Flexible perovskite scintillators and detectors for X-ray detection

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SUMMARY

X-ray detection and imaging technology has been rapidly developed for various fields since 1895, offering great opportunities to scientific and industrial communities. Particularly, flexible X-ray detectors have drawn numerous attention in medical-related applications, solving the uniform issues of traditional rigid X-ray detectors. Out of all the potential materials, metal halide perovskites (MHPs) have been emerged as excellent candidates as flexible X-ray scintillators and detectors owing to the advantages including low temperature solution processable, strong X-ray absorption coefficient, large mobility lifetime product and tunable bandgap. In this review, the recent advances of MHP-based flexible X-ray detectors are comprehensively summarized, focusing on the scalable synthesis technologies of materials and diverse device architectures, and covering both direct and indirect X-ray detection. A brief outlook that highlights the current challenges impeding the commercialization of flexible MHP-based X-ray detectors is also included with possible solutions to those problem being provided.

INTRODUCTION

Nowadays, ionizing radiation and its detectors are widely used in medical, industrial, and scientific research fields. As one type of ionizing radiation, X-ray is a high-energy electromagnetic wave with a photon energy ranging from 0.12 to 124 keV (corresponding to a wavelength between 10 and 0.01 nm). Because the energy of X-ray is much higher than that of visible light, it is relatively difficult to accurately detect X-rays. According to the different conversion principles of photon-to-photon and photon-to-electric, X-ray detectors can be divided into indirect (scintillator) and direct type.

The contrast-based X-ray imaging using a scintillation screen-film is a classical technique that greatly advances the noninvasive medical imaging. Despite great efforts and tremendous achievements have been made in the past decades, the field of X-ray imaging is still in search of low-dose, high-resolution, large-area and flexible X-ray detectors. To date, traditional scintillator materials, include alkali metal halides (CsI, NaI), bismuth germanate (Bi4Ge3O12, BGO), gadolinium oxysulfide (Gd2O2S, GOS), cadmium tungstate (CdWO4), often require the use of high temperature and high vacuum to realize thick crystalline structures, suffering drawbacks such as harmful scintillation decay, harsh synthesis processes, unsatisfied light yields and being not capable with flexible systems.

As for the applications in direct X-ray detection, the material should have a large stopping power ability, high mobility-lifetime (µτ) products and large resistance. However, the drawbacks in current commercial materials, i.e. Si, α-Se and CdZnTe (CZT) still impede their further development. For example, Si has a small atomic number and a small stopping power. Despite α-Se has a larger atomic number, the µτ products are relatively low. Although the increase of mobility can be done by boosting the bias voltage, this would sacrifice the dark current and hence increase the noise level.5 Besides, CZT needs a high processing temperature and is not cost-effective.6 Therefore, the development of novel semiconductors as active layer in both indirect and direct X-ray detectors are quite urgent. Recently, metal halide perovskites (MHPs) have attracted considerable attention in various optoelectronic applications, including solar cells,7 light emitting diodes (LEDs),8 lasers,9 and radiation detectors.10–12 Meanwhile, they have a relatively high atomic number, moderate density and tunable bandgaps with some of the properties even superior to conventional materials, making them great candidates as active materials in X-ray detectors.13 Their relatively low deposition temperature also makes the realization of flexible X-ray detectors possible. Actually, MHPs have already...
been regarded as an alternative material in X-ray detectors with some magnificent work being already published. For example, Meng et al. reported metal halide scintillators based on manganese (II) complexes, showing a spatial resolution of 4.6 lp mm\(^{-1}\) and a detection limit of 65.1 nGy\(_{air}\) s\(^{-1}\).\(^{1,2}\) Peng et al. reported lead-based MHP thick films for direct detection of X-rays, showing a high X-ray sensitivity of 13.6 mC Gy\(_{air}\)\(^{-1}\) cm\(^{-2}\) and ultra-low detection limit of 4.2 nGy\(_{air}\) s\(^{-1}\).\(^{1,2}\) Therefore, it is of quite urgent to have a review summarizing the recent progress and propose useful strategies to further enhance the performance of MHP-based flexible X-ray detectors.

In this work, the recent progress of flexible X-ray detectors based on MHPs and their outstanding potentials are reviewed and discussed, covering the applications in both direct and indirect X-ray detection. Figure 1 gives a general view of MHP-based X-ray detectors. After an overview of this field, a brief introduction on the chemical and physical properties of perovskite materials is given, focusing on their composition and structure, methodology of synthesis, and pointing out the advantages of using them in radiation detections. Then, according to the detection type, the key performance of MHPs X-ray detectors is given with the working principles being discussed in detail. After that, representative MHP-based flexible X-ray detectors are summarized, covering both indirect and direct direction, and aiming to give the readers an insight view of this field. Finally, the current challenges impeding the commercialization of flexible MHP-based X-ray detectors are highlighted with possible solutions to those problems being provided.

**BASIC OF PEROVSKITES**

Until now, the advantages such as solution processable, cost-effective synthesis, tunable bandgaps\(^{1,6}\) and outstanding optoelectronic properties have enabled considerable attention of MHPs in research fields of materials science, physics, and optoelectronics.\(^{1,7}\) To give an insight view of this kind of material, in this section, we review the basic of MHPs, covering their crystal structures and typical synthesis methods.
Crystal structure of perovskites

According to their crystal structures, MHPs materials can be divided into three-dimensional (3D) perovskites and low-dimensional perovskites, where low-dimensional perovskites include two-dimensional (2D), one-dimensional (1D) and zero-dimensional (0D) ones. Notably, the nomenclature of 3D, 2D, 1D, and 0D herein means the structural dimensionality of MHPs at the molecular level. As shown in Figure 2, the structure of 3D perovskites can be described by the cubic contractual formula $A^+B^{2+}(X^-)_6$, where each A cation (either an organic group or an inorganic cation) has twelve neighboring X halide ions (e.g., Cl$^-$, Br$^-$, I$^-$), and each B cation (e.g., Pb$^{2+}$, Sn$^{2+}$) connects with six adjacent X through ionic bonds. When a suitable organic molecule, such as CH$_3$NH$_3^+$ (methylammonium, MA$^+$) or CH$_3$(NH$_2$)$_2^+$ (formamidinium, FA$^+$) is employed as the A cation, the resulted material is an inorganic-organic hybrid MHP, whereas an inorganic MHP is resulted when an inorganic atom such as cesium (Cs$^+$) and rubidium (Rb$^+$) is applied as the A cation.

Reducing the perovskite structure from 3D to 2D produces a general chemical formula of $A_0^2A_{n-1}B_nX_{3n+1}$ or $A^0_{n-1}B_nX_{3n+1}$ ($A^0 = ^+ \text{ or } ^2+$ cation, $A = \text{MA}^+$, FA$^+$, Cs$^+$, and $B = \text{Pb}^{2+}$, Sn$^{2+}$, Ge$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, etc.). The structure of 2D perovskites is separated by thin sheets of spacer materials, which could be either organic or inorganic cations. Further structural reduction of 2D MHPs generates 1D and 0D MHPs such as (C$_7$H$_{16}$N)$_2$PbBr$_3$ and Cs$_4$PbBr$_6$. 1D perovskites contain numerous edge-shared BX$_4$ tetrahedra and isolated A cation, leading to the formation of 1D chain-like sharp. The basic unit of 0D perovskites is a B$_m$X$_n$ polyhedron (mostly octahedron, hexahedron and tetrahedron), which is separated by A cations to form a 0D crystal structure. Generally, for low-dimensional MHPs like constructing 2D and 0D, the enhanced quantum confinement effect enables MHPs to obtain an efficient room temperature scintillation.

The formability and stability of MHPs can be evaluated by two important parameters, namely tolerance factor (TF) and octahedral factor (OF). TF is used to evaluate the symmetry and phase stability of perovskite structures according to:

$$TF = \frac{r_A + r_B}{\sqrt{2(r_B + r_X)}}$$

where $r_A$, $r_B$, and $r_X$ are ionic radii of A, B, and X, respectively. For an ideal cubic perovskite lattice, TF is close to 1. When $TF > 1$, a hexagonal structure is typically formed whereas a non-perovskite phase is formed at $TF \leq 0.8$.

OF is the ratio between the ionic radius of B site and A site, which is also of great importance, especially in the design of lead-free metal halides, because it provides a measure of the octahedral stability of the perovskites. OF is usually found in the range of $0.44 \leq OF \leq 0.9$.

