Metal Halide Perovskite Nanosheet for X-Ray High-Resolution Scintillation-Imaging Screens

Yuhai Zhang, Ruijia Sun, Xiangyu Ou, Kaifang Fu, Qiushui Chen, Yuchong Ding, Liang-Jin Xu, Lingmei Liu, Yu Han, Anton V. Malko, Xiaogang Liu, Huanghao Yang, Osman M. Bakr, Hong Liu, and Omar F. Mohammed

ACS Nano, Just Accepted Manuscript • DOI: 10.1021/acsnano.8b09484 • Publication Date (Web): 05 Feb 2019

Downloaded from http://pubs.acs.org on February 10, 2019
Metal Halide Perovskite Nanosheet for X-Ray High-Resolution Scintillation-Imaging Screens

Yuhai Zhang,¹,² * Ruijia Sun,¹ Xiangyu Ou,³ Kaifang Fu,¹ Qiushui Chen,⁴ Yuchong Ding,⁵ Liang-Jin Xu,² Lingmei Liu,⁶ Yu Han,⁶ Anton V. Malko,⁷ Xiaogang Liu,⁴ Huanghao Yang,³ Osman M. Bakr,² Hong Liu,¹ * and Omar F. Mohammed,² *

¹Institute for Advanced Interdisciplinary Research (iAIR), University of Jinan, Jinan 250022, Shandong, China
²King Abdullah University of Science and Technology, Division of Physical Sciences and Engineering, Thuwal 23955-6900, Saudi Arabia
³MOE Key Laboratory for Analytical Science of Food Safety and Biology, State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350002 China.
⁴Department of Chemistry, National University of Singapore, Singapore 117543, Singapore
⁵Research & Development Center of Material and Equipment, China Electronics Technology Group, Corporation No. 26 Research Institute, Chongqing 400060, China
⁶King Abdullah University of Science and Technology (KAUST), Advanced Membranes and Porous Materials Center, Physical Sciences and Engineering Division, Thuwal 23955-6900, Saudi Arabia.
⁷Department of Physics, The University of Texas at Dallas, Richardson, TX, 75080, USA

Corresponding Authors

ifc_zhangyh@ujn.edu.cn, ifc_liuh@ujn.edu.cn, omar.abdelsaboor@kaust.edu.sa
ABSTRACT

Scintillators, which are capable of converting ionizing radiation into visible photons, are an integral part of medical, security, and commercial diagnostics technologies such as X-ray imaging, nuclear cameras, and computed tomography. Conventional scintillator fabrication typically involves high-temperature sintering, generating agglomerated powders or large bulk crystals, which pose major challenge for device integration and processability. On the other hand, colloidal quantum dot scintillators cannot be cast into compact solid films with the necessary thickness required for most X-ray applications. Here, we report the room-temperature synthesis of a colloidal scintillator comprising CsPbBr₃ nanosheets of large concentration (up to 150 mg/mL). The CsPbBr₃ colloid exhibits a higher light yield (~21000 photons/MeV) than the commercially available Ce:LuAG single-crystal scintillator (~18000 photons/MeV). Scintillators based on these nanosheets display both strong radioluminescence (RL) and long-term stability under X-ray illumination. Importantly, the colloidal scintillator can be readily cast into a uniform crack-free large-area film (8.5×8.5 cm² in area) with the requisite thickness for high-resolution X-ray imaging applications. We showcase prototype applications of these high-quality scintillating films as X-ray imaging screens for a cellphone panel and a standard central processing unit (CPU) chip. Our radiography prototype combines large-area processability with high resolution and a strong penetration ability to sheath materials, such as resin and silicon. We reveal an energy transfer process inside those stacked nanosheet solids that is responsible for their superb scintillation performance. Our findings demonstrate a large-area solution-
processed scintillator of stable and efficient RL as a promising approach for low-cost radiography and X-ray imaging applications.

