Millimeter-Sized Single-Crystal CsPbBr$_3$/CuI Heterojunction for High-Performance Self-Powered Photodetector

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Supporting Information

ABSTRACT: Millimeter-sized CsPbBr$_3$ single crystals were prepared via a facile solvent-evaporation method in ambient environment. The heterojunction between p-type CuI and n-type CsPbBr$_3$ was formed by a simple immersion process. The as-integrated CsPbBr$_3$/CuI device exhibits a good rectifying behavior (ratio of 250 at ±2 V). In particular, the photodetector shows excellent self-powered characteristics under 540 nm light illumination, including high photocurrent (near 100 nA); high photosensitivity (on/off ratio of 1.5 × 10$^3$); fast response speed (0.04/2.96 ms); and good wavelength selectivity ($65$–$255$ nm), responsivity (1.4 mA W$^{-1}$), and detectivity ($6.2$ × $10^{10}$ Jones). This work provides a simple, low-cost, and effective method for preparing millimeter-level CsPbBr$_3$ single crystals. The simple device architecture further provides a promising approach for fabricating high-performance self-powered photodetectors.

Recently, metal halide perovskites have attracted growing attention in the field of optoelectronics because of their remarkable optical and electronic properties, including tunable direct band gap, high electron mobility, long electron–hole diffusion length, simple processing technique, and facile integration with various semiconductor materials.$^{1–8}$ These unique features allow such perovskite materials to be promising candidates for various optoelectronic devices, such as photovoltaics, luminescent devices, and photodetectors.$^{9–13}$ Particularly, photodetectors (PDs), as one of the most significant optoelectronic devices that can directly transform light illumination into an electrical signal, show a wide range of applications such as machine vision, surveillance, and imaging.$^{13–16}$ It is noteworthy to mention that the organic–inorganic hybrid perovskites are unstable and degenerate rapidly when they are exposed to air or heat. Among the various perovskites, CsPbBr$_3$, an inorganic perovskite, exhibits many advantages, such as a remarkable stability besides the superior features inherited from the hybrid perovskite structure, thereby drawing great attention in the field of photodetection.$^{17,18}$ The micrometer-level CsPbBr$_3$ crystals can be prepared by chemical vapor deposition.$^{19}$ Moreover, CsPbBr$_3$ single crystals with a well-defined structure possess a clear cutting band edge, reduced trap densities, and high carrier diffusion lengths, resulting in high-performance photodetectors.$^{20–22}$ Therefore, the preparation of large-size CsPbBr$_3$ single crystals is urgent for high-performance photodetectors.

Large-size perovskite crystals are critical for both fundamental properties and efficient photodetection. The CsPbBr$_3$ single crystals were usually prepared through a variety of solution-based methods, such as inversion temperature crystallization, antisolvent vapor-assisted crystallization, and seeded solution crystal growth,$^{22–25}$ which rely on high temperature, complex processes, and vacuum. Recently, Yang et al. developed a low-temperature, space-limited, and substrate-independent growth technique for millimeter-sized CsPbBr$_3$ monocrystalline films, which presents excellent stability and high photodetection performance.$^{26}$ Saidaminov et al. presented a rapid low-temperature and solution-based synthesis of millimeter-level CsPbBr$_3$ single crystals, and the device showed self-powered behavior with a high on/off ratio by sandwiching CsPbBr$_3$ between Au and Pt contacts.$^{27}$ These experiments still require complex experimental processes and external tools. Therefore, preparing large-size CsPbBr$_3$ single crystals via a simple and low-cost method is still in demand. Meanwhile, many composite photodetectors based on CsPbBr$_3$ (quantum dots, nanosheets, and polycrystalline films) such as CsPbBr$_3$/ZnO and CsPbBr$_3$/TiO$_2$ have been reported with enhanced performance.$^{28–32}$ However, the fabrication of composite devices based on large-size CsPbBr$_3$ single crystals is rarely noticed, and it is still worth researching to boost device performance and develop integrated features.