Synthesis methods of perovskites

Perovskite materials are generally developed in powder crystals, films and single crystals for X-ray applications with unique properties being found for all of them. For example, powder crystals are easily blended with other polymer materials in preparing composite films for scintillators without needing an extra substrate. Perovskite films could be fabricated on a flexible substrate for special X-ray detections. With no grain boundaries existed, perovskite single crystals generally possess excellent μ products, ideal for direct detection. Note that no matter what kind of MHPs being used, a high quality is required for pursuing high...
performance X-ray detection. Therefore, in this subsection, we introduce the most commonly used synthesizing methods for perovskite materials.

**Powder crystals (nanocrystals and micron crystals)**

Powder crystals have shown a great potential as active layer in radiation detections owing to their advantages of high absorption coefficient, high conversion efficiency, and easy integration with flexible substrates. Out of all the synthesis methods for nano and micro particles, hot-injection and room temperature anti-solvent methods are the most used ones. For example, as shown in Figure 3A, \[^{23}\] CsPbBr\(_3\) nanocrystals (NCs) can be formed after the injection of cesium-oleate into precursors at 150°C. Similarly, Chen et al. also synthesized CsPbBr\(_3\) NCs using hot-injection methods and successfully applied them in X-ray detectors.\[^{26}\] However, a high temperature, inert gases and sometimes even vacuum are generally required in a hot-injection method,\[^{27}\] which not only enhances the synthesizing cost, but also complicates the synthesis, limiting the potential applications in mass production.

Alternatively, one can synthesize powder crystals using anti-solvent methods at room temperature. As shown in Figure 3B, an anti-solvent method involves the adding a large amount of anti-solvent to a solvent system, thereby reducing the solubility of the substance to be crystallized in the solvent, and then crystallizing the solid from the liquid phase and separating the two solvents.\[^{24}\] For example, CsPbX\(_3\) were successful synthesized by an anti-solvent method, as reported by Pan et al., showing an efficient emission, rendering them attractive for applications in fields such as lighting and scintillation.\[^{28}\] Xu et al. reported the synthesis of CH\(_3\)NH\(_2\)PbBr\(_3\) and CsPbBr\(_3\) quantum dots (QDs), and demonstrated their potential in scintillation applications of high-energy ray radiation and a wide range dosimeters.\[^{29}\] However, the impurities in this method tend to precipitate out with the product because of the involved high supersaturation, thus additional washing steps or recrystallizations are usually required to obtain a product with the desired purity, complicating the deposition process.

Besides solution-based methods, MHPs nanoparticles can also be synthesized with a solvent-free mechanochemical reaction. One typical mechanochemical reaction is grinding, which forcing the chemical reaction between the precursor particles by the strong impact and stirring of the raw materials through the energy of rotation or vibration, as shown in Figure 3C. Leupold’s group, as an example, synthesized MAPbI\(_3\)
powders with a good optoelectronic performance and stability from a ball milling approach. Similarly, Palazon et al. also reported the synthesis of CsPbBr$_3$ and CsSn(BrCl)$_3$ powders by a ball-milling mechano-chemical reaction, achieving intense and narrow Photoluminescence (PL) peak. However, despite such a mechanical grinding method offer advantages of high-temperature-free and solvent-free, the optical performance is generally unsatisfactory, which needs further improvement.

Polycrystalline films

For X-ray detections, a high-quality film is generally required for enhancing the detection performance. However, the previously mentioned powder crystals normally require a further mixture with other polymers to obtain a uniform film, resulted in a complicated process. To solve such an issue, one can directly synthesis MHP films through chemical or physical methods. Out of all the potential methods, spin coating (Figure 4A) is the most reported one, not only in detectors, but also in solar cells. As early as 2016, Wang et al. already reported the use of spin-coated lead-based perovskites in photodetectors, achieving both a high sensitivity and an ultrafast response. However, the large-area uniformity is still a serious issue of such a method.

An effective alternative to spin-coating is blade coating (Figure 4B), which has been widely reported especially in solar cells, owing to the advantages of high uniformity over large areas and compatibility with roll-to-roll processing techniques. Recently, such a method has also applied in the deposition of X-ray detectors, as reported by Dong et al. and Li et al., achieving low dark currents and low detection limits. However, the precise control of film thickness in such a method is still quite challenging.

As shown in Figure 4D, ink-jet printing is also a method highly reported in the preparation of MHP films because it offers advantages of easy patterning, selective printing location, and low cost. In 2021, Glushkova et al. reported the preparation of MAPbI$_3$ X-ray detectors using aerosol-jet-printing, showing an ultrahigh sensitivity.
of $2.2 \times 10^5 \text{mGy}_x^{-1} \text{cm}^2$ when detecting 8 keV photons at a low dose rate. However, similar to other solution-based methods, the film quality is not satisfactory with pinholes and a rough surface might exist.

Besides the above mentioned solution-based methods, one can also deposit MHP films through a chemical vapor deposition (Figure 4D). For example, Li et al., achieved X-ray detectors consisting of CsPbBr$_3$/Cs$_4$PbBr$_6$ films by such a method. However, the polycrystalline nature of MHP films might result in defects and traps at grain boundaries and film surfaces, degrading the overall performance.

Single crystals (millimeter or centimeter crystals)
Single crystals with less grain boundaries, show advantages of improved carrier mobility, lower bulk defect state density, and more adequate light absorption. Main techniques that were reported capable of synthesizing high performance single crystals include high-temperature Bridgeman (Figure 5A), heating precursor solution crystallization (inverse temperature crystallization, Figure 5B), cooling precursor solution crystallization (Figure 5C), hot process (Figure 5D), solvent volatilization, anti-solvent-assisted crystallization, vapor phase epitaxial growth, space-limited crystallization, cavitation triggered asymmetrical crystallization methods. For example, Chung et al. successfully grew pure CsSnI$_3$ crystals in evacuated fused silica tubes at a rate of 2 cm h$^{-1}$ through a single-zone Bridgman furnace. Peng et al. grown CsPbBr$_3$ crystals by inverse-temperature crystallization, exhibiting a distinct crystal habit and superior charge transport properties in X-ray direct detection. Wang et al. dissolved the precursor at 100 °C and then lowered the temperature of the saturated precursor to room temperature at a rate of 1 °C h$^{-1}$ to obtain cesium-copper-iodine single crystals with a centimeter scale. However, the above-mentioned methods generally result in single crystals with a large size/thickness, limiting their applications in flexible X-ray detections. To solve such an issue, Zhang et al. reported the preparation of CsCu$_2$I$_5$ films and X-ray scintillators by a close-space sublimation through a bulk crystal, opening the door for achieving flexible X-ray detectors. However, the slow growth rates of MHP single crystals still limits their practical applications. Alternatively, one can try thermal evaporation to achieve high-performance MHP single crystals. In 2021, Li et al. reported flexible X-ray detectors based on FAPbI$_3$ single crystals synthesized through co-evaporation of FAI and PbI$_2$, showing extremely low dark current and noise, fast response and high sensitivity.

PERFORMANCE CHARACTERIZATION
To meet the needs of various applications, X-ray detectors with different architectures have been constructed. According to the detection principle, high-energy radiation detectors can be divided into two types, namely indirect and direct detectors. Table 1 summarizes the merits and disadvantages of both detectors.

Recent years, MHPs have exhibited great potentials in direct X-ray detection because of their exceptional properties such as large X-ray attenuation coefficients, large $\mu r$ products, low-cost solution processable,
high photoluminescence quantum yields (PLQYs), tunable optical bandgaps, and short decay times. However, such detectors generally require MHPs with a high quality to achieve a high performance, resulting in an increased manufacturing cost. MHP based X-ray scintillators despite showing a more complex device structures, the ability of them to convert high-energy photons into lower-energy visible photons make them especially suitable for medical-related applications.

### Operation mechanism

#### Indirect detection

As shown in the top of Figure 6, for indirect detection, a light-emitting material (also called a scintillator) is placed in the middle of a high-energy ray source and a photodetector, and is used to convert the high-energy radiation into visible or near-visible light for it to be detected by a standard photodetector. The basic principle of an X-ray projection imaging is to record the attenuation of X-rays after penetrating subjects. When X-rays travel through a matter, they are transmitted, absorbed, or scattered. The processes of scattering and absorption depend on the attenuation ability of the matter and are governed by Lambert-Beer’s Law:2,56,57

$$I = I_0 e^{-\mu d}$$

where $I$ is the intensity of transmitted X-ray photons, $I_0$ is the initial intensity of X-ray photons, $\mu$ is the linear attenuation coefficient, and $d$ is the thickness of the matter. The attenuation ability is dominated by a combination of the Compton scattering, Rayleigh scattering, photoelectric effect, and pair production.58 Their ratios are determined by both the nature of the matter and the energy of income X-rays. Typically, in a low-energy X-ray region, X-ray photons are mainly absorbed by the object through the photoelectric effect, whereas Compton scattering and pair production dominate at high-energy regions (>1.02 MeV).

