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Micro/nano engineering advances next-generation flexible X-ray detectors

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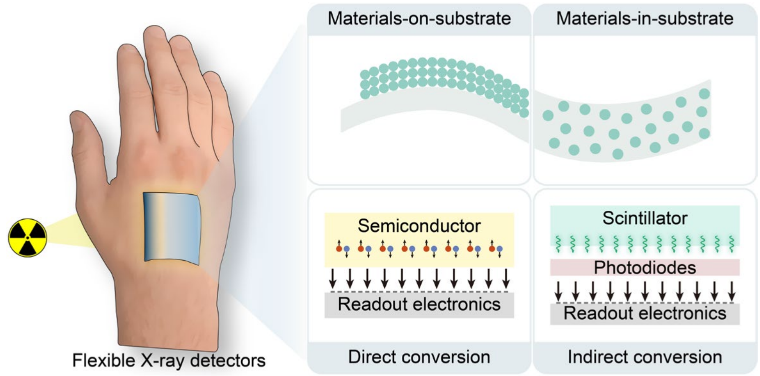
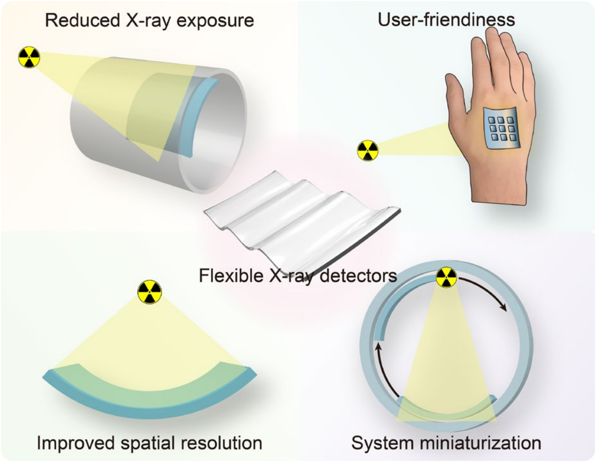
ABSTRACT: The growing demands for X-ray imaging applications impose diverse and stringent requirements on advanced X-ray detectors. Among these, flexibility stands out as the most expected characteristic for next-generation X-ray detectors. Flexible X-ray detectors can spatially conform to non-flat surfaces, substantially improving the imaging resolution, reducing the X-ray exposure dosage, and enabling extended application opportunities that are hardly achievable by conventional rigid flat-panel detectors. Over the past years, indirect- and direct-conversion flexible X-ray detectors have made marvelous achievements. In particular, microscale and nanoscale engineering technologies play a pivotal role in defining the optical, electrical, and mechanical properties of flexible X-ray detectors. In this Perspective, we spotlight recent landmark advancements in flexible X-ray detectors from the aspects of micro/nano engineering strategies, which are broadly categorized into two prevailing modalities: materials-in-substrate and materials-on-substrate. We also discuss existing challenges hindering the development of flexible X-ray detectors, as well as prospective research opportunities to mitigate these issues.



KEYWORDS: X-ray imaging, flexible X-ray detectors, nanoengineering, scintillator, semiconductor

Flat-panel X-ray detectors have made significant contributions across a wide range of applications, such as medical care, security check, industrial inspection, and universe exploration.[1, 2] As a critical component of the X-ray imaging system, digital flat-panel X-ray detectors convert incoming X-rays into electrical signals, followed by the signal storage, processing, and readout by image sensor arrays such as complementary metal oxide semiconductors (CMOS) or thin-film transistor backplanes (TFTs) to generate digital X-ray images.[3, 4] At present, most flat-panel detectors are exclusively constructed on rigid glass substrates.[5, 6] The spatial incompatibility between rigid X-ray flat-panel detectors and three-dimensional (3D) objects usually results in compromised spatial resolution, intrinsic image vignetting, and increased X-ray exposure dosage.[7, 8] As a result, the



Scheme 1. The merits of flexible X-ray detectors. Flexible X-ray detectors can be curved to fit on the internal surface of an object, enabling X-ray imaging without interference from non-target objects, which reduces overall X-ray exposure. The homogeneous distribution of X-rays over the curved surface can effectively mitigate vignetting, thus improving spatial resolution. Furthermore, flexible X-ray detectors can conform to the patient's skin, significantly enhancing the user experience. Their spatial compatibility also allows for installation in more miniature protective housings, minimizing the size requirements of medical facilities.

effectiveness of rigid flat-panel detectors is compromised in complicated scenarios involving highly curved surfaces, confined spaces, and non-planar objects.

Nowadays, a growing number of X-ray imaging applications require large-area detectors that can flexibly fit to non-flat surfaces of 3D objects. These requests call for the development of large-area flexible X-ray detectors that offer superior imaging performance and overcome the limitations of conventional rigid X-ray flat-panel detectors.[9] Particularly, flexible X-ray detectors exhibit several advantages, enabling extended application opportunities that are hardly available with their rigid counterparts (Scheme 1): i) ***Reduced radiation exposure***: Since flexible X-ray detectors can be intentionally shaped to fit irregular surfaces, a closer proximity to the imaging region without disturbance by non-target objects leads to reduced X-ray exposure.[10] ii) ***Improved spatial resolution***: It is worth noting that vignetting in X-ray imaging can be caused by the decreasing angle of incidence X-rays from the center to the edge of the detector. The homogeneous irradiation of X-rays across the flexible X-ray detectors improves spatial resolution by suppressing the vignetting effects.[11] iii) ***User-friendliness***: Flexible X-ray detectors, built on highly durable and lightweight polymer substrates, provide expanded application opportunities. Examples include compression-free mammography for patients with breast diseases, rapid wound evaluation in outdoor emergencies and on the battlefield, health dosimeters for surgeons exposed to radiation, and medical wearables for patient-centered and real-time monitoring. These innovations improve user comfort and broaden the applicability of X-ray technology.[12] Besides medical purposes, the aerospace industry, which still adopts time-consuming and labor-intensive radiographic films rather than flat-panel detectors, has an urgent need for digital flexible X-ray detectors. Taking advantage of mechanical flexibility and portability, flexible X-ray detectors are well-suited for scanning and identifying injuries, including cracks, voids, and delamination in components with complex geometries (*e.g.,* engine, wing, and undercarriage). iv) ***System miniaturization***: The structural flexibility of X-ray detectors enables the miniaturization of the entire X-ray imaging system because of their spatial compatibility with more compact and smaller external housing compared to rigid X-ray flat-panel detectors with equivalent effective imaging areas.[13] Moreover, the size of flexible X-ray detectors can be readily customized and tailored to meet specific requirements of applications, which significantly saves space for detection and imaging.

