Combination of solution-phase process and halide exchange for all-inorganic, highly stable CsPbBr₃ perovskite nanowire photodetector

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ABSTRACT The synthesis of high quality all-inorganic perovskite nanowires needs the harsh conditions, complex process and precision instruments, which are not beneficial to their extensive application. Here, all-inorganic perovskite cesium lead bromine (CsPbBr₃) nanowires (NWs) are demonstrated with the combination of solution-phase process and halide exchange technology. A metal-semiconductor-metal structure CsPbBr₃ nanowire photodetector was prepared, which showed a detectivity as high as $1.7 \times 10^{11} \text{ cm Hz}^{1/2} \text{ W}^{-1}$ (Jones) with rapid response time (The rise and decay time are 10 ms and 22 ms, respectively). Moreover, our photodetectors have high stability under ultraviolet (UV) light, high temperature and humidity.

Keywords: solution-phase process, halide exchange, perovskite nanowires, photodetector

INTRODUCTION

In the past few years, halide perovskite materials, both hybrid organo-inorganic and all-inorganic perovskites, have gained a lot of interest in the optoelectronic fields due to their tunable wavelength and long carrier diffusion length, etc. [1–4]. The efficiency of hybrid bulk perovskite-based solar cells reached 23.58% up to date [5]. However, the stability of organic-inorganic hybrid materials is still an obstacle because the organic cation MA⁺ is susceptible to degradation under the oxygen, moist heat and UV light [6–9]. As a kind of more stable new perovskite materials, all-inorganic lead halide perovskites CsPbX₃ (X=I, Br, Cl) is considered to be the most suitable alternative of organic-inorganic perovskites. Recently, CsPbX₃ based optoelectronic devices have been widely reported in solar cells [10,11], light-emitting diodes (LEDs) [1,12,13], photodetectors (PDs) [14–18] and other

fields [19–21].

Compared with the perovskite films, perovskite nanostructures, such as nanowires, nanoplates and quantum dots, have attracted more attention due to their special nanostructures [22–24]. In these nanostructures, the devices based on nanowires may have better performance due to their large surface-to-volume ratio and direct conduction path for carriers [24–26]. Therefore, they have better photoelectric characteristics than film-based devices [27,28]. In the family of halide perovskites, CsPbBr₃ is particularly attractive in the field of photodetectors and light-emitting diodes due to its suitable band gap and high quantum efficiency [14,29]. Thus, nanowires based on CsPbBr₃ have been reported widely [28,30–33]. In these reports, most of the nanowires were prepared by the traditional hot-injection technique [32], but when these nanowires are used for films, complex vacuum coating technology will be necessary [26]. Also, high-speed centrifugation, used to improve the purity of nanowires, may destroy the ligands [31]. Additionally, nanocrystals will be synthesized firstly before the preparation of nanowires, in which redundant nanosheets will exist in this process [12]. From above, the synthesis of inorganic CsPbBr₃ NWs relies on harsh strips, complex processes, and sophisticated instruments, which block its widespread application.

Recently, Yang's group reported a surfactant free solution process to synthesize cesium lead iodine (CsPbI₃) NWs directly on the substrate at room temperature. In this process, the edge-shared PbI₆ octahedra in CsPbI₃ form a 1D chain structure along the [010] direction [33]. However, this method can only produce non-perovskite phase iodine-based perovskite nanowires. In order to achieve the transition from non-perovskite phase to

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perovskite phase, high temperature annealing (310–350°C) will be used and the yellow CsPbI_3 with non-perovskite phase can be transformed to the black CsPbI_3 with perovskite phase [34]. However, the high temperature annealing process results in many defects in nanowires, and the uniform heating at high temperature is very difficult. After the transformation, the phase is unstable and easy to degrade back to non-perovskite phase. The structural phase transition from the non-perovskite phase to a perovskite phase might be stabilized by a fast thermal quenching method [33]. But the harsh preparation conditions and the high temperature are not available at any time. In addition, if the iodine precursor is substituted by bromine precursor directly, the product will be mixture of nanowires and nanoplates with various sizes [35]. Herein, P-CsPbBr₃ NWs (P stands for perovskite phase) have been obtained by introducing anion exchange strategy [36,37] and Yang's method [33] with low temperature annealing. The principle comparison of the two methods is illustrated in Fig. S1. Our method led to the direct growth of P-CsPbBr₃ NWs on the substrate at lower temperature. Subsequently, P-CsPbBr₃ NWs PDs exhibited photocurrent (I_p) and dark current (I_d) without obvious deterioration after the devices was exposed to UV illumination (2.2 mW cm⁻²) for 10,000 s. Moreover, when the device was placed in the atmospheric environment with average temperature of 32°C and average relative humidity of 75% for about 200 h, the I_p of devices decreased less than 4.9%, suggesting the excellent stability of the P-CsPbBr₃ NW PDs.