**Keywords:** perovskite, colloidal scintillator, self-assembly, X-ray imaging, energy transfer, nanosheets
Scintillating materials are widely used for radiation-detection applications in many fields, including interstellar particle detection, X-ray security, nuclear cameras, and computed tomography, due to their ability to convert ionizing radiation into visible or ultraviolet photons.\textsuperscript{1, 2} Conventional scintillators, such as CsI(Tl) crystals and cerium-activated glass, are usually synthesized under high-temperature conditions,\textsuperscript{3, 4} which is neither cost-effective nor user-friendly. Additionally, the resulting powder scintillator suffers from severe agglomeration while a precisely sliced single crystal is required to be easily incorporated into device architectures.\textsuperscript{5, 6}

An ideal scintillator with a controllable thickness should be solution-processable. Organic dye solutions, such as $p$-terphenyl (C\textsubscript{18}H\textsubscript{14}), PBD (C\textsubscript{20}H\textsubscript{14}N\textsubscript{2}O), and PPO (C\textsubscript{15}H\textsubscript{11}NO), have been used as scintillators to detect neutrons.\textsuperscript{7-9} However, the detection efficiency is substantially low due to their low stopping power because of their low atomic number constituents. Moreover, organic dyes are intrinsically susceptible to both the photobleaching effect and oxygen quenching,\textsuperscript{10} hindering their practical application in many areas. It is worth pointing out that hybrid perovskite films incorporating heavy-metal ions became an excellent candidate for X-ray detection.\textsuperscript{11-17} For instance, all-inorganic perovskite nanocrystals have recently emerged as promising semiconductor materials for efficient scintillators due to their high stopping power, low detection limit, and multicolor RL.\textsuperscript{18} However, these nanocrystals are difficult to cast into compact solid form films with the requisite thickness (due to the long penetration depth of X-rays) and area sizes for commercially viable applications. Thus, only small device areas were possible to be fabricated and tested.\textsuperscript{1, 11, 14, 15, 19}
Here, we report the room-temperature synthesis of a high-quality scintillator in both colloidal and solid film forms, designed and self-assembled from highly concentrated solutions of perovskite nanosheets. The colloidal form of concentrated CsPbBr$_3$ nanosheets exhibits equivalent brightness of RL to the film counterpart and shows long-term stability under both storage and X-ray exposure conditions. Due to their high concentration and nanosheet morphology, our scintillators are readily solution-processable and tend to assemble into a crack-free film over a large area up to 72 cm$^2$, allowing for high-resolution (< 0.21 mm) X-ray imaging applications. Finally, we used time-resolved photoluminescence spectroscopy to reveal an energy transfer process inside those stacked nanosheets that enhances the scintillation performance beyond what is typically expected in nanocrystal scintillators.

RESULTS AND DISCUSSION

The CsPbBr$_3$ nanosheets were synthesized using a modified coprecipitation method.$^{20}$ Briefly, an excessive amount of PbBr$_2$ precursor was injected into a cesium acetate precursor at room temperature under an ambient atmosphere (see the Supporting Information for further details). A bright green color appeared immediately, indicating the formation of CsPbBr$_3$ nanosheets. Conventionally, the purification process of CsPbBr$_3$ nanocrystals requires breaking the colloidal stability by the addition of a poor solvent, ethyl acetate for example, which inevitably induces severe degradation of the particles.$^{21,22}$ In this work, however, the nanosheets could be easily collected by low-speed centrifugation (< 4000 rpm) without using any polar solvents. The collected
Nanosheets were dispersed in toluene with a high concentration of up to 150 mg/mL, and the resulting colloid could be kept in a capped vial for one month without any noticeable degradation (Figure S1).

