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Colloidal Synthesis of Lead-free Cs₂TiBr₆-xIₓ Perovskite Nanocrystals

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Abstract. Cesium titanium halide perovskites are novel lead-free optoelectronic materials that have attracted attention in the last two years for their application in solar cells with power conversion efficiencies reaching 3.3%. We report here the first colloidal synthesis of pure and mixed bromide-iodide cesium titanium perovskite nanocrystals with bandgap tunable from 2.3 eV till 1.2 eV.

Since their first introduction in solar cells in 2009, APbX₃ (where A = Cs⁺, CH₃NH₃⁺, CH(NH₂)₂⁺; X = Cl⁻, Br⁻, I⁻) perovskites have acquired a pivotal role as emerging class of semiconductors, thanks to their remarkable optoelectronic properties combined with the ease of solution processability. Their first synthesis as nanocrystals (NCs) dates back to 2015, with their outstanding properties when applied in several devices, such as solar cells light emitting diodes, photodetectors and lasers being already documented. Despite the compelling performance achieved, the use of lead imposes regulatory and environmental concerns. To tackle this problem, in recent years the computational research community has focused on the search of alternative elements to lead, with a focus on those that are not toxic and that can produce a stable perovskite structure. Among them so far only Sn-based perovskites offer direct bandgap with values useful for solar cell applications, yet suffering by the notorious oxidation of the Sn⁴⁺.

Vacancy-ordered halide perovskites are one of the alternative structures that have been designed to replace Pb⁴⁺ with tetravalent cations. They have general formula A₂BX₆, which is obtained by the removal of half the B⁴⁺ cations in the archetypical ABX₃ perovskite structure, and the use of tetravalent cations instead in order to balance the charges (see Scheme 1). Over the last 5 years, vacancy-ordered perovskites containing tin, palladium, tellurium, zirconium and titanium have been synthesized and characterized. Among them, cesium titanium halide perovskite stands out as promising candidate for lead-free perovskite solar cells in view of its favorable bandgap for solar cell applications. Cs₂TiBr₆ solar cells have been reported with Power Conversion Efficiency (PCE) of 3.3%, higher than what has been reached with double perovskites that have been studied for a longer time, such as tin vacancy-ordered perovskites, whose solar cells reached a maximum of 2.1% PCE, or Cs₂AgBiBr₆, which has received a big interest due to its stability and straightforward synthesis but whose bandgap is not optimal for solar harnessing and reported solar cells achieved a maximum PCE of 2.84%.

To date, Cs₂TiBr₆ perovskite has been synthesized with different methods, none of which is a low temperature and easily scalable solution method that leads to stock solutions suitable for making low-cost thin films for optoelectronic devices. While Cs₂TiBr₆ with a bandgap of 1.8 eV has been grown via vapor deposition at high temperatures, Cs₂TiBr₆-Iₓ that offer bandgap tunability down to 1.2 eV have only been grown by melt-crystallization at high temperatures yielding crystal powders and preventing their application to devices. A solution method has yet to be reported due to the difficulty in finding a solvent in which both CsBr/CsI and TiBr₄/TI₄ are soluble, since cesium halides dissolve only in highly polar solvents while titanium halides react with them.

