Ultrathin lead bromide perovskite platelets spotted with europium(II) bromide nanodots

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We describe here the preparation of a novel nanohybrid comprising a two-layer cesium lead bromide nanoplatelet, $[\text{CsPbBr}_3]\text{PbBr}_4$ NPL, containing europium(II) bromide (EuBr_2) nanodots, by ultrasound/heating treatment of toluene dispersions of CsPbBr_3 nanomaterial in the presence of EuBr_2 nanodots. The hybrid nanoplatelet exhibits the strong excitonic and narrow emission peaks characteristic of ultrathin NPLs at 430 and 436 nm, respectively, and remains mainly non-stacked after prolonged standing in solution.

Lead halide perovskites are relevant semiconductor materials with the APbX_3 formula, where A is a small-sized monocation (such as methylammonium, formamidinium, or cesium), and X is a halide (Cl^- , Br^- and/or I^-). These materials present a three-dimensional (3D) inorganic framework consisting of corner-sharing PbX_6 octahedra and the small-sized cations in the voids between them. They can easily be prepared with 3D morphology (bulk material) by simply mixing AX and PbX_2 , and also with other morphologies¹: nanoparticles (0D material) and low-dimensional materials (such as nanowires and nanoplatelets, 1D and 2D materials, respectively). Recently the preparation of colloidal nanoparticles has been reported with photoluminescence quantum yields (Φ_{PL}) of up to 100%, by using coordinating ligands which confine the material to the nanoscale and provide dispersibility; such nanoparticles are suitable for preparing thick films with a Φ_{PL} close to that of the colloid.²⁻¹⁰ Their exceptional electronic and optical properties make them of great interest in light-emitting devices, photodetectors and photovoltaics.^{9, 11, 12}

Currently, there is an increasing interest focused on perovskites with 2D morphology, in particular, nanoplatelets (NPLs) with a few lead halide layers and the $\text{L}_2[\text{APbX}_3]_{n-1}\text{PbX}_4$ formula, where "L" represents the ligand and "n" stands for the number of layers.^{13, 14} As long as the NPL thickness is homogeneous, they exhibit the same emission peak, independently of their lateral dimensions, as well as exceptionally narrow absorption and emission (full width at half maximum (FWHM) ca. 10 nm) and small Stokes shift (<10 meV). They have been prepared as colloids following different strategies: i) exfoliation of the bulk material by sonication in the presence of coordinating solvents¹⁵; ii) hot-injection crystallization¹³; and iii) non-solvent crystallization¹⁶.

We devised that the ultrasound treatment of a mixture of two different materials could be used not only for the exfoliation of one of the materials, which might lead to a novel nanohybrid, but also for avoiding the stacking of the exfoliated material.

Figure 1: Transformation of CsPbBr_3 nanoparticle nanowires (NPNWs) into ultrathin nanoplatelets (NPLs) under ultrasound/heating treatment in the presence of a EuBr_2 solid. Top: conventional TEM image of the NPNWs (scale bar 50 nm), absorption and emission spectra of the NPNWs; inset: TEM image at scale bar of 2 μm . Bottom: conventional TEM image of the NPLs (scale bar 200 nm), absorption and emission spectra of the NPLs.

In particular, we report here that ultrasound/heating treatment of a toluene colloid of CsPbBr_3 nanoparticles capped with dodecylamine (DDA) in the presence of europium(II) bromide nanodots (EuBr_2 NDs) lead to the formation of blue, highly stable two-layer $[\text{CsPbBr}_3]\text{PbBr}_4$ NPLs spotted with EuBr_2 nanodots.