In recent years, copper-based compounds (CuO, CuS, CuI, and CuSCN) have attracted significant attention because of simple preparation technology and special physicochemical properties.$^{33–35}$ Owing to point defects (copper vacancies) in the crystals, these materials typically exhibit excellent p-type conductivities. Among them, CuI has a direct wide band gap of 3.1 eV, a high exciton binding energy (62 meV), a high hole mobility, a low resistivity, and the advantages of simple preparation and low cost. Thus, it has wide variety of applications in the field of optoelectronic devices, such as
light-emitting diodes, field effect transistors, and dye-sensitized solar cells.36−38 Yang et al. have reported bipolar diodes based on an epitaxial thin-film heterojunction of p-CuI/n-ZnO with a high rectification of $2 \times 10^9$ (±2 V) and a low saturation current density of $5 \times 10^{-9}$ A cm$^{-2}$.39 CuI is usually used as a hole injection layer and can be directly contacted with other semiconductor materials, while CsPbBr$_3$ has balanced electron–hole diffusion lengths and a high absorption coefficient over the visible region. However, there is very limited work on photodetectors based on CsPbBr$_3$/CuI, and exploring the device feasibility and special properties is worthwhile.

In this work, we synthesized millimeter-level CsPbBr$_3$ single crystals by a simple solution processing technique at a low temperature in ambient environment. The CsPbBr$_3$/CuI heterojunction was formed by a facile immersion and heating process. The as-fabricated CsPbBr$_3$/CuI device was examined to determine its photoelectric performances. It was found that the device demonstrates a good photodiode behavior. More importantly, the CsPbBr$_3$/CuI photodetector exhibits excellent self-powered characteristics at 540 nm light illumination. In addition, both CsPbBr$_3$ and CsPbBr$_3$/CuI devices present high performance at −3 V at 540 nm light illumination. This work provides a facile and low-cost method to fabricate high-performance, self-powered photodetectors based on CsPbBr$_3$ single crystals.

Millimeter-sized CsPbBr$_3$ single crystals were synthesized by direct evaporation of an equimolar CsBr/PbBr$_2$ solution (prepared in dimethyl sulfoxide) at a low temperature (40 °C) in ambient environment. A small amount of aqueous HI solution was added to promote crystal growth prior to the solvent evaporation. As shown in Figure 1a, the yellow CsPbBr$_3$ single crystals were obtained with the prolongation of heating time. Most crystals are cuboid in shape, ranging in length from 4 to 10 mm, with an average length of 6 mm and the longest length of up to 1.5 cm (Figure S1a). Some small CsPbBr$_3$ crystals are self-assembled into a big flower-like crystal. The crumbly CsPbBr$_3$ crystals were carefully cleaned and employed to construct devices. The fabrication of an individual CsPbBr$_3$/CuI heterojunction was achieved by dipping a part of a long CsPbBr$_3$ crystal into CuI acetonitrile solution for 1 min followed by heating at 60 °C for 10 min. The as-prepared millimeter-sized CsPbBr$_3$ single crystals provide a promising platform to integrate with other semiconductor materials for various devices. Figures 1b and S1b display the scanning electron microscopy (SEM) images of the CuI particles with different magnifications. The results show that the CuI particles are spheroidal with the diameter...
ranging from 50 to 150 nm. Moreover, some particles are aggregated together to form agglomerates, and a few nanoparticles are also formed, as shown in Figure S1b. The CsPbBr3 crystals and CuI nanoparticles are all prepared by a facile cost-effective method. Panels c and d of Figure 1 demonstrate the X-ray diffraction (XRD) patterns of the CsPbBr3 crystals and the CuI particles, respectively. As shown in Figure 1c, the diffraction peaks for the CsPbBr3 single crystal appearing at 15.2°, 21.5°, 30.5°, 30.8°, 38.0°, and 43.8° are assigned to (001), (010), (210), (002), (102), and (020) crystal planes of monoclinic cesium lead bromide (JCPDF No. 54-0571), respectively. All the peak positions of the CsPbBr3 crystal planes of monoclinic cesium lead bromide (JCPDF No. 54-0571) are indexed to the (001), (010), (210), (002), (102), and (020) crystal planes of monoclinic cesium lead bromide (JCPDF No. 54-0571), respectively. All these results demonstrate the X-ray diffraction (XRD) patterns of the CsPbBr3 and CuI nanoparticles are all prepared by a facile cost-effective method. As shown in Figure 1e,f, the band gaps of as-prepared CsPbBr3 crystals and CuI particles are estimated to be 2.23 and 3.0 eV, respectively, both of which are close to the theoretical values. The simplicity of our method will permit promising use of millimeter-sized CsPbBr3 single crystals for in-depth fundamental studies and a wide range of practical applications.