**Figure 1.** a) Schematic showing the self-assembly process of CsPbBr$_3$ nanosheets. The bottom panel shows the photographs of a heavily loaded colloid (150 mg/mL) in toluene and a wafer-sized thin film on a glass slide. b) TEM image of the assembled CsPbBr$_3$ nanoplatelets, featuring an interplane spacing of 2.1 nm. c) HRTEM image of the assembly, showing a clear lattice fringe of (200) facets. d) Low-angle XRD diffraction pattern of the assembled CsPbBr$_3$ thin film, showing a series of interplane diffraction peaks of the stacked CsPbBr$_3$ nanoplatelets. The peak spacing of 3.82° suggests an interplane spacing of 2.32 nm, in line with the TEM results. e) SEM image showing the flatness of the thin film. f) Steady-state absorption and photoluminescence (excitation at 365 nm) spectra of the colloid and thin-film samples.
The large-area thin film was fabricated through a self-assembly process of CsPbBr$_3$ nanosheets. Typically, the concentrated colloid was drop cast on a clean glass substrate under ambient conditions and allowed to dry naturally. A crack-free perovskite thin film was obtained in 12 minutes, showing a green tint under ambient light (Figure 1a). The TEM image reveals the face-to-face packing manner of CsPbBr$_3$ nanosheets with an interplane gap of 2.1 nm (Figure 1b). Moreover, the HRTEM image shows the lattice fringes of both a lateral nanosheet and an aligned nanosheet, featuring a (002) d-spacing of 0.30 nm (Figure 1c). Importantly, we were able to accurately measure both the thickness of the nanosheets (2.8 ~ 4.2 nm) and the gap between them (2.1 nm). Considering the lattice constant (0.59 nm) of a single unit cell, we were able to identify the number of monolayers (5-7 layers) comprising an individual nanosheet, which was in good agreement with both the HRTEM observation and the Scherrer broadening effect (Figure S2). The thin film was rather flat, featuring a surface roughness of approximately 13 nm and a thickness of approximately 4.0 μm (Figure 1e, Figure S3), which is critical for high-resolution radiography.

To further confirm the self-assembly nature of the thin film, low-angle powder XRD was conducted. The XRD pattern shows three peaks with an equal spacing of 3.82°, indicating that the slit of the superstructure is approximately 2.3 nm. This value is in line with our result obtained from HRTEM (2.1 nm), suggesting that there are two layers of passivating ligands (octylamine or octanoic acid) occluding the gap. It is worth noting that the result is in good agreement with the value obtained from the reported relationship $d$ (Å) = 8.06 + 1.59 × n, where n is the number of carbon atoms in the
alkylamine (for octylamine or octanoic acid, n = 8).\textsuperscript{23} The thin film showed intense luminescence centered at 515 nm under 365-nm excitation, which is slightly spectrally redshifted compared to that of the colloidal counterpart. Interestingly, the absorption of the colloid exhibited an excitonic peak at 460 nm, together with a long tail extending to 570 nm (Figure 1f). This broadening can be ascribed to the inhomogeneous distribution of the nanosheet thickness, as evidenced by HRTEM.

**Figure 2.** Streak camera measurement of transient PL from the thin film of the CsPbBr\textsubscript{3} nanosheet assembly (Pb/Cs: 5/1). a) 2D pseudocolor transient emission map, excitation at 410 nm, flux at 1 pJ/cm\textsuperscript{2}. b) Transient PL profiles at 3 ns, 6 ns, and 15 ns, showing the recombination center shifting of excitons. PL decay traces extracted at 460 and 500-nm windows (±5 nm). c) Magnified image of PL decay traces in the first 3 ns, where the building-up lifetime of 500-nm emission is comparable to the short component of 460-nm emission, indicating an efficient energy transfer. The dashed box highlighted the building-up stage of 500-nm emission. d) The effective lifetime was plotted against the wavelength, with two plateau lifetimes (dashed box) ascribable to thin and thick nanosheets, respectively. e) Magnified image of PL decay traces in the first 3 ns, where the building-up lifetime of 500-nm emission is comparable to the short component of 460-nm emission, indicating an efficient energy transfer. f) Schematic showing the energy transfer process from thin to thick nanosheets, with a FRET efficiency of 74%.
The coexistence of both thin and thick CsPbBr$_3$ nanosheets, as indicated by HRTEM, implies an energy transfer process inside the stacked thin film. To quantitatively evaluate the energy transfer efficiency, we used a streak-camera system to collect the transient PL signal in both wavelength and time domains (Figure 2a). The time-delayed PL profile shows a clear redshift from 460 nm to 510 nm, indicating that the exciton recombination center shifted from a high energy level to a low one in 15 ns (Figure 2b).