#### Direct detection

Semiconductors with suitable band gaps can absorb high-energy rays and generate free carriers (electron-hole pairs) because of the inelastic collisions and photoelectric effects. If the electron-hole pairs are separated by an external circuit, the current can be collected, leading to the direct conversion of the incident ionizing radiation to an electric current. Depending on the interaction of energetic particles with semiconductors, this process can be operated in either current or voltage modes. The magnitude of the maximum photocurrent, $I_{CC}$, accounting for such a carrier generation and collection process is described by:

$$I_{CC} = \Phi nq$$

where $\Phi$ is the photon absorption rate, $n$ is the number of the generated electron-hole pairs per absorbed photon, and $q$ is the elementary charge.59,60

For direct detection, three generally device structures are used, namely photodiodes, photoconductors and phototransistors. According to the transmission direction of the current, the photoelectric conversion part of the ionizing radiation detectors can be divided into two types: vertical and lateral structures, as shown in the bottom of Figure 6. Detectors with vertical structures are mainly vertical-type photoconductors and photodiodes, whereas those with lateral structures include lateral-type photoconductors and phototransistors. Vertical geometries are widely applied because of their easy integration with pixelated matrices, but lateral structures offer advantages of low driving voltage because the intensity of the electric field depends only on the electrode spacing but not on the film thickness.60

| Table 1. The advantages and disadvantages of indirect and direct X-ray detectors |
|---|---|
| **Indirect detection** | **Direct detection** |
| **Advantages** | **Simple device structure** |
| Low manufacturing costs | High sensitivity |
| Easy manufacture | High spatial resolution |
| Good operating stability | Short theoretical response time |
| Low detection limit | |
| **Disadvantages** | **High preparation cost** |
| Dependent on the performance of visible light detectors | |
Phototransistors are three-terminal architectures with gate, source and drain electrodes. In such structures, the charging current flow within the channel of the transistor (that is, the current between the source and drain) can be adjusted not only by the polarization of the gate, but also by the charge generated through the interaction with radiation. In addition, when the gate voltage is set below the threshold, the charge carrier density in the transistor channel is lower, and the photocurrent at this time comes from the separation and collection of ionized charges of high-energy ray photons. The advantage of this structure is that a gate electrode is applied to amplify the signal, thus enlarging the obtained photocurrent. However, there are very few works reported so far about MHP-based X-ray phototransistors, which might relate to the performance degradation caused by the ion migration.

**Key performance parameters**

**Absorption coefficient**

It reflects the ability of a detection material to stop high-energy rays. X-ray absorption capability depends on the effective atomic numbers ($Z_{eff}$) and the density ($\rho$) of absorption materials, which means the larger the atomic numbers, the greater the attenuation of X-rays.\(^{61,62}\) The absorption coefficient can be calculated using

$$\text{Absorption coefficient} = \frac{\mu Z_{eff}^2}{AE^3}$$

where $A$ is the atomic mass and $E$ is the X-ray photon energy.

**Spatial resolution**

The ability to distinguish adjacent details in an object and their relative sharpness. For digital imaging systems, the spatial resolution is affected by the pixel size in the matrix, meaning that the higher the spatial resolution, the higher the image quality.\(^{61}\) Typically, this parameter can be measured by slanted edge, slits, and line-pairs standard cards.\(^2\) Generally, a modulation transfer function (MTF) equals to 0.2 is extracted from the X-ray imaging to characterize the spatial resolution, which is the limit of discernibility to the naked eye.
Detection limit
The equivalent dose rate to generate a signal three times greater than the noise level according to the International Union of Pure and Applied Chemistry (IUPAC). For medical radiation imaging, this value should be as low as possible. The detection limit is affected by signal sensitivity and system noise, suggesting that a precise monitoring of tiny currents may improve the performance of detectors.

Indirect detection
Light yield. The ability of scintillators to convert a certain number of high-energy radiations into low-energy lights, which can be measured by integrating sphere according to the following equation:

\[
\text{Light yield} = 1000000 \frac{SQ}{\beta E_g}
\]

where \(S\) is the efficiency of transport for electron-hole pairs to the optical (emissive) center, \(Q\) is the luminescence efficiency, \(\beta\) is a constant with a typical value of 2.5, and \(E_g\) is the energy bandgap.

Radioluminescence wavelength. Radioluminescence (RL) is the visible or near-visible light emitted from scintillators when excited by an ionizing radiation. If the central wavelength of RL coincides with that of PL, it means that the two emitted lights come from the same energy level. Generally, the RL intensity boosts linearly with the enhancement of dose rate. The RL spectra should match the absorption spectra of the photodetectors, such as: charge coupled device (CCD), complementary metal oxide semiconductor (CMOS), photomultiplier tube (PMT), thin film transistor (TFT) array, silicon probe, and so on.

Afterglow. The RL intensity at a given time after X-ray radiation, which is mainly caused by material defects (i.e., impurities, flaws). Generally, the RL intensity at a given time (e.g., 3 ms) less than 0.1% is required after X-ray excitation. Long afterglow can lead to imaging artifacts, owing to the signal superimposition on the previous exposure. With negligible afterglow, MHPs show great potential in dynamic X-ray imaging.

Direct detection
Dark current. The dark current, or leakage current, is an important parameter for direct X-ray detection. Smaller dark currents imply less scattering noise, which contribute to a higher signal-to-noise ratio. Typically, we require dark current densities as low as \(10^{-10}\) A cm\(^{-2}\).

Sensitivity. It reflects the efficiency of a detector to convert incident X-ray photons into collected charges. High sensitivity can generate better imaging contrast with low incident dosage, which is essential for applications particularly in medical-related fields. The sensitivity, \(S\), can be estimated by

\[
S = \frac{Q}{AD},
\]

where \(Q\) is the collected charges, \(A\) is the effective area, and \(D\) is the radiation exposure.

Response time. The response time includes rise time (\(t_{\text{rise}}\), defined as the time for signal intensity to increase from 10% to 90%) and fall time (\(t_{\text{fall}}\), defined as the time for signal intensity to decrease from 90% to 10%). A detector with a shorter response time is preferred because it offers advantages of improved work efficiency, conducive to real-time monitoring or imaging, and reduced radiation dose to the tested object.

\(\mu t\) product. A key parameter that directly affects the carrier collection efficiency of X-ray detectors. The larger the \(\mu t\) product, the higher the charge collection efficiency of a direct detector.