EXPERIMENTAL SECTION

All chemicals, including acetone (AR, Sinopharm Chemical Reagent Co. Ltd), alcohol (AR, Sinopharm Chemical Reagent Co. Ltd), lead iodide (PbI_2 , 99.99%, Xi'an Polymer Light Technology Core), *N,N*-dimethylformamide (DMF, 99.9%, Sigma-Aldrich), cesium iodide (CsI, 99.9%, Aladdin), methanol (99.9%, Aladdin), isopropanol (AR, Sinopharm Chemical Reagent Co. Ltd), and cesium bromide (CsBr, 99.999%, Aladdin), were used as received without any further purification.

Glass substrates was cleaned using deionized water, acetone and alcohol in sequence for 20 min, and then cleaned in UV ozone atmosphere for 30 min. 460 mg PbI_2 was dissolved in 1 mL anhydrous DMF, stirred at 70°C for 15 h until the PbI_2 was completely dissolved. The PbI_2 solution was spin-coated on glass substrates at 5,000 rpm for 60 s, then annealed at 100°C for 15 min. When PbI_2 film was cooled to room temperature, it was carefully dipped into a glass vial with 8 mg mL⁻¹ CsI/methanol,

Figure 1 Schematic illustration of the synthesis of P-CsPbBr₃ NWs film.

with the PbI_2 side facing up and the glass vial capped closely. The reaction was carried out at room temperature (about 20–30°C) for 3–12 h. Then the glass substrate was taken to other glass vial with isopropanol carefully. After waiting for 10 s, it was spun at 2,000 rpm for 30 s. Then the substrate was placed on the hot plate under 50°C until the surface was completely dry. The whole preparation process was in Ar.

The CsPbI_3 nanowire mesh film grown on glass substrate was dipped into a glass vial with 10 mg mL⁻¹ CsBr/methanol at room temperature (about 20–30 °C) for about 5 min, with the nanowire mesh side facing up and the glass vial capped closely. When the yellow films transformed into white translucent films completely, the substrate was taken out and placed on the hot plate under 50°C until the surface was completely dry. Then the hot plate with substrates was heated quickly to 145–200°C, and the temperature was remained for 10 min. The whole CsPbBr_3 nanowire mesh samples were annealed at 165°C for 10 min except special explanation. The whole preparation process was in a Ar filled glove box. The schematic illustration of the synthesis of P-CsPbBr₃ NWs film is shown in Fig. 1.

80-nm-thick Au electrode was deposited by thermal evaporation under a pressure of 5×10^{-5} Torr with interdigital electrode. The morphology and crystallinity of the samples were characterized by field emission scanning electron microscopy (SEM, JSM-7100F) and X-ray diffraction (XRD, D8 FOCUS X-ray diffraction), respectively. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) measurements were implemented with FEI Tecnai G20 on a Cu grid. The current-voltage (I - V), and current-time (I - t) curves characteristics were measured by Agilent Technologies B1500A. The UV-vis absorption spectra were characterized by UV-vis spectrophotometer (MPC-3100 SHIMADZU). The photosensitivity was tested using a 66984 Xe Arc source (300 W Oriel) and Oriel CornerstoneTM 260

Figure 2 (a–c) SEM images of CsPbI₃ NWs film, W-CsPbBr₃ NWs film and P-CsPbBr₃ NWs film on glass substrates. Scale bars are 5 μm. (d–f) XRD patterns of CsPbI₃ NWs film, W-CsPbBr₃ NWs film and P-CsPbBr₃ NWs film. The insets are the corresponding photographs of NWs films.

