Defect Passivation on Lead-Free CsSnI₃ Perovskite Nanowires Enables High-Performance Photodetectors with Ultra-High Stability

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HIGHLIGHTS

• Through materials analysis and theoretical calculations, the defects of CsSnI₃ nanowires (NWs) were effectively passivated via incorporating 1-butyl-2,3-dimethylimidazolium chloride into perovskites.

• The high-performance CsSnI₃ NW photodetectors (PDs) were achieved with a responsivity of up to 0.237 A W⁻¹, a high detectivity of 1.18 × 10¹² Jones and a linear dynamic range of 180 dB. These values are comparable to the reported high-performance Pb-based perovskite PDs and higher than those of the Pb-free perovskite PDs.

• Our unpackaged devices exhibit ultra-high stability with no degradation after 60 days of storage in air (25 °C, 50% humidity).

ABSTRACT In recent years, Pb-free CsSnI₃ perovskite materials with excellent photoelectric properties as well as low toxicity are attracting much attention in photoelectric devices. However, deep level defects in CsSnI₃, such as high density of tin vacancies, structural deformation of SnI₆⁻ octahedra and oxidation of Sn²⁺ states, are the major challenge to achieve high-performance CsSnI₃-based photoelectric devices with good stability. In this work, defect passivation method is adopted to solve the above issues, and the ultra-stable and high-performance CsSnI₃ nanowires (NWs) photodetectors (PDs) are fabricated via incorporating 1-butyl-2,3-dimethylimidazolium chloride salt (BMIMCl) into perovskites. Through materials analysis and theoretical calculations, BMIM⁺ ions can effectively passivate the Sn-related defects and reduce the dark current of CsSnI₃ NW PDs. To further reduce the dark current of the devices, the polymethyl methacrylate is introduced, and finally, the dual passivated CsSnI₃ NWPDs show ultra-high performance with an ultra-low dark current of 2 × 10⁻¹¹ A, a responsivity of up to 0.237 A W⁻¹, a high detectivity of 1.18 × 10¹² Jones and a linear dynamic range of 180 dB. Furthermore, the unpackaged devices exhibit ultra-high stability in device performance after 60 days of storage in air (25 °C, 50% humidity), with the device performance remaining above 90%.

KEYWORDS Pb-free; Perovskite; CsSnI₃; Photodetector; Nanowire
1 Introduction

Because of excellent photoelectronic properties and low fabrication cost, organic–inorganic hybrid perovskites have become a hot topic in recent years and are widely used in solar cells [1–4], photodetectors (PDs) [5–7], light-emitting diodes (LEDs) [8, 9], etc. Until now, the highest certified power conversion efficiency of perovskite solar cells has exceeded 25% [10, 12], and the LEDs based on lead-containing perovskite materials also show high performance; for example, the highest external quantum efficiency of green LEDs has exceeded 20% [13–15]. However, the presence of heavy metal lead severely limits the commercialization of lead halide materials, which will face security risks of heavy metal lead leakage during mass production, transportation, installation and operation.

In this context, lead-free perovskite materials based on tin (Sn) [14], bismuth [15], germanium [16], antimony [17] or copper [18] have attracted much attention. Among these lead-free perovskite materials, CsSnI3 is more popular in photovoltaic applications due to its similar crystal and electronic structure to its Pb-based counterpart. Besides, inorganic perovskite CsSnI3 has a narrow optical band gap close to the Shockley–Queisser limit, with long lifetime and high charge carrier mobility [19, 20]. Moreover, the melting point of the CsSnI3 is up to 451 °C, which means that it has excellent inherent thermal stability. Therefore, the development of the inorganic perovskite CsSnI3 shows great prospect, and many scientists have achieved meaningful results [21–23]. Jin et al. [24] reported the growth of CsSnX3 (X = Br, I) perovskite semiconductors with controlled orientation and size by high-temperature vapor-phase epitaxy on mica sheets. Yang et al. [25] reported the preparation of CsSnX3 (X = Cl, Br, and I) perovskite nanowire (NW) arrays by chemical vapor deposition with a responsivity of 54 mA W−1, a detectivity of 3.85 × 10−5 Jones, and fast rise and decay time constants of 83.8 and 243.4 ms, respectively. However, the efficiency of the solution-processed CsSnI3 devices was much lower than that of the Pb-based analogs, mainly due to the weak Sn-I bond of inorganic CsSnI3, which causes lower tin vacancy formation energy and the easy oxidation of Sn2+ to Sn4+, leading to a high level of self-P doping in inorganic CsSnI3 perovskites, and the reduction in the device performance and the decrease in the output stability [26]. Therefore, strategies to passivate the Sn defects in inorganic CsSnI3 perovskites while maintaining their environmental stability are urgently needed.