The PL decay trace at 500 nm shows a nearly monoexponential decay with a lifetime of 8.09 ns (Figure 2b). In stark contrast, the PL decay trace at 460 nm comprises both a short component of 0.67 ns (67%) and a long component of 2.57 ns (33%) (Figure 2, e and f). The long component is likely the intrinsic excited-state lifetime of the thin nanosheets (donor), which are isolated from the thick ones (acceptor), with a lifetime value similar to that of five-layer nanoplatelets, as reported by Akkerman et al.$^{24}$ On the other hand, the short component can be attributed to the energy transfer from the thin to the thick nanosheets.

To validate the assumption that the short-component lifetime of 460-nm emission is due to FRET, we fitted the rising time of 500-nm emission (Figure 2e). Indeed, the rise time of 0.58 ns at 500 nm (acceptor) is quite similar to the short component of 0.67 ns at 460 nm (donor), confirming the abovementioned assumption about FRET.$^{25}$ It is worth noting that the effective lifetime is wavelength dependent with two plateaus, suggesting the existence of both thin and thick nanosheets (Figure 2d). Now, the assembly can be viewed as a donor-acceptor system where the donor has an intrinsic
lifetime of 2.57 ns ($\tau_d$), and the donor-acceptor assembly has a lifetime of 0.67 ns ($\tau_{da}$).

The FRET efficiency (E) can be calculated by the following equation:\textsuperscript{26}

$$E = 1 - \frac{\tau_{da}}{\tau_d} = 74\% \quad (1)$$

In the thin film of the stacked nanosheet assembly, the donor-acceptor distance ($r$) is equivalent to the interplane distance, approximately 2.3 nm, as indicated by the small-angle XRD measurement. By using equation (2), we calculated the Förster distance ($R_0$) of CsPbBr$_3$ nanosheets to be 2.74 nm.\textsuperscript{27-29}

$$E = \frac{1}{1 + (r/R_0)^6} \quad (2)$$

Next, we investigated the RL of both colloidal and solid forms of CsPbBr$_3$ nanosheets, as well as the transformation process. As shown in Figure 3a and Figure 4b, the concentrated colloidal nanosheets showed bright green luminescence under X-ray excitation as well as the ensuing thin film. In fact, most perovskite nanocrystals tend to compromise on PLQY after colloid-solid transformation due to ligand-detachment induced trap states. For example, due to the ligand loss, the CsPbBr$_3$ tethered with oleic-acid ligands dramatically drops its original PLQY from 56 to 18% after solidification.\textsuperscript{30,31} The stacked nanosheets in this work, however, retained a high PLQY of up to 63%, mainly because the ligands tethered on nanosheets were well shielded among the assembly.
Figure 3. RL of the colloidal and solid forms of CsPbBr$_3$ nanosheets. (a) Photographs of the concentrated colloid (0.15 g/mL) under ambient light and an X-ray. The exposure time for the RL photo was set to 2 s. (b) Pulse height spectra of a standard commercial scintillator (Ce:LuAG) and a CsPbBr$_3$ colloid. Note that the Compton edge for the colloidal scintillator is significantly weak. The RL spectra (c), peak (d), and intensity (e) were monitored during the transformation from a colloid to a solid in 12 min. (f) Small-angle XRD shows the emergence of the superstructure during the drying process of the colloid.

In an attempt to quantify the RL light yield, a commercially available scintillator of cerium-doped lutetium–aluminum garnet (Ce:LuAG) single crystal was used as a reference standard,$^3$ and exhibited a similar RL peak to colloidal CsPbBr$_3$ nanosheets, both centered at 520 nm (Figure S7). Both samples were excited by γ-rays with an energy of 662 keV ($^{137}$Cs source). The signal was fed into a multichannel analyzer (MCA) (ORTEC 926) and plotted into a pulse height spectrum (Figure 3b). Therefore, the channel number at the full energy peak represents the relative light yield of the scintillator.$^{32}$ Importantly, the CsPbBr$_3$ colloid exhibits a higher light yield (~21000
photon/MeV) than the commercially available Ce:LuAG single-crystal scintillator (~18,000 photons/MeV). In stark contrast to most of the conventional scintillators, the colloidal scintillator did not show any pronounced Compton edge, which may need further investigation.

