New Lead-free Organic—Inorganic Hybrid Semiconductor Single Crystals for a UV—Vis—NIR Broadband Photodetector

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1. INTRODUCTION

Organic—inorganic hybrid semiconductor (OIHS) materials have demonstrated remarkable potential for numerous fields such as energy, solid-state lasers, resistive switching, and highly sensitive photodetectors. This is due to the synergy of desirable properties of both organic and inorganic components within a single molecular scale composite such as high intrinsic carrier mobility and broadband absorption of inorganic component, as well as tunable properties, excellent mechanical reliance, and easy processing of the organic materials. The unique properties and advantages of OIHS enable their prospects in several applications, particularly, they possess remarkable potential to realize the photodetectors capable of detecting a broad spectral range from ultraviolet (UV) to near infrared (NIR) regions. Hence, their potential in optoelectronic applications is highly demanded to be explored.

Currently, organic—inorganic hybrid perovskite materials, as one of the most glaring OIHS materials, have superior photovoltaic properties such as tunable band gap, longer carrier lifetime, and high carrier mobility, showing great potential in photovoltaics, light-emitting, photodetection, memory, lasing, and high energy detection. For instance, perovskite-based photodetectors have demonstrated excellent performance, such as their optimal photoresponsivity exceeds $10^9$ A/W, the detectivity is over $10^{16}$ Jones, and the response time reaches the nanosecond level. However, the environmental toxicity of crucial element lead (Pb) of the perovskite severely limits their commercialization. To overcome this issue, tin (Sn) and bismuth (Bi) have been explored to replace Pb, due to the similar electronic structures and comparable ionic radius with that of Pb. However, Bi-based perovskite materials have a relatively wide band gap, such as Cs$_2$AgBiBr$_6$ (2.1 eV) and (NH$_4$)$_2$BiI$_6$ (2.04 eV), which are not suitable for fabricating NIR light photodetectors. Whereas, despite the narrow band gap ($\sim$1.3 eV) of Sn-based perovskites that contributes to achieving a broadband spectral response, the high-lying 5s
orbitals of Sn$^{2+}$ in tin-based perovskites are known to easily undergo oxidation even in the presence of trace amounts of oxygen, raising a significant barrier against the viability of these materials.\textsuperscript{22} For example, the MASnI$_3$ film photodetectors gain zero photocurrent only 30 min after device fabrication in the air with 70% humidity at 26 °C.\textsuperscript{28} Nevertheless, another important aspect is to realize devices capable of detecting the ultraviolet–visible–near infrared (UV–vis–NIR) spectral range, which is highly desired for a variety of applications, for instance broadband photodetectors are critical for a variety of applications including biomedical imaging, communications, environmental monitoring, remote control, and so forth.\textsuperscript{29–32}

However, separate materials are required for different subbands within the UV (GaN) to the visible (Si) and NIR (InGaAs) wavelength ranges in the industry.\textsuperscript{33} Although, the heterojunction structures\textsuperscript{34} and doping methods\textsuperscript{29} broadened the absorption range, which are often employed in the development of broadband photodetectors. Nevertheless, these methods need the assembly of two materials by a complex and tedious fabrication process, which vastly impedes their practical applications. Therefore, using a single material capable of detecting the UV–vis–NIR spectral range is greatly demanded for low-cost and practical UV–vis–NIR broadband photodetectors. Moreover, a high-performance photodetector usually exhibits high detectivity, short response time, and good stability at room temperature. Semiconductor single crystals with higher phase purity, fewer grain boundaries, and defects are more desirable than polycrystalline films for high-performance photodetectors.\textsuperscript{35} In this context, a novel OIHS single crystal with a narrow band gap, non-toxic element, and great stability can circumvent the above-mentioned issues due to synergy of both the organic and the inorganic desirable properties and enables the development of high-performance UV–vis–NIR broadband photodetectors.