In this work, 1-butyl-2,3-dimethylimidazolium chloride (BMIMCl) salt is introduced to passivate the defects of perovskite CsSnI3 NWs. Through materials analysis and theoretical calculations, the BMIMCl has a strong passivating effect on Sn-related defects via large π-bonds in N–C = N, and the lone pair of electrons in large π-bonds enhances the electron density around Sn2+ in CsSnI3 and protects it from oxidation to Sn4+; thus, the fabricated CsSnI3 NWs with BMIMCl show high light absorption, low defect density and air stability. To further reduce the dark current of the devices, the polymethyl methacrylate (PMMA) was applied, and finally, the dual passivated CsSnI3 NW PDs show ultrahigh performance with an ultra-low dark current of 2 × 10−11 A, a high responsivity of 0.237 A W−1, a high detectivity of 1.18 × 1012 Jones and a linear dynamic range (LDR) of 180 dB. Besides, our unpackaged devices exhibit good stability with less than 10% degradation in device performance after 60 days of storage in air (25 °C, 50% humidity), demonstrating good application potential.

2 Experimental and Calculation

2.1 Device Fabrication

A pre-etched indium-tin oxide (ITO) glass substrate was ultrasonically cleaned with detergent, deionized water, ethanol and iso-propyl alcohol for 15 min, respectively. To prepare the SnO2 precursor solution, the SnO2 stock solution (1 mL) was diluted in deionized water (4 mL). The as-cleaned ITO substrate was treated with UV ozone at 100 °C for 10 min. A compact layer of SnO2 was spin-coated on top of the ITO at 4000 rpm for 30 s. Then, it was heated at 150 °C for 30 min in air. After that, the samples were treated with UV ozone for 10 min. Subsequently, the samples were transferred into a N2 filled glovebox with H2O and O2 concentrations of < 0.1 ppm. A layer of PbI2 film was fabricated by spin-coating PbI2/BMIMCl (1 mol mL−1/0, 5, 8, 10 and 15 mg mL−1) in DMF at 3000 rpm for 30 s, followed by annealing at 70 °C for 10 min. Then, the substrate was soaked in the prepared CsI/SnI2/SnF2 (5 /4 /0.4 mg mL−1) solution in anhydrous methanol for 2 h. After that, the substrates were placed in an isopropyl alcohol solution for 20 s and then annealed at 180 °C for 10 min. Finally, a layer of
PMMA was coated on the samples by spin-coating PMMA in CB (20 mg mL\(^{-1}\)) at 2000/3000/4000/5000/6000/7000 rpm for 30 s, followed by annealing at 100 °C for 10 min. Then, a layer of carbon electrode was scraped on the samples and annealed at 120 °C for 15 min in air.

### 2.2 Calculations

All the calculations are performed in the framework of the density functional theory (DFT) with the projector augmented plane-wave method, as implemented in the Vienna ab initio simulation package. The generalized gradient approximation proposed by Perdew, Burke and Ernzerhof is selected for the exchange–correlation potential. The long-range van der Waals interaction is described by the DFT-D3 approach. The cutoff energy for plane wave is set to 400 eV. The energy criterion is set to 10\(^{-5}\) eV in iterative solution of the Kohn–Sham equation. The Brillouin zone integration is performed at the Gamma point for structural optimization, and a 3 × 3 × 1 k-mesh grid is used for electronic structure calculations. All the structures are relaxed until the residual forces on the atoms have declined to less than 0.05 eV Å\(^{-1}\).