Figure 4. Radiography property of the perovskite thin film comprising CsPbBr$_3$ nanosheets. (a) The dose-dependence of the RL intensity shows a linear relationship. (b) The thickness dependence of the RL intensity suggests an optimal value at 25 μm, above which the added thickness is not able to gain more RL intensity. The insets show the photographs of a 25 μm-thick film under room-light and X-ray illumination, respectively. (c) Intensity record of the thin-film RL over 2-hour exposure of X-ray radiation at 18 μGy/s, showing a robust stability. (d) Photograph of a transistor panel in a cellphone. (e) The interior structure of the resin-covered panel (red dashed square)
can be clearly revealed by the perovskite thin-film screen under our homemade radiography setup. (f) The point spread function (red line) of the intensity profile is fitted with a Gaussian function (blue line), and the full width at half-maximum (FWHM) is taken as the resolution. (g) Photograph of a standard CPU panel with a silicon chip integrated underneath. (h) X-ray imaging of the covered part (red dashed square) by the silicon chip, showing an unharmed resolution.

To monitor the RL change during self-assembly in real time, we used a fiber coupled spectrometer to record the RL of CsPbBr3 nanosheets during the transition from a colloid to a solid. As seen, the RL peak remains the same at 525 nm during the drying process (Figure 3d). Surprisingly, the RL of the colloidal scintillator is 20% higher than that of its solid form. The slight decrease in thin-film RL intensity is ascribable to the enhanced reabsorption between thin and thick nanosheets as the self-assembly proceeds.33 To elucidate the self-assembly process, a real-time XRD measurement was conducted (Figure 3f). As the colloid solidifies, the peaks at 7.6° and 11.4° emerged and intensified as the time evolved, confirming the formation of a highly ordered superstructure (Figure S8). We also observed that the XRD peaks are significantly broadened due to the reduced grain size (Figure S2). Based on the Scherrer equation, the mean thickness of the nanosheets is calculated to be 2.95 nm, which is in good agreement with the HRTEM result.

X-ray radiography is an imaging technique that uses the dose-dependence of scintillator RL to generate a phase contrast image. To assess the dose response of the perovskite film, we record the RL of a film (25 µm in thickness) under varied X-ray dose rates. The RL intensity shows an exceptional linearity to the dose rate in a broad
range of 1 to 140 μGy/s (Figure 4a and Figure S4). Importantly, the RL intensity increases with increasing thickness of the film in the range of 5-25 μm (Figure 4b). The intensity reaches a plateau when the thickness is above 25 μm, suggesting an optimal thickness of the active layer for the perovskite scintillator screen. This value is significantly smaller than those previously reported values, indicating the strong X-ray stopping power of our thin film. Importantly, the perovskite film under investigation shows no radio-degradation effect under continuous X-ray irradiation for 2 hours (Figure 4c), exhibiting a long-term radio-stability. On a separate note, the lifetime of the perovskite scintillator is wavelength-dependent, ranging from 2 to 13 ns with varied wavelengths from 460 to 550 nm (Figure 2d). This is two orders of magnitude shorter than that of the conventional standard scintillator (NaI:Tl, decay time ~ 200 ns), which allows for significantly shortened deadtime for radiodetection devices. Holding these features, the perovskite thin film of stacked CsPbBr$_3$ nanosheets qualifies for a potential candidate for radiography applications.