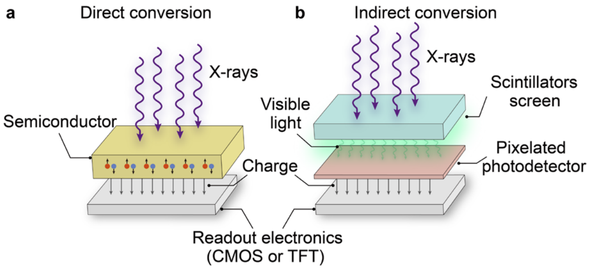


Figure 1. Working principles of X-ray detectors. (a) Direct X-ray detectors convert incoming X-rays into charge carriers (depicted as blue and red circles) via semiconductors. These charge carriers drift to bottom electrodes and are then processed by readout electronics, such as CMOS or TFT, to produce X-ray images. (b) Indirect X-ray detectors introduce a layer of scintillators to convert incoming X-rays into visible photons (green arrows) and subsequently into charge carriers through pixelated photodetectors, which are shortly extracted by readout electronics.

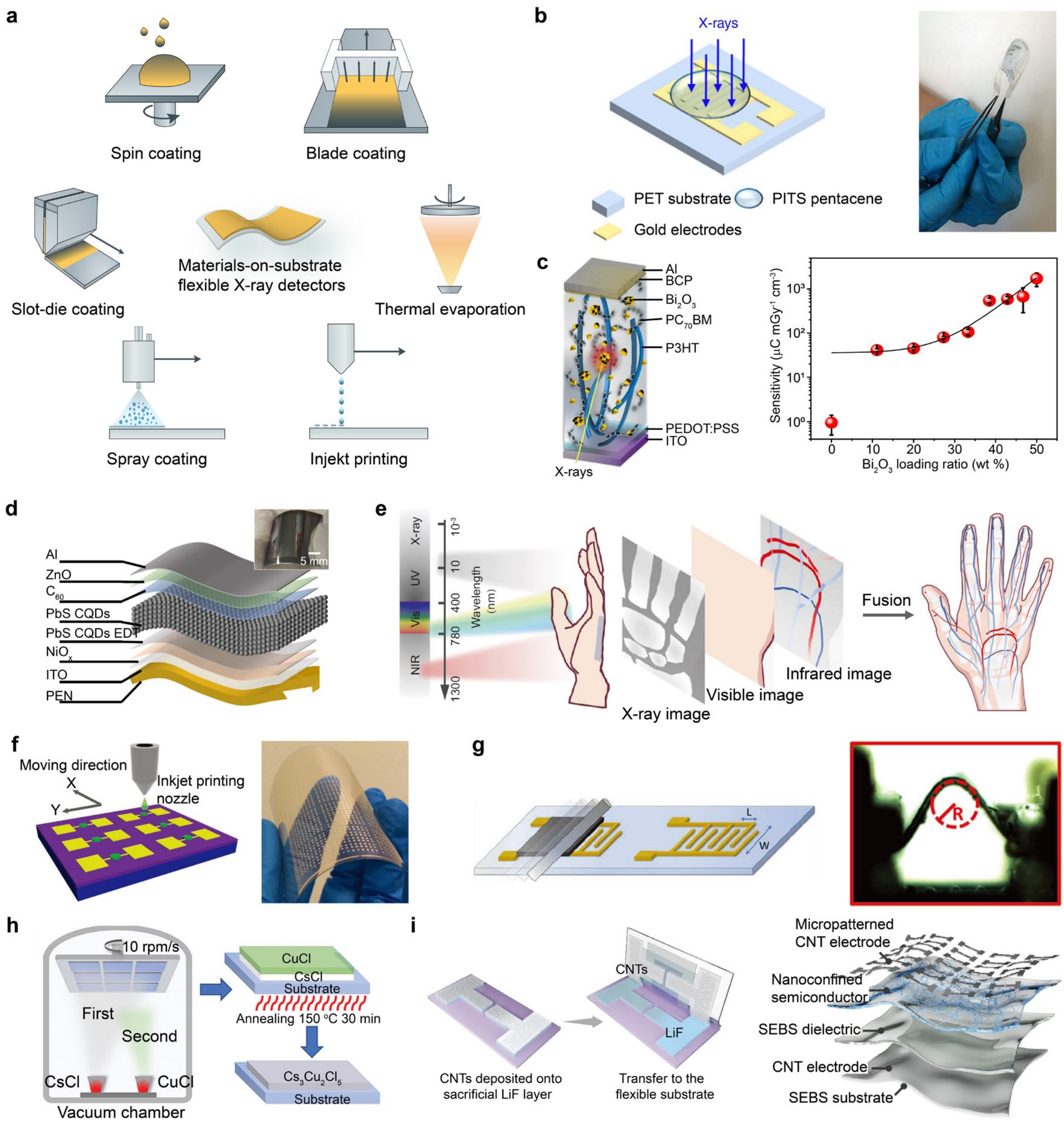


Figure 2. Materials-on-substrate type flexible X-ray detectors. (a) Micro/nano engineering-related film deposition techniques for materials-on-substrate flexible X-ray detectors. Reproduced with permission from ref ([14]). Copyright 2020, Springer Nature Limited. (b) Schematic of the device architecture with a thin layer of TIPS-pentacene drop-cast onto a flexible PET substrate with interdigitated gold electrodes (left) and optical image of the flexible organic X-ray detector (right). Reproduced with permission under a Creative Commons CC BY 4.0 License from ref ([15]). Copyright 2016, The Author(s). (c) Schematic of the device architecture. The Bi_2O_3@P3HT: PC70BM BHJ composite is sandwiched between indium tin oxide (ITO) and aluminum (Al) electrodes with BCP and PEDOT: PSS as the electron transport layer and hole transport layer, and the corresponding sensitivity of the device depending on the loading ratio of Bi_2O_3. Reproduced with permission under a Creative Commons CC BY 4.0 License from ref ([16]). Copyright 2018, The Author(s). (d) Schematic illustrating the device configuration of PbS CQDs photodetector. (e) X-ray to infrared image fusion through a single flexible and broadband photodetector. Panels (d) and (e) are Reproduced with permission under a Creative Commons CC BY 4.0 License from ref ([17]). Copyright 2023, The Author(s). (f) Schematic illustration of the procedures for $CsPbBr_3$ X-ray detectors via inkjet printing. Reproduced with permission from ref ([18]). Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (g) Sketch of the flexible $MAPbI_3$@PEN X-ray detectors fabricated by blade coating (left) and optical photograph of the bent detector. Reproduced with permission from ref ([19]). Copyright, 2021 Wiley-VCH GmbH. (h) Schematic illustration of $Cs_3Cu_2Cl_5$ scintillator layers fabricated by thermal evaporation followed by annealing. Reproduced with permission from ref ([20]). Copyright 2023, Wiley-VCH GmbH. (i) Schematic illustrating the device structure of high-density stretchable organic transistors and the synergy of detachable interface and LiF sacrifice layer to transfer stretchable CNTs electrodes. Reproduced with permission under a Creative Commons CC BY 4.0 License from ref ([21]). Copyright 2024, The Author(s).