Figure 1. [Ga(C$_6$H$_5$-NO)$_3$](I$_3$)$_3$ single crystal growth. (a) Procedure for single crystal growth. (b) Photograph of [Ga(C$_6$H$_5$-NO)$_3$](I$_3$)$_3$ single crystal. (c) The frequency-dependent capacitance curve for the [Ga(C$_6$H$_5$-NO)$_3$](I$_3$)$_3$ single crystal. (d) Dark I–V response of a [Ga(C$_6$H$_5$-NO)$_3$](I$_3$)$_3$ single crystal.

Herein, to the best of our knowledge for the first time, a novel non-toxic millimeter-sized OIHS Ga-based single-crystal [Ga(C$_6$H$_5$-NO)$_3$](I$_3$)$_3$ is grown by using the room-temperature liquid diffused separation (LDS) method.\textsuperscript{34} The novel OIHS single crystal [Ga(C$_6$H$_5$-NO)$_3$](I$_3$)$_3$ exhibiting a quasi-zero-dimensional structure of crystal structure has a considerably narrow band gap (1.32 eV), which enables UV–vis–NIR broadband photodetection. This single crystal has been employed to develop a UV–vis–NIR broadband photodetector and the corresponding device has been systematically studied by varying wavelengths and intensity of incident light. It showed a broadband response range from UV to NIR (325–1064 nm) and fast response time ($t_{rise}/t_{decay} = 3.8$ ms/5.4 ms). This performance was upheld even after 130 cycles and 41 h of air storage, which indicates its promising operational stability plus tremendous reproducibility. Such a great photodetection performance can be ascribed to a narrow band gap and good crystalline quality of [Ga(C$_6$H$_5$-NO)$_3$](I$_3$)$_3$ single crystals plus inherent attributes of OIHS materials, which highlight its potential to develop low-cost, non-toxic, stable, and fast speed broadband photodetectors.

2. RESULTS AND DISCUSSION

2.1. Growth of [Ga(C$_6$H$_5$-NO)$_3$](I$_3$)$_3$ Single Crystals. The high-quality [Ga(C$_6$H$_5$-NO)$_3$](I$_3$)$_3$ single crystals were grown by the room-temperature LDS-induced crystallization method that has been previously reported to grow high-quality perovskite single crystals.\textsuperscript{34} Figure 1a,b illustrates the growth process and the photograph of [Ga(C$_6$H$_5$-NO)$_3$](I$_3$)$_3$ single crystal, respectively. The detailed procedure has been presented in the Experimental Section. The change of color from transparent to red probably indicates the coordinate bond between dissociative Ga$^{33+}$ ions and O atoms in DMF.
molecules and the formation of I$_3^-$ ions by isolated iodide in the precursor.$^{35-38}$ This led to the formation of well-shaped and high-quality black single crystals of [Ga(C$_3$H$_7$NO)$_6$](I$_3$)$_3$. The dimensions of this large single crystal are measured to be about 7 mm in length, 6 mm in width, and 0.6 mm in height.

To demonstrate the high quality of this crystal, trap state density of the [Ga(C$_3$H$_7$NO)$_6$](I$_3$)$_3$ single crystal was measured. First, the dielectric constants ($\varepsilon$) from the capacitance–frequency measurement (between 1 Hz and 8 MHz) were estimated, as shown in Figure 1c. The relative dielectric constant $\varepsilon = 105$ of the single crystal is calculated by eq 1:

$$\varepsilon = \frac{cd}{\varepsilon_0 A}$$

where $c$ is the measured capacitance, $d$ is the thickness of the single crystal, $A$ is the surface area, and $\varepsilon_0$ is the permittivity constant ($8.85 \times 10^{-14}$ F/cm). Moreover, the size of [Ga(C$_3$H$_7$NO)$_6$](I$_3$)$_3$ single crystal is measured to be $d = 0.06$ mm and $A = 3.1$ mm $\times$ 1.57 mm. The trap state density ($n_{trap}$) of [Ga(C$_3$H$_7$NO)$_6$](I$_3$)$_3$ single crystal was measured using the dark current–voltage ($I$–$V$) measurement for a hole-only device (Figure 1d inset). The dark $I$–$V$ curve is shown in Figure 1d. There are three regions in the $I$–$V$ curve: ohmic, trap-filled limit (TFL), and child, respectively. As the applied voltage exceeds the first kink point voltage, the current exhibits a fast nonlinear increase ($n > 3$), showing all trap states are filled by the injected carriers. The bias voltage at the first kink point is defined as the TFL voltage ($V_{TFL}$), which is