First, CsPbBr_3 nanoparticles were prepared by the re-precipitation technique with some modifications.^{17, 18} Briefly, we prepared a solution containing an equimolar concentration of cesium bromide (CsBr) and lead bromide (PbBr_2) in a 9:1 dimethylformamide/dimethylsulfoxide mixture. Then, 200 μL of this solution were mixed with DDA (0.053 mmol) to obtain the precursor solution, which was added dropwise to a toluene solution of myristic acid (MA, 0.709 mmol); therefore, the DDA:MA molar ratio used in this preparation was 7:94 (see

experimental section for further details). Finally, the dispersion was centrifuged at 5500 rpm for 5 min and the precipitate was redispersed in 2 mL of toluene for further use and the supernatant was discarded. This combination of ligands led to the formation of micrometer-sized wires with a width of ca. 100 nm, together with square-shaped nanoparticles of ca. 7 nm deposited at the edges of the wires; see Figure 1(top).

This material presented an exciton peak at 500 nm, an emission maximum at 510 nm with a FWHM of 20 nm (Figure 1(top)), a Φ_{PL} of 31% and an average PL lifetime (τ_{av}) of 34.4 ns (the PL decay fitted to 3 exponential decays, see details in the experimental section); for further characterization data see thermogravimetry analysis (TGA), proton nuclear magnetic resonance (H-NMR), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and X-ray powder diffraction (PXRD) (Figure S1-S4).

In the TGA spectrum, the weight loss of 76% in the 100-200 °C range, assigned to the DDA ligand, was followed by a small loss (4%) ascribed to MA, and then a loss of 20% in the 500-600 °C range attributed to the inorganic components (PbBr₂ and CsBr) (Figure S1). The ¹H-NMR spectrum corroborated that DDA was practically the only capping ligand on the CsPbBr₃ NPNW's surface (Figure S2).

The XPS analysis of Pb 4f showed two symmetrical peaks at 138 and 143 eV attributed to Pb 4f_{7/2} and Pb 4f_{5/2}, respectively (Figure S3). The presence of two additional symmetrical bands at a lower energy, specifically at 137.7 and 142 eV, cannot be attributed to metallic lead or lead oxide¹⁹ and therefore, they could be indicative of perovskite Pb in a different environment. The peaks at 68.8 and 67.7 eV were assigned to the Br 3d present in the perovskite and are similar to those observed by other authors.²⁰ The N 1s spectrum showed two peaks at 401.5 and 399.8 eV that corresponded to DDA as ammonium and amine, respectively.²¹

The O1s spectra showed three peaks at 533.7, 532.4 and 531.3 eV attributed to the equivalent O atoms of the carboxylate, non-equivalent O of carboxylic acid, and to the O-O bond. The C 1s spectra exhibited an intense peak at 284.6 eV assigned to the C-C aliphatic chain, which was used as a reference. Two small contributions at 288.3 and 286.7 eV were ascribed to the carbonyl group and C-O bond of the MA and the peak at 285.4 eV corresponded to the C-N signal.²² Finally, the typical peaks at 737 and 723 eV were attributed to the Cs 3d.⁹

The powder XRD spectrum showed the presence of peaks at 15.08° (002), 15.22 (110), 21.50° (112), 30.38° (004), 30.71° (220) and 34.37° (222); which are characteristic of the orthorhombic phase of CsPbBr₃ (Figure S4).^{23, 24}

Secondly, the first attempt to prepare a hybrid material consisted of mixing a small amount of the freshly prepared CsPbBr₃ colloid (0.5 mL) with the EuBr₂ salt (1.2 mg) in a vial and submitting the mixture to ultrasound/heating treatment. Small aliquots (50 µL) were extracted after 1, 3, 5 and 7h and their UV-visible and PL spectra were systematically recorded (Figure S5). The absorption spectrum of the material after 7 h of treatment showed the appearance of a peak at 430 nm together with that of the excitonic peak of the CsPbBr₃ perovskite at 500 nm (Figure SX). The PL spectrum showed two main peaks at 436

nm and 510 nm; the first can be ascribed to the formation of two-layer caesium lead bromide nanoplatelets. Similar results were obtained when the treatment was performed for 7 h without sampling. Table S1 resumes the PL quantum yield of the reaction along the time.

