X-ray Lithography on Perovskite Nanocrystals Films: From Patterning with Anion-Exchange Reactions to Enhanced Stability in Air and Water

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Supporting Information

ABSTRACT: Films of colloidal CsPbX₃ (X = I, Br or Cl) nanocrystals, prepared by solution drop-casting or spin-coating on a silicon substrate, were exposed to a low flux of X-rays from an X-ray photoelectron spectrometer source, causing intermolecular C=C bonding of the organic ligands that coat the surface of the nanocrystals. This transformation of the ligand shell resulted in a greater stability of the film, which translated into the following features: (i) Insolubility of the exposed regions in organic solvents which caused instead complete dissolution of the unexposed regions. This enabled the fabrication of stable and strongly fluorescent patterns over millimeter scale areas. (ii) Inhibition of the irradiated regions toward halide anion exchange reactions, when the films were exposed either to halide anions in solution or to hydrohalic vapors. This feature was exploited to create patterned regions of different CsPbIₓBrᵧClₜ compositions, starting from a film with homogeneous CsPbX₃ composition. (iii) Resistance of the films to degradation caused by exposure to air and moisture, which represents one of the major drawbacks for the integration of these materials in devices. (iv) Stability of the film in water and biological buffer, which can open interesting perspectives for applications of halide perovskite nanocrystals in aqueous environments.

KEYWORDS: perovskite, nanocrystals, X-ray, anion-exchange, patterning

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This enhances the film stability in several manners. First, such "graphitization" creates a network of NCs interconnected with each other and renders the exposed regions insoluble in solvents that are able to disperse the starting "as synthesized" NCs. It is therefore easy to "lift-off" the nonexposed regions, as they remain soluble, such that luminescent patterns extending over millimetric areas can be fabricated easily. Second, the irradiated regions become refractory to anion exchange reactions when exposed to either liquid or gaseous halide precursors, whereas the nonirradiated regions exchange rapidly the anions, as reported by various groups (including ours). This makes it possible to "draw" regions of CsPbI\textsubscript{3}Br\textsubscript{2}Cl\textsubscript{y} with varying \textit{x}, \textit{y}, and \textit{z} stoichiometries starting from a single CsPbX\textsubscript{3} film, which may be exploited to elicit broadband photoluminescence from a suitably patterned film. Furthermore, the irradiated regions exhibit good resistance toward aging in air, water and even in a biological buffer (phosphate buffer saline, PBS 1x). Such stability is currently one of the most sought-after aspects concerning these materials.

RESULTS AND DISCUSSION

In the present work, cesium lead halide NCs, synthesized as previously described (procedure adapted from Protesescu et al.), were deposited on a silicon substrate either by drop-casting or spin-coating and were then inserted in a X-ray photoelectron spectrometer, where they were irradiated with X-rays from the monochromatic Al K\alpha source of the spectrometer (photon energy = 1486.6 eV). At the same time, we monitored the chemical changes in the ligand shell that took place while irradiating the film by \textit{in situ} X-ray photoelectron spectroscopy (XPS). As can be seen from Figure 1a, upon irradiation over several hours (up to 2 days), the C 1s peak shifted to lower binding energies (BE) and broadened, while the so-called \textit{D}-parameter, which is extracted from the derivative curve of the C KLL peak, increased to 16.4 eV from 12.3 eV of the starting, nonirradiated film (Figure 1b). This parameter is sensible to the sp\textsuperscript{2}/sp\textsuperscript{3} carbon hybridization ratio, with higher values of the \textit{D}-parameter corresponding to a higher fraction of sp\textsuperscript{2} carbon. According to published calibration curves, this change corresponds to the transformation from roughly all-sp\textsuperscript{3} hybridization (consistent with a layer of oleylamine/oleic acid molecules capping the pristine particles) to a 50% sp\textsuperscript{2} hybridization. This partial graphitization can be assigned to the loss of hydrogen and the formation of intra- and intermolecular C=C bonds, induced by X-ray irradiation (see Scheme 1 for a schematic view of the graphitization process). It is reasonable to think that the electrons generated...
by the interaction of the primary X-ray beam with the sample are causing the transformation rather than (or in combination with) the X-rays themselves. Indeed, primary and secondary electrons have already been reported to induce transformations in thin organic self-assembled monolayers.\textsuperscript{35,36} Furthermore, we observed a similar effect upon exposure to electron beams on these NCs (see Figure S1 of the Supporting Information) as well as on NCs of other inorganic materials but coated with the same ligand shell as the one studied here.\textsuperscript{29}