Figure 2. Structural characterization of [Ga(C$_3$H$_7$NO)$_6$](I$_3$)$_3$ single crystal. (a,b) Ball-and-stick diagrams of crystal structures and their [GaO$_6$]$^{3+}$ octahedral structure units in the [Ga(C$_3$H$_7$NO)$_6$](I$_3$)$_3$ single crystal, respectively. (c) Experimental and calculated XRD spectra of [Ga(C$_3$H$_7$NO)$_6$](I$_3$)$_3$. (The wavelength of X-ray: 0.043 nm).

Figure 3. Optical characterizations and DFT calculations. (a) Absorption and transmittance spectra of a [Ga(C$_3$H$_7$NO)$_6$](I$_3$)$_3$ single crystal. (b) Tauc plot with band gap calculated. (c) Band structures of [Ga(C$_3$H$_7$NO)$_6$](I$_3$)$_3$. (d) PDOSs indicating Ga, I, C, N, O, and H orbitals.
2.2. Structural Characterization of [Ga(C₃H₇NO)₆](I₃)₃

Single Crystal. The crystal structure of [Ga(C₃H₇NO)₆](I₃)₃ was determined and refined using single-crystal X-ray crystallography. Figure S1a shows the diffraction pattern of [Ga(C₃H₇NO)₆](I₃)₃ single crystal [ε = 105]. The n_{trap} of [Ga(C₃H₇NO)₆](I₃)₃ single crystal is 5.48 × 10⁻¹⁵ cm⁻³, which is lower than Si and CdTe traditional semiconductors.

2.3. Optical Properties and Density Functional Theory Calculations. For a better understanding the optical properties of [Ga(C₃H₇NO)₆](I₃)₃ single crystal, the absorption spectrum of this material has been recorded between 300 and 1080 nm. Figure 3a reveals that this material has a wide (UV–vis–NIR) absorption range at room temperature. Moreover, [Ga(C₃H₇NO)₆](I₃)₃ shows the characteristics of a quasi-zero-dimensional structure.
an indirect band gap semiconductor owing to a shallow absorption region between 800 and 1080 nm. The homologous Tauc plot, assuming an indirect allowed transition, is demonstrated in Figure 3b. The linear region of the plot shows the expected phonon-assisted processes, with transitions at 1.15 and 1.48 eV occurring with absorption and emission of a phonon. Moreover, the band gap has been estimated to be 1.32 eV (representative phonon energy = 0.165 eV), which is far smaller than that of the Bi-based halide perovskites reported in the literature (around 2.0 eV). As a result, this [Ga(C₃H₇NO)₆]I₃ single crystal possesses great potential for UV–vis–NIR broadband photodetection. To further inquire the electronic origin of optoelectronic properties of hybrid [Ga(C₃H₇NO)₆]I₃, the electronic band structure and partial density of states (PDOS) were estimated by the Ab initio density functional theory (DFT) calculations. Because the conduction band minimum (CBM) and the valence band maximum (VBM) are not localized at the same k-vector in the Brillouin zone, DFT results depicted in Figure 3c indicate that [Ga(C₃H₇NO)₆]I₃ is an indirect semiconductor with a 1.26 eV band gap, which is near the experimental data (1.32 eV). In addition, from the $E(k)$ curves of the band edges in Figure 3c, the effective mass of carriers can be expressed as

![Figure 5](https://example.com/figure5.png)