In this paper, we present a new approach for the synthesis of Cs₂TiBr₆ and mixed bromide/iodide Cs₂TiBr₆-Iₓ nanocrystals, which consists on performing a colloidal synthesis using the hot-injection method. With this method, we were able to synthesize...
stable solutions of mixed bromide/iodide Cs₂TiBr₆Iₙ NCs that can be easily deposited as thin films. Cs₂TiBr₆Iₙ NCs have a bandgap tunable from 2.3 eV to 1.2 eV and Cs₂TiBr₆ NCs solution shows emission at 580 nm. For the synthesis of Cs₂TiBr₆ NCs, cesium acetate and titanium octaoleate were loaded in a flask together with oleic acid, 3-(N,N-Dimethyloctadecylammonio)propanesulfonate and octadecene. Bromotrimethylsilane (TMSBr) was swiftly injected at 140 °C under argon and after few seconds the reaction was quenched by diluting the nanocrystals in toluene while lowering the temperature. After the injection, the solution changed color from pale orange to dark red. Figure 1(a) shows the XRD pattern of the as-synthesized nanoparticles and the simulated XRD pattern of Cs₂TiBr₆, which indicates that the crystal possesses Fm3m space group symmetry. Using Bragg’s law, a lattice constant of 10.72 Å was calculated, very close to the values reported in the literature for bulk Cs₂TiBr₆. The optimized synthesis required a Cs/Ti/Br molar ratio of 2:2.5:13.5, otherwise CsBr peak was detected in the bulk synthesis, producing a white powder, while quaternary amines or organic acids did not react with CsBr. The synthesis procedure was designed to control the shape of the nanoparticles. Indeed, in the first attempts to synthesize Cs₂TiBr₆ NCs, only oleic acid was used as ligand and produced very similarly shaped nanoparticles with a homogeneous size distribution (Figure SI6). However, the as-prepared nanoparticles were very sensitive to any antisolvent used during the washing. On the contrary, with the use of the zwitterionic ligand the nanoparticles are stabilized so that can be precipitated with acetone and then easily redispersed in toluene. This ligand was preferred to the classically used long chain organic amines, for instance oleylamine or octylamine, because when using the latter, XRD showed CsBr contamination and the dark red solution turned milky few seconds after the reaction occurred. The production of CsBr as byproduct and the change of color from dark red to milky diminishes when the temperature of TMSBr injection is lowered or when the ligand is added after the synthesis at room temperature (Figure S17). To understand the reactivity of these amines with Cs₂TiBr₆, we mixed different ligands with a solution of TiBr₄ dissolved in toluene, and observed that amines with the lone pair in the nitrogen atom available reacted with TiBr₄ producing a white powder, while quaternary amines or organic acids did not produce any change in the color of the TiBr₄ solution (Figure S18). From these experimental observations, we hypothesized that the strong electrophilic nature of titanium in oxidation state +4 combined with the nucleophilicity of primary, secondary or ternary amines, could give rise to adducts of amines and Ti(IV)Br₄ as already observed in literature for the case of Ti(IV)Cl₄. The zwitterionic ligand contains a quaternary amine group, so that this possible secondary reaction is completed carrying out a TEM analysis. Figure 1(b) shows that the synthesis produces well-dispersed nanoparticles with a controlled size distribution, with an average diameter of 12.9 nm, a size deviation of ±1.7 nm and symmetrical shape (Figure S13). Figure 1(c) is a High Resolution TEM (HRTEM) image of the same sample from where d-spacings can be calculated through a Fast Fourier Transform (FFT) of the image, represented in the inset of Figure 1(c). The d-spacings calculated from the image match those ones obtained considering a lattice parameter of 10.72 Å, inferred from the XRD pattern. Moreover, STEM-EDS analysis performed on ensembles of NCs detected the presence of Cs, Ti and Br (Figure SI4), and inductively coupled plasma optical emission spectroscopy (ICP-OES) results confirm the ratio Cs/Ti is very close to 2, as expected from the stoichiometry (Table S1). To investigate the optical properties of the Cs₂TiBr₆ colloidal solution, absorption and emission of the washed solution were measured and are shown in Figure 1(d). Taking into account the quasi-direct bandgap nature calculated for Cs₂TiBr₆, the optical bandgap was extracted from the Tauc Plots, considering both direct and indirect bandgap, and it is equal to 2.3 eV and 2 eV respectively (Figure S15), around 0.5 eV higher than the values reported for bulk Cs₂TiBr₆. The absorption spectrum has the same shape observed for the bulk material, with two peaks at 390 nm and 483 nm representing the two parity-allowed transitions. The emission peak falls at 580 nm (2.1 eV) and should represent a band-edge transition. The PLQY was measured at the excitation wavelength of 480 nm using Rhodamine 6G in absolute ethanol as reference, and has a value far below 1%. Such a low value is consistent with the calculated parity-forbidden nature of the bandgap.
Figure 2. (a) XRD patterns of mixed halide Cs₂TiBr₆ₓIₐ, NCs with the corresponding standards of pure bromide (bordeaux) and pure iodide (black) perovskites. (b) Expanded XRD pattern. (c) TEM image of Cs₂TiBr₆₋ₓIₓ NCs prepared using TMSI and TMSBr in ratio 0.7. (d) HRTEM image of Cs₂TiI₆ NCs. In the two insets of (d), FFT images of two NCs.

avoided; moreover, this ligand demonstrated to stabilize colloidal perovskite solutions better than the common oleic acid/oleylamine system.

Lastly, it was observed that when the reaction is quenched with a water bath, the nanocrystals grow with the irregular shape of big rods, both when using only oleic acid and when adding the zwitterionic ligand (Figure SI9). Lowering the temperature without diluting the precursors is not effective in quenching the reaction because the Cs₂TiBr₆ NCS are produced also at lower temperature (Figure SI10) but they grow with less symmetrical shapes (Figure SI11). On the contrary, diluting the solution with toluene quenches fast the reaction because it decreases the temperature and dilute the precursors simultaneously, preventing further growth of the NCS. With this method, only NCS grown at high temperature, which are the most symmetrical ones, are produced.