INDIRECT DETECTION (SCINTILLATORS)
Ever since the discovery of X-rays, the detection of ionizing radiations has become extremely important due to their wide applications in medicine, nuclear industry, industrial nondestructive detection, safety inspection and scientific research. Down-conversion scintillators, which can be used to convert X-rays into visible light or near-visible light, are relatively mature detection methods for ionizing radiation. Efficient scintillator materials require several key parameters, including a high absorption coefficient, a high light output, a fast response, a high spatial resolution, and a linear relationship between emission intensity and incident photon energy. However, current commercial scintillators, such as CsI:Tl and CdWO\(_4\), still suffer
| Scintillators                        | Synthesis method          | Emission (nm) | PL Decay time (ns) | Light yield (photons MeV$^{-1}$) | Detection limit (nGy s$^{-1}$) | Spatial resolution (lp mm$^{-1}$) | RL stability | Reference                                       |
|------------------------------------|---------------------------|---------------|-------------------|---------------------------------|-------------------------------|---------------------------------|-------------|-------------------------------------------------|
| CsPbBr$_3$ NCs/PDMS               | Hot-injection             | 530           | 44.6              | –                               | 13                            | 5 (MTF = 0.4)                   | 35.3 h @80 kV, 10 keV          | (Chen et al., 2018)           |
| CsPbBr$_3$ NCs/methyl methacrylate/photoinitiator | Hot-injection             | 550           | 2.87              | 177000                           | –                             | 9.8 (MTF = 0.2)                 | 40 Gy s$^{-1}$                | (Heo et al., 2018)           |
| Cs$_2$Cu$_3$I$_5$ NC films/glass   | Hot-injection             | 445           | 1920              | 79279                           | –                             | 1.5 (0.32 mm)                   | –                        | (Lian et al., 2020)           |
| (Cs$_3$H$_7$NH$_3$)$_2$SnBr$_4$/PMMA | Cooling/spin-coating      | 596           | 3340              | –                               | 2.5 (0.2 mm)                  | 0.22 h @40 kW/0.07 mA           | –                        | (Cao et al., 2020b)          |
| (Cs$_3$H$_7$P$_2$)MnBr$_4$ powder/PDMS | Antisolvemold            | 517           | 318000            | 66256                           | 46.1                          | 1.5 (0.322 mm)                  | 4 h @0.0894mGy s$^{-1}$       | (Xu et al., 2020a)           |
| CsPbBr$_3$ QD-acrylate-resin sheets | Laminated                | 534           | 1.07              | 21500                           | –                             | 4 (MTF = 0.2)                   | 1 h@45 kV 10 mA, 8 keV         | (Maddalena et al., 2021)     |
| UCNP$_5$@mSiO$_2$@MAPbX$_3$/PDMS  | Antisolvemold             | 504           | 2.6–93.7          | –                               | –                             | 20                              | 6 h                      | (Xie et al., 2021)            |
| MAPbBr$_3$/lauryl methacrylate     | Spin-coating              | 525           | 63.7              | –                               | 1.57                          | 5.35 (MTF = 0.3)                | 21 h @125mGy s$^{-1}$          | (Xu et al., 2021b)           |
| (TBA)CuBr$_2$/PVDF                | Solvent evaporation       | 498           | 232050            | 24134                           | –                             | 3 (0.166 mm)                    | –                        | (Lian et al., 2021)          |
| CsPbBr$_3$: Lu$^{3+}$/B$_2$O$_3$-SiO$_2$-ZnO | Melt-quenching process   | 516           | 27               | –                               | 50                            | 16.8 (MTF = 0.2)                | 30 h @8mGy s$^{-1}$           | (Zhang et al., 2021a)        |
| Rb$_2$CuBr$_5$/polystyrene        | Anti-solvent              | 400           | 61040             | 91056                           | –                             | 1.7 (0.29 mm)                   | –                        | (Han et al., 2022b)          |
| Cu$_2$CuI$_3$/PDMS                | Ball-milled               | 445           | 960              | 12376                           | –                             | 6.8 (MTF = 0.2)                 | 1 h @0.1838mGy s$^{-1}$        | (Li et al., 2022b)           |
| Cs$_3$H$_7$NCuBr/PDMS             | Antisolvemold             | 464, 630      | 2230, 2520        | 25000                           | 40.4                          | 5.6                            | 0.5 h @0.0104mGy s$^{-1}$      | (Mao et al., 2022)           |
| Cs$_3$Cu$_2$I$_5$/polymethylsiloxane/PDMS | Anti-solvent/spin-coating/blade-coating | 445, 969   | 48800             | 48.6                            | 17 (MTF = 0.2)                 | –                              | –                        | (Zhou et al., 2022)          |
| Cs$_3$CuCl$_5$: 2% K$^+$/polystyrene | Hot-injection             | 530           | 107.57            | –                               | 63.5                          | 5                               | –                        | (Han et al., 2022a)          |
| BA$_2$PbBr$_4$: 10% Mn$^{2+}$/PMMA | Solid-state grinding      | 430, 610      | 737830            | 85000                           | 16                            | 10.7                           | –                        | (Shao et al., 2022)          |
| CsPbBr$_3$ NCs/PMMA               | Spin-coating              | 513           | –                | –                               | 120                           | 12.5                           | 1 h @0.6mGy s$^{-1}$           | (Chen et al., 2022b)         |
| CsPbBr$_3$ NCs/PMMA               | Spray-coating             | 516           | 35.68             | 30000                           | 2971                          | 5                              | 0.5 h @28.76mGy s$^{-1}$       | (Chen et al., 2022b)         |
| PVDF/CsPbBr$_3$: Ce$^{3+}$/PS     | Suction filtration        | –             | 7.09              | 33000                           | –                             | 580                           | 0.3 h @4mGy s$^{-1}$           | (Wu et al., 2022)           |
| CsPbBr$_3$ NCs/PMMA               | Template dispense         | 532           | 8.25              | –                               | 40.1                          | 8 (MTF = 0.2)                   | 108 h @0.005mGy s$^{-1}$       | (Wang et al., 2022a)         |
disadvantages of high cost, toxicity and non-flexibility. As a promising alternative, MHPs can be synthesized through a facile method at a relative low temperature and thus being considered as star materials for flexible scintillators. Table 2 summarizes the recent progress of MHP-based scintillators.

All-inorganic MHPs films
Out of all potential MHPs, inorganic CsPbX₃ (X = Cl, Br, I), especially CsPbBr₃ NCs have gained numerous attention as scintillators because of their high PLQYs and low cost. The easy solution processability also makes them being easily integrated into pixel silicon photodiode arrays, and thus suitable for large-scale production of ultra-sensitive, large-area, flexible X-ray detectors and imagers. As early as 2018, Heo et al. already reported flexible CsPbBr₃ NCs-based scintillators. As an alternative to original terbium-doped GOS scintillator films in the system, such scintillator films were prepared by photopolymerizing a mixed solution of CsPbBr₃ NCs, methyl methacrylate (MMA) and a photoinitiator, as shown in Figure 7A. The prepared CsPbBr₃ NCs-based X-ray scintillators were found to show a high stability even under an X-ray irradiation of over 40 Gy air s⁻¹/C₀, comparable to conventional GOS scintillators. Also, a shorter response time (≈ 200 ns) and a higher spatial resolution (9.8 lp mm⁻¹ at MTF = 0.2) were found for the prepared CsPbBr₃ scintillators, mainly due to the shorter average PL lifetime and stronger emission than that of GOS.67

In the same year, Chen et al. prepared a series of CsPbX₃ NCs (X = Cl, Br, I) using hot-injection methods and demonstrated their applications in ultra-sensitive scintillators. These scintillators showed a strong X-ray absorption and intense RL at visible lights and could generate X-ray-induced emission across the whole visible spectra by simply tuning the anionic component of the colloidal precursors during synthesis. Under an X-ray beam excitation, the NCs showed a narrow and tunable emission, and thus being suitable for realizing multicolor and high-efficiency X-ray scintillations. With a high flexibility and a low detection limit of 13 nGy air s⁻¹/C₀, the prepared scintillators would no doubt have great potential in medical-related fields.66

Similar works were also reported by Xu et al., who proposed a nucleation suppression strategy to prevent perovskite crystals from agglomeration and Ostwald ripening during the subsequent precipitation process, resulting in a uniform dispersed CsPbBr₃ NCs based polymer-ceramics film. The use of such films as the scintillators achieved a detection limit of 120 nGy s⁻¹ and a spatial resolution of 12.5 lp mm⁻¹. Interestingly, the scintillator films could be renewed after a long-time (≥ 3 h) and a high-dose irradiation (8 mGy s⁻¹) because of the anchoring effect of exfoliated atoms provided by the polymer matrix. This

Figure 7. All-inorganic lead-based scintillators
(A) CsPbBr₃ NCs scintillators and X-ray images of ball-point pens. Adapted with permission from Heo et al. Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
(B) Flexible scintillator films based on CsPbBr₃ NCs and X-ray images of a chip and a fish. Adapted with permission from Wang et al. Copyright 2022, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
inherent property sort of overcoming the long-term stability issues of MHP-based scintillators, paving the way for achieving highly sensitive, renewable and flexible MHPs scintillators with a low cost.  

Large-scale fabrication is a key factor for commercializations of X-ray detectors. This year, our groups reported a facile and low-cost template assembled method to prepare large-area flexible CsPbBr3 NCs@poly(methyl methacrylate) (PMMA) films in ambient conditions (Figure 7B). The composite films could maintain 94 and 81% of their initial PL intensity even after 2000 bending cycles and 2500 h storage in water, respectively, suggesting the excellent flexibility and stability. The application of such films as the scintillators enabled not only a low detection limit (40.1 nGy/s) and a high spatial resolution (8.0 lp mm1), but also an excellent tolerance against radiation (108 h), demonstrating the great potential of such methods and materials in flexible X-ray imaging.

However, the above mentioned works still use an external photodiode, where the device performance is highly limited by the performance of the used photodiode. To solve such an issue, one can directly combine CsPbX3 with an organic photodetector to form an indirect-type X-ray detector. For example, Xiang et al. deposited CsPbBr3 NCs on a flexible PET substrate, and then bonded an organic photodetector with a structure of ITO/PEDOT:PSS/P3HT:PC61BM/LiF/Al with it. When exposing to X-rays, the NCs converted the X-rays to green light, which was then absorbed by the attached organic photodetector to generate a photocurrent as the detection signal. The results showed that the dark current and photocurrent could maintain their original levels even after 1200 bending cycles, indicating the good flexibility of this high-energy ray detector.