**Figure 5.** Photodetector with fast response and stability. (a,b) Time-dependent photoresponse at a voltage of 1 V under a 830 nm laser. (c,d) On–off photoresponse under 473 nm at 1 V bias voltage. (e) Long-term storage stability test of a single-crystal-based photodetector in N₂ and air (RH: 30%) environments. (f) Photostability measured under 633 nm of 600 μW after storing for about 144 h.
The rise time is defined as the time that is required to increase the current at 10% from 0 to 90% of its final value, and is important in ultrafast optical communication, image pixel readout, or for other ultrafast applications. The rise time is one of the key parameters to determine the response efficiency of the photodetector to incident light. The representative equations to calculate the detectivity ($D^*$) and the responsivity ($R$) of the photodetector as a broadband device.

$$m = \frac{\hbar}{dE}$$

where $\hbar$ is the reduced Planck constant and $m$ is the effective mass of carriers. This material has a larger effective mass of carriers, leading to low carrier mobility, which is consistent with its quasi-zero-dimensional structure. The contributions from all atomic orbitals to the band structures of [Ga(C$_2$H$_3$NO)$_6$]$\text{(I)}_3$ and the PDOS of every I atom orbital are shown in Figure 3d. The data manifests that I-p orbital significantly contributes to the VBM and CBM, which implies that I$^-$ ions are the main origin of the material’s semi-conducting characteristics.

### 2.4. Performance Evaluation of Single-Crystal Photodetector

The high crystallinity and narrow band gap of the [Ga(C$_2$H$_3$NO)$_6$]$\text{(I)}_3$ single crystal indicate its potential for a broadband photodetector. Hence, a photoconductive-type photodetector was fabricated on [Ga(C$_2$H$_3$NO)$_6$]$\text{(I)}_3$ single crystals and corresponding performance has been evaluated. While the UPS and absorption spectra plus Tauc plots of the corresponding [Ga(C$_2$H$_3$NO)$_6$]$\text{(I)}_3$ film fabricated by dissolving the single crystals in the DMF solution have been shown in Figure S3. In addition, Figure S3e also shows a schematic energy level diagram of the photodetector. $E_{VAC}$ denotes the vacuum energy level. The data have been explained in Note 1 of the Supporting Information. To investigate effective photoresponse spectrum of photodetectors, current–voltage ($I-V$) measurements under the visible to NIR illumination range were carried out. The photoelectric performance has been evaluated in the dark as well as at different power intensities and wavelengths. The $I-V$ curves for visible regions are presented in Figures 4a and S4a,b for $\lambda = 473, 514,$ and $633$ nm, respectively. While the UV region has been recorded at $\lambda = 325$ nm, as shown in Figure S5. Moreover, the $I-V$ and $I-T$ curves for NIR are presented in Figures 4b and S4c,d for $\lambda = 830, 940,$ and 1064 nm, respectively. For all the curves, high current has been recorded under light (photocurrent) as compared to the dark current under the UV–vis–NIR range. The standard linear characteristic of the curves under different illumination powers clearly indicates the existence of a strong Ohmic contact that enables an efficient electronic transport path between Au electrodes and [Ga(C$_2$H$_3$NO)$_6$]$\text{(I)}_3$ single crystals. Importantly, the photodetector exhibited a broadband photoelectric response from UV (325 nm) to NIR (1064 nm), which is well consistent with the absorption spectrum of the [Ga(C$_2$H$_3$NO)$_6$]$\text{(I)}_3$ single crystals. These results prove the remarkable potential of the [Ga(C$_2$H$_3$NO)$_6$]$\text{(I)}_3$-based photodetector as a broadband device.

To further investigate the performances of the [Ga(C$_2$H$_3$NO)$_6$]$\text{(I)}_3$ photodetector, photoresponsivity ($R$), and detectivity ($D^*$) were also calculated, which actually indicate the response efficiency of the photodetector to incident light. The representative equations to calculate $R$ and $D^*$ are described in the Supporting Information. Figure 4c shows the $R_i$ for photodetectors based on single crystals as a function of the light intensity ranging from 2.2 to 220 $\mu$W at 473 nm under a 10 V bias voltage. It is found that $R_i$ increases linearly as the light power decreases, which is consistent with the photogating mechanism implying that high light intensity leads to more carrier recombination.