1/4 m monochromator. The sample was under direct illumination and the optical power of light was measured by a UV-enhanced Si detector.

RESULTS AND DISCUSSION

To investigate the changes of NWs in the process of translation, we have characterized their morphology by SEM (Fig. 2a–c), TEM and HRTEM (Fig. S2). Compared with the CsPbI₃ NWs film, the W-CsPbBr₃ NWs (The prefix W indicates it is white and non-perovskite phase) film gained from the anion exchange process exhibit significant differences in the morphology, while the effect of annealing process on the morphology of W-CsPbBr₃ NWs film is weak. From the HRTEM images of single nanowire, it could be obviously observed that crystal lattice spacing of CsPbI₃ between two adjacent planes is 0.34 nm, corresponding to (105) planes, while the W-CsPbBr₃ shows a lattice fringe of 0.30 nm, in agreement with the (213) facet of tetragonal CsPb₂Br₅ structure. For P-CsPbBr₃ NW, its lattice-spacing is about 0.29 nm, which matches well with the standard value for the (200) facet of bulk orthorhombic CsPbBr₃. From the HRTEM results, the orthorhombic perovskite can be successfully synthesized through solution-phase process and ion-exchange technology. In addition, compared with CsPbI₃ NWs film, the surface of P-CsPbBr₃ NWs is rough, and the diameter becomes smaller (Fig. S3) with a small amount of fracture. The reason for the breakage of some

nanowires is probably the destruction of internal structures during the substitution of I[−] by Br[−]. Fortunately, we can reduce breakage of nanowires by optimizing the parameters, such as growth time and the concentration of the solution during anion exchange. Compared with the previous reports, a large number of nanowires being fractured [32,33], and bottom of nanowires films becoming turbid owing to high temperatures [35], our method can protect the morphology of nanowires successfully and provide convenience for fabricating nanowire-based devices.

The XRD patterns (Fig. 2d–f) further confirmed the transformation process of our nanowires through halide-exchange of I[−] by Br[−]. After the accomplishment of anion substitution of I[−] by Br[−], the XRD patterns of as-formed white film illustrated no diffraction peaks corresponding to the CsPbI₃ phase or any products from decomposed CsI and PbI₂, confirming the success of the halide-exchange. XRD patterns of W-CsPbBr₃ could not be assigned to the phase of any perovskite recorded in the previous literature. The crystalline phase of W-CsPbBr₃ in our experiments should be between the non-perovskite tetragonal structure CsPb₂Br₅ (obtained from the JCPDS database (No. 25-0211)) and orthorhombic phase CsPbBr₃ (obtained from the JCPDS database (No. 18-0364)). The orthorhombic phase CsPbBr₃ should be formed by the direct substitution of I[−] by Br[−] in the halide-exchange. It inherited the edge-shared PbI₆ octahedra

Figure 3 SEM images of CsPbI₃ NWs Films with different growth time: (a) 10 min, (b) 3 h, (c) 6 h, (d) 9 h, (e) 12 h. Scale bars are 5 μm. The inset is the corresponding enlarged SEM image. (f) XRD patterns of CsPbI₃ NWs films with different growth time.

[38], which is fundamental structure of original orthorhombic phase CsPbI₃. In addition, some of I[−] dissociated from the edge-shared PbI₆ octahedra was replaced by the free Br[−] directly and CsPb₂Br₅ with tetragonal phase was formed. After that, the W-CsPbBr₃ NWs film was annealed at 165°C, which led to the transformation from the non-perovskite phase to the P-CsPbBr₃ NWs film and the color changing from white to orange. The obvious split peaks in Fig. 2f indicated a lower symmetry orthorhombic perovskite phase (obtained from the JCPDS database (No. 18-0364)). The structure of the orthorhombic perovskite phase is similar to the ideal cubic phase, where PbBr₆ octahedra are slightly distorted and corner-shared in three dimensions (Fig. S1). In addition, the XRD patterns (Fig. 2d–f) matched well with the HRTEM results (Fig. S2). And both XRD and TEM confirmed that not only CsPbI₃ NWs but also W-CsPbBr₃ and P-CsPbBr₃ NWs are polycrystalline, with uniform growth direction.