To achieve high-performance flexible X-ray detectors, researchers have dedicated enormous efforts to exploring highly sensitive X-ray sensing materials, including scintillators and semiconductors (*e.g.*, metal halide perovskites, metal-organic frameworks, rare-earth fluorides, *etc.*).[3, 22-24] Notably, thick X-ray sensing layers varying from tens to hundreds of microns, with embedded X-ray sensing materials ranging from nanometers to micrometers, are required for the effective absorption of highly penetrating X-rays. This request dramatically complicates the fabrication of flexible X-ray detectors compared to other solution-processed flexible devices with thin active layers (*e.g.,* solar cells, light-emitting diodes, and thin-film transistors). In this case, nano/micro engineering, involving design, fabrication, manipulation, and refinement of materials and devices at the nano/micro scale, profoundly influences the performance of flexible X-ray detectors.[25, 26] For instance, it affects radioluminescence intensity, self-absorption, and light outcoupling efficiency in indirect X-ray detectors,[27] as well as conductivity, charge carrier mobilities, and dark current in direct X-ray detectors.[28] A thorough understanding on advanced nano/micro engineering is critical to fully explore the potential of flexible X-ray detectors for future applications.

This Perspective highlights recent advances and challenges in flexible X-ray detectors based on micro/nano engineering. To begin with, we provide a brief description of the working mechanism of direct and indirect X-ray detectors. As follows, we give an overview of state-of-the-art flexible X-ray detectors within currently prevalent paradigms: materials-on-substrate and materials-in-substrate. In the end, we discuss the existing barriers that restrain the progress of flexible X-ray detectors and outline promising strategies to settle out these challenges.

ENERGY CONVERSION MODE OF X-RAY DETECTORS

Typically, there are two primary types of X-ray detectors depending on X-ray energy conversion mode: indirect and direct conversion. In direct X-ray detectors, semiconductors directly convert X-ray photons into charge carriers.[29] Since charge carriers drift along the electric field with nearly no signal crosstalk, direct X-ray detectors exhibit a higher spatial resolution than indirect X-ray detectors (Figure 1a).[30] Unfortunately, the development and practical application of large-area direct X-ray detectors have been primarily constrained by the limitations of conventional semiconductors, such as the poor X-ray absorption of amorphous selenium (α-Se)[31] and the extremely stringent fabrication requirements of cadmium zinc telluride (CdZnTe).[32] Therefore, searching for next-generation semiconductors that satisfy the prerequisites of X-ray detection is highly desirable.[33]

Alternatively, scintillator materials such as terbium-doped gadolinium oxysulfide (GOS: Tb) and thallium-doped cesium iodide (CsI: Tl) are employed to convert X-rays into visible photons, which are then detected and converted into charge carriers by the amorphous silicon photodiodes in indirect X-ray detectors (Figure 1b).[4, 34] While indirect X-ray detectors are prevalent in the market, they encounter inherent obstacles such as severe light scattering and delayed radioluminescence, both originating from scintillators, which result in an inferior spatial resolution and unavoidable image lag. These shortcomings limit their utilization in X-ray imaging requiring high spatial resolution and fast response.[35, 36]

STATE-OF-THE-ART FLEXIBLE X-RAY DETECTORS

While commercial X-ray sensing materials have shown their capabilities in rigid X-ray flat-panel detectors, they are stiff, brittle, and incompatible with flexible substrates. Fortunately, recent advances in materials science and nano/micro engineering provide excellent opportunities for the development of large-area flexible X-ray detectors. Currently, flexible X-ray detectors are mainly fabricated by either depositing solution-processable nano-to-micro-sized X-ray sensing materials onto the surface of flexible organic substrates or incorporating them into soft polymers, which are hereby categorized as materials-on-substrate and materials-in-substrate, respectively.

Materials-on-substrate flexible X-ray detectors

On the basis of conventional fabrication procedures for flexible electronics, surface deposition of X-ray sensing materials onto flexible supporting substrates offers a general approach for the fabrication of flexible X-ray detectors.[37] According to the properties of materials for coating and application requirements, a wide range of thin-film fabrication techniques can be implemented, such as drop casting, spin coating, blade coating, slot-die coating, spray coating, inkjet printing, and thermal evaporation, as shown in Figure 2a.[14] To fabricate a compact, continuous, and homogeneous X-ray sensing layer, deposition parameters such as solution concentration and viscosity, interface wettability, deposition temperature, speed, annealing duration, humidity, and environmental atmosphere, are required to be comprehensively modulated. Borrowing extensive experience from plastic electronics, organic polymers known for their excellent mechanical flexibility and strength, *e.g.*, polyimide (PI),[38] polyethylene terephthalate (PET), polyethylene naphthalate (PEN),[39, 40] biodegradable paper, and cellulose-based substrates, are applicable to flexible X-ray detectors.

Organic materials, featuring structural versability, solution processability, low cost, and environmental friendliness, are natural candidates for large-area flexible X-ray detectors. As shown in Figure 2b, 0.5 wt% of bis-(triisopropylsilylethynyl)pentacene (TIPS-pentacene) dissolved in toluene was drop cast onto a 125 μm thick flexible PET substrate patterned with thermally evaporated and interdigitated gold electrodes, followed by thermal annealing at 80 °C for 1 hour to remove the toluene, giving rise to a high-quality TIPS-pentacene film with a thickness of 100 nm, characterized by atomic force microscopy. The resulting TIPS-pentacene flexible X-ray detectors, operating at low voltage, are highly sensitive and are promising for large-area wearable electronics.[15] However, pure organic materials, composed of carbon (C), oxygen (O), and nitrogen (N), present poor X-ray absorption for hard X-rays (above 40 keV) and inferior charge carrier diffusion length due to tightly bound excitons.