Thus, the maximum values of $R_i$ and $D^*$ can reach 0.23 mA/W and 3.5 $\times$ 10$^7$ Jones, respectively, at the lowest irradiance power of 2.2 $\mu$W. The specific spectral photoresponsivity of the crystal-based photodetector ($R_i$) at different wavelengths ranging from 473 to 1064 nm are shown in Figure 4d. The power density and bias voltage are 13 $\mu$W and 1 V, respectively. Similar to the absorption spectrum, the photoresponsivity decreases by increasing wavelength values. While, $R_i$ sharply declined from 830 to 1064 nm, which could be attributed to a smaller absorption coefficient than the UV–vis range in the absorption spectrum.

The response time ($\tau$), which includes the rise and decay times, is one of the key parameters to determine the performance and capability of a photodetector. Particularly, it is important in ultrafast optical communication, image pixel identification, rapid imaging, and dynamic monitoring. The rise time is defined as the time that is required to increase from 10 to 90% of maximum photocurrent, and the decay time is the time that is required to decrease from 90 to 10% of
maximum photocurrent. In this context, the response time of the crystal-based detector was investigated under a light wavelength of 830 nm at 1 V bias voltage, as shown in Figure 5a,b. The detector showed rapid response time with a rise time of 3.8 ms and a decay time of 5.4 ms for NIR light, which is faster than many reported photodetectors based on organic—inorganic hybrid halide perovskites, organic photodetectors, and nanocrystal-based photodetectors and even comparable with some inorganic detectors. For example, (n-butylammonium)PbI$_2$ and FAPbI$_3$ single-crystal photodetectors showed 28 and 17 ms response time, respectively. Table 1 summarizes the photoelectric performances of typical photodetectors based on some recent perovskite-based photodetectors and comparatively, the current [Ga(C$_3$H$_7$-NO)$_3$]$_3$ single-crystal photodetector demonstrated a much faster response time than Sn-based photodetectors. In general, the response time is related to efficient charge transport. Hence, the fast response time of devices is probably attributed to the single crystal with low defects, which improves the charge transport. Thus, [Ga(C$_3$H$_7$-NO)$_3$]$_3$ single-crystal photodetector with a fast response time is a very promising candidate to realize a broader application scope.

Additionally, the reproducible response to light illumination and long-term stability are crucial to practical photodetectors. As shown in Figure 5c, the photoresponse curves of the fresh crystal-based photocolector were measured under periodic illumination of a light source at $\lambda$ = 473 nm and at 1 V bias voltage. The photocurrent had sharply increased under light illumination and had fallen rapidly in the dark. Moreover, under different irradiation intensities, [Ga(C$_3$H$_7$-NO)$_3$]$_3$ photodetector exhibited excellent repeatability and stability during the on–off switching cycles. The operational stability of the devices was further evaluated by increasing the number of on–off switching cycles to 24 at the first instance and then prolonged to even 130 cycles, as depicted in Figures 5d and 5e. The decay in the on–off switching was insignificant, which indicates the high reproducibility and operational stability of the fabricated photodetector. The devices were further tested for their storage stability and the photoresponse was recorded in regular intervals for 144 and 41 h in a N$_2$ glovebox and air environment (relative humidity: 30%) without any encapsulation, respectively, as shown in Figure 5e. The device showed no significant degradation in the first 96 h and retained 60% of initial photoresponse even after 144 h of N$_2$ storage and retained 40% of initial photoresponse even after 25 h in the air environment (RH: 30%). In addition, the response speed of the detector almost maintained the initial values even after 144 h, as shown in Figure S7. Moreover, the device was tested for the photostability after being stored in the N$_2$ glovebox and air environment (RH: 30%), as shown in Figures Sf and S8. Pleasantly, it showed profound photostability (almost no degradation) under constant illumination for 70 s after storing for about 144 h and in the N$_2$ glovebox at a power of 600 $\mu$W and 0.1 V bias voltage. Moreover, it showed excellent photostability for 200 s measured under 633 nm of 600 $\mu$W after storing in air (RH 30%) for 41 h. It has been observed that when the [Ga(C$_3$H$_7$-NO)$_3$]$_3$ single crystal was stored for long time, its surface had changed from black to pale yellow. On account of Ga$_3^+$ powders being pale yellow, it was deduced that the weak coordination bond between C$_3$H$_7$-NO and Ga$^+$ and the easy volatility of the organic group led to the material degradation. The excellent reproducibility, storage, and photostability are probably ascribed to the fact that this single crystal has very few defects and is free from grain boundaries (Figure S9), which contributes to the structural stability of materials. Such results obviously indicate the superior stability of this innovative single crystal than the conventional Sn-based perovskites.