The band gap of the NWs films is measured by UV-vis absorption spectrum and shown in Fig. S4. The absorption edge of solution-phase synthesized CsPbI₃ NWs is located at 450 nm with a bandgap of 2.76 eV, which matches well with the previous report [34]. The absorption edge of W-CsPbBr₃ NWs after the accomplishment of halide substitution blue shifted to 385 nm, corresponding to a bandgap of 3.23 eV. For P-CsPbBr₃ NWs film, its absorption edge is located at about 540 nm with a bandgap of 2.30 eV.

The morphology of P-CsPbBr₃ NWs is mainly de-

termined by the initial CsPbI₃ NWs, which can be optimized by the corresponding preparation process. The diameter of the CsPbI₃ NWs can be adjusted by changing the concentration of the CsI/methanol solution. The length of the nanowires can be controlled by changing the thickness of PbI₂ and dipping time. It was reported [33] that the concentration of CsI/methanol solution in 4–10 mg mL^{−1} could produce the NWs with adequate diameter, and the higher concentration the smaller diameter. Once the diameter of nanowires is too small, it will be vulnerable to destruction during ion exchange; If the diameter is too large, the inner structure will be hard to transform thoroughly and a higher annealing temperature will be required. So CsI/methanol solution with 8 mg mL^{−1} was chosen.

The growth time of CsPbI₃ NWs (the dipping time of PbI₂ film in CsI/methanol solution) is a critical factor to obtain high quality nanowires. Five time durations (10 min, 3, 6, 9 and 12 h) were chosen to investigate the morphology and crystal structure of CsPbI₃ nanowire mesh films (Fig. 3). As seen from the SEM in Fig. 3a, the morphology of nanowires grown with 10 min is good and the length is about 3.5 μm. After the growth with 3–12 h, the length of the NWs ranges from 5 to 40 μm, and their diameters are between 100 and 200 nm (Fig. 3b–e). The XRD patterns of CsPbI₃ NWs films with different growth time were shown in Fig. 3f and it can be seen that the NWs films grown for 10 min have strong diffraction peaks of PbI₂ at 12.67°, 38.66° and 52.39°, indicating that

Figure 4 (a) Schematic demonstration of P-CsPbBr₃ NW PD device configuration. (b) The microscope image of interdigitated electrodes with finger width of 100 μm. (c) Band profile of the P-CsPbBr₃ PD. (d) The logarithmic I - V and (e) I - t curves at 5 V bias of the P-CsPbBr₃ PD at different growth times (3–12 h) under UV illumination with the light intensity of 2.7 mW cm⁻².

the dipping time of 10 min is not enough as the PbI₂ on the substrate does not react fully. When longer time is used, the diffraction peaks of PbI₂ are significantly reduced. And the XRD patterns of corresponding P-CsPbBr₃ NWs are illustrated in Fig. S5. There is an obvious peak of PbI₂ at 12.67° for the sample prepared at 10 min, and the peak at 11.56° is assigned to the tetragonal phase of CsPb₂Br₅. When the dipping time is too short, the thin PbI₂ film left at the bottom of the CsPbI₃ NWs reacts with the CsBr directly and the CsPb₂Br₅ is formed. Due to the poor quality of 10 min NWs film, we do not do further research in the following research. In addition, the P-CsPbBr₃ NWs film grown with 6 h showed a strongest peak. Also from the UV-vis absorption spectra (Fig. S6a), the P-CsPbBr₃ NWs grown with 6 h NWs showed a strongest absorption curve. So we think 6 h is the best for growth of CsPbI₃ NWs.

SEM images of P-CsPbBr₃ NWs films with a growth time of 3–12 h were shown in Fig. S6b–e where the NWs are not uniform and their morphologies are poor when the growth times are 9 and 12 h and the surface of nanowires would be damaged seriously. For the P-CsPbBr₃ NWs films grown for 3 and 6 h, their nanowire morphology is well (Fig. S7). The CsPbI₃ NWs film with non-perovskite phase can be divided into two parts: the denser

NRs at the bottom and the sparse NRs at the upper part. When CsPbI₃ NWs are transformed into P-CsPbBr₃, the above sparse parts will be lodged down. For NWs film grown for 9 and 12 h, according to their SEM (Fig. S8), the bottom parts are too dense, which will result in the NRs sticking together more easily during halide substitution. We concluded 6 h for growth of P-CsPbBr₃ NWs film is the best.