Partial ligand transformation was observed already after 30 min of irradiation with a $2.4 \times 10^{11}$ photons/mm$^2$·s X-ray flux. Therefore, in the experiments that follow, typical irradiation times were between 30 min and 5 h. It must be noted that, since the X-ray intensity profile on the sample has a Gaussian distribution,\textsuperscript{37} the area affected by the irradiation becomes

Figure 2. (a) Schematic representation of X-ray lithography for perovskite NC film patterning (see Scheme 1 for additional details). The stencil mask is a 3 mm honeycomb copper grid. Confocal PL microscopy (b; 515 nm emission), SEM (c), and XPS (d; Br 3d intensity mapping at BE = 68 eV) demonstrating selective stabilization of the CsPbBr$_3$ NCs in the exposed regions corresponding to the hexagonal apertures of the stencil mask. Scale bars are 300 $\mu$m.

Figure 3. Photoluminescence (PL) microscopy image (a) and XPS chemical mapping of iodine (orange) and bromine (green) (b) on a CsPbBr$_3$/CsPbI$_3$ NC patterned film, prepared from an initial CsPbBr$_3$ NC film by a sequence of two irradiation sessions (masked irradiation at high dose to inhibit anion-exchange on selected regions followed by unmasked irradiation at low dose to prevent dissolution of the film in toluene). The hexagonal areas remained indeed Br rich, while the stripe regions between the hexagons became I rich. (c, d) PL microscopy images recorded by integrating in a wavelength range from 500 to 600 nm (c) and from 410 to 500 nm (d) on a patterned CsPbBr$_3$/CsPbCl$_3$ NC film by single masked irradiation and followed by anion-exchange (Br $\rightarrow$ Cl) using HCl vapors as source of Cl$^-$ ions. PL microscopy image (e) and emission spectra of different regions of interest (f) on a film of CsPbI$_3$ NCs after having undergone sequential irradiations and anion-exchange with HBr and HCl. Due to the deposition technique (drop-casting) the film had high roughness. Since the image was acquired with a confocal microscope, the appearance of dark spots on the image is due to out-of-focus regions that were cut-out by the pinhole setup. Scale bars are 300 $\mu$m.
larger with increasing irradiation time, as regions far from the spot center (>1–2 mm) may receive a high enough dose even at low flux. This range of irradiation times proved enough for the stabilization of the film. At the same time, X-ray irradiation under vacuum did not lead to noticeable changes in the chemical composition of the film (see Figure 1c) or in the crystalline structure of the particles’ cores, as demonstrated by X-ray diffraction (XRD, see Figure 1d). Also, irradiation with X-rays under the higher vacuum conditions of the XPS setup does not lead to the deposition of any additional carbon layer, which may be the case when the irradiation is performed with electron beam lithography. Interestingly, the regions of the NCs films irradiated by X-rays became insoluble in toluene, while the nonexposed regions could be easily lifted-off from the substrate in a process similar to that presented by Nandwana et al.38 and by others.39–41 We used this property to demonstrate large-scale patterning of a CsPbBr3 NC film. A 3 mm copper grid with a honeycomb network of 150 μm hexagonal apertures was used as stencil mask during the irradiation of the film. The mask was then removed and the whole film was rinsed in toluene (see Figure 2a for a schematic representation of the process). Scanning electron microscopy (SEM), confocal photoluminescence (PL) imaging, and XPS chemical mapping of the bromine 3d peak corroborated the selective etching of the film only at the nonirradiated regions between the hexagons (see Figure S1), although for the reasons mentioned above e-beam lithography was not investigated further in this work.

The dose of X-ray irradiation on the NC films regulated the extent to which the films could engage in anion exchange reactions. As an example, a “mild” dose (i.e., 30 min at 1011 photons/mm²·s) was enough to modify the ligand shell so that the irradiated regions could not be dissolved by dipping the whole sample in toluene, while at the same time the ligand shell remained permeable enough to enable anion exchange. Higher doses (achieved by a few hours exposure at same photon flux) could then block the exchange. Starting from a CsPbBr3 NC film, using a long masked irradiation followed by a short “flood” (maskless) exposure of the whole film and then by immersion of the sample in a iodine precursor (I-OLAM) solution in toluene,18,19 we could fabricate patterns of bromide-rich (unexchanged) and iodide-rich (exchanged) regions, as shown in Figure 3a,b. This methodology has two drawbacks: it requires two irradiation steps (masked and unmasked), which makes the process elaborate, and additionally the flood irradiation can cause some undesired anion exchange inhibition.