### 3 Results and Discussion

A schematic diagram of the preparation of CsSnI\(_3\) NWs by a two-step solution method is shown in Fig. 1a. The aqueous SnO\(_2\) solution was first spin-coated onto a clean ITO substrate and then annealed on a hot table at 150 °C for 30 min to obtain the SnO\(_2\) films. The PbI\(_2\)/BMIMCl (1 mol mL\(^{-1}\)/0, 5, 8, 10 and 15 mg mL\(^{-1}\)) DMF solution was spin-coated on the SnO\(_2\)/ITO substrate and then annealed at 70 °C for 10 min to obtain the PbI\(_2\)/BMIMCl films. The PbI\(_2\)/BMIMCl film-covered substrates were immersed in a methanol solution of CsI/SnI\(_2\)/SnF\(_2\) (5/4/0.4 mg mL\(^{-1}\)) for 2 h. The yellow phase CsSnI\(_3\) (γ-CsSnI\(_3\)) was obtained by the B-position exchange reaction. During the reaction, the perovskite also grows in a specific direction because of the strong anisotropy of γ-CsSnI\(_3\) and eventually forms one-dimensional γ-CsSnI\(_3\) NWs [27, 28]. After that, the CsSnI\(_3\) NWs-covered substrates were placed in an isopropyl alcohol solution for 20 s to wash away the impurities on it and then annealed at 180 °C for 10 min to obtain the black phase CsSnI\(_3\) NWs (B-CsSnI\(_3\) NWs). The top-view scanning electron microscopy (SEM) images of CsSnI\(_3\) NW films with different soaking times (2, 4, 8, 16, 24, and 48 h) are shown in Figs. 1b and S1, which show little changes in surface morphology. Besides, the energy-dispersive spectroscopy (EDS) results (Table S1) show that when the soaking time is above 2 h, the perovskite NWs indicate very little Pb content (~ 0.21%) and we think our perovskite nanowires are basically all converted to CsSnI\(_3\) NWs and 2 h of soaking time are enough.

When different BMIMCl concentrations (5, 8, 10 and 15 mg mL\(^{-1}\)) are incorporated (Fig. S2), the surface coverage of the nanowires is more obvious with the increase in the concentration. In order to further study the effect of the incorporation of BMIMCl, the high-resolution transmission electron microscopy (HRTEM) is performed, and the results are shown in Figs. 1c and S4. From these figures, all perovskite NW samples show high crystallinity. The d-spacing value of the CsSnI\(_3\) without BMIMCl is estimated to be 0.31 nm, corresponding to the (202) plane of CsSnI\(_3\). For the BMIMCl + CsSnI\(_3\) sample, the spacing between the lattice fringe is 0.35 nm, which corresponds to the (220) plane of CsSnI\(_3\), and shows clearer lattice fringes of the perovskite grains, indicating higher crystallinity of the perovskite grains [29, 30]. Besides, the NW is covered by an amorphous BMIMCl molecular layer with a thickness of about 1.2 nm. This thin layer of BMIMCl will protects the underlying CsSnI\(_3\) from degradation when exposed to ambient air.

Figures 1d and S3a show the X-ray diffraction (XRD) patterns of CsSnI\(_3\) NW films with different concentrations of BMIMCl, which match well with the orthorhombic perovskite crystal structure. After the addition of BMIMCl, the peak intensity of the (220) plane of the CsSnI\(_3\) NW film is slightly enhanced compared with that of the unincorporated CsSnI\(_3\) NW film, the better crystal quality of the perovskite may improve the carrier transmission of the CsSnI\(_3\) [31]. Figures 1e and S3b show the optical properties of the perovskite with different concentrations of BMIMCl, which show the CsSnI\(_3\) NWs have capacity of absorbing from visible to infrared light. Steady-state photoluminescence (PL) spectroscopy is then performed to examine the emission characteristics of the CsSnI\(_3\) NW thin films (Figs. 1f and S3c). Compared with the CsSnI\(_3\) NW film without BMIMCl, the peak intensity of the CsSnI\(_3\) NW film gradually increases with increasing the concentration of BMIMCl and reaches a maximum at the concentration of 8 mg mL\(^{-1}\). Then, the peak intensity gradually decreases after further increasing the concentration of BMIMCl. This can be explained that
the moderate BMIMCl concentration can effectively passivate the defects of the CsSnI\textsubscript{3} NWs and suppress the non-radiative recombination of the perovskites [23, 32]. Besides, the time-resolved PL indicates that the CsSnI\textsubscript{3} NW film with 8 mg mL\textsuperscript{-1} BMIMCl shows longest carrier lifetime (Fig. S4d), which further confirms moderate BMIMCl concentration is beneficial for passivating the defects of the CsSnI\textsubscript{3} NWs.