To enhance the optoelectronic performance of a large-size CsPbBr3 single crystal device and explore its self-powered characteristics, CuI was integrated with CsPbBr3 single crystals. Figure 2a shows the schematic illustration of the photodetectors based on an individual CsPbBr3/CuI composite. Part of the cuboid CsPbBr3 single crystal was covered with a CuI particle film to form a heterojunction, and the device was manually fabricated by using silver paste with a small area as the electrodes. The photoelectric properties of CsPbBr3/CuI devices were carefully studied using a two-probe method at room temperature. Figure 2b demonstrates the typical current–voltage (I–V) curves of the individual CsPbBr3/CuI heterojunction in a logarithmic plot in the dark and upon 540 nm light illumination. The dark current of the CsPbBr3/CuI device exhibits an on-state at the forward bias and an off-state at the reverse bias, which indicates the successful formation of heterojunction and reveals a typical photodiode behavior. The photodiode shows a high rectification ratio of 250 at ±2 V, similar to the transparent p-CuI/n-ZnO diode reported by Yang et al.39 The photocurrent could reach 4.5 μA under 540 nm light illumination (power density of 1.276 mW cm−2), which is much higher than the dark current under the reverse bias and slightly lower than the forward bias. More importantly, the remarkable difference between the dark-current and photocurrent at zero bias demonstrates the
symmetrical features, which indicate that the Schottky junction CuI devices under dark conditions and light illumination show mainly originates from the heterojunction between CsPbBr3/CuI device irradiated with 540 nm light at zero bias. In electric power supply and is a photovoltaic detector, because the built-in electric field can act as the driving force to separate the electron–hole pairs by the built-in electric field near the heterojunction. The photocurrent of the device can reach up to 100 nA at zero bias under 540 nm light illumination. The photosensitivity (defined as the ratio of photocurrent to dark current, Iph/Id) of the device is calculated to be 1.5 × 103. Furthermore, the accurate response time of the CsPbBr3/CuI device under zero voltage bias was recorded by a photoresponse measurement system, as shown in Figure S4. As the pulse laser (355 nm) irradiates the photodetectors with pulse duration of 3–5 ns, the loop current increases, leading to an increase of partial voltage on the series resistor. The partial voltage is measured in real-time by the oscilloscope. Figure 3b shows the normalized curve as a function of time. The rise time (the peak photocurrent rises from 10 to 90%) and the decay time (the peak photocurrent decays from 90 to 10%) are estimated to be 0.04 and 2.96 ms for an individual CsPbBr3/CuI device at zero bias, respectively. The high photocurrent, good repeatability, large on/off ratio, and fast speed of the self-powered CsPbBr3/CuI photodetector provide a promising route for developing future photodetectors based on CsPbBr3 single crystals.

The spectral responsivity (Rλ) and detectivity (D*) are also important parameters to evaluate the performance of self-powered photodetectors. The responsivity is defined as the photocurrent (Iph) per unit of irradiation power, indicating the sensitivity of a detector responding to incident light signals. The detectivity (D*, typically quoted in Jones) reflects the ability of a detector to detect weak signals from the noise environment. The noise current of a photodetector should comprise all noise sources, but only short noise current is normally considered in the estimation. The responsivity and the detectivity of a photodetector are defined by the following equations:

\[ R_\lambda = \frac{I_{ph} - I_d}{P_{IS}} \]  
\[ D^* = \frac{R_\lambda}{(2e\lambda/\gamma)^{1/2}} \]
where $\lambda$ is the irradiation light wavelength, $e$ the electronic charge, $I_{ph}$ the photocurrent, $I_d$ the dark current, $P_\lambda$ the light power density, and $S$ the effective area under light illumination (measured to be about 0.05 cm$^2$ in our experiment). The spectral responsivity and detectivity of the CsPbBr$_3$/CuI device with incident wavelength ranging from 700 to 300 nm at zero bias are shown in panels c and d of Figure 3, respectively. The maximum responsivity of the device is 1.4 mA W$^{-1}$ at the wavelength of 540 nm corresponding to the UV−vis absorption spectra of CsPbBr$_3$, which indicates that the device exhibits a high detecting responsivity to signals in the visible region. It is clear that the responsivity increases rapidly from 580 nm (0.1 mA W$^{-1}$) to 540 nm (1.4 mA W$^{-1}$) and then decreases dramatically at 520 nm (0.28 mA W$^{-1}$) in the range of 700−300 nm. As seen in Figure 3c, the sharp cutoff wavelengths defined as the ratio between the maximum and the natural constant ($e \approx 2.718$) appear at 565 and 525 nm, respectively. The detectivity ($D^*$) has a similar trend as that of the responsivity ($R_\lambda$) with a maximum value of 6.2 $\times$ 10$^{10}$ Jones (Figure 3d). The detectivity also shows a narrow detection band at around 540 nm and slowly drops from 500 to 300 nm. These results imply the self-powered CsPbBr$_3$/CuI device has excellent spectral selectivity and is a green-light-sensitive (565−525 nm) photodetector.