The device structure of P-CsPbBr₃ NW PD is illustrated in Fig. 4a. After the perovskite NWs film was prepared on a glass substrate, the interdigital Au electrodes were deposited by thermal evaporation using mask plate with spacing of 100 μm, as shown in Fig. 4b. The schematic band diagram of the device is displayed in Fig. 4c. To study the light response ability of the P-CsPbBr₃ NW PD, we tested it with different grown time of CsPbI₃ NWs. Fig. 4d, e show the logarithmic I - V and I - t curves of the P-CsPbBr₃ NW PDs obtained from PbI₂ films dipping in CsI/methanol solution for different time (3–12 h), respectively. From the logarithmic I - V curves (Fig. 4d), all of the dark currents reach the pA level. The device prepared with 6 h exhibits the minimum dark current and maximum photocurrent of 0.1 and 16 nA at 5 V, respectively. From the I - t curves (Fig. 4e) at 5 V bias, the differences between the four PDs in the dark and under

UV illumination can be observed. Obviously, the PD with the growth time of 6 h exhibits the on/off ratio more than 150, due to the P-CsPbBr₃ NWs film grown for 6 h with the best crystal quality, strongest absorption and the most uniform morphology with minimal damaged surface.

The optimization of the annealing temperature is necessary for our perovskite NWs film because too high temperature will lead to increasing costs and change the crystal morphology [39]. Compared with organic lead halide perovskites, Cs-based lead trihalide perovskites are known to have higher stability under harsh environmental conditions [40,41]. For example, Cs-based single crystal perovskites have demonstrated thermal stability up to 600°C [40]. Once the samples based on CsPbBr₃ are heated upon about 450 K (177°C), irreversible structural changes will occur [42]. Therefore, based on P-CsPbBr₃ NWs Films grown for 6 h, seven temperature ranging from 145°C to 205°C were displayed to investigate the relationship between performance of the device and annealing temperature.

Annealing at 145–205°C for 10 min, the color of the W-CsPbBr₃ NWs films changes from white to orange. The XRD pattern curves were shown in Fig. S9a. There are no obvious impurity peaks, indicating that W-CsPbBr₃ NWs films are transformed into P-CsPbBr₃ with perovskite orthorhombic phase. Also with the increase of temperature, the intensity of XRD diffraction peak continuously increases at first, and then decreases at 195°C. When the annealing temperature reaches 205°C, a peak at 11.5°, attributed to the tetragonal CsPb₂Br₅ with non-perovskite phase, indicates the structure of P-CsPbBr₃ changed under high temperature.

The photocurrent and dark current of perovskite PD devices with different annealing temperatures are shown in Fig. S9b. Except the device annealed at 205°C, the others showed good photoelectric properties. In addition, the on/off ratio of the device annealed at 165°C reached maximum of 150. Combining with XRD analysis, the poor photoelectric performance of the device annealed at 145 and 155°C are probably owing to the poor crystallinity of the NWs films. When the temperature exceeds 170°C, the decrease of the performance is attributed to photoluminescence (PL) loss mechanisms [42]. The increased mobility of Br ions in the CsPbBr₃ crystal at high temperature results in irreversible changes of NW composition.

Fig. 5 showed the detailed photoelectric properties of the optimal P-CsPbBr₃ NW photodetector. The spectral responsivity curve under the reverse bias of 5 V is presented in Fig. 5a. From the curve, the device showed a