In order to circumvent these issues, we carried out anion exchange by exposing the NC films to hydrohalic vapors, as this procedure avoids the intermediate unmasked irradiation step. Films of CsPbBr3 could be converted to CsPbCl3 and then converted back to their original composition simply by placing the film a few mm above a vial of HCl or HBr for less than a minute (see Figure S2 and Video). Thus, as the stability of the film was no more an issue in this case, we could easily fabricate patterns of different compositions after a single masked irradiation, followed by anion exchange with gaseous reagents (see Figure 3c, d). Eventually, starting from a red-emitting CsPbI3 film it was also possible to obtain a gradient of different colors after subsequent irradiations and anion-exchanges with HBr and HCl, resulting in a film with broadband photoluminescence between 500 and 700 nm (see Figure 3e, f). In this case, no stencil mask was applied. However, as the X-ray spot on the surface has an uneven intensity distribution, a “gradient of anion-exchange inhibition” could be obtained from a single exposure (see Figure S3 for more details on the dose-dependent anion exchange inhibition from a single irradiation).

It must be noted that long exposures to X-rays (5 h with a flux of 2.4 × 1011 photons/mm²·s in case of the sample shown in Figure 4) could lead to a loss of photoluminescence on the central region of the irradiated spot (maximum dose). This deleterious effect does not appear to be related to any specific lability of halide perovskites, since we observed the same behavior on giant shell CdSe/CdS NCs,42 which are systems that have a documented photostability (see Figure S4). Furthermore, we could not detect any changes in chemical composition, crystallinity (Figures 1 and S5) or film morphology (Figures S5 and S6) in the regions that suffered such loss in photoluminescence. Therefore, we can only speculate that the prolonged exposure to “high” X-ray flux is likely inducing the formation of trap states which lead to nonradiative recombination. On the other hand, it is clear that at lower doses (which is the case either for regions further away from the center of irradiation, see Figure 4; or for samples at shorter irradiation times, see Figures S4 and S7) the photoluminescence was preserved. From a practical point of view, it is plausible that a less-focused X-ray source could lead to a more homogeneous stabilization (i.e., prevention from redispersion or anion-exchange, while conserving the photoluminescence properties) over larger areas.

While recent reports have stressed the instability of lead triiodide perovskites, especially toward moisture,18,30–32 we demonstrate here that the same sample of irradiated NCs remained stable after several weeks in air (room temperature, ambient humidity), then after 1 day in ultrapure Milli-Q water and then finally after 3 days in a biological buffer (PBS 1X). This is in striking contrast to the rapid degradation of the same crystals deposited on the same conditions, but not irradiated (or irradiated at lower dose, see Figure 4). At the end of the aging procedure, the irradiated sample was rinsed with ultrapure water to remove deposited salts from the PBS solution and the PL spectrum was recorded (see Figure S7):
the emission peak from this sample was still at around 670 nm, consistent with the spectral position of the pristine CsPbI₃ NC sample.

**CONCLUSION**

We have demonstrated how low flux X-ray irradiation can greatly enhance the stability of cesium lead halide NC films by inducing the formation of C–C bonds between the organic ligands present at the NC surfaces. This enhanced stability can be useful for a number of applications. It was shown that PL patterns of one or several colors could be easily obtained either by redispersion of nonirradiated areas or by selective anion-exchange using either liquid or gaseous reagents. Furthermore, we demonstrated that irradiated cesium lead triiodide films could be remarkably protected from degradation when exposed to air, moisture, pure water, and even biologic buffers. This stability is especially promising for further exploitation of these NCs to different fields, including applications in aqueous environments. Although these films may not be suitable as such for applications where electrical conductivity is needed (due to their high organic content), great promise is coming from hybrid approaches incorporating organic molecules to organic-free films.²⁷,²⁸ X-ray induced stabilization could also play a key role in the development of these approaches.

**METHODS**

**Materials.** Lead(II) bromide (PbBr₂, 99.999% trace metals basis), lead(II) iodide (PbI₂, 99.999% trace metals basis), cesium carbonate (Cs₂CO₃, reagentPlus, 99%), iodine (I₂, 99.99%), hydrochloric acid (HCl, ACS reagent, ≥98%), tetrapropylammonium hydroxide (Tol-H₂O, 100% purity 98% in H₂O), hydrochloric acid (HCl, 48 wt % in H₂O, ≥99.9%), octadecene (ODE, technical grade, 90%), oleylamine (OLAM, 70%), and oleic acid (OA, 90%) were purchased from Sigma-Aldrich. Toluene (TOL, anhydrous, 99.8%) was bought from Carlo Erba reagents. All chemicals were used without any further purification, except for ODE, OA, and ODE, which were degassed at 100 °C for 2 h in vacuum.

