Large-Area Perovskite-Related Copper Halide Film for High-Resolution Flexible X-ray Imaging Scintillation Screens

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ABSTRACT: Flexible copper halide films of 400 cm² area were fabricated with outstanding mechanical stability, excellent film uniformity, nearly 100% photoluminescence quantum yields, and resistance to water and heat. The re-absorption-free X-ray imaging scintillators engineered based on these films exhibit superior scintillation performance with a detection limit as low as 48.6 nGy/s and 17 lp/mm X-ray imaging resolution, representing the highest imaging resolution for powder-based screens.

X-ray imaging scintillation is a critical technology for medical diagnosis as well as industrial and security inspection. Lead halide perovskite X-ray imaging scintillators have attracted a great deal of attention since the initial report of using all-inorganic CsPbX₃ (X = I, Br⁻, Cl⁻, or mixed halides) solution-processed nanocrystals as multicolor scintillators. To guarantee a high light yield, the ideal imaging scintillators should possess a large absorption cross-section for X-ray radiation and simultaneously a large Stokes shift to minimize the re-absorption of the radioluminescence (RL). Although the presence of high-Z ions (such as Cs, Pb, and I) endows perovskites with a considerable X-ray absorption capacity, the significant re-absorption behavior caused by band-edge transitions seriously attenuates the utilizable light yield, leading to a poor scintillation performance. Moreover, the toxicity of lead and poor air- and light-stability are also serious problems that severely limit their commercialization potential. Therefore, the development of new stable lead-free scintillation materials is urgently needed.

Recently, the lead-free Cs₃Cu₂I₅ perovskite-related compound has emerged as a promising candidate for X-ray scintillators because it is eco-friendly and has a high light yield. By virtue of its low-dimensional electronic structure, the Cs₃Cu₂I₅ can easily form self-trapped excitons (STEs) due to the lattice’s Jahn–Teller distortion. The ensuing, large Stokes shift between emission and absorption spectra renders re-absorption-free candidate materials for high-performance X-ray imaging scintillators. Specifically, the Cs₃Cu₂I₅ single crystals grown by the Bridgman method showed a high light yield of ~32 000 photons/MeV, and the X-ray imaging spatial resolution of 6.8 lp/mm was realized using Cs₃Cu₂I₅ film made of ball-milled powder. However, the zero-dimensional (0D) Cs₃Cu₂I₅ phase with blue emission is extremely sensitive to moisture, and it readily transforms into 1D CsCu₂I₃ phase with yellow emission under moisture treatment due to the high solubility of CsI in water. Unfortunately, the light yield of the CsCu₂I₃ phase is much lower than that of the Cs₃Cu₂I₅ phase, which limits the actual scintillation applications.

Here, the highly stable flexible X-ray scintillation screens with a 400 cm² area based on the Cs₃Cu₂I₅-polydimethylsiloxane (CCl-P) films were realized. Due to their re-absorption-free, high phase purity, and nearly 100% photoluminescence quantum yields (PLQYs), the films exhibited very promising scintillation properties with a low detection limit of 48.6 nGy/s and 17 lp/mm X-ray imaging resolution. Cs₃Cu₂I₅ polycrystalline powders with high phase purity were synthesized by a modified solution process using 2-propanol as the antisolvent (see SI for details, Figures S1–S3). It is noteworthy that the product yield is more than 85%, which provides a favorable condition for low-cost, large-scale fabrication (Figure S4). The Cs₃Cu₂I₅ powders were ground with a mortar and pestle to further refine the particle sizes (Figure S5).