Figure 2a shows the CsSnI\textsubscript{3} NWPD with an ITO/SnO\textsubscript{2}/perovskite NWs/carbon structure, in which SnO\textsubscript{2} is used as the electron transport layer, perovskite NWs are the photoactive layer, and carbon is as the top electrode also protects perovskites from corrosion by water and oxygen in air. As a high-performance PD, low dark current is essential, which has a positive impact on the linear dynamic range, signal-to-noise ratio and detectivity of the device. The relationship between the light and dark current of the PDs is shown in Fig. 2b, and 8 devices are used for the light/dark current statistic. The dark current gradually decreases as the BMIMCl concentration increases, and the dark current reaches a minimum until the concentration is at 8 mg mL\textsuperscript{-1}. The drop in dark current is attributed to the passivation of the surface defects of perovskite, especially the Sn vacancies, which are the main culprit for the material to appear metallic [21]. However, too much ionic liquid will cause additional impurities, which will increase the dark current of the device. For the photocurrent, it shows a slightly downward trend. Considering the light and dark currents comprehensively, we believe that the NWPDs prepared at 8 mg mL\textsuperscript{-1} are best.

To investigate the passivation interaction of the BMIMCl on Sn-related defects and verify our conjecture, Fourier transform infrared spectroscopy (FTIR) measurements are performed on BMIMCl and BMIMCl+CsSnI\textsubscript{3}. The peak of the pure BMIMCl sample is located at 1589 cm\textsuperscript{-1} (Fig. 3a), which corresponds to the N–C = N stretching vibration of the imidazole ring. For the BMIMCl+CsSnI\textsubscript{3} sample, this peak is red-shifted to 1584 cm\textsuperscript{-1}, indicating a strong interaction between N–C = N and CsSnI\textsubscript{3}. It is inferred that the
N–C=N of BMIM+ has a strong passivating interaction with Sn-related defects such as Sn vacancies. The trap density of the Sn-based perovskites is strongly associated with the Sn⁴⁺ content, which is considered as the Sn vacancies and can be distinguished by X-ray photoelectron spectroscopy (XPS) measurement. As shown in Fig. 3b, compared with ordinary CsSnI₃ samples, the proportion of Sn⁴⁺ in the BMIMCl + CsSnI₃ sample is greatly reduced, and the proportion of Sn²⁺ rises, which indicates that the oxidation of Sn²⁺ to Sn⁴⁺ in the BMIMCl + CsSnI₃ sample is significantly suppressed. In order to further verify our conjecture, the DFT calculations are used to study the effect of the introduction of BMIMCl on CsSnI₃. Since the BMIMCl is coated on the surface of CsSnI₃ perovskite, a model of BMIMCl on CsSnI₃ is established, and the calculated differential charge density of BMIMCl + CsSnI₃ (220) indicates the effective charge extraction of BMIMCl, as shown in Fig. 3c. Besides, the density of state (DOS) of CsSnI₃ perovskites with or without BMIMCl is calculated, as shown in Fig. 3d. It can be clearly observed that compared with CsSnI₃, the DOS of CsSnI₃ after BMIMCl passivation is significantly reduced in electron defects near the Fermi level, indicating the reduction in charge carrier recombination in CsSnI₃ after BMIMCl passivation and the promotion of electron transport in the perovskite.

Previous reports showed that the PMMA can fill the voids of the nanowires, passivate the surface defects of the perovskites [33] and can also generate Fowler–Nordheim tunneling to enhance device performance [34]. Based on these, we further adopt the PMMA to reduce the dark current and enhance the device performance. Through optimize the rotational speed, the appropriate thickness of the PMMA
is obtained at 5000 rpm (Fig. S5a), and at this rotational speed, the device filled by the PMMA shows the lowest dark current and the biggest light current.

The detailed device performances are shown in Fig. 4. As shown in Fig. 4a, under the irradiation of 405 nm laser with different illumination intensities, our device exhibits good photoresponse characteristics to both strong and weak light. From this figure, there is a three-order-of-magnitude difference in dark current under different light intensities. We think the main reason of the three-order-of-magnitude increase in dark current is attributed to the perovskite CsSnI$_3$, in which a few Sn vacancies still exist. When the device is illuminated by light, a large number of photo-generated carriers will be generated, and some of them may be trapped by these vacancies and remain. After the light is removed, these remaining photo-generated carriers will be slowly released and cause the rise of the dark current. When stronger light is applied, more photo-generated carriers are generated and more left, resulting in a three-order of magnitude difference in dark current under different light intensities.