The subsequent experiments were performed using 7 h of heating/ultrasonic treatment. Then, the synthesis was carried out using different amounts of: i) EuBr₂ (0.6 mg, 1.6 mg), ii) CsPbBr₃ colloid volume (125 µL, 250 µL, 500 µL), and iii) total volume of the mixture (500 µL). The best results, in terms of dispersibility and emissive properties, were obtained using 0.6 mg of EuBr₂, 125 µL of CsPbBr₃ NPNWs and 500 µL of the total volume. Figure 1(bottom) shows the absorption and emission spectra that correspond to the colloid obtained after ultrasound/heating treatment of the CsPbBr₃ NPNWs in the presence of EuBr₂ for 7 h. The PL (λ_{ex} = 365 nm) spectrum of the optimal sample exhibited an emission at 436 nm and 510 nm with a total Φ_{PL} of 41 %. The PL decays fitted to three components and the PL τ_{av} was 16 ns and 8 ns for the emissions at 436 nm and 510 nm, respectively. Table S2 contains the luminescence lifetime of the colloid obtained after ultrasound/heating treatment of CsPbBr₃ NPNWs in the presence EuBr₂ for 7 h, recorded at λ_{ex} 510 nm and 436 nm. The

Figure 2: HAADF-HRSTEM images and EDS spectra recorded on different nanostructures present in the samples. (a) HAADF-STEM micrographs of: (i) a cesium lead bromide platelet, (ii) two EuBr₂ nanodots, (iii) an EuBr₂ nanoparticle, (iv) a perovskite NP, (v) an amorphous agglomerate containing europium and (vi) PbBr₂ NP, respectively. (b) EDS spectra recorded rastering the electron beam on the highlighted red areas of each of the previous images.

luminescence kinetics decays are shown in Figure S6. Furthermore, the relative intensity between the emission peaks did not change when exciting at 280 nm, where EuBr₂ does not absorb, thus ruling out the contribution of EuBr₂ to the emission at 436 nm.²⁵ Remarkably, the emission spectrum of the sample showed negligible changes after two weeks in air atmosphere (Figure S7).

Figure S8 shows the emission spectra (λ_{ex} at 365 nm) of the

Figure 3: a,b) Atomic force topography and height profile of the film prepared from the colloid obtained after sonication the CsPbBr₃ NPNWs in the presence of EuBr₂ (method 1). c,d) Atomic force topography, 3D-view and height profile of the film prepared from the colloid (method 2).

starting CsPbBr₃ NPNWs in toluene and of the colloid obtained after ultrasound/heating treatment of the CsPbBr₃ NPNWs in the presence of EuBr₂ for 7 h, as well as the excitation spectra of the NPNWs (λ_{em} at 510 nm) and of the colloid obtained after sonication of the CsPbBr₃ NPNWs in the presence of EuBr₂ (λ_{em} at 515 nm and 430 nm). All these data, together with the optical features reported for [CsPbBr₃]PbBr₄ NPLs, are consistent with the assignment of the emission at 436 nm to the NPLs.

Control experiments were carried out i) at a lower temperature and ii) in the absence of EuBr₂. We found that the sonication bath at 70 °C was crucial for the formation of the NPLs, since the corresponding excitonic peak was not detected when the reaction was carried out at 50 °C (Figure S9a, b). TEM images corroborated the nanoplatelets were not formed under this temperature (Figure S9c,d). This indicates that a suitable

temperature during the ultrasound treatment is required. In addition, in the absence of EuBr₂, the CsPbBr₃ NPNWs transformed into micro-sized perovskite particles after 7 h of ultrasound/heating treatment. In keeping with this, the colour of the dispersion changed from yellow to orange and a drastic decrease in the sample dispersibility was observed. In addition, the excitonic peak at 500 nm shifted to 540 nm, whereas the PL emission peak at 510 nm shifted to 550 nm, and the PL decreased (Figure S10). TEM images in Table S3 show the different morphological evolution of the NPNWs in the presence than in the absence of EuBr₂, under ultrasound/heating treatment. Figure S11 shows the HRTEM images of the colloid obtained after 7 h, before and after centrifugation; it mainly consisted of [CsPbBr₃]PbBr₄ NPLs. The hypothesis is that sonication fragments the CsPbBr₃ NPNWs as well as the EuBr₂ solid and the europium salt helps in the exfoliation of the perovskite material.

