RESEARCH HIGHLIGHTS

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Perovskite films for X-ray detection

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X-ray detection is widely used in research[1–3], product inspection[4], nuclear station, and medical imaging. Si[5], α-Se[6], PbI_2[7], and CdZnTe[8] are conventional semiconductors, and some problems limit their applications. For instance, Si and α-Se have low stopping power for X-ray[8], which hinders their application in high-energy range over 50 keV. Moreover, the complicated preparation, high operating voltage, and high fabrication cost of these materials are the negative issues.

Perovskite materials are promising candidates for X-ray detection due to facile synthesis[9–14] and large mobility-lifetime ($\mu\tau$) products for highly sensitive detection. The $\mu\tau$ product of $MAPbBr_3$ single crystal reaches 1.2×10^{-2} cm^2 V^{-1}[12], which is comparable to the $\mu\tau$ value of CdZnTe[3]. Perovskite-based X-ray detectors also exhibited a record X-ray sensitivity[15] of ~710 000 μC Gy^{-1} cm^{-2} and an ultralow detection limit[16] of 0.62 nGy s^{-1}. Tang *et al.* developed a hot-pressing method to grow quasi-monocrystalline $CsPbBr_3$ films, which exhibits a superior sensitivity of 55 684 μC Gy^{-1} cm^{-2} and a low detection limit of 215 nGy s^{-1}[17]. To date, halide perovskites in various forms like polycrystalline films, single crystals, and nanocrystals have been used in X-ray detectors. Especially, polycrystalline films prepared by hot-pressing, coating or printing have attracted great interests due to their superior flexibility, lightweight and facile synthesis.

In comparison to brittle single-crystal films, polycrystalline films can be curved to fit non-flat substrates, thus showing potential for flexible X-ray detectors[18, 19]. Some high-quality flexible perovskite films were prepared, presenting high performance. Liu *et al.*[20] reported a flexible and printable X-ray detector based on colloidal $CsPbBr_3$ QDs. To enhance the sensitivity, they effectively reduced the surface defects and tuned crystallinity *via* chemical engineering. This detector can sense a very low X-ray dose rate (~17.2 μGy s^{-1}) with a high sensitivity of 1450 μC Gy^{-1} cm^{-2} at 0.1 V bias. Meanwhile, the vignetting issues can be effectively alleviated, leading to reduced misdiagnosis. 400 cm^2 $MAPb(I_{0.9}Cl_{0.1})_3$-filled nylon membranes were used to make X-ray detectors[21]. The devices exhibited a high sensitivity of ~8696 μC Gy^{-1} cm^{-2} and could be bent at 2 mm radius without performance loss (Figs. 1(a)–1(d)).

For polycrystalline films, besides flexibility, the facile preparation of large-area and thick films by solution processing is another advantage over single crystal films. Blade coating is one of the common methods. Kim *et al.*[22] made a thick polycrystalline $MAPbI_3$ film by this method, and it had excellent optoelectronic properties, which are comparable to single crystal films. The device had a thickness of 830 μm and an active area of ~100 cm^2 (Figs. 1(e)–1(g)). In order to minimize dark current drift, the polycrystalline films should have high crystallinity and large grain to reduce grain boundaries. He *et al.*[23] made a quasi-2D perovskite film with low defects and suppressed ion migration. The average grain size was 31.88 μm. Such large grain size resulted from colloidal particles aggregating in the slurry with PEA^+, which can decrease nucleation sites. The resulted $\mu\tau$ value was 2.6×10^{-5} cm^2 V^{-1} and the minimum current drift was 1.5×10^{-2} pA cm^{-1} s^{-1} V^{-1}.

The perovskite films should give low dark current to ensure high X-ray sensitivity. The patients under a high level of radiation exposure may face cancer risk[24]. To capture clear X-ray images under a low dose of X-ray is desired[25]. The detection limit is the minimum signal which can be reliably identified by X-ray detectors and is defined as the equivalent dose rate of a signal 3 times greater than the noise. A low detection limit results from high current signal with low noise current dominated by dark current, which can reduce the imaging capability of detectors under weak X-ray. Most polycrystalline perovskite detectors[17, 26] have large dark current densities of 50–500 nA cm^{-2} under an electrical field of 0.05 V μm^{-1} due to the defective structures as compared to single crystals. To solve this problem, great efforts have been devoted to improve the quality of perovskite films. Zhou *et al.*[27] reported a heterojunction structure formed by laminating membranes filled with perovskites with different bandgaps. The membranes reduced dark current density of the devices by over 200 times without compromising their sensitivity. They captured clear X-ray images at a low dose rate of 32.2 nGy s^{-1} (Figs. 2(a)–2(c)). Tang *et al.*[23] also proposed a new strategy to suppress ion migration by inserting 2D Ruddlesden-Popper layer into 3D perovskite film. The quasi-2D perovskite X-ray detector offered a sensitivity of 10 860 μC Gy^{-1} cm^{-2} with a stable dark current.