Alternatively, the introduction of high atomic number (Z) elements in organics offers a feasible strategy to enhance X-ray absorption and improve optoelectronic properties. Bismuth oxide (Bi_2O_3; Z_{Bi} = 83) nanoparticles were selected as an ideal dopant for organic bulk heterojunction (BHJ) X-ray detectors due to their high X-ray attenuation coefficient, direct conversion of X-rays, and low environmental and health risks (Figure 2c). A P3HT:PC70BM and Bi_2O_3 blender solution was deposited onto a PEDOT: PSS-coated Kapton substrate through drop casting. To maximize the performance of Bi_2O_3@P3HT:PC70BM BHJ X-ray detectors, the loading ratio of Bi_2O_3 within BHJ is optimized to 33 wt% (Bi_2O_3-40) through comprehensively evaluating the film formation quality, X-ray absorption, dark current level, charge collection efficiency, response time, and detection sensitivity. The depletion region formed between Bi_2O_3 nanoparticles and highly crystalline P3HT:PC70BM BHJ generates a high local electric field of up to 200 V μm^{-1}, facilitating the extraction of electrons and holes under low reverse bias. Flexible X-ray detectors based on Bi_2O_3-40@P3HT:PC70BM BHJ, capable of detecting broad X-ray energy, exhibit comparable X-ray detection performance with conventional rigid X-ray flat-panel detectors.[16]

Although drop casting is a low-cost and convenient method, variations in evaporation rate and concentration fluctuation of solvent across the substrate may lead to uneven film, therefore degrading device performance. Instead, spin coating offers a reproducible, controllable, and high-efficiency technique for homogeneous thin-film deposition, which has been widely used for the fabrication of various optoelectronic devices spanning light-emitting diodes, solar cells, photodetectors, and thin-film transistors. Owing to their solution processability, high-Z lead sulfide quantum dots (PbS QDs) were utilized to fabricate flexible X-ray detectors through layer-by-layer spin coating, resulting in a 1 μm active layer and enabling ~5 % of X-ray absorption (Figure 2d).[17] Notably, the as-synthesized PbS QDs are capped with long-chain ligand oleic acid (OA), which hinders efficient charge transport. The OA was subsequently replaced by short inorganic ligands PbX_2 (X = Br, I) through a solution-phase ligand exchange strategy before the film deposition. Zinc oxide (ZnO) and nickel oxide (NiO_x) were sequentially deposited by magnetron sputtering and employed as the electron transport layer and hole transport layer to achieve the energy band alignment for efficient charge extraction. Intriguingly, PbS QDs are highly efficient semiconductors for detecting a broad spectral range from X-rays to near-infrared (NIR) light due to their tunable bandgap and high absorption coefficient. In particular, flexible PbS QDs photodetectors built on poly(ethylene naphthalate) (PEN) present excellent tolerance to cyclic bending and continuous X-ray exposure. The combination of structural flexibility and multi-spectral imaging dramatically boosts the capabilities of flexible PbS QDs X-ray detectors, resulting in valuable fusion imaging that significantly amplifies diagnostic outcomes (Figure 2e).

