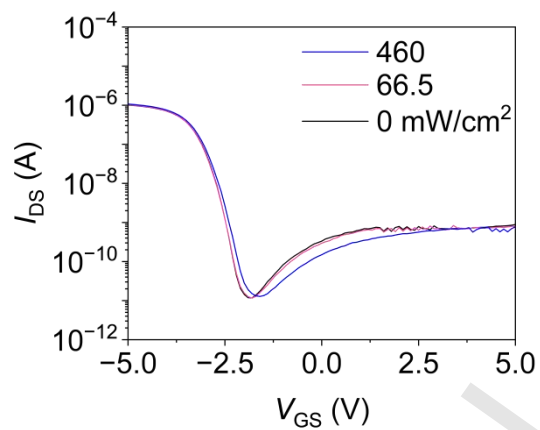


Figure S10. Photoresponse of the CNTs transistor under 405 nm laser illumination at various power densities. The I_{DS} - V_{GS} characteristics of the CNTs transistor exhibit typical electrical behavior; however, it shows negligible photoresponse under 405 nm laser illumination with a power density of 460 mW/cm².

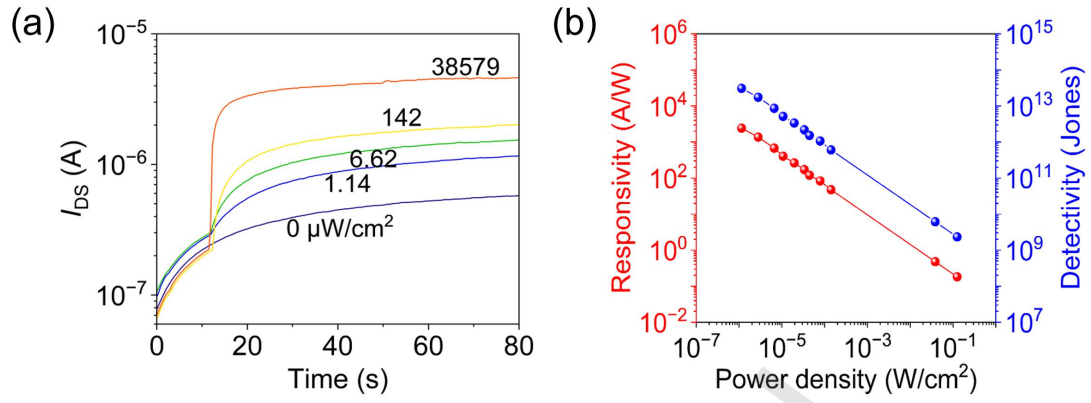


Figure S11. Optoelectronic performance using a light with a wavelength of 516 nm. (a) I_{DS} - T curves of the device under 516 nm monochromatic illumination with different power densities at $V_{DS} = -1$ V and $V_{GS} = 5$ V. (b) Dependence of the responsivity (R) and the detectivity (D^*) on light power density (P). $R = 2.41 \times 10^3$ A/W, $D^* = 3.07 \times 10^{13}$ Jones at $P = 1.15 \mu\text{W}/\text{cm}^2$.

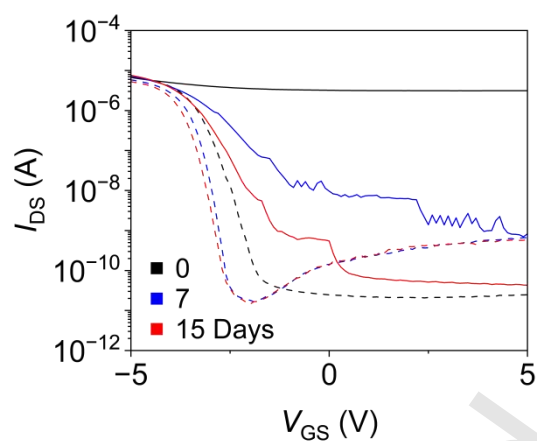


Figure S12. Long-term stability test of the $\text{Cs}_3\text{Bi}_2\text{I}_9/\text{CNTs}$ photodetector. Comparison of dark current (dashed lines) and current under 405 nm illumination at 460 mW/cm^2 (solid lines) of unpackaged devices after being stored in an environment with 30% humidity and 25°C for 0, 7, and 15 days.

Table S3. Performance comparison of Cs₃Bi₂I₉-based photodetectors.