In comparison with some conventional perovskite photodetectors with a similar device structure, as listed in Table 1, [Ga(C$_3$H$_7$-NO)$_3$]$_3$ detector exhibits obvious advantages including a broadband response, fast response time, and great stability, raising greater potential in relevant applications compared to those reported in the literature.

3. CONCLUSIONS

In summary, a Pb-free OIHS [Ga(C$_3$H$_7$-NO)$_3$]$_3$ single crystal, with high crystalline quality, regular shape, and millimeter size, was successfully grown for the first time through a simple room-temperature LDS method in the ambient environment. A quasi-zero-dimensional crystal structure based on the [GaO$_6$] octahedron and I$_3^-$ chains was revealed by single-crystal XRD. The optical properties of the single crystal were investigated by the experiment and further elucidated by DFT calculations. The narrow band gap (1.32 eV) of this semiconductor single crystal makes it an attractive candidate for UV–vis–NIR broadband photodetection. Thus, the photoelectric performances of the [Ga(C$_3$H$_7$-NO)$_3$]$_3$ single-crystal photodetector was also evaluated. More importantly, the [Ga(C$_3$H$_7$-NO)$_3$]$_3$ single-crystal photodetector exhibited stable and fast UV–vis–NIR broadband photoresponse ranging from 325 to 1064 nm, excellent reproducible response (130 cycles) and air storage stability (41 h), as well as fast response time ($t_{\text{rise}}$ = 3.8 ms, $t_{\text{decay}}$ = 5.4 ms, at 830 nm and 1 V bias voltage), exceeding the most common Sn-based perovskite photodetectors. Additionally, this device has a responsivity of 0.23 mA/W and a detectivity of 3.5 $\times$ 10$^7$ Jones. These results open up broad opportunities and can inspire future evolution of this innovative organic–inorganic hybrid [Ga(C$_3$H$_7$-NO)$_3$]$_3$ single crystals for low-cost, non-toxic, stable, and fast speed UV–vis–NIR broadband photodetectors.

4. EXPERIMENTAL SECTION

4.1. Chemicals and Regents. Gallium iodide (GaI$_3$, 99.9% purity), methylammonium iodide (MAI, 99.9% purity), and N,N-dimethylformamide (DMF, 99.5%) were purchased from Sigma-Aldrich. All the chemicals were used as received without further purification.

4.2. Crystallization of [Ga(C$_3$H$_7$-NO)$_3$]$_3$ Single Crystals. A stock solution of 0.5 M precursor was prepared by dissolving GaI$_3$ and MAI in 500 $\mu$L DMF and stirred overnight at room temperature to ensure complete dissolution. The next day, the fully dissolved precursor was filtered and a small amount of silicone oil was added to the liquid level of the precursor. Owing to the density value of silicone oil is between that of the solvent and precursor, the solvent in the precursor diffused into silicone oil and then appeared over its surface, which led to increasing the concentration of precursors beneath the silicone oil. The precursor was then placed in the air for 3 weeks at room temperature. Oversaturation that was identified by its temperature and concentration led to the formation of small seed single crystals. This seed crystal gradually grew up with time; however, no other crystal nuclei appeared during that time. The little seed crystal gradually became larger as a function of time and eventually transformed into a large single crystal of outstanding quality. During the whole process of the single-crystal growth, the precursor should
remain stationary. Failure to ensure a stationary precursor can lead to growth of irregular crystals with stacking of many small single crystals.