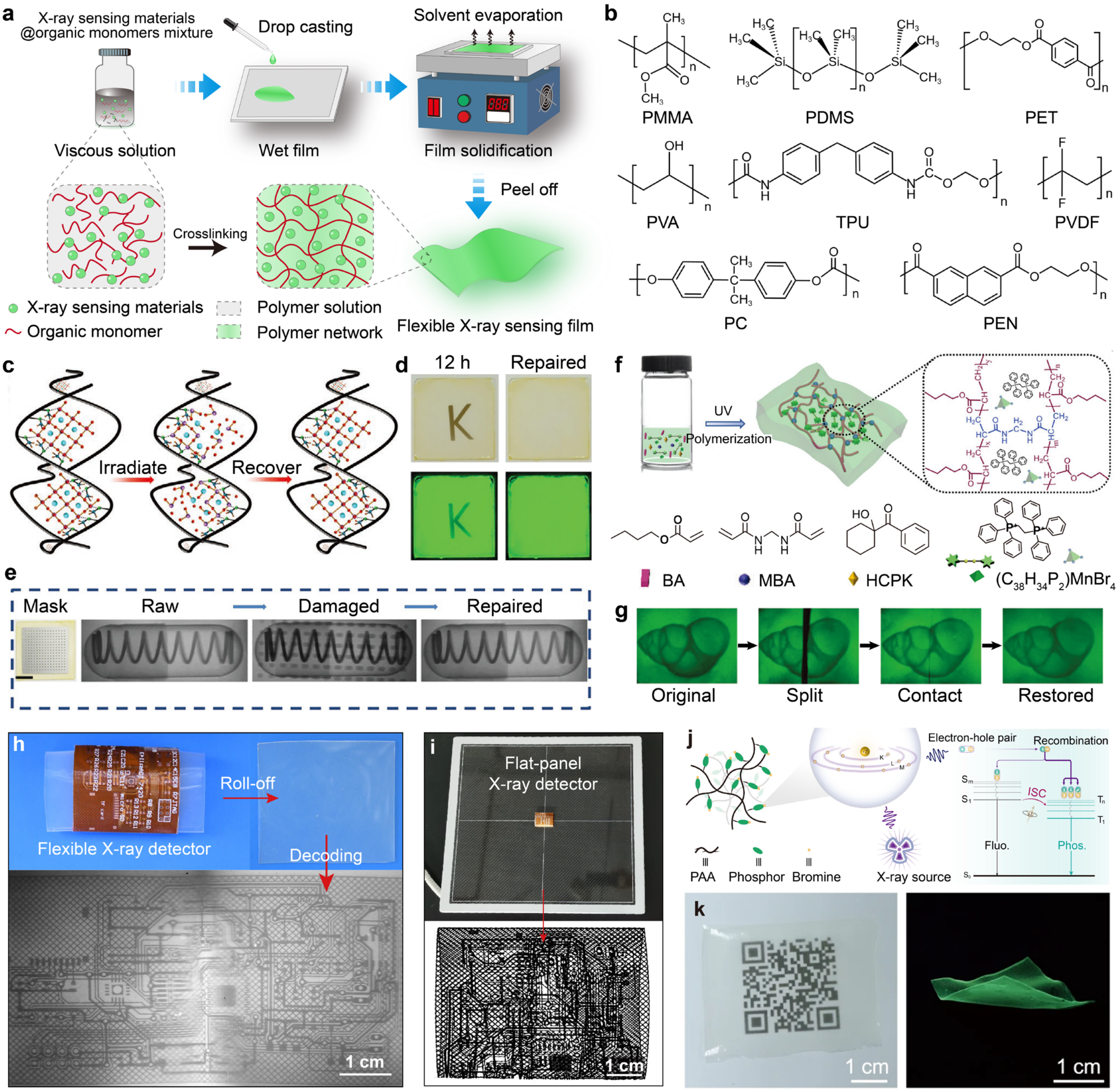


Figure 3. Materials-in-substrate type flexible X-ray detectors. (a) Schematic illustration of the preparation procedures of the flexible X-ray sensing films. (b) Molecular structure of widely used polymer substrate for flexible X-ray detectors. (c) Schematic diagram of the damage-repair process due to the fixation of exfoliated atoms with the assistance of anchor sites within PMMA substrate. (d) The optical and fluorescence image of as-fabricated scintillator ceramics after long-term X-ray exposure for 12 h with a design mask patterned with the letter "K" exhibit the damage-repair process. (e) X-ray imaging of an encapsulated spring by raw, damaged, and repaired scintillator ceramics. The scintillator ceramic was irradiated by X-rays to form damaged arrays through a mask. Panels (c) to (e) are reproduced with permission from ref ([41]). Copyright 2021, Wiley-VCH GmbH. (f) Schematic of UV-induced polymerization of scintillator organogel and its monomer, crosslinker, and photoinitiater. (g) Schematic diagram of self-healing of organogel scintillator by facial contact. Panels (f) and (g) are reproduced with permission from ref ([42]). Copyright 2023, Wiley-VCH GmbH. (h) Sketch of a $NaLuF_4$:Tb@$NaYF_4$ flexible X-ray detectors inserted into the inner surface of a circular circuit board (top) and the full-view X-ray image after thermal stimulation (bottom). (i) Schematic representation of an overlapped X-ray image of a circular circuit board taken by a rigid flat-panel detector. Panels (h) and (i) are reproduced with permission from ref ([43]). Copyright 2021, The Author(s), under exclusive license to Springer Nature Limited. (j) The design principles of PAA/phosphor copolymers and its X-ray-excited radioluminescence mechanism. (k) Photographs of transparent and large-area flexible copolymer scintillator film under room light (left) and UV light (right). Panels (j) and (k are reproduced with permission under a Creative Commons CC BY 4.0 License from ref ([44]). Copyright 2022, The Author(s).

While spin coating has demonstrated its competence in single-pixel devices, it is hardly available for large-area fabrication, an imperative prerequisite for practical optoelectronic devices. To overcome this limitation, researchers have turned to techniques suitable for large-area fabrication, such as blade coating,[45] screen printing,[46] inkjet printing,[47] spray coating,[48] and thermal evaporation.[49] For example, after surface passivation and crystallinity modulation through chemistry engineering, cesium lead bromide ($CsPbBr_3$) QDs were printed at the center of counter gold electrode pairs using inexpensive inkjet printing.[18] Taking advantage of inkjet printing, a continuous and uniform $CsPbBr_3$ array was deposited on the flexible PET, showing good durability against bending circles (Figure 2f). In addition, doctor blade coating, which is highly compatible with industrial-scale production, has demonstrated a robust technology for fabricating thick films with well-defined thicknesses, which is especially suitable for X-ray detection devices.[50] In previous research, methylammonium lead iodide ($MAPbI_3$) dispersed in isopropanol with a concentration of 100 mg mL^{-1} was directly printed onto the flexible PEN substrate through doctor blade coating. Shortly, 10 mg L^{-1} of [6,6]-Phenyl C61 butyric acid methyl ester (PC60BM) was drop cast on the printed $MAPbI_3$ to passivate the intrinsic surface defects, followed by an 80 °C thermal annealing process, giving rise to a homogeneous $MAPbI_3$ layer with a thickness of 10 microns (Figure 2g).[19] Although the dark current increased by a factor of 2 after the first bend with a radius of 0.63 mm, the performance of the devices remained consistent in subsequent bend cycles.

In addition to solution process techniques, thermal evaporation provides a useful strategy for dealing with insoluble raw materials for large-area fabrication. Thermal evaporation allows precise manipulation of the composition and thickness of the target film by controlling the evaporation rate and duration.[51] Zero-dimensional cesium copper chloride ($Cs_3Cu_2Cl_5$) has emerged as an excellent scintillator emitting green lights at 530 nm with a significant Stokes shift of 276 nm ascribed to self-trapped excitons emission, contributing to enhanced light output due to their reduced self-absorption. However, the insolubility of raw materials restricts its solution processability for film deposition. Therefore, sequential vacuum thermal evaporation was performed to fabricate large-area flexible $Cs_3Cu_2Cl_5$ scintillator screens. As shown in Figure 2h, cesium chloride (CsCl) and copper chloride (CuCl) crystals were placed in two separate tungsten boats. After that, CsCl and CuCl were deposited onto the substrate in sequence under vacuum, followed by thermal annealing at 150 °C for 30 min to form $Cs_3Cu_2Cl_5$ scintillator film with a thickness of approximately 2 microns. The as-prepared $Cs_3Cu_2Cl_5$ flexible X-ray detectors resolve the vignetting and distortion issues commonly encountered in rigid X-ray detectors.[20]

Furthermore, stamp transfer printing provides a facial option for thin-film deposition. Currently, uneven and destroyed interfaces during the transfer printing process irreversibly cause the deterioration of device performance and stability. To address this challenge, a thin layer of lithium fluoride (LiF) was introduced as a sacrificial layer for stretchable carbon nanotube electrodes (CNTs), leveraging the weak Li-O dipole interaction between LiF and CNTs. Therefore, the detachable interface strategy allows for the non-destructive transfer of micropatterned CNTs to flexible substrates (Figure 2i).[21] In a typical procedure, the sacrificial LiF and CNTs are sequentially deposited onto the photolithographically patterned photoresist template by vacuum thermal evaporation and spray coating, respectively. Then, the micropatterned CNTs can be easily transferred to stretchable styrene-ethylene-butylene-styrene elastomer blends (SEBS) substrate by mechanical stripping. The synergy of high-precision microlithography and innovative damage-free transfer technique enables the fabrication of pixel-dense intrinsically stretchable organic transistor arrays for high-resolution X-ray imaging.