To further investigate photoelectric properties, the current−time, response time, and spectra responsivity characteristics of a single CsPbBr$_3$ crystal and individual CsPbBr$_3$/CuI photodetectors were recorded under −3 V bias, and the results are displayed in Figure 4. For the time-resolved photocurrent of the devices under −3 V with the illumination of 540 nm light, they all exhibit a stable and reproducible response (Figure 4a,b). The current of the CsPbBr$_3$ and CsPbBr$_3$/CuI devices rapidly rises to 0.5 and 5 μA, then quickly declines to 1.5 and 30 nA with the light on and off, respectively. The ratios of photocurrent to dark current are calculated to be 320 and 160 under 540 nm light illumination, respectively. Note that the CsPbBr$_3$/CuI device has higher photocurrent than that of the CsPbBr$_3$ device. This result confirms that coating CuI on individual CsPbBr$_3$ crystals can enhance the photocurrent in the visible region. The pure CuI device has high photocurrent and dark current (Figure 2d), but it has a very small on/off ratio and slow speed of response (Figure S5). The formation of a heterojunction is favorable for improving the photocurrent of a CsPbBr$_3$/CuI device. For the response time of the devices, as shown in Figure 4c,d, they all exhibit fast response speed. The rise time from 10% to 90% and the decay time from 90% to 10% of CsPbBr$_3$/CuI devices are 20 μs and 1.85 ms, respectively, which are slightly faster than those at zero bias because of the strengthened built-in electric field. Moreover, the rise time of the CsPbBr$_3$ device is 0.4 μs and the decay time is 0.46 ms, which are much faster than those of the CsPbBr$_3$/CuI device. These results demonstrate that the CsPbBr$_3$ device shows excellent performance, higher photocurrent, and faster speed than that of CsPbBr$_3$ devices previously reported prepared by solution processing methods. The CsPbBr$_3$ and CsPbBr$_3$/CuI photodetectors all have good photo-
sensitivity and fast response speed, indicating their potential for developing future microscale photodetectors.

For the wavelength-dependent responsivity of the two devices under −3 V bias, as seen in Figure 4e,f, both CsPbBr3 and CsPbBr3/CuI devices show excellent spectral selectivity. The responsivity peaks of the CsPbBr3 and CsPbBr3/CuI photodetectors are both located at 540 nm, which is the same as that under zero bias, and the responsivities are 5.2 and 82 mA W−1, respectively. Because of enhanced photocurrent, the responsivity of the CsPbBr3/CuI device is much higher than that of the CsPbBr3 device. With the decrease of wavelength (from 700 to 300 nm), the responsivity of the CsPbBr3 photodetector increases rapidly from 0.26 mA W−1 (580 nm) to 5.2 mA W−1 (540 nm), decreases dramatically to 2.52 mA W−1 (520 nm), and fluctuates slightly to 2.35 mA W−1 (300 nm). Similarly, the responsivity of the CsPbBr3/CuI device increases quickly from 2.5 mA W−1 (580 nm) to 82 mA W−1 (540 nm), decreases rapidly to 32 mA W−1 (520 nm), and declines stepwise to 7.8 mA W−1 (300 nm). In addition, a considerable drop centered at 420 nm corresponds to the band gap of CuI (3.0 eV). Upon light illumination, the pure CsPbBr3 photodetectors exhibit response at 540 nm while CsPbBr3/CuI devices also show high performance upon visible light illumination (540 nm), suggesting that CsPbBr3 plays a key role in the photodetection performance of CsPbBr3/CuI devices. Interestingly, the CsPbBr3 and CsPbBr3/CuI photodetectors showed notable difference in responsivity in the range of 520–300 nm wavelength. The CuI particles deposited on the surface of the CsPbBr3 crystal might have decreased the light penetration distance, and part of the photogenerated charge carriers may be quenched by the holes of CuI under light illumination (<400 nm). Therefore, the corresponding response signals at short wavelength region were further weakened. All these results suggest that the CsPbBr3/CuI photodetector exhibits an enhanced performance and modified responsivity.