Figure 8. All-inorganic lead-free scintillators. (A) The X-ray absorption coefficients of Cs3Cu2I5, CsPbBr3, CsI:Tl and carbon dots as a function of photon energy. The photographs and X-ray images of a circuit board, a universal board, and a ball-point pen. Adapted with permission from Lian et al. Copyright 2020. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (B) Cs3Cu2I5-PDMS flexible films under UV lights. X-ray images of a flexible copper grid under flat and bending states. Adapted with permission from Zhou et al. Copyright 2022, American Chemical Society. (C) Curved films at different angles (0 ≤ θ ≤ 80°) and a composite film during four weeks’ exposure to air. Adapted with permission from Han et al. Copyright 2022. Elsevier.
Although CsPbX₃ scintillators exhibit many scintillator advantages, such as a large stopping power, tunable RL, a fast scintillation response, a sensitive X-ray sensing, and a high-resolution imaging, the self-absorption effects, small Stokes shifts and the intrinsic toxicity can severely limit the optical output efficiency of the prepared scintillators and seriously restrict their wide applications. Therefore, the development of next generation scintillators with large Stokes shifts, high PLQYs and environmental friendly nature are of quite urgent.

Substituting lead with other elements, such as Mn, Cu, Zn, Ag, Sn, Sb, Bi, are expected to be a better choice in the field of radiation detections because of their low toxicity and small re-absorptions. As shown in Figure 8A, the occurrence of multiple local lattice distortions leads to multiple trapped excitons in both Cs₃Cu₂I₅ and CsPbBr₃, thus resulting in similar absorption coefficients for both materials. Besides, the multiple self-trapped excitons (STEs) are localized and separated by the 0D structure of Cs₃Cu₂I₅, avoiding the Auger recombination. Lian et al. reported Cs₃Cu₂I₅ NCs produced with the assistance of InI₃ through hot-injection, which exhibited a PL peak of 445 nm, matching the response peak of silicon photomultipliers, a large Stokes shift of 161 nm, a PLQY of 73.7% and a highly light yield of 79,279 photons MeV⁻¹. The use of such NCs successfully worked as scintillators, with the internal structure of a circuit board and a spring pen being clearly revealed, as shown in Figure 8A.

Similar works were also reported by Li et al., who prepared a flexible scintillator film by mixing the ball-milled Cs₃Cu₂I₅ powders with poly(dimethylsiloxane) (PDMS), which exhibited a high PLQY of >90%, a high spatial resolution of 6.8 lp mm⁻¹@0.2 MTF in X-ray imaging and a good stability under steady X-ray illuminations. The obtained high performance combined with the easy large-scale production guarantees the great potential of the reported strategies in building reabsorption-free, large-size, low-cost and flexible scintillation films for high spatial resolution X-ray imaging systems.

Very recently, Mohammand’s group reported highly stable and flexible Cs₃Cu₂I₅ films with a large area of 400 cm² prepared by mixing Cs₃Cu₂I₅ with PDMS, as shown in Figure 8B. Owing to the advantages including reabsorption-free, high phase purity and nearly 100% PLQYs, the films were found to exhibit a very promising scintillation performance, including a low detection limit of 48.6 nGy s⁻¹ and an X-ray imaging resolution of 17 lp mm⁻¹. Most importantly, the rubber-like nature of PDMS also enabled the composite films to show a negligible physical damage in response to mechanical deformations, including stretching, crumpling, bending, twisting and folding. The prepared films not only possessed a better resolution at bending state compared with films under a flat state, but also maintained a high resolution at stretching state, confirming the promising features of the reported flexible films in non-flat, flexible target X-ray detections.

Apart from the well-known Cs, Rb cations were also reported in Cu-based perovskites in preparing high-performance X-ray scintillators, as reported by Han et al., using Rb₂CuX₃ (X = Br, Cl). The prepared Rb₂CuBr₃ exhibited a quite high mass yield of 90% with a high PLQY of 59.06% and a large Stokes shift of 90 nm, mainly originated from the formation of STEs. By composing with polystyrenes, the films showed a high uniformity with a good flexibility and an excellent stability. As shown in Figure 8C, the use of such films as an X-ray imaging screen clearly presented a sensitive scintillation response to X-ray signals with targeted objects being clearly observed even after storage in air for 30 days, further confirming the high stability.

Currently, high-performance perovskite X-ray detectors are mainly based on lead-containing halide perovskites (CsPbX₃, X = Cl, Br or I). Commercialization of such ionizing radiation detectors is still limited because of the toxicity of lead. Despite the substitution of lead with other elements could solve the toxicity issue, the severe ion migration in all-inorganic perovskites is still a serious issue limiting the overall performance.

Organic-inorganic MHPs films

An alternative choice to all-inorganic MHPs is organic-inorganic MHPs, which were also highly reported as scintillator materials mainly because of the advantages of rich sources of materials and low manufactory cost. As shown in Figure 9A, by designing a sandwich structure, Xu et al. reported a polymer-MAPbBr₃-polymer (PPP) scintillation screen, using the outer polymer layer to provide high mechanical stability and encapsulation for the internal perovskite QDs layer. The prepared PPP showed a good flexibility with 93 ± 0.5% of its initial light outputs remaining even after 600 times’ bending to a radius down to
2.5 mm. The scintillation performance of such PPP was then demonstrated, with the clear interior details of the objects being revealed through a digital CCD. Also, the PPP exhibited an ultra-high sensitivity to low energy X-rays with a detection limit of 1.57 nGyair s\(^{-1}\) and a spatial resolution of 5.35 lp mm\(^{-1}\) (MTF = 0.3) being achieved under an exposure dose of 12 \(\mu\)Gyair.\(^{73}\)

In 2021, Xie et al. synthesized an upconversion nanoparticles (UCNPs)-perovskite nanotransducer, namely UCNPs@mSiO\(_2@MAPbX_3\) (X = Cl, Br, or I) through in situ crystallization and deliberately tuning the material composition in the lanthanide core and perovskites, and reported photodetectors with a broadband detection through ultraviolet (UV) to near-infrared (NIR) and even X-rays. The detection of X-ray was achieved by embedding the perovskite-lanthanide nanoparticles into a PDMS substrate \((8 \times 8 \text{ cm})\), which showed an excellent flexibility and a high uniformity, as shown in Figure 9B. The internal structures of an encapsulated metallic spring, an electronic circuit board and chicken feet could be clearly visualized through the prepared X-ray scintillator and the spatial resolution was found to be up to 20 lp mm\(^{-1}\).\(^{72}\)

Clearly, these high resolution scintillators will have great advantages in practical applications.

Similar to all-inorganic MHPs, lead-based hybrid perovskites also show an unavoidable self-absorption phenomenon caused by the intrinsic small Stokes shift, limiting the light output efficiency. From commercial scintillators, such as NaI:Tl, CsI:Tl, and LaBr\(_3\):Ce, it is found that the introduction of an external emitter into the crystal host can provide an additional radiative recombination channel to enhance the scintillation performance. Applying such a method to MHPs, Shao et al. reported highly efficient and low-cost X-ray scintillators based on Mn (II) activated 2D butylammonium lead bromide perovskites-BA\(_2\)PbBr\(_4\):Mn (II).\(^{81}\)

Several Mn doping concentrations were tested by them with the optimized condition being obtained at a doping content of 10%, showing an X-ray scintillation light yield of up to 85000 photons MeV\(^{-1}\), the highest value reported for long-wavelength emission among perovskite scintillators. BA\(_2\)PbBr\(_4\):10% Mn/PMMA composite scintillation screen with a size of 95 \(\times\) 95 \(\times\) 0.5 mm\(^3\) was fabricated by them through blade-coating, realizing a high-resolution X-ray imaging for both planar and nonplanar objects, demonstrating the great potential for high-resolution X-ray imaging applications.

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**Figure 9. Organic-inorganic lead-based scintillators**

(A) Preparation processes of polymer-MHPs-polymer thin films. X-ray images of LEDs, springs, and screws. Adapted with permission from Xu et al.\(^{73}\) Copyright 2021. Elsevier.