Materials-in-substrate flexible X-ray detectors

Compared to surface deposition strategies, incorporating X-ray sensing materials inside the polymer substrates offers a straightforward approach for the fabrication of materials-in-substrate type flexible X-ray detectors. In general, pre-synthesized X-ray sensing materials or their precursors are homogeneously blended with a viscous polymer monomer solution by stirring and then either poured into a template or spread into a wet film onto a substrate. From the aspects of deposition techniques, the viscous mixture containing X-ray responsive materials and polymer monomers can be uniformly coated onto the substrate using blade coating, spin coating, drop coating, and so on. After air bubbles are removed under vacuum, the solidification of the film is initiated by thermal treatment or light irradiation for a certain duration. Eventually, the as-fabricated free-standing flexible X-ray sensing films are detached from the template or substrate, as depicted in Figure 3a.[52] Accordingly, the thickness and the size of flexible X-ray sensing films can be easily customized by tuning the weight of the mixtures and the dimension of the template. The selection of polymers is crucial for the mechanical and optoelectronic properties of flexible X-ray detectors. As shown in Figure 3b and Table 1, polymers such as polydimethylsiloxane (PDMS),[53] polymethyl methacrylate (PMMA),[54] thermoplastic polyurethane (TPU),[55] poly(vinyl alcohol) (PVA),[56] PET,[57] poly(vinylidene fluoride) PVDF,[58] polycarbonate (PC), and poly(ethylene naphthalate) (PEN) are promising for accommodating X-ray sensing materials for flexible X-ray detectors. These functional polymers serve as natural outer shells for X-ray sensing materials, protecting them from external forces, humidity, and oxygen.

Table 1. The properties of commonly used polymers for flexible X-ray detectors.

Property (Unity)	PDMS	TPU	PVDF
Density (g cm^{-3})	9.7	1.22	1.78
Tension strength (MPa)	2.24 – 6.7	20	35 – 50
Young's modulus (MPa)	2 – 3	162	2500
Hardness	42 (Shore A)	60 (Shore A)	50 – 80 (Shore D)
Contact angle (°)	~108	94	127.3
Melting point (°C)	-50 – -40	200	170
Thermal conductivity (W m^{-1}K^{-1})	0.19 – 0.24	0.15	0.041
Poisson ratio	0.5	0.38	0.35
Index of refraction	1.4	1.54	1.42
Reference	53, 59	55, 60	58, 61

Considering potential radiation damage to X-ray sensing materials during detection, functional organic hosts that provide anchors for exfoliated atoms caused by X-ray exposure are beneficial for the repair processes that prolong the lifetime of X-ray detectors. For instance, $CsPbBr_3$ nanocrystals can grow in situ within PMMA substrates as the carbonyl and ester groups provide anchors for the nucleation of lead bromide ($PbBr_2$), resulting in transparent flexible $CsPbBr_3$@PMMA scintillator ceramics (Figure 3c). Notably, even though the flexible $CsPbBr_3$@PMMA scintillator ceramics were damaged by high-intensity X-ray irradiation (8 mGy s^{-1}), the fixation of exfoliated atoms within the solidified PMMA film promotes the damage-repair process following post-annealing treatment at 80 °C, and the injured regions are almost repaired (Figure 3d & e).[41] The inherent refreshable characteristic of the scintillator ceramics allows for long-term operation and cost savings.

In addition to employing common organic polymers as host materials, researchers have made considerable efforts to endow the host materials with extraordinary properties, such as self-healing and expansion enabled by intramolecular interactions, to meet the increasing demands for X-ray imaging in complex scenarios. In a recent study, n-butyl acrylate (BA), N, N'-methylenebisacrylamide (MBA), and 1-hydroxycyclohexyl phenyl ketone (HCPK) were utilized as the monomer, crosslinker, and photoinitiator, respectively, for the construction of organogel. After introducing 20 wt% of ethylenebis-triphenylphosphonium manganese (II) bromide ($(C_{38}H_{34}P_2)MnBr_4$), a 3D scintillator organogel was formed upon the ultraviolet light irradiation, characterized by flexibility, stretchability, and bendability (Figure 3f).[42] The abundant coordination bonds between $(C_{38}H_{34}P_2)MnBr_4$ and the organic network ensure the uniform distribution of $(C_{38}H_{34}P_2)MnBr_4$ throughout the organic network with nearly no aggregation. Furthermore, the dynamic synergies of hydrogen bonds and coordination bonds in the scintillator organogels contribute to not only the excellent mechanical strength but also the self-healing capability without compromising the luminescence property of $(C_{38}H_{34}P_2)MnBr_4$ scintillators. Even when the organogels were split off, they can recover through facile interface contact for 20-30 mins, maintaining their mechanical properties and scintillation performance unchanged (Figure 3g). As opposed to traditional scintillators that are sensitive to thermal and moisture, hydrophobic $(C_{38}H_{34}P_2)MnBr_4$ scintillator organogels can survive in the water for at least 750 min while preserving 72% of their original photoluminescence intensity.

Although flat-panel detectors have significantly contributed to various fields over the past two decades, they suffer from difficulties in imaging irregular and non-flat objects in limited spaces because of their bulky, thick, and rigid architecture. In a pioneering study, researchers developed a series of ultralong afterglow nanoscintillators using sodium lutetium fluoride ($NaLuF_4$) as host and lanthanide ions as emitting centers.[43] To enhance radioluminescence, the surface of $NaLuF_4$ was passivated by coating a thin layer of sodium yttrium fluoride ($NaYF_4$) through a high-temperature coprecipitation method. The excellent solution processability, as well as superior afterglow performance, inspire researchers to fabricate flexible X-ray detectors by embedding the afterglow nanoscintillators into the PDMS substrate. As a proof of concept, the as-fabricated X-ray detector was attached to the internal surface of a circular circuit board. Compared to the overlapped X-ray image produced by rigid and large flat-panel detectors, the conformable flexible X-ray detectors can clearly