According to the Beer–Lambert law, the number of charge carriers in the crystal decreases exponentially with increasing light penetration distance. The high extinction coefficient of CsPbBr3 crystal within the short wavelength indicates a narrow region of photogenerated carriers near the irradiated side, whereas the low extinction coefficient within the long wavelength reveals a broad region. In general, the narrowband response signals at short wavelength region were further weakened. All these results suggest that the CsPbBr3/CuI photodetector exhibits high performance and fast response speed (0.04/2.96 ms) at 540 nm at zero bias. In addition, narrowband response. Such filter-free narrowband devices are potentially crucial for a wide range of applications, including imaging, optical communications, machine vision, and many more.

In summary, millimeter-sized CsPbBr3 single crystals were prepared by a facile solvent evaporation method in ambient environment. The CsPbBr3/CuI heterojunction was simply obtained by immersing CsPbBr3 crystals into a CuI solution followed by heat treatment. The device demonstrates a high rectification ratio of 250 at ±2 V. Particularly, the CsPbBr3/CuI photodetector shows high photocurrent (near 100 nA), high photosensitivity (on/off ratio of 1.5 × 103), good wavelength selectivity (565–525 nm), and fast response speed (0.04/2.96 ms) at 540 nm at zero bias. In addition, both CsPbBr3 and CsPbBr3/CuI devices exhibit fast and reproducible responses at 540 nm at −3 V, rise time of 0.4 and 20 μs, decay time of 0.46 and 1.85 ms, respectively, and the latter exhibit significantly increased responsivities. This work provides a simple, low cost, and effective method to prepare millimeter-level CsPbBr3 single crystals. All these promising features reveal that both the pure CsPbBr3 and composite CsPbBr3/CuI devices could be potential candidates for wide practical applications in optoelectronic devices.

**EXPERIMENTAL METHODS**

**Preparation of CsPbBr3 Crystals.** All the chemicals were purchased from Aladdin, and the solvents were purchased from Sinopharm. Chemicals were used as received without further purification. First, 0.5 M CsBr (99.9%) and 0.5 M PbBr2 (99.99%) were dissolved in dimethyl sulfoxide (DMSO, 99.9%). The solution was stirred until it was saturated. Then, CsPbBr3 single crystals were obtained by immersing CsPbBr3 crystals into a CuI solution prepared by dissolving CuI in DMSO. The device demonstrates a high rectification ratio of 250 at ±2 V. Particularly, the CsPbBr3/CuI photodetector shows high photocurrent (near 100 nA), high photosensitivity (on/off ratio of 1.5 × 103), good wavelength selectivity (565–525 nm), and fast response speed (0.04/2.96 ms) at 540 nm at zero bias. In addition, both CsPbBr3 and CsPbBr3/CuI devices exhibit fast and reproducible responses at 540 nm at −3 V, rise time of 0.4 and 20 μs, decay time of 0.46 and 1.85 ms, respectively, and the latter exhibit significantly increased responsivities. This work provides a simple, low cost, and effective method to prepare millimeter-level CsPbBr3 single crystals. All these promising features reveal that both the pure CsPbBr3 and composite CsPbBr3/CuI devices could be potential candidates for wide practical applications in optoelectronic devices.
solution, and the mixture was stirred for 30 min. Subsequently, the solution was transferred to a Petri dish and heated on a heating platform at 40 °C in ambient conditions. With the slow evaporation of DMSO and the prolongation of heating time, the yellow crystals were gradually precipitated. Finally, the large-size CsPbBr₃ crystals were carefully washed with isopropanol three times to remove unreacted precursors and dimethyl sulfoxide. Most CsPbBr₃ crystals are cuboid in shape, ranging from 4 to 10 mm in length.

Preparation of CsPbBr₃/CuI Heterojunction. First, 0.1 M Cu (99.5%) acetoniitrole solution was prepared by ultrasonication dissolution. Subsequently, a long CsPbBr₃ crystal was selected for device fabrication. Half of the CsPbBr₃ crystal was dipped into the as-prepared CuI solution for 1 min. Later the CsPbBr₃/CuI heterojunctions were heated at 60 °C in the surrounding environment for 10 min to promote CuI crystallization. Two drops of silver paste were dropped onto the composites as electrodes to construct CsPbBr₃/CuI PDs.

Characterization. Field emission scanning electron microscopy (FE-SEM, Zeiss Sigma) was performed to investigate the crystallization. Two drops of silver paste were dropped onto the composites as electrodes to construct CsPbBr₃/CuI PDs. The active area is about 0.05 cm². The diameter of electrodes and channel length are about 0.15 cm and 0.33 cm, respectively. The active area is about 0.05 cm².

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