**CsPbX₃ Nanocrystals and OLAM-I Synthesis.** CsPbI₃ and CsPbBr₃ NCs were synthesized as described by Protescu et al.¹ with some minor adaptations. In a typical synthesis, 69 mg of PbBr₂ (0.188 mmol) or 87 mg of PbI₂, 5 mL of ODE, 0.5 mL of OA, and 0.5 mL of OA were loaded in a 25 mL three-neck flask and stirred under vacuum for 2 h in vacuum. After degassing, the temperature was raised to 165 °C and a 0.6 mL ODE with 0.4 mL of previously synthesized Cs-octylate (0.4 g Cs₂CO₃ degassed in 15 mL ODE and 1.75 mL OA at 150 °C) mixture was swiftly injected. Immediately after the injection, the NC solution was quickly cooled down to room temperature with an ice bath, and the NCs were transferred to a glovebox. The OLAM-I precursor was prepared by reacting 0.5 mmol of I₂ (1 mmol 1⁻) with 0.250 mL OLAM overnight. The solid OLAM-I was dissolved in 5.75 mL TOL.

**Film Deposition.** Nanocrystals were deposited either by spin-coating or drop-coating onto piranha-cleaned silicon wafers. Typically, 1 mL of CsPbBr₃ solution in ODE was centrifuged for 10 min at 14 000 rpm, the supernatant was removed, and the particles were redispersed in 100 μL of toluene. For spin-coating, 20 μL of solution was dropped on the substrate which was then spun at 2500 rpm for 40 s.

**X-ray Irradiation.** Nanocrystal films were irradiated in vacuum with the Al Kα monochromatic source of the X-ray Photoelectron Spectrometer (photoelectron energy = 1486.6 eV) with an emission current of 10 mA or 20 mA, corresponding to photon fluxes of 1.2 × 10¹¹ photons/mm² s or 2.4 × 10¹¹ photons/mm² s.

**E-beam Lithography.** CsPbBr₃ nanocrystal films were irradiated by an electron beam from a Raith 150-two lithography system with an acceleration voltage of 10 kV and exposure dose of 1 mC/cm².

**Anion-Exchange.** Br ↔ I anion-exchange was performed in toluene by immersing the sample film in a 0.17 M solution of OLAM-I for 5 min, followed by rinsing with fresh toluene and drying under a stream of nitrogen. Br ↔ Cl, I ↔ Br, and I ↔ Br ↔ Cl exchanges were performed from the gas phase simply by holding the sample (film) a few mm on top of a vial of hydrobromic or hydrochloric acid for ca. 30 s.

**XPS Characterization.** XPS characterization was performed using a Kratos Axis Ultra DLD spectrometer with a monochromatic Al Kα source (15 kV, 20 mA). Wide scans were acquired at an analyzer pass energy of 160 eV. High resolution narrow scans were performed at a pass energy of 20 eV and steps of 0.1 eV. The photoelectrons were detected at a takeoff angle Φ = 0° with respect to the surface normal. The pressure in the analysis chamber was maintained below 5 × 10⁻⁹ Torr for data acquisition. The data were recorded with VAMAS format and processed using CasaXPS software. For the monitoring of the carbon graphitization, films were deposited on a gold substrate and the binding energy scale was referenced to the Au 4f₇/₂ peak (BE = 84.0 eV).

**SEM Characterization.** SEM images were recorded using a JEOL JSM-7500F (JEOL, Tokyo, Japan) instrument equipped with a cold field emission gun (FEG), operating at 10 kV acceleration voltage.

**PL Microscopy.** Confocal PL microscopy images and spectra were recorded with a Nikon A1 microscope with a laser excitation of 405 or 488 nm.

**XRD.** XRD analysis was performed on a PANalytical Empyrean X-ray diffractometer equipped with a 1.8 kW Cu Kα ceramic X-ray tube and PIXcel2D 2 × 2 area detector, and operating at 45 kV and 40 mA. The diffraction patterns were collected in air at room temperature using parallel-beam (PB) geometry and symmetric reflection mode. XRD data analysis was carried out using HighScore 4.1 software from PANalytical.

**ASSOCIATED CONTENT**

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.5b06536.

Table of main XPS peaks found on CsPbX₃ nanocrystals wide spectra, PL microscopy image of e-beam patterned CsPbBr₃ film, high-resolution XPS spectra of nanocrystals during irradiation and after anion-exchange from gas phase, XPS semi-quantitative analysis of dose-dependent stabilization, photograph and SEM images of stabilized chalcogenide nanocrystal films, high-resolution SEM images of CsPbI₃ film before and after irradiation, photographs of irradiated CsPbI₃ films under various aging conditions, and PL spectra of aged CsPbI₃ films and pristine solution (PDF)

Video showing sequential Br ↔ Cl exchanges from hydrobromic vapors (AVI)

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**Notes**

The authors declare no competing financial interest.

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