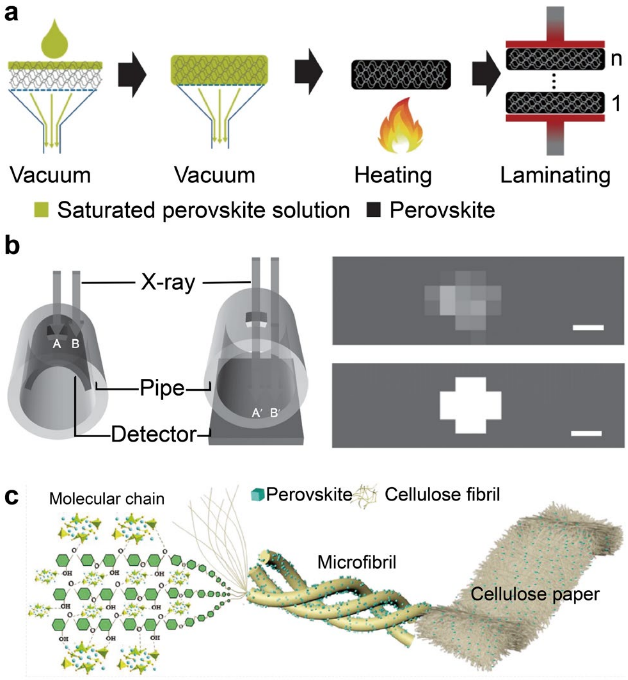


Figure 4. Materials-in-substrate type flexible X-ray detectors based on as-fabricated polymer networks. (a) Schematic illustrating the fabrication process of flexible perovskite-filled membranes. The flexible X-ray sensing films were fabricated by infiltrating the saturated perovskite precursor into the nylon membrane, then thermal annealing and laminating. (b) Schematic diagram of X-ray imaging of a tube with a '+' shape hole by placing the detector inside the tube (voltage: 60 kV; left) and outside the tube (voltage: 100 keV; right) along with X-ray imaging results (top: inside the tube; bottom outside the tube). Panels (a) and (b) were reproduced with permission from ref ([10]). Copyright 2020, The Author(s), under exclusive license to Springer Nature Limited. (c) Schematic of the $Cs_3Cu_2I_5$:2%In^+ perovskite crystals-loaded cellulose fibrils. Reproduced with permission under a Creative Commons CC BY from ref ([62]). Copyright 2023, The Authors, Advanced Science published by Wiley-VCH GmbH.

unveil the fine structure of the circuit board in a tight space (Figure 3 h & i).

Apart from their use as host materials, polymers can independently form luminescent flexible films and are competitive candidates for flexible X-ray detectors due to their structural diversity, solution processability, film-formation ability, and low cost. Polyacrylic acid (PAA) was chosen as a versatile polymeric backbone, capable of accommodating various chromophores through radical copolymerization, as its carboxyl groups can suppress non-radiative recombination via hydrogen bonding.[44] The incorporation of bromine (Br) in 4-(allyloxy)−4′-bromo-1,1′-biphenyl (BBr) enhances the spin-orbit coupling (SOC) for efficient intersystem crossing, as well as improved X-ray absorption. The synergies of enhanced X-ray stopping capability, suppressed non-radiative recombination, and strong SOC make PAA/BBr (PBBr) an efficient copolymer scintillator (Figure 3j). A transparent, homogeneous, and flexible copolymer X-ray detector was then fabricated to demonstrate its X-ray imaging capabilities (Figure 3k).

While the as-fabricated X-ray sensing materials or their precursors are premixed with polymer monomers, they can also be directly incorporated into readily available 3D porous polymer networks (e.g., nylon, cotton fabric, natural cellulose, *etc.*) through immersion or infiltration processes.[63] As presented in Figure 4a, the saturated $MAPbI_3$ perovskite precursor was infiltrated into the high-strength porous nylon membranes by vacuum pumping. Thanks to the low formation energy of perovskites, $MAPbI_3$ crystals can grow within the pores of the nylon membrane at low temperatures following the evaporation of the solvent by thermal annealing and lamination. The thickness of the $MAPbI_3$@nylon composite membranes can be easily tailored by increasing the lamination cycles. The large-area $MAPbI_3$@nylon composite flexible X-ray detectors exhibit excellent flexibility and optoelectronic properties, which overcome the limitations of traditional rigid flat-panel detectors, especially in imaging non-planar objects, as demonstrated in Figure 4b.[10]

From the perspective of green growth and sustainable development, utilizing natural products as organic hosts that perform as well as synthetic organics is expected to substantially reduce the environmental burden, manufacturing cost, and recycling difficulties.[64] As renewable products, cellulose papers are ideal candidates for flexible X-ray detectors because of their flexibility, portability, and biocompatibility. The exposed lone electron pairs of hydroxyl and ether groups on the cellulose microfibril chains facilitate the coordination with copper atoms, enabling the uniform dispersion and crystallization of indium-doped cesium copper iodide ($Cs_3Cu_2I_5$: 2%In; Figure 4c) via a two-step process including immersion and thermal annealing. During the immersion, Cu ions were tightly bonded on the microfibril chains through coordination. The subsequent thermal treatment leads to the evaporation of solvent molecules and then the crystallization of $Cs_3Cu_2I_5$: 2%In microcrystals, forming a large-area $Cs_3Cu_2I_5$: 2%In@cellulose scintillator paper (4800 cm^2). Furthermore, in-situ crystal growth within cellulose networks provides a versatile strategy for accommodating a variety of perovskites, such as cesium copper chloride ($Cs_3Cu_2Cl_5$) and cesium copper bromide ($Cs_3Cu_2Br_5$).[62] The compatibility of cellulose microfibrils with industrial roll-to-roll manufacturing techniques provides the possibility of fabricating large-area and low-cost flexible X-ray detectors.

CHALLENGES AND OPPORTUNITIES

Despite tremendous achievements in flexible X-ray detectors over the past few years, alongside the promising applications in health care, industrial nondestructive inspection, and security checks, several challenges continue to hamper their development and practical implementation.

Low loading ratio and severe phase segregation. Currently, the majority of materials-in-substrate type flexible X-ray detectors are fabricated by mixing inorganic X-ray sensing materials with organic monomer viscous solution. However, the loading ratio of the X-ray sensing materials within organic substrate remains low, typically less than 20 wt%, which is primarily attributed to the phase incompatibility between inorganic and organic substances. Especially, the phase separation becomes more severe as the dopant ratio of X-ray sensing materials increases, resulting in serious light scattering in indirect X-ray detectors and electrical insulation in direct X-ray detectors, respectively, thus degrading the detection and imaging performance. Until now, little research has been directed toward improving the phase compatibility between organic and inorganic substances in flexible X-ray detectors. Given the crucial role of the interface between organics and inorganics, elaborate modification of surface properties of X-ray sensing materials or functional groups of organic substrates is essential. Strategies like ligand exchange, core-shell structures, and surface in situ polymerization can effectively modify the surface properties of X-ray sensing materials. Furthermore, surface modification can mitigate luminescence quenching effects caused by surface chemical reactions and surface defects in scintillators, contributing to enhanced radioluminescence in indirect X-ray detectors.[65, 66] However, excessive organic ligands will impede charge carrier transport in semiconductors. Hence, manipulating the balance between surface modification and electrical properties in direct X-ray detectors is of critical importance. Simultaneously, tailoring the side chains of organic substrates according to the 'like dissolves like' principle can improve their solubility with X-ray sensing materials. By adopting these strategies, it is anticipated that the loading ratio of X-ray sensing materials in the organic substrate will considerably increase, thus enhancing the performance of flexible X-ray detectors.[67]