peak response at 463 nm with the value of about 7.26 mA W⁻¹. When the dark current is dominated by shot noise, the detectivity (D^*) is given by the following equation [43], $D^* = R / (2qJ_d)^{1/2} = (J_{ph} / L_{light}) / (2qJ_d)^{1/2}$ where R is the responsivity of the PD, J_d is the dark current, J_{ph} is the photocurrent density, L_{light} is the light intensity. Our perovskite NW film PDs exhibit lower dark current (Fig. 5b). At 463 nm, the PDs show the highest spectral detectivity of 1.7×10^{11} cm Hz^{1/2} W⁻¹ (Jones). To study the relationship between illumination intensity and photocurrent, the I - V curves (Fig. 5c) are presented with various light intensities. The photocurrent increases with increasing illumination intensity, (Fig. S10). When the light turns on or off, the current sharply increases or decreases, showing that our devices have fast response speed. The photocurrent and responsivity vs. light intensity curves at different bias are displayed in Fig. 5d. The red curve shows a linear response from 0 to 68 μ W with increasing light intensity, and the curve slope increases with the reverse bias, showing that higher bias has better carrier collection capability. The blue curve in Fig. 5d shows linear changes for R and the values decrease with the increase of light intensity. Under weak light (0.5 mW cm⁻²), it shows good response with $R = 5.5$ mA W⁻¹. The fast response time is presented in Fig. 5e. The rise time (from 10% to 90% of the saturated value) is about 10 ms, and the decay time (from 90% to 10% of the peak value) is 22 ms. Due to the good single-crystalline, the detectivity and responsivity of our NWs film PDs are at the same level as the reported CsPbBr₃ single crystal PDs [44,45]. Meanwhile, the response time is better than those of other PDs reported with metal-semiconductor-metal (MSM) structure (Table S1). The outstanding stability of the PD during more than 10,000 s under 5 V bias under UV light (2.7 mW cm⁻²) is shown in Fig. 5f. The photocurrent and dark current of P-CsPbBr₃ NW PDs are both quite stable during the UV irradiation. The inset of Fig. 5f shows the I - t curves after being placed in atmospheric environment (July in Wuhan, average temperature of 32°C and average relative humidity of 75%) for a long time. Notably, after being placed for more than 200 h, the photocurrent only changes from 16.0 to 15.2 nA, and the degradation rate is less than 5%, exhibiting an excellent stability to oxygen and moisture. So the PDs using our method show high photoelectric performances and excellent stability under UV irradiation, oxygen and moisture.

CONCLUSION

In summary, the morphology and performance of in-

Figure 5 The spectral responsivity (a) and detectivity (b) curve under 5V bias. (c) I - V curves of the devices measured under illumination of UV light with different light density. (d) Photocurrent under 10 V bias and responsivity under 5 V bias *versus* light intensity curves of the PD under illumination of UV light. (e) The photoresponse time curve of CsPbBr₃ perovskite NW PD. (f) Stability of the device under illumination of UV light (2.2 mW cm⁻²) after more than 10,000 s. The inset shows the current of device after more than 200 h.

organic P-CsPbBr₃ NWs films directly grown on glass by combining solution-phase process and halide exchange technology were investigated under various synthesis conditions. The optimal metal-semiconductor-metal structure CsPbBr₃ NW photodetector showed the detectivity as high as 1.7×10^{11} cm Hz^{1/2} W⁻¹ with rapid response time (The rise and decay time are 10 ms and 22 ms, respectively). Moreover, our photodetectors have high stability under UV light, high temperature and humidity.

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结合液相合成与离子交换技术制备的全无机高稳定的铯铅溴钙钛矿纳米线光电探测器

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摘要 高质量全无机钙钛矿纳米线的合成往往依赖于苛刻的条件、复杂的工艺和精密仪器, 这不利于其广泛的应用. 本文首次将液相法和卤素交换技术相结合, 合成出了全无机钙钛矿铯铅(CsPbBr_3)纳米线, 并详细阐述了在不同条件下合成的 CsPbBr_3 纳米线薄膜的形貌和性能. 通过场发射扫描电子显微镜和X射线衍射等分析技术, 表征了纳米线的形貌和晶体结构. 最后通过工艺优化, 制备了最佳的金属-半导体-金属结构 CsPbBr_3 纳米线光电探测器, 其探测度高($1.7 \times 10^{11} \text{ cm Hz}^{1/2} \text{ W}^{-1}$ (Jones)), 响应时间快(上升和衰减时间分别为10毫秒和22毫秒). 此外, 我们的光电探测器对紫外光(UV)、温度和湿度具有高稳定性, 因此具有巨大的应用潜力.