(B) A photograph of a flexible X-ray scintillation screen under UV excitation. X-ray images of chicken feet and an electronic board. Adapted with permission from Xie et al.\(^{72}\) Copyright 2021. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
Besides, one can introduce a large Stokes shift by substituting Pb with Sn, Cu, Mn, Sb, etc., to solve the toxicity issue. For example, Gu et al. prepared 2D Sn-based halide perovskites \((\text{C}_8\text{H}_{17}\text{NH}_3)_2\text{SnBr}_4\) by a cooling precursor solution method, exhibiting a PL peak of 596 nm, a PLQY of 98% and a PL decay time of 3.34 ms. They also reported for the first time the preparation of flexible 2D \((\text{C}_8\text{H}_{17}\text{NH}_3)_2\text{SnBr}_4\) scintillator films by mixing the perovskites with PMMA, and tested the detection performance of such composite films. As shown in Figure 10A, images of a spring, a circuit board and a crab can be acquired with a resolution of 200 mm (low dose 104.23 μGy s⁻¹/C0) using a low cost standard CCD camera, demonstrating the promising features of the prepared perovskites as next-generation scintillators in X-ray imaging applications.

Similar to Sn substitution, the introduction of Cu as the B-site ions also enables the realization of STEs emission and hence enlarging the Stokes shift. For example, Zhang et al. blended \((\text{TBA})\text{CuX}_2\) \((\text{TBA} = \text{tetrabutylammonium cation, X = Cl, Br})\) synthesized by a slow solvent evaporation method with Poly(vinylidene fluoride) (PVDF) and achieved flexible scintillation screens with a spatial resolution of 3 lp mm⁻¹ (166 μm). As shown in Figure 10B, such scintillators enabled the clear visible of a spring inside the ball pen through an X-ray image. Most importantly, the prepared flexible scintillator screens were found able to image nonplanar objects more accurate than flat scintillators, which was crucial for commercial applications. Similar works were also reported by Wang et al., who synthesized flexible scintillators based on 0D \(\text{C}_9\text{H}_{20}\text{N}\text{CuBrI}\) by a facile antisolvent diffusion method.

Apart from STE emissions, the incorporation of Mn into the perovskite structure could also cause a big Stokes shift owing to the induced d-d transition. Ma et al. blended 0D ethylenebis-triphenylphosphonium manganese (II) bromide \(((\text{C}_{38}\text{H}_{34}\text{P}_2)\text{MnBr}_4)\) powders prepared by an anti-solvent method with PDMS, and achieved a highly flexible scintillation films with a spatial resolution of 1.5 lp mm⁻¹ (322 μm). Such flexible scintillator films also exhibited excellent linearity to X-ray dose rates with a light yield of 66256 photons MeV⁻¹ and a detection limit of 461.1 nGy s⁻¹, comparable to those of single crystals. As shown in Figure 10C, the scintillators based on \((\text{C}_{38}\text{H}_{34}\text{P}_2)\text{MnBr}_4\) provided an excellent visualization toll for X-ray imaging applications.
radiography, with the wrench and the inner structure of a chip being clearly visible through the flexible scintillator screens. Significantly, lead-free scintillators with a long afterglow and a low spatial resolution need to be further investigated.

Because the detector has been bombarded by high-energy particles for a long time, its radiation stability must be considered. The radiation stabilization time of the reported scintillators has been summarized in Table 2. The RL stability of the reported MHP-based scintillators are found still not enough to meet the requirement of long-term commercialization, which might relate to the poor stability of the perovskite material itself. Further radiation stability enhancement might be doable by doping or coating strategies.

**DIRECT DETECTION**

Although MHPs-based flexible X-ray scintillators have shown a great potential in medical-related applications, offering advantages of convenience, low cost, abundant option, flexible conversion rate and compatible with mature sensor arrays, they still suffer limitations in spatial and energy resolutions because of lateral spread of light-scattering crossable in the converting layer as well as the low conversion efficiency. As an alternative detectable method, direct X-ray detection offer advantages of a wide linear response range, a fast response speed, a high-energy resolution, and a high spatial resolution. Here in this section, we review the recent progresses of flexible X-ray direct detectors with Table 3 summarizing the main performance.

**Inorganic MHP detectors**

Compared with indirect schemes, in which X-rays are converted into photons by scintillating phosphors before detecting by photodiode arrays, direct detection with a direct generation of electrical signals by X-rays, shows advantages such as a higher spatial resolution and a simpler system configuration. To realize a high sensitivity, the semiconductors used for X-ray detections require a large average atomic number (Z), a large carrier mobility-charge product, and a high resistivity. In particular, Z decides the X-ray absorption coefficient, \( \mu \) determines the charge collection efficiency at a given electric field and a high resistivity enables a low dark current and hence reduces the noise current and increases signal-to-noise ratio.

As early as 2019, Bao et al. already reported flexible X-ray detectors based on CsPbBr\(_3\) NCs by an inkjet printing method, which demonstrated a large-scale fabrication of arrays containing multichannel detectors, as shown in Figure 11A. The prepared detectors achieved a high sensitivity of 1.45 mC Gy\(_{air}\)^{-1} cm\(^{-2}\) under a low X-ray dose rate of 0.0172 mGy\(_{air}\) s\(^{-1}\) and a bias voltage of 0.1 V, which were 70 times more sensitive than conventional \( \alpha \)-Se devices. To study the flexibility of the detectors, different bending angles ranging from 0 to 120° were tested, showing only 25% reduction of current at a bending angle of 120°. The durability of the detectors was measured against cycles and found despite strain was produced via 200 bending cycles, it only degraded the current by 12% (Figure 11A), indicating the high conductivity, robustness and stability of this X-ray detector.

The ion migration behaviors in the perovskites would seriously impact the X-ray detection performance. With inhibited ion migration effects, low-dimensional perovskites were found capable of achieving high performance X-ray detection, as reported by Liu et al. using 0D Cs\(_3\)Bi\(_2\)I\(_9\)\(^{105}\) and Wu et al. using 0D Cs\(_3\)Cu\(_2\)I\(_5\)\(^{106}\). Recently, Xu et al. reported flexible polymer-encapsulated Au/Cs\(_4\)PbI\(_6\)/Au X-ray detectors by a spin coating method, as shown in Figure 11B. Such detectors exhibited a high sensitivity of 0.2562 mC Gy\(_{air}\)^{-1} cm\(^{-2}\) at the bias of 10 V irradiated by an X-ray of 30 keV. The excellent protection from the polymer films also enabled the devices to show good air stability and durable flexibility with negligible changes of sensitivity after being placed in air for 60 days or bending for 600 cycles.