Poor X-ray absorption of organic substrates. Since flexible X-ray sensing layers primarily consist of organic materials with light elements such as C, H, O, and N, showing poor overall X-ray absorption capability. In practical applications, 90 % of incoming X-rays are required to be absorbed by the detectors with sufficient thickness. At present, strategies aimed at increasing the thickness of flexible X-ray sensing layers for better X-ray absorption inevitably reduce the flexibility of the devices and complicate the fabrication processes. Conversely, an alternative strategy associated with integrating heavy metal atoms in organic substrates provides a ‘two birds with one stone’ strategy to increase the X-ray absorption without increasing the thickness of the X-ray sensing layer.[68] In particular, organometal complexes are ideal candidates for flexible X-ray detectors as host materials due to their excellent X-ray absorption capability.[69] Specifically, the energy or electron transfer processes between the heavy atoms and the X-ray sensing materials upon X-ray irradiation must be thoroughly investigated by combining advanced techniques such as transient absorption and ultrafast spectroscopy to establish the guidelines on the design of highly efficient flexible X-ray detectors.[70, 71]

Limited flexibility in materials-on-substrate type flexible X-ray detectors. Materials-on-substrate type flexible X-ray detectors, where X-ray sensing materials are directly coated onto the surface of flexible supporting substrates, commonly exhibit limited flexibility due to the fragility of the pure X-ray sensing layer. A critical challenge lies in balancing the thickness and flexibility of the active layer, as increased thickness generally results in reduced flexibility. Consequently, the thickness of active layers in current materials-on-substrate flexible X-ray detectors is only tens of microns, which is insufficient to block hard X-rays effectively. One available strategy to improve flexibility and enhance the X-ray stopping power is to introduce crosslinking polymers that can form a 3D supporting network for X-ray sensing materials.[72] Considering that the presence of organic insulators may block charge transport in direct X-ray detectors, developing flexible organic binders that provide excellent flexibility while maintaining electronic properties is highly desirable. Additionally, incorporating a protective polymer cover over the active layer can further enhance the flexibility of the active layer and prevent the active layer from ambient conditions, thereby improving the operational stability of flexible devices.[73]

Light scattering in flexible scintillator layers. In contrast to direct X-ray detectors, where charge carriers move along the electric field without signal crosstalk, indirect flexible X-ray detectors suffer from anisotropic light scattering-induced signal crosstalk among pixels, severely degrading the spatial resolution. To mitigate this challenge, several engineering strategies can be implemented. Various strategies such as additives engineering,[74] solvent engineering,[75] and interfacial engineering[76] have been demonstrated to effectively improve the crystallinity of X-ray sensing materials, thereby inhibiting nonradiative recombination, reabsorption, and light scattering. Furthermore, anisotropic light scattering can be restricted by constructing light waveguide photonic structures to inhibit light crosstalk between pixels. For example, columnar scintillator crystals with light waveguide effect, inspired by needle-like CsI: Tl arrays, can be constructed onto the flexible substrate through controllable thermal evaporation, mist deposition,[77] laser printing,[78] or lithography[79] to confine light propagation.[80, 81] Simultaneously, the integration of X-ray sensing materials inside the as-fabricated flexible substrate with highly ordered channels, similar to anode aluminum oxide (AAO) array, provides a relatively convenient approach to suppress lateral light spreading by directing light propagation.[82] By implementing these light management strategies, the light output of flexible scintillator layers in indirect X-ray detectors can be significantly boosted.[83]

The spatial mismatch between rigid image sensors and flexible X-ray sensing layers. In principle, flexible X-ray detectors present higher spatial resolution than their rigid counterparts because they can conform to non-planar surfaces. However, indirect flexible X-ray detectors commonly integrate a flexible scintillator layer with a commercial digital camera with rigid planar image sensors like charge-coupled devices (CCD) and CMOS. This combination fails to fully exploit the capabilities of flexible X-ray detectors due to spatial non-conformity between the flexible scintillator layer and the planar image sensor, leading to discrepancies in incident angular light on the planar image sensor, thus causing a vignetting effect. To address this issue, it is necessary to develop flexible image sensors that can spatially adapt to the geometry of flexible scintillator layers to eliminate the vignetting effect.[84] In addition, previous research on flexible scintillator films with long electron-trapping effects is expected to address the vignetting issue in current indirect flexible X-ray detectors. In a typical imaging procedure, a flexible scintillator film with nanoscintillators featuring long-lived energy trapping is attached to a non-planar surface of the object before X-ray exposure. After X-ray exposure, the flexible scintillator film is taken out, unfolded, and placed on a flat surface to extract the latent image by thermal or light stimulation. The separation of X-ray exposure and signal readout resolves the spatial incompatibility between the flexible scintillator composite films and the planar image sensors.[43, 85] Additionally, current flexible X-ray detectors fail to retrieve accurate surface information of the objects due to the lack of motion-sensing detectors. Therefore, integrating shape-sensing systems into flexible X-ray detectors offers a possible solution for precisely capturing the distortions and deformations of the detector as well as the spatial information about the object's surface.[86-88]

CONCLUSIONS

Large-area flexible X-ray detectors, exhibiting higher spatial resolution, reduced radiation exposure, user-friendliness, miniaturized systems, and low cost, undoubtedly stand for a prospective research frontier and cutting-edge technique anticipated to reform the X-ray imaging industry. Significantly, flexible X-ray detectors can intentionally conform to the surface of 3D objects, promising to extend X-ray imaging applications in various fields, including health care, industrial inspection, homeland security, and more. Notably, the past decade has witnessed the extensive advancement of flexible X-ray detectors either in materials-on-substrate type, where the X-ray sensing materials are deposited onto the surface of the flexible substrate, or in materials-in-substrate type, where the X-ray sensing materials are incorporated into the flexible matrix, through various micro/nano engineering strategies. Despite these brilliant achievements, a considerable gap exists between laboratory research and commercialization. Critical scientific issues such as low loading ratio, phase separation, poor X-ray absorption, limited flexibility, light scattering, and spatial mismatch in different kinds of flexible X-ray detectors are required to be thoroughly investigated and addressed. We are optimistic that the strategic guidance proposed in this Perspective will attract the attention of the communities and inspire more researchers to contribute to facilitating the commercialization of large-area flexible X-ray detectors.

Author Contributions

X.O. and Z.H. contributed equally to this manuscript.

Notes

The authors declare no competing financial interest.

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