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The preparation of CCI-P-x% (i.e., the mass ratio of Cs$_3$Cu$_2$I$_5$ is x%) films is illustrated in Figure S6. Upon addition of ethyl acetate (EA), a very uniform flexible film can be fabricated by the spin-coating or blade-coating method. In contrast, the film without adding EA exhibited poor surface morphology due to the aggregation of Cs$_3$Cu$_2$I$_5$ particles (Figure S6). Figure 1a shows the uniform large-area (20 × 20 cm$^2$) CCI-P-5% film with a thickness of 300 μm. Under UV excitation, the film exhibited bright blue emission (Figure 1b). Thanks to the rubber-like nature of polydimethylsiloxane (PDMS), the flexible films have no physical damage in response to mechanical deformations (Figure 1c–g). Furthermore, the XRD pattern of CCI-P-5% film demonstrated that the Cs$_3$Cu$_2$I$_5$ structure remains well after mixing with PDMS (Figure S7). To reveal the photophysical properties of the film, we first investigated the absorption spectra of CCI-P-5% film, which showed a sharp absorption edge at approximately 325 nm (Figure S8). Next, we measured the steady-state photoluminescence (PL) spectra. Under UV excitation, the CCI-P-5% film displayed a broad PL spectrum ranging from 350 to 580 nm, peaking at ca. 445 nm and with a full width at half-maximum of 81 nm (Figure S8). The PLQY of CCI-P-5% film was measured to be about 97.4%. Note that a large Stokes shift of 120 nm was observed, as shown in Figure S8.

To further understand the PL behavior, we measured the PL lifetime for CCI-P-5% film. As shown in Figure S9, the decay curve of the CCI-P-5% film can be fitted by a single-exponential function, with a time constant of 969 ± 8.6 ns. All of the above photophysical characteristics, including long lifetime, large Stokes shift, and broad PL range originate from the STEs. To evaluate the stability of the engineered flexible film for real-
life applications, we studied its resistivity to water and high temperature. As shown in Figure S10, the blue emission of Cs$_3$Cu$_2$I$_5$ powders quickly quenched and evolved to yellow emission under high humidity (~95%) treatment, while the CCI-P-5% film showed outstanding stability and still maintained strong blue emission even when immersed in deionized water. On the other hand, the PL intensity of CCI-P-5% film remained almost the same under long-time heat treatment (Figure S10).

Both the excellent photophysical properties and high stability of the flexible films manifested a great potential as X-ray imaging scintillators. For instance, the light yield of CCI-P-20% film was calculated as ~48 800 photons/MeV as compared with the commercial LYSO: Ce scintillator (~33 000 photons/MeV) (Figure 2a). The RL intensity of CCI-P-20% film was measured under various X-ray doses, showing a well linear correlation with the dose rate of X-rays; and a detection limit of 48.6 nGy/s was achieved, which was even better than that of commercial LYSO: Ce scintillator (60.1 nGy/s) (Figure 2b–d, Figure S11). We further evaluated the X-ray imaging capability of the flexible films. As shown in Figure 2e,f, the X-ray image of a flexible copper grid recorded by the bending film possesses much better resolution, especially on the edge of copper grid, as compared with that taken by the film under a flat state. Interestingly, the X-ray image still maintained high resolution when the film was under stretching state (Figure S12). These confirmed that our flexible films have huge potential for non-flat, flexible target X-ray detection. Finally, the excellent resolution ability of the films was demonstrated using a copper grid with honeycomb structure as an imaging object (Figure 2g). An excellent X-ray spatial resolution of 17 μm/mm was achieved with a modulation transfer function (MTF) value of 20%, representing the highest imaging resolution for powder-based screens (Figure 2h, Table S1). It is noteworthy that the flexible film based on PDMS not only possesses the homogeneous distribution of Cs$_3$Cu$_2$I$_5$ particles that mitigates the scattering of emitted X-ray but also enables the fabrication of a thickness down to 50 μm, which is critical to achieve high-resolution X-ray imaging.

In summary, we present lead-free large-area flexible Cs$_3$Cu$_2$I$_5$ films with high PLQYs, negligible re-absorption, and high air and heat stability. These features make the flexible films excellent X-ray scintillators with a low detection limit of 48.6 nGy/s, ~1.13 times lower than a typical standard dose for X-ray medical imaging. More importantly, the highest X-ray imaging spatial resolution of 17 μm/mm was achieved, demonstrating the films’ promise for medical radiography and security screening applications.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.2c00075.

Details of powder preparation, film fabrication, and characterization; Figures S1–S12 and Table S1 (PDF)

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**Notes**

The authors declare the following competing financial interest(s): O.M.B. is a founder of Quantum Solutions, a nanotechnology company that develops and manufactures quantum dot materials for optoelectronics.

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