Once the synthesis of Cs₂TiBr₆ NCS was optimized, we used the same colloidal method to attempt the synthesis of pure Cs₂TiI₆ and mixed-halide Cs₂TiBr₆₋ₓIₓ NCS, by partially or fully replacing TMSBr with TMSI. Figure 2(a) illustrates the XRD patterns of pure bromide Cs₂TiBr₆, pure iodide Cs₂TiI₆ and of the mixed-halide species. All crystals possess Fm-3m space group symmetry and, as expected, the diffraction angles decrease going from the pure bromide to the pure iodide perovskite, indicating an increase in the unit cell parameter, from 10.72 Å to 11.5 Å for Cs₂TiI₆ (Figure 2(b)). Using Vegard’s law, we calculated the amount of iodide inserted for each different precursors’ ratio (Figure SI12). The XRD pattern of TiI₄ powder confirms TiI₄ was not present in the NCS solution (Figure SI2). TEM images of the mixed-halide perovskites and of the pure iodide perovskite illustrate the synthesis produces polydispersed nanoparticles with less regular shapes than the bromide NCS (Figure 2(c) and Figure SI13). A HRTEM image of pure iodide Cs₂TiI₆ perovskite shows d-spacings matching the lattice parameter extracted from the XRD pattern (Figure 2(d)). Additionally, STEM/EDS analysis on pure iodide and mixed-halide samples confirmed the presence of Cs, Ti and both Br and I (Figure SI14 and SI15) and ICP-OES that the ratio of Cs and Ti in the structure is around 2 (Table SI1).

Figure 3(a) shows the absorption spectra of the mixed-halide perovskite solutions. When increasing the amount of iodide in the structure, the absorption onset shifts towards longer
wavelengths, and two characteristic peaks at around 570 nm and 790 nm appear. This redshift of the absorption onset is clearly visible already when just 24% of bromide has been replaced by iodide (Figure 3(b)). The direct bandgaps for all the combinations were extracted from Tauc Plots (Figure S116) and plotted against the ratio of iodide and bromide in the structure (Figure 3(c)). It is possible to tune the bandgap from 2.3 eV to 1.2 eV when 87% of bromide has been replaced by iodide. The bandgap decreases until 87% replacement but then increases to 1.3 eV for pure iodide perovskite. This trend is in agreement with previously reported theoretical values\(^2\), plotted in Figure 3(c), and is ascribed likely to bandgap reduction from Urbach tailing due to anionic disorder in the crystal structure.

In the literature there are contradictory results about the stability of \(\mathrm{Cs}_2\mathrm{TiBr}_6\) in air. Some studies claim that this material is intrinsically and environmentally stable\(^{23,24,27}\), while others found that it decomposes fast in air, producing CsBr and amorphous titanium oxide\(^{26,32}\). The colloidal Cs\(_2\)TiBr\(_6\) NCs solution and films prepared by drop-casting the solution on silicon or glass substrates are stable for weeks when prepared and stored under nitrogen atmosphere. However, we observed fast degradation of the films into CsBr when exposing them to air (Figure SI17 and Figure SI18). Such a fast decomposition probably occurs because the nanoparticles own a much bigger surface to volume ratio compared to the bulk, and therefore are more susceptible to decomposition due to the interaction with humidity and oxygen. To further investigate the stability of Cs\(_2\)TiBr\(_6\) NCs films under environmental conditions, we exposed them to UV-light and heat under nitrogen atmosphere. The NCs films are stable after 4 hours under UV light at 395 nm with power density of 15 mW/m\(^2\), and for 1 hour at 100 °C (Figure SI18). We heated the films for 1 hour at increasing temperatures and observed a partial degradation at 150 °C, and a complete degradation into CsBr and most probably into amorphous titanium oxide at 300 °C (Figure SI19).

Conclusions

In summary, we have reported the first colloidal route to synthesize \(\mathrm{Cs}_2\mathrm{TiBr}_6\) vacancy-ordered perovskite NCs with good control over their size distribution and shape, bandgap of 2.3 eV and emission peak at 580 nm. Moreover, we demonstrated that by partially or fully replacing the bromide precursor with the corresponding iodide precursor, it is possible to synthesize mixed- and pure- halide \(\mathrm{Cs}_2\mathrm{TiBr}_6:\mathrm{I}_x\) NCs, with tunable bandgap between 1.2 eV and 2.3 eV. All the NCs show the expected cubic crystal structure, with lattice parameter increasing from 6.22 to 6.38 Å, consistent with the increase of halide content. The NCs show a high surface to volume ratio compared to the bulk, and therefore are more susceptible to decomposition due to the interaction with humidity and oxygen. To further investigate the stability of Cs\(_2\)TiBr\(_6\) NCs films under environmental conditions, we exposed them to UV-light and heat under nitrogen atmosphere. The NCs films are stable after 4 hours under UV light at 395 nm with power density of 15 mW/m\(^2\), and for 1 hour at 100 °C (Figure SI18). We heated the films for 1 hour at increasing temperatures and observed a partial degradation at 150 °C, and a complete degradation into CsBr and most probably into amorphous titanium oxide at 300 °C (Figure SI19).

Experimental section

Preparation of titanium oleate solution. For the synthesis of titanium oleate, 16 ml of oleic acid were added in a 50 ml three-neck flask and degassed through 3 cycles of argon and vacuum. 2 ml of titanium (IV) isopropoxide taken from the glovebox were slowly added while stirring and the solution was heated under argon for 1 hour at 140°C. Afterwards, the solution was left under