4.3. XRD Analysis. Single-crystal X-ray crystallography. A suitable crystal was chosen to perform the data collection. Single-crystal XRD measurements were performed on a Bruker D8QUEST diffractometer equipped with Mo Kα radiation. The diffraction data were collected at room temperature by the ω- and θ-φ scan methods. The crystal structure was determined and refined using the APEX3 program. Absorption corrections were performed using the multi-scan method (SADABS). The powder XRD dates were collected by a RIGAKU DMAX-3A diffractometer.

4.4. Absorption and Transmission. The absorption and transmission spectra were measured using an F20-UV thin-film analyzer (FILMETRICS) at a wavelength range between 300 and 1100 nm. Tauc plots of the absorption spectra to determine the type of band gap for new materials are calculated from the absorption spectra.

4.5. Scanning Electron Microscopy. The top-view scanning electron microscopy (SEM) images of perovskite films were recorded by ZEISS Sigma HD SEM equipment.

4.6. DFT Analysis. The Ab initio method based on the DFT is performed for all the calculations with the Vienna ab initio simulation package. In structural relaxation and electronic band structure calculations, the Perdew–Burke–Ernzerhof version of the generalized gradient approximation is used to describe the exchange–correlation functional with a kinetic energy cutoff of 600 eV, and the projector-augmented-wave pseudopotential is used to describe the interaction between valence electrons and core charges. The K points in the Brillouin zone are sampled with the smallest k-mesh interval of 0.2 under the Monkhorst–Pack scheme. The convergence thresholds are set to $10^{-5}$ eV/Å for the Hellman–Feynman force convergence and $10^{-6}$ eV for electronic energy difference convergence.

4.7. Photodetection Fabrication and Measurement. An films were deposited as electrodes on the surface of $[\text{Ga}(_2\text{H}_5\text{NO})_3]_2(\text{I}_3)_6$ single crystal by using a copper screen mask in vacuum evaporation coating equipment (Shenyang Huiyu Co. Ltd., China) at a rate of 0.5 Å s$^{-1}$ ($2 \times 10^{-5}$ Pa). The dimensions of the square electrode are 420 × 420 μm and thickness is 80 μm, while the interelectrode spacing is determined to be 80 nm (the width of single-crystal conductive channel). The schematic illustration of the photodetector is shown in Figure 4b. In this study, lasers with different wavelengths (Raman spectrometer and Metatext corporation) were used as the light source with power varying from 2.2 to 600 μW for all photodetector tests. The effective illumination area for the detector is around 0.005 mm$^2$. The $I$–$V$ curves of a $[\text{Ga}(_2\text{H}_5\text{NO})_3]_2(\text{I}_3)_6$ single crystal photodetector were obtained using a semiconductor parameter analyzer (B1500A, Agilent Technologies). Notably, all photoelectric measurements were carried out in ambient air with a temperature of 20–23 °C and a relative humidity level of about 30%.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.2c08116.

Crystallographic structural data of $\text{C}_18\text{H}_{26}\text{GaI}_5\text{N}_9\text{O}_8$ (CIF)

Single-crystal XRD data, XRD scans, UPS spectra, Tauc plots, absorption spectrum, current-voltage and current-time curves, SEM image, and crystal data and details of the structure refinements (PDF)

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Y.Z., F.L., and X.C. conceived the idea and designed the experimental protocols. F.L. performed the device fabrication and characterization, analyzed the data, and wrote the original draft under K.L. help. K.B., X.L., and J.W. provided the structure data acquisition of single crystals. S.W., X.W., H.S., and J.W. conducted the NIR photodetection measurements. X.L., Y.P., Y.C., J.Z., and Z.Q. performed UV–vis photodetection measurements. S.R., F.B., A.Y., and K.L. participated in the discussion and manuscript editing. Y.Z. and A.Y. directed the whole research. All authors reviewed the manuscript.

Notes
The authors declare no competing financial interest.

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