Generally, perovskite films should have a thickness of hundreds micrometers for sufficient X-ray absorption[28]. However, it is very difficult to make such films by spin-coating or blade-coating methods. First, it is difficult to deposit a very thick wet film due to the limitations of surface tension and viscosity[29]. Second, even though a thick wet film could be made, it is still difficult to obtain perovskite films with high crystallinity and low defect density (Figs. 2(d) and 2(f)).

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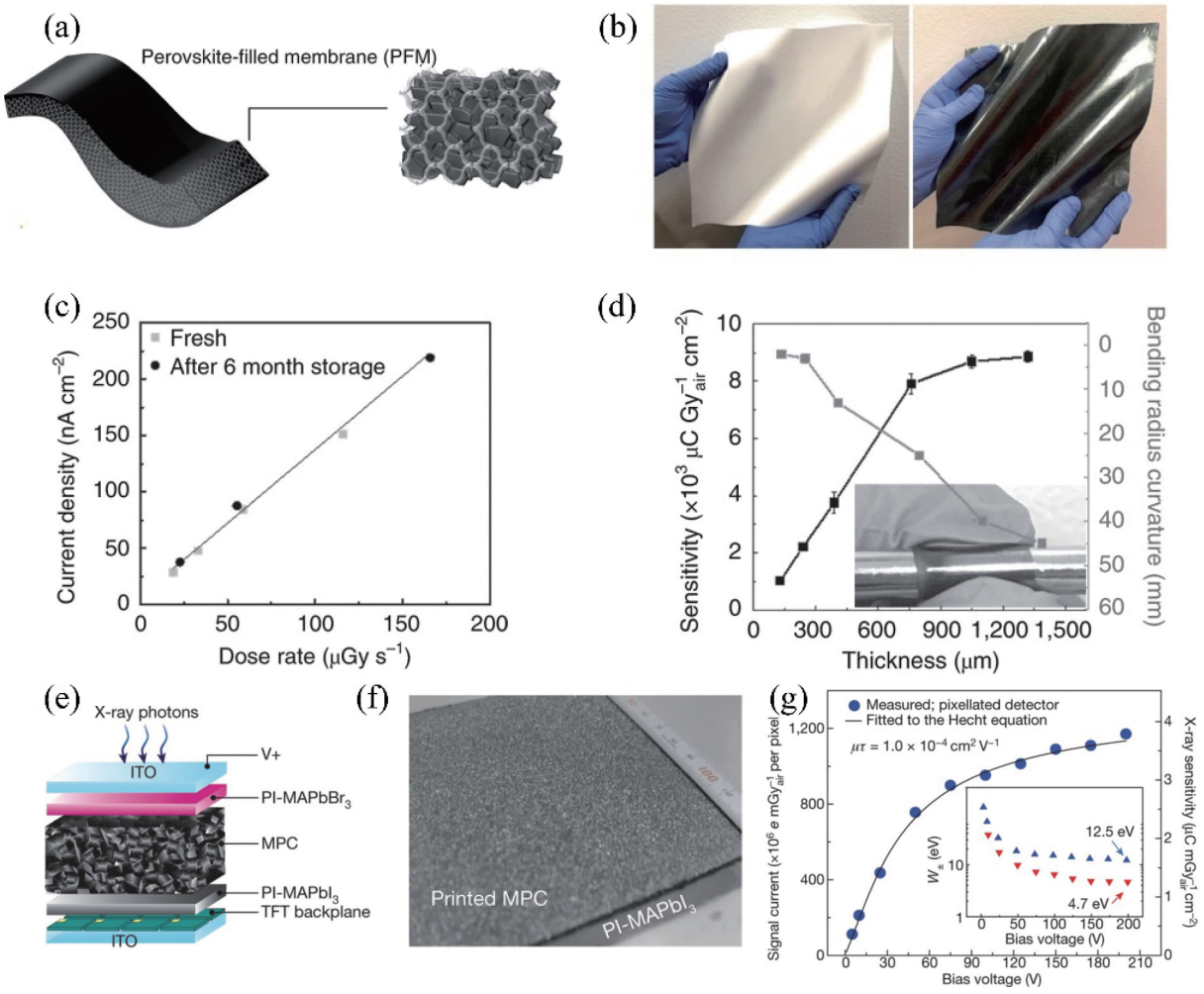

Fig. 1. (Color online) (a) Perovskite-filled membrane (PFM). (b) A 400 cm^2 nylon membrane without (left) and with (right) perovskites. (c) Current density for the PFM device changes with the dose rate. (d) Dependence of the sensitivity and flexibility of PFM devices on device thicknesses. Inset: the bending of a PFM device. The error bars were obtained from three devices. Reproduced with permission[21], Copyright 2020, Springer Nature. (e) Illustration for an all-solution-processed X-ray detector. (f) Printed MPC on PI-MAPbI$_3$. (g) Signal current and sensitivity change with bias voltage. Reproduced with permission[22], Copyright 2017, Springer Nature.