The optimal precipitate was also analysed by high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) HAADF-HRSTEM combined with energy-dispersive X-ray spectroscopy (EDS) to determine its composition.²⁶⁻²⁸ These measurements, see Figure 2, showed the formation of ultrathin cesium lead bromide platelets of different lateral sizes spotted with EuBr₂ nanodots, homogeneously distributed throughout the platelet. In addition, the presence of CsPbBr₃ NPs, EuBr₂ NPs, and PbBr₂ NPs, and amorphous material containing europium were clearly identified. A close inspection of the selected area electron diffraction (SAED) patterns of the [CsPbBr₃]PbBr₄ NPLs revealed the presence of orthorhombic CsPbBr₃, preserving the main planes of the starting NPNWs. In addition, the plane (211), 4.21 of EuBr₂ was detected in the sample, in agreement with the proposed NPLs spotted with EuBr₂ (see Table S4 and Figure S12).

It is worth noting that europium vanished under prolonged irradiation of the NPL-EuBr₂ dots with the laser beam, while no evidence of damage of the perovskite layer was detected. Likewise, the EuBr₂ nanodots were also damaged by electron beam. However, crystalline EuBr₂ NPs, the EuBr₂ covered with organic material and the Eu salts detected within the amorphous material remained stable under irradiation. Consequently, the EDAX analysis of NPLs-EuBr₂ dots cannot be used to determine the stoichiometry of these species.

AFM experiments (Figure 3) demonstrated that although we did not perform any further purification, deposition of a drop of the colloid on a glass substrate followed by spinning (method 1) led to homogeneous film, as demonstrated the roughness analysis of the AFM image and the 3D-AFM view (Figures 3a,b), with only few unfilled features, and the height profile gives a value of 8.6 nm. This can be attributed to the tendency of the NPLs to lie flat on the substrate and stack together. Moreover, deposition of the colloid drop on a spinning glass (method 2) enabled the observation of some NPLs. Figures 3c,d show the AFM topography and height profile with an average roughness of 3.1 nm for the NPLs.

Conclusions

In summary, we report here the preparation of a novel hybrid material consisting of a two-layer caesium lead bromide nanoplatelet with small EuBr_2 dots homogeneously distributed in the structure. The strong excitonic and narrow emission peaks characteristic of ultrathin NPLs at 430 and 432 nm, respectively, remained unchanged after two weeks under air atmosphere, thus showing no evolution towards more bulk-like structures. EuBr_2 plays a key role in the formation of the perovskite nanoplatelet and the EuBr_2 dots increase the chemical and colloidal stability of the platelets. The herein reported strategy opens the possibility to the development of hybrid materials with novel properties for application in photocatalysis and/or optoelectronics.

Experimental section

Chemicals

Cesium bromide (99.999%, Sigma Aldrich, USA), lead bromide (99.999%, Sigma Aldrich, USA), Europium(II) bromide (99.99%, Alfa Aesar, Germany), Dodecylamine (98%, Sigma Aldrich, USA), Myristic acid ($\geq 99\%$, Sigma Aldrich, USA), N,N-Dimethylformamide (99.8%, VWR, USA), Dimethyl Sulfoxide ($\geq 99\%$, VWR, USA), Toluene anhydrous (99.8%, Sigma Aldrich, USA).

Characterization

Absorption measurements. UV-vis spectra were recorded at room temperature using quartz cuvettes of 1 cm $\times$ 1 cm using a UV-visible spectrophotometer Jasco V-670.