Despite showing a great potential as active layers in direct X-ray detection, the toxicity of Pb in inorganic perovskites still limit their potential applications. Replacing Pb\(^{2+}\) with other lead-free ions, either one ion or double ions in the unit cells of perovskites could solve such an issue.\(^{107}\) For example, Yu’s group reported the replacement of Pb\(^{2+}\) with Ag\(^+\) and Bi\(^{3+}\), which not only solved the toxicity issue but also maintained the corner-sharing metal-halide octahedral network of perovskite crystals. The prepared X-ray photoconductors with an Au/Cs\(_2\)AgBiI\(_6\)/PVA/Au structure exhibited a sensitivity of 0.04 mC Gy\(_{air}\)^{-1} cm\(^{-2}\) and an excellent flexibility with a negligible performance degradation after flexing/bending at a radius of 2 mm (Figure 12A), corresponding to a maximum 5% tensile/compressive strain.\(^{92}\)
| Device structure | Preparation methods | Preparation time (ms) | m product (cm² V⁻¹) | Response time (ms) | Sensitivity (mC Gy⁻¹ cm²) | Detection limit (nGy s⁻¹) | Spatial resolution (lp mm⁻¹) | Electric field (V mm⁻¹) | Work stability | References |
|------------------|---------------------|-----------------------|--------------------|-------------------|--------------------------|---------------------------|---------------------------|--------------------------|----------------|------------|
| Au/Cs₃AgBr₃/PVA/Au | Antisolvent         | -                     | -                  | 0.04              | -                        | -                         | 4000                      | -                        | -             | (Li et al., 2018)⁹² |
| Au/CsPbBr₃/Cr     | Inkjet printing     | 27                    | 27                 | 0.0177            | -                        | -                         | 0.1 V                     | -                        | -             | (Liu et al., 2019)⁹³ |
| Au/CsPbBr₃/Cr     | Inkjet printing     | 2 x 10⁻⁴              | 248                | 0.0599            | 12000                    | -                         | 27                        | 1 h ø 1.1 mGy s⁻¹     | -             | (Mescher et al., 2020)⁹⁴ |
| Au/PEDOT/Cs₃AgBr₃/PbI₃/Br₃/PCBM/BCP/Au | Spin-coated | -                     | -                  | 0.0075            | 580                      | -                         | 0                         | -                        | -             | (Demchyshev et al., 2020)⁹⁵ |
| Cr/BP/C₆P/MAPbI₃/C₁₀Cl₁₃/PFM/Cr | laminating process | 1.5 x 10⁻³          | 0.0065             | 8.696             | -                        | -                         | 50                        | 85.5 h ø 1.2 mGy s⁻¹ | -             | (Zhao et al., 2020)⁹⁶ |
| Au/Cs₄PbI₃/Au     | Spin-coated         | -                     | -                  | 0.2562            | -                        | -                         | 4.8                       | -                        | -             | (Li et al., 2021)⁹⁷ |
| ITO/poly-TPD/Cst/FAPbI₃/C₁₀/CBP/Cu | Thermal coevaporation | -                   | 0.1421             | -                 | -                        | -                         | 100                      | -                        | -             | (Li et al., 2021)⁹⁸ |
| Au/MAPbI₃/Au      | Inkjet Printing     | 48                    | 0.494              | 27                | -                        | -                         | 400                      | -                        | -             | (Ciavatti et al., 2021)⁹⁹ |
| Au/PEA₂PbBr₃/Cr   | Blade-coating       | 10⁻⁴                 | 13                 | 6.74              | 10                       | 30 V                      | 3.3 h ø 1.6 mGy s⁻¹     | 50                        | -             | (Jang et al., 2021)¹⁰⁰ |
| CsPbBr₃ NCs/PET/ITO/PEDOT/PSS/MAPbI₃/PCBM/Ai | Spin-coated | -                     | 0.0003             | 600               | -                        | -                         | -                         | -                        | -             | (Hoe et al., 2021)¹⁰¹ |
| FTO/TiO₂/Cs₂TeI₆/Au | Inkjet Printing     | -                     | 0.07627            | 170               | -                        | 10                        | 1h                        | -                        | -             | (Guo et al., 2021)¹⁰² |
| Au/PEDOT:PSS/MAPbBr₃/Au | Screen-printing procedure | -                   | 150               | 0.0122            | 3000                     | -                         | 17                        | 0.42 h ø 8 mGy s⁻¹     | -             | (Possanzini et al., 2022)¹⁰³ |
| Au/PTAA/BA₂MAPbI₃/C₁₀/BCP/Au | Printing | -                     | 1.214              | 6.25 (80 µm)      | 5                        | 12 h ø 0.035 mGy s⁻¹     | 12 h ø 0.035 mGy s⁻¹     | -                        | -             | (Tsai et al., 2022)¹⁰⁴ |
Alternatively, Cs₂TeI₆ was reported for direct X-ray detection, not only because of its low toxicity but also because of the low ion migration. Using an electrospray method at a low temperature of 160°C, Xu et al. prepared Cs₂TeI₆ detectors on a flexible polyimide (PI) substrate. The obtained X-ray detectors with Au as the electrodes showed a detection limit of 170 mGyair s⁻¹, a sensitivity of 0.07627 mC Gy⁻¹ cm⁻² under 20 kV X-rays at a bias voltage of 5 V, and satisfactory X-ray images of original samples (i.e. the pattern letters, the nut and the copper leaf in Figure 12B). Most importantly, the detectors could maintain a high stability even after being bent for 100 times at a low bending radius of 10 mm as well as being stored in air for 6 months, demonstrating the great potential in large-scale, low-cost, low-toxic X-ray detection and imaging. There is still a huge room for performance enhancement of all-inorganic X-ray detectors before achieving their real commercialization.

Organic-inorganic detectors

Although the use of low-dimensional all-inorganic perovskites could reduce the ion migrations and improve the overall detection performance, with a small size of A-site ion, inorganic perovskites generally suffer more severe ion migrations than organic-inorganic halide counterparts. Besides, hybrid perovskites offer additional advantages such as cost-effective and low-temperature solution-processability. Thus, researchers have now putting more attention on depositing direct X-ray detectors based on organic-inorganic hybrid MHPs with unpressed dark current.

A magnificent work regarding this field was reported by Huang et al., who prepared perovskite-filled membranes (PFMs) for highly sensitive, flexible and large-area X-ray detectors (Figure 13A). The good connectivity and crystallization of MAPb(ClI)₃ in the porous nylon membranes enabled the prepared large-area X-ray detectors to show a high sensitivity of 8.689 mC Gy⁻¹ cm⁻² under a field of 0.05 V μm⁻¹. Such detectors also showed a high flexibility without losing performance even after being bent to 2 mm, and an excellent stability with no degradation of detection performance after storing for over 6 months. As shown in Figure 13A, by putting the stand-alone detector arrays inside metal pipes, the defects of material can be clearly detect with the imaging quality superior to those flat-panel detectors, suggesting the potential implications in X-ray imaging where accurate diagnosis are required under unconventional conditions. Similarly, MA-based direct X-ray detectors were also reported by Petrozza and Fraboni’s group, using a device architecture of Au/MAPbI₃:PC₆₀BM/Au on flexible PEN substrates, as shown in Figure 13B. Such detectors exhibited a high X-ray sensitivity up to 2.27 mC Gy⁻¹ cm⁻², a radiation tolerance over 2.2 Gyair of total dose, and a response time as low as 48 ms. The stability tests also suggested that the detectors could suffer a strong bending stress of >10% as well as a high X-ray energy up to 150 keV, opening the way for achieving flexible real-time direct radiation detectors and imagers with a low-operation-voltage and large-area compatibility.
Generally, there is a trade-off relationship between X-ray absorption and charge transport, making the thickness control of quite important. However, traditional solution-based methods are found relatively hard to precisely control the thickness. Thermal co-evaporation technique, as a potential alternative, could be used to solve such an issue, with the thickness being able to be effectively controlled by tuning the evaporation time and rates. Using FAI and PbI$_2$ as the evaporation sources, Lin et al. optimized the resulted thickness of FAPbI$_3$ and achieved large-area and flexible X-ray detectors. Those detectors with an additional CsI film being deposited before the evaporation and an in situ annealing of the substrate, enhanced the resulted quality of black-phase FAPbI$_3$. They found that a fast response of <100 ns could be achieved at an active layer thickness less than 3 $\mu$m. Thicker films might limit the charge transport but increasing the sensitivity and reducing the dark current and noise with the highest sensitivity of 0.142 mC Gy$^{-1}$ cm$^{-2}$/C$^{-2}$ being achieved at a film thickness of 5 $\mu$m. The work clearly demonstrated the importance of precise thickness control in achieving high-performance direct X-ray detectors.

Despite MA and FA based 3D perovskites have been proved to show great potential in X-ray detectors, they have issues concerning stability. Numerous efforts have been made to solve such an issue. For example, Park et al. reported a mixed A-cation approach using guanidinium (GA, C(NH$_2$)$_3$)-doped MAPbI$_3$ as the X-ray sensitive layer. The stability was enhanced because of the difference in the number of hydrogen bonds between MA and GA. With six hydrogen atoms, one GA molecule can form six hydrogen bonds with neighboring iodides as compared with the two hydrogen bonds by an MA molecule, thus strengthening the host lattice and enhancing the stability of MAPbI$_3$ upon GA.
incorporation. As a result, this GA-doped MAPbI3 not only presented a high X-ray sensitivity of 6.74 mC Gy\(^{-1}\) cm\(^{-2}\) at an X-ray tube voltage of 50 kV, but also exhibited an outstanding stability over a year at ambient conditions.\(^9^9\)

Further reducing the dimension of the perovskites could be another effective method to improve the stability. Recently, Fraboni et al. reported solid-state ionizing radiation direct detectors by directly integrating 2D layered hybrid perovskites, namely PEA\(_2\)PbBr\(_4\) (PEA = C\(_6\)H\(_5\)C\(_2\)H\(_4\)NH\(_3\)), onto a pre-patterned flexible substrate, as shown in Figure 13C. The grains that compose the perovskite films exhibited high crystallinity and provided an optimal electrical contact with the electrode, both of which were beneficial for enhancing the carrier collection and stability. As a result, the flexible detectors showed a good sensitivity of 0.806 mC Gy\(^{-1}\) cm\(^{-2}\) and a low detection limit down to 42 nGy s\(^{-1}\), a high bending stability even under a bending radius of 3.5 mm, and an excellent air stability of 80 days.\(^1^0^0\)