The LDR of the PD is an important parameter for evaluating the performance of the PD, which can be calculated by the formula:

$$LDR = 20 \log_{10} \frac{P_{\text{sat}}}{P_{\text{low}}}$$

where $P_{\text{sat}}$ and $P_{\text{low}}$ are the strongest and weakest light intensities, respectively, when the incident light begins to deviate from the linear photocurrent. The calculated LDR is as high as 180 dB, indicating that our device can work stably in a
wide range of the light intensity (Fig. 4b), and the ultra-
low dark current of \(2 \times 10^{-11} \) A of the device is obtained.
Besides, the noise of the device affects the sensitivity of
the PD to light, and shot noise is an important noise source
which affects the dark current. The device noise power spec-
trum (Fig. 4c) shows that the noise \( (i_n) \) of the CsSnI\(_3\) NW
PD is very low with the value of about \(4 \times 10^{-13} \) A Hz\(^{-1}\).
Through the dark current, the shot noise of the device is
further calculated, and it is close to the total noise, indicat-
ing that the main device noise is the shot noise. To further
study the performance of the device, the responsivity
\(R\) and the detectivity \(D^*\) are measured to evaluate the sensitivity
of the photoelectric response of the device to incident light,
which are calculated by the formulas:

\[
R = \frac{I_{ph}}{AP_{opt}} \tag{2}
\]

\[
D^* = \frac{R \sqrt{AB}}{i_n} \tag{3}
\]

where \(I_{ph}\) is the photocurrent, \(A\) is the effective light irradia-
tion area of the PD, \(P_{opt}\) is the light intensity, and \(B\) is the
detection line width. As shown in Fig. 4d, both the \(R\) and
the \(D^*\) show a linear drop with increasing the light intensity.
Under weak light, our PD shows high device performance
with a \(R\) of 0.237 A W\(^{-1}\), and a \(D^*\) of up to \(1.18 \times 10^{12}\) Jones,
which are comparable to the reported high-performance
Pb-based perovskite PDs and higher than those of the Pb-
free perovskite PDs [35–44]; the detailed comparison is
shown in Table S2. The achievement of the high perfor-
mane is due to the dual passivation of perovskite defects
through the BMIMCl and the PMMA, which greatly reduce
the dark current, thereby reduce the device noise level and
improve the detection capability of the device. Moreover, the
broad light absorption range of the CsSnI\(_3\) enables the wide
work region of our PD ranging from ultraviolet to infrared
radiation, as shown in Fig. S5b. Furthermore, our device
shows the \(f_{3 \, dB}\) bandwidth of 1196 Hz (Fig. 4e) and the rise/
fall time (\(\tau_{rise}/\tau_{fall}\)) of 0.23/0.19 ms (Fig. 4f).

Device stability is a key parameter of the PD, which is
an important reference for commercialization. To confirm
the improvement in device stability by the dual passivation
strategies, we perform the stability of the unpackaged PDs
under different conditions in air (25 °C, 50% humidity), as
shown in Fig. 5. We find the performance of the passivated
device shows no degradation when it is exposed to continuous
light in air for more than 1200 s, but the light current of
the original device indicates a significantly decline (Fig. 5a).
We further place the devices in air for more than 60 days,
and the performance of the original CsSnI\(_3\) PDs decreases to
about 30% of the initial value. However, the device perfor-
mane of the passivated devices remains 90% of the initial
value after the same storage time. These results demonstrate
that the introduction of the BMIMCl and PMMA not only enhances the optoelectronic performance of the device, but also improves the stability of the device.

4 Conclusions

In conclusion, the BMIMCl was introduced in CsSnI$_3$ NWs to passivate the Sn vacancies and reduce the dark current of the CsSnI$_3$ NWPDs. Experimental analysis and theoretical calculation demonstrate that BMIM$^+$ ions can effectively suppress the oxidation of Sn$^{2+}$ to Sn$^{4+}$ in the BMIMCl + CsSnI$_3$ sample. For further reduce the dark current of the devices, the PMMA was applied, and finally, the dual passivated CsSnI$_3$ NW PDs show ultra-high performance with an ultra-low dark current of $2 \times 10^{-11}$ A, a responsivity of up to 0.237 A W$^{-1}$, a high detectivity of $1.18 \times 10^{12}$ Jones and a linear dynamic range of 180 dB. Furthermore, our unpackaged devices exhibit ultra-high stability in device performance after 60 days of storage in air (25 °C, 50% humidity), with the device performance remaining above 90%. This work provides a simple and effective method for the preparation of high-performance, highly stable Pb-free perovskite photoelectric devices.

Acknowledgements We acknowledge grants from the National Natural Science Foundation of China (Nos. 51972101, 62074117, 12134010) and the Shenzhen Fundamental Research Program (No. JCYJ20190808152609307).

Funding Open access funding provided by Shanghai Jiao Tong University.

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Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s40820-022-00964-9.

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