As a proof-of-concept experiment, we construct an X-ray imaging system with a projection configuration (Figure S5). By using a commercial camera and a 50-keV X-ray source, the prototype X-ray imager can reveal the detailed structural information of a transistor panel under a resin cover (Figure 4e). To measure the resolution ability of our prototype, the point spread function of the intensity profile (red arrow in Figure 4e) is fitted with a Gaussian function. Impressively, such a simple prototype is able to provide a spatial resolution as high as 0.21 mm (Figure 4f), mainly due to the crack-free virtue of the thin film. Apart from organic masks (i.e., resin), inorganic materials...
such as a silicon chip (~300 μm in thickness, Figure S6) can also be penetrated by X-rays without compromising any resolution ability (Figure 4, g and h).

**CONCLUSIONS**

In conclusion, this work presented the room-temperature synthesis for a CsPbBr$_3$ nanosheet colloid on the gram-scale. The concentrated colloid shows strong luminescence under both X-ray and UV light illumination. In addition, our colloidal perovskite nanosheets are readily cast into a crack-free thin film of a large area up to 72 cm$^2$. The thin film consisting of self-assembled perovskite nanosheets not only exhibited a high PLQY but also showed long-term stability under continuous X-ray irradiation. The ensuing radiography prototype demonstrated a high-quality imaging ability with resolution down to 0.21 mm. Our findings offer a colloidal scintillator to the screen industry, holding potential for low-dose radiography or even liquid scintillating displays.

**METHODS**

**Synthesis of CsPbBr$_3$ Nanosheets**

CsPbBr$_3$ nanosheets was synthesized by a significantly modified procedure reported by Konstantatos and co-workers.$^{20}$ Typically, Cs precursor and PbBr$_2$ precursor were prepared separately, and the reaction was initiated by injecting the latter into the former in a molar ratio of 4:1. Firstly, Cs precursor solution was prepared by dissolving 32 mg CsAc in 1-mL 1-PrOH in a 20-mL vial under stirring in air at room temperature, followed by addition of 6-mL Hex and 2-mL 1-PrOH. Secondly, PbBr$_2$ precursor
solution was prepared by dissolving 245-mg PbBr$_2$ into a mixture solution of 0.45-mL 1-PrOH, 0.45-mL OcAc and 0.45-mL OcAm at 90°C in air under vigorous stirring.

Thirdly, the hot PbBr$_2$ precursor was injected into Cs precursor swiftly under vigorous stirring at room temperature. The system turned green immediately, and the reaction completed in 2 minutes. The CsPbBr$_3$ NCs were isolated by centrifugation at 4000 rpm, and the pellet was dispersed into 2-mL toluene. The synthesis has been successfully scaled up by 20 times, producing ~3 grams of CsPbBr$_3$ nanosheets in one single trial.

**RL and X-ray Imaging**

RL were obtained by an Edinburgh FS5 fluorescence spectrophotometer (Edinburgh Instruments Ltd., UK) equipped with a miniature X-ray source (AMPEK, Inc.). The X-ray screen was made by drop casting colloid (~150 mg/mL) onto a thin glass slide (150 μm in thickness). The thin-film screen was formed under ambient condition by slow evaporation of toluene. The photographs of X-ray-excited luminescence were acquired with a digital camera (Canon 600D with EF-S 35mm f/2.8 IS STM lens).

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: xxx

Stability test, SEM cross-section image, Scherrer equation, dose-dependence of RL intensity, projection configuration of home-made prototype X-ray imager, RL spectra
of CsPbBr$_3$ colloidal and Ce:LuAG single crystal, large-area TEM image of nanosheet assemblies.

The authors declare no competing financial interests.

AUTHOR INFORMATION

Corresponding Authors

*Y. Z.: Email: ifc_zhangyh@ujn.edu.cn
*H. L.: Email: ifc_liuh@ujn.edu.cn
*O.F.M: Email: omar.abdelsaboor@kaust.edu.sa

ACKNOWLEDGMENT

This work was supported by both University of Jinan and King Abdullah University of Science and Technology (KAUST). Y. Z. has been supported by both National Natural Science Foundation of China (grant # 21805111) and Taishan Scholar Fund. A. V. M. has been supported by the US NSF-CAREER grant #1350800. He gratefully acknowledges travel support from CRDF Global at early stages of the work.
REFERENCES