To solve this issue, Wei *et al.*[30] developed an aerosol–liquid–solid (ALS) method to make perovskite films on TFT substrates by spray coating. This method solved the problem of uncontrolled crystallization of perovskites (Figs. 2(e) and 2(g)). The detectors demonstrated a high sensitivity (~1.48 × 10^5 μC Gy^{-1} cm^{-2}), a low detection limit (280 nGy s^{-1}), and they could also realize high-resolution imaging.

In summary, high-quality perovskite films featuring large area, sufficient thickness, flexibility and high sensitivity are prerequisites for high-performance X-ray detectors. Perovskite X-ray detectors may find applications in security inspection, medical imaging, and nondestructive checking in the future.

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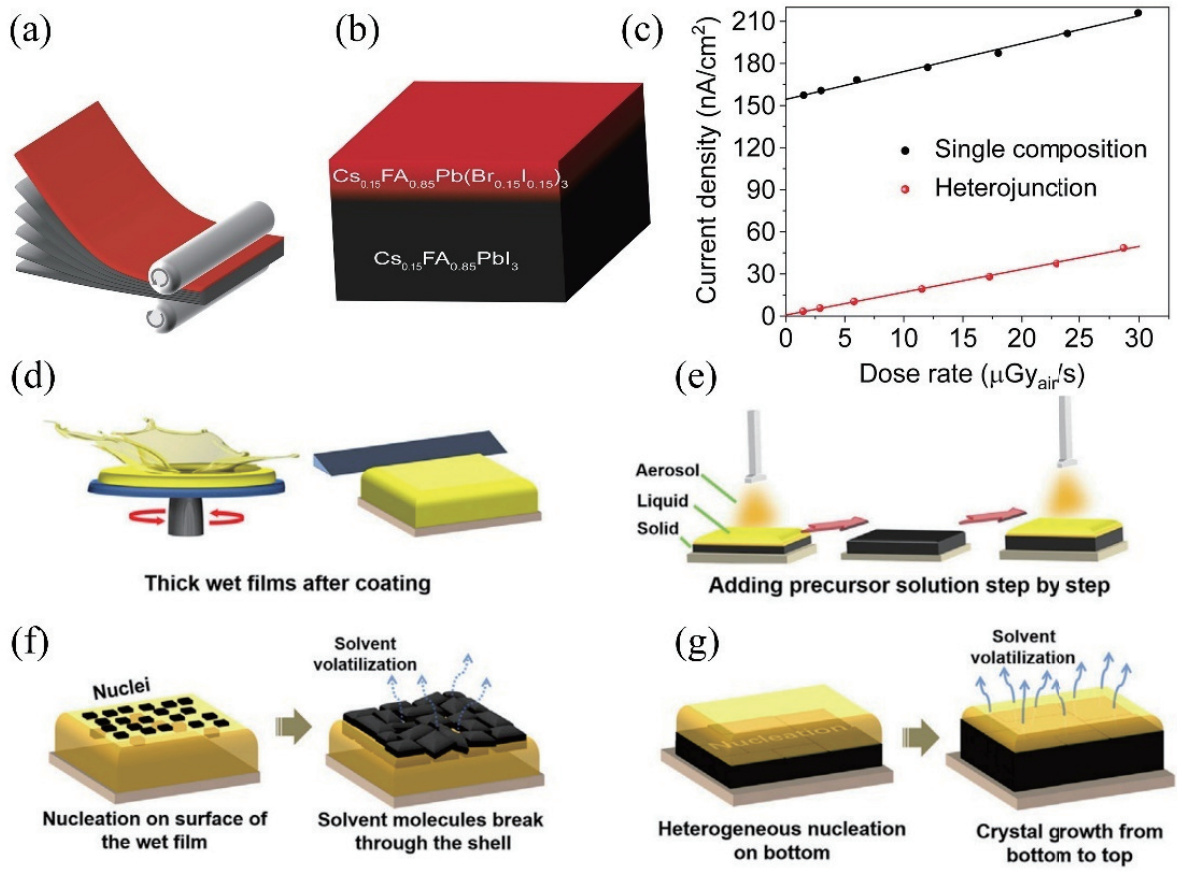

Fig. 2. (Color online) (a) The lamination technique. (b) Heterojunction perovskite film. (c) Response of single-composition and heterojunction perovskite detectors. Reproduced with permission[27], Copyright 2021, AAAS. (d) Wet film fabrication by spin-coating or blade-coating. (e) The ALS method. (f) The nucleation and growth process in (d). (g) Nucleation and growth process in ALS method. Reproduced with permission[30], Copyright 2021, Elsevier.

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