Alternatively, one can try to use perovskites with organic-inorganic mixed-cations to solve the instability issue, which could also offer advantages of reduced ion migration as compared with those fully inorganic perovskites. For example, Basirico and Kaltenbrunner’s group reported the first flexible, lightweight, and highly conformable X-ray detectors based on mixed-cations mixed-halides perovskite composition. Several electron and hole transport layers were examined by them and found that the resulted detectors could achieve a sensitivity of 0.009 mC Gy\(^{-1}\) cm\(^{-2}\) operated at 0 V using a PEDOT/C\(_{50.05}(F{A_0.83M{A_0.17})_{0.95}}\)
PbI$_3$xBr$_y$/PTCDI/C$_2$O$_3$ structure, a dark current as low as 0.03 ± 0.004 nA cm$^{-2}$ using a NiO$_x$/Cs$_{0.05}$ (FA$_{0.83}$MA$_{0.17}$)$_{0.95}$PbI$_3$Br$_x$/PCBM/BCP structure, and a detection limit down to 580 nGy s$^{-1}$ using a PEDOT/C$_{0.05}$ (FA$_{0.83}$MA$_{0.17}$)$_{0.95}$PbI$_3$Br$_x$/PCBM/TIO$_x$ structure. Similar works were also reported by Lemmer et al., who used an inkjet printing method to prepare triple cation perovskite X-ray detectors. As shown in Figure 13D, the devices with an ITO/NiO$_x$/Cs$_{0.1}$ (FA$_{0.83}$MA$_{0.17}$)$_{0.9}$Pb(Br$_{0.17}$I$_{0.83}$)$_{0.1}$C$_{60}$/BCP/Au structure presented a sensitivity of 0.0599 mC Gy$^{-1}$ cm$^{-2}$ at a low operating voltage of 0.1 V. Besides, the detectors were found to show a high bending stability and an excellent operating stability with a high performance being maintained even under a bending radius of 3 mm and after a cumulative X-ray exposure above 4 Gy$_{air}$ (corresponds to more than 13000 chest radiographic examinations).

So far, the spatial resolution of direct X-ray detectors is still lower than that of indirect type scintillators. To enhance the stability of flexible MHPs-based X-ray detectors, the factors of temperature, humidity, light, and bending should also be systematically studied. All in all, the above works show that MHPs, as alternative detection materials, need to be balanced at all aspects to accelerate their commercial applications.

### CHALLENGES AND PERSPECTIVES

Halide perovskites have achieved some meaningful and representative works as flexible X-ray detectors. However, there are still several challenges remained that need to be tackled to realize the commercialization.

#### Resolution

The spatial resolution of X-ray detectors is limited by many factors, i.e., charge carrier trapping and reabsorption of K-fluorescent X-ray photons and primary photoelectrons. Out of them, the pixel cross-talk is the most significant one. For indirect detection, this is caused by the scattering of visible photons. To control the light scattering phenomenon and improve the resolution, one can try to control the grain size to prevent light scattering and achieve an effective output. Alternatively, one might reduce the thickness of the perovskite scintillators to improve the imaging resolution.

As for the direct X-ray detection, charge cross-talk is related to anisotropic carrier mobility and electric field. The diffusion length, $L$, can be calculated using

$$L = 2d\sqrt{D/\mu V}$$

where $d$ is the thickness, $D$ is the diffusion constant, and $V$ is the applied voltage. Thus, an effective way to do is applying a higher voltage or using a guard ring, so the charges can be limited within the pixel. The charge trapping in semiconductors might also cause an induction of charges on the neighboring pixels, which might be solvable using perovskites with a uniform structure and a large grain size to reduce the charge sharing between neighboring pixels.

#### Sensitivity

The biggest obstacle in pursuing a high sensitivity and a small detection limit is the dark current, which inevitably induces noise and deteriorates the X-ray detector performance. Thus, to increase the sensitivity, one could either increase the intensity of the signal through increasing the quality of perovskites or decreasing the dark current and noise directly. The quality of perovskites is mainly affected by the grain boundaries and to increase it, one might try designing device structures by introducing passivation layers or interface treatments to passivate the defect states and reduce the influence of ionic migration. The introduction of interfacial layers might also reduce carrier injection and hence the noise level.

#### Large-area

Generally, the X-ray refractive index is about 1.0 and difficult to focus, so large-area detectors with sizes comparable to the object are the future trend. However, although there were some reports showing that large-area and flexible properties can be conquered in perovskite films, the quality and thickness control remained big problems, leaving a vast distance in the detection level between MHP detectors and the existing commercial radiation detectors. The thickness of perovskite layers should be large enough to efficiently absorb X-ray and the grain boundaries inside the perovskite films should be reduced to avoid the effects to charge transportation. Perovskite single crystals with no grain boundaries might be a potential choice, but the limited technology and expensive cost makes flexibility a great challenge. The recent works...
reported by Tang et al. provided a potential method to solve the above-mentioned issue, with single crystals being grown first and then used as the source to prepare perovskite films through thermal evaporation. Great efforts should be taken on this field to overcome the shortcomings and achieve large-area and flexible X-ray detectors with a high performance.

**Stability**

To pursue commercialization of perovskite X-ray detectors, the instability issue of them at harsh environment should be systematically studied because they might cause a degradation of detection performance and hence an additional cost being required to replace the related component in commercial operations. For indirect detection, the inherent high sensitivity of perovskite scintillators to light, heat, humidity and other environmental species, the phase transitions issues, and aggregation issues of NCs/QDs would cause the formation of carrier traps, making them unstable especially when exposed to X-ray irradiations. Enormous efforts have been reported so far regarding to doping, coating, and ligand modification in enhancing the stability of the perovskites, which might also be applicable to perovskite scintillators in preparing more stable materials. Besides, the synthesis of perovskite/polymer composite films have been proved not only enabling the high flexibility but also enhancing the stability owing to the encapsulation of MHPs. However, it is now still quite challenging to obtain MHP scintillators with both a high stability and an excellent optoelectronic performance.

As for direct detection, an external bias is typical applied to MHP-based X-ray detectors to optimize the charge generation and collection, which might severely affect the long-term stability. Developing new structure-function relationships specific to X-ray detections might be the solution to such an issue. Apply a self-powered photodiode structure normally used in detecting X-ray light might be a possible choice, but the performance reported so far were relatively poor. One might therefore introduce heterojunctions by inserting an electron/hole transport layer at electrodes/perovskite interfaces to enhance the charge carrier separation and reduce the required voltage in X-ray detectors.

**Response time**

Last but not least, response time is also a key factor for X-ray detectors. A shorter response time of an X-ray detector means a faster operation and a less radiation dose being received by the target object. Typically, the response time of a detector should not exceed the millisecond order. However, the time at which the rays hit the material to generate electron-hole pairs is not controllable. Therefore, to shorten the response time, a subsequent separation process should be considered.

**OUTLOOK**

At present, commercial X-ray detectors are mainly based on NaI:Tl and CsI:Tl, which are generally rigid-based and have a low light yield and a complex and expensive deposition process. Compared with them, MHPs can be formed through a simple and low-cost process at a relatively low temperature, making them capable of depositing with a high flexibility. Thus, MHPs hold a great potential to replace the existing radiation detection devices especially in Computed tomography technologies of medical diagnostic, therapeutic tools, and security check. Here, in this review, the compressive progress of MHP-based flexible X-ray detectors is described and discussed in terms of morphologies and synthesis of materials, architectures and operating mechanisms of devices and applications in direct and indirect detections.

However, despite MHPs showing a great advantage as flexible X-ray detectors in a very short time, there is room for further improving the preparation method and the device performance, achieving commercialization. This particularly offers to the resolution and sensitivity, which requires the development of high-quality perovskites to minimize the defect states and scattering. Similar to perovskite solar cells, the stability is also a serious issue, and might be solved by developing chemical stable materials as well as a device structural design. As an alternative for traditional rigid-based X-ray detectors, the development of large-area and flexible detectors are of quite importance, for applications in medical diagnostic.

Therefore, knowledge is still required on properties, technological pathways and bottlenecks to improve the performance of MHP-based flexible X-ray detectors. We hope that this timely review could guide and boost the future development of perovskites in X-ray-related applications and pave the road to commercialization.
Research Funds for the Central Universities (2021CDJQY-022).

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B.W. conceived the idea and initiated the project. X.Y., S.C., S.L., S.Z., and Q.Q. conducted the literature review. B.W. and W.C. wrote the manuscript. B.W. and X.Y. prepared the figures. S.W. and Z.Z. guided this work.

DECLARATION OF INTERESTS

The authors declare no competing interests.

ACKNOWLEDGMENTS

This work is funded by National Natural Science Foundation of China (61904023, 11974063); Fundamental Research Funds for the Central Universities (2021CDJQY-022).

AUTHOR CONTRIBUTIONS

B.W. conceived the idea and initiated the project. X.Y., S.C., S.L., S.Z., and Q.Q. conducted the literature review. B.W. and W.C. wrote the manuscript. B.W. and X.Y. prepared the figures. S.W. and Z.Z. guided this work.

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