Category	Device structure	Responsivity (R , A/W)	Detectivity (D^* , Jones)	Response time (τ_r/τ_d)	Ref.
Film	Au/Cs ₃ Bi ₂ I ₉ /CNTs/Au	1.44×10^5	1.60×10^{16}	336 /456 ms	This work
	Ag/Cs ₃ Bi ₂ I ₉ /FTO	3.80×10^{-3}	1.60×10^{12}	63 /90 ms	[1]
	ITO/SnO _x /MA ₃ Bi ₂ I ₉ /Spiro-O MeTAD/Au	2.80×10^{-1}	8.80×10^{12}	380 /450 ms	[2]
	Au/CsPbBr ₃ -QDs/CNTs/Au	5.10×10^7	2.00×10^{16}	3.3 /1.1 ms	[3]
	ITO/SnO ₂ /CsSnI ₃ /C	2.40×10^{-1}	1.18×10^{12}	0.23 /1.19 ms	[4]
	Au/Cs ₃ Cu ₂ I ₅ /PEDOT:PSS/ITO /PET	1.70×10^{-1}	1.00×10^{13}	0.18 /0.19 ms	[5]
	Ag/FTO/Cs ₃ Bi ₂ I ₉ /C-Ag	5.0×10^{-6}	5.93×10^8	1.52 /2.29 s	[6]
	Au/Cs ₃ Bi ₂ I ₉ /ZnO/FTO	3.30×10^{-2}	1.07×10^{10}	220 /270 ms	[7]
	Au/Copper phthalocyanine/Cs ₃ Bi ₂ I ₉ /Au	1.96	6.99×10^{11}	3 /7 ms	[8]
	FTO/ZnO/Cs ₃ Bi ₂ I ₉ /C	1.05×10^{-2}	7.68×10^{10}	0.9 /1 ms	[9]
	Si/Cs ₃ Bi ₂ I ₉ /Au	1.97×10^{-4}	9.00×10^{11}	-	[10]
	FTO/CdS/Cs ₃ Bi ₂ I ₉ :Bi ₂ S ₃ /C-Ag	5.90×10^{-4}	8.18×10^9	-	[11]
	ITO/CuO _x /Cs ₃ Bi ₂ Br ₉ / PC61BM/BCP/Ag	8.00×10^{-4}	2.95×10^{10}	0.274 /1.01 ms	[12]
	ITO/PEDOT: PSS/Cs ₃ Bi ₂ I ₉ /Ag	3.29	6.49×10^{10}	13 /21 ms	[13]
Single crystal	Au/CsPbBr _{3-x} I _x /Graphene/Au	1.00×10^8	2.40×10^{16}	0.81 /3.65 s	[14]
	Au/MAPbI _{3-x} Cl _x /Graphene/Au	5.60×10^8	2.80×10^{16}	20 /445 μ s	[15]
	Au/Cs ₃ Bi ₂ I ₉ /Au	1.10	4.70×10^{12}	9.6 /10.4 s	[16]
	Ag/Cs ₃ Bi ₂ Cl ₉ /Ag	1.70×10^{-2}	6.63×10^{11}	-	[17]
	Au/Cs ₃ Bi ₂ I ₉ /Au	3.15×10^{-3}	8.70×10^8	-	[18]
	Si/Cs ₃ Bi ₂ I ₉ /Graphene	23.60	1.75×10^{13}	31 /34 μ s	[19]
	Ag/CsCu ₂ I ₃ /CuI/Ag	1.20	4.96×10^{10}	119 /287 ms	[20]

Nano plate	ITO/Cs ₃ Bi ₂ I ₉ /ITO	3.31×10^{-2}	1.00×10^{10}	10.2 /37.2 ms	[21]
	Graphene/Cs ₃ Bi ₂ I ₉	1.38×10^{-2}	5.24×10^{11}	11.6 /14.9 ms	[22]
	Au/Cs ₂ AgBiBr ₆ /Au	54.60	7.40×10^{14}	1.7 /1.7 ms	[23]
	Mxene/Cs ₃ Bi ₂ I ₉ /MXene	6.45	9.45×10^{11}	0.27 /2.32 ms	[24]
	FTO/Al-doped ZnO/Cs ₃ Bi ₂ I ₉ /poly 3-hexylthiophene 2,5-diyl(P3HT)/C	2.90×10^{-2}	2.20×10^{13}	90 /140 ms	[25]
	FTO/NiO _x /Cs ₃ Bi ₂ I ₉ /PCBM/Ag	4.74×10^{-2}	2.47×10^{11}	0.86 /2.21 ms	[26]
	Au/Cs ₃ Bi ₂ I ₉ /TiO ₂	1.10	1.96×10^{11}	0.2 /0.4 s	[27]

Table S4. Performance comparison of Cs₃Bi₂I₉ based X-ray detectors.

Category	Device structure	Bias voltage (V)	Dose rate ($\mu\text{Gy}_{\text{air}}/\text{s}$)	Sensitivity (S , $\mu\text{C}/(\text{Gy}_{\text{air}} \cdot \text{cm}^2)$)	Ref.
Film	Au/Cs ₃ Bi ₂ I ₉ /CNTs/Au	1	57.36	3.49×10^3	This work
	Au/Cs ₃ Bi ₂ I ₉ /Au	80	2900	1.10×10^4	[28]
	Au/Cs ₂ AgBiBr ₆ /Au	5	937.7	1.80×10^4	[29]
	FTO/TiO ₂ /SnO ₂ /Cs ₃ Bi ₂ I ₉ /Au	6	799	1.27×10^2	[30]
Single crystal	ITO/MAPbBr ₃ /C60/BCP/Au	1	9.5	2.10×10^4	[31]
	Au/Cs ₃ Bi ₂ I ₉ SC/Au	90	829.2	1.12×10^2	[32]
	Ag/(NH ₄) ₃ Bi ₂ I ₉ /Ag	10	0.41	8.20×10^3	[33]
	Au/Cs ₃ Bi ₂ I ₉ SC/Au	60	36.2	1.65×10^3	[34]
	Au/Cs ₃ Bi ₂ I ₉ SC/Au	156	11.5	9.64×10^2	[16]
	Au/Cs ₃ Bi ₂ I ₉ SC/Au	40	270	4.38×10^3	[35]
	Au/Cs ₃ Bi ₂ I ₉ SC/Mxene/Au	-	11.5	3.68×10^2	[36]
	Au/Cs ₃ Bi ₂ I ₉ SC/Au	150	395.12	5.95×10^4	[37]
	Au/Cs ₃ Bi ₂ I ₉ SC/Au	40	395.12	2.31×10^4	[38]
	Au/Cs ₃ Bi ₂ I ₉ SC/Au	40	34.85	1.74×10^2	[39]
	Au/Cs ₃ Bi ₂ I ₉ SC/Au	100	217	9.30×10^1	[40]
Poly-crystal	Au/MA ₃ Bi ₂ I ₉ /Au	-	70	5.63×10^2	[41]
	Au/Cs ₃ Bi ₂ I ₉ /Au	40	14.6	2.30×10^2	[42]

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