Luminescence measurements. Photoluminescence spectra were measured on an Aminco Browman series 2 Luminescence spectrometer, equipped with a xenon lamp (150 W). AB2 software (version 5.5) was used to register the data. Time-resolved PL were measured using a Compact fluorescence lifetime spectrometer C11367, Quantaurus-Tau. Fluorescence lifetime software U11487 was used to register the data. All of the data of PL decay of perovskite dispersed in ethyl acetate were acquired using 1 cm $\times$ 1 cm path length quartz cuvettes and light-emitting diode excitation wavelength of 365 nm. The PL decays of colloidal perovskite nanoparticles were fitted with a triexponential function. The average lifetimes (τ_{av}) were calculated as $\tau_{av} = \sum A_i \tau_i^2 / \sum A_i \tau_i$, where τ_i are the decay times and A_i represents the amplitudes of the components, values obtained from the fitted PL kinetic decay traces.

Transmission electron microscopy

Transmission electron microscopy (TEM) was performed on a Tecnai G2 F20 microscope operated at 200 keV.

Quantum yield measurements. The photoluminescence (PL) quantum yields were measured using a Hamamatsu C9920-02 absolute PL quantum yield measurement system with monochromatic light source (150 W) and integrating sphere. All of the data were acquired using 1 cm $\times$ 1 cm path length quartz cuvettes, at room temperature, using an excitation wavelength at 365 nm.

Preparation of CsPbBr_3 perovskite nanocrystals. The source of Cs used in this work was CsBr, which was stored and manipulated in a glove box. After gridding of the salt, 8 mg (0.037 mmol) were dissolved in 1 mL of dimethylformamide

(DMF)/dimethyl sulfoxide (DMSO) mixture in a ratio 9:1, during 4 hours under ultrasound. The solution was transferred into a vial that contained 13.8 mg of PbBr_2 and the solution was called “precursor solution”, with a molar ratio 1:1. An aliquot of this solution (0.2 mL) was mixed with 9.86 mg (0.053 mmol) de dodecylamine (DDA). Finally, this mixture was injected into a toluene solution (2 mL) of myristic acid (MA, 162 mg) and the CsPbBr_3 nanocrystals were formed. The molar ratio used between the ligands was 7:94 for DDA:MA. The nanocrystals were purified by centrifugation steps (5500 rpm for 5 min) and the pellet redispersed in 2 mL of toluene.

Preparation of $[\text{CsPbBr}_3]\text{PbBr}_4$ NPLs. An aliquot of the CsPbBr_3 nanocrystals (125 μL) dispersed in toluene (0.5 mL) was mixed with 0.6 or 1.2 mg of EuBr_2 in a small vial. Then, the mixture was submitted to ultrasound/heating treatment for 7 h in a Branson 2510 Ultrasonic Cleaner. The final molar ratio between the components (PbBr_2 :CsBr: EuBr_2) was 1:1:2 and 1:1:4 when using 0.6 mg and 1.2 mg of EuBr_2 , respectively. Finally, the nanomaterial formed was separated by centrifugation at 5500 rpm for 5 min. The pellet obtained was redispersed in toluene (0.5 mL) to further characterization.

Scanning transmission electron microscopy (STEM) analyses. STEM (energy-dispersive X-ray spectroscopy (EDS) and high-angle annular dark field (HAADF) STEM imaging) measurements were performed on probe-corrected FEI Titan Low-Base 60-300 operating at 300 keV (fitted with a X-FEG[®] gun and Cs-probe corrector CESCOR from CEOS GmbH). The convergent semi-angle was of 25 mrad.

Atomic Force Microscopy. The AFM measurements were performed in a Nanoscope IVa Multimode Scanning Probe Microscope (Bruker, former Veeco); the microscope allows to measure surface characteristics as topography. The samples were prepared using 20 μL of the colloid obtained after ultrasound/heating treatment of CsPbBr_3 NPNWs in the presence EuBr_2 for 7 h.

Conflicts of interest

“There are no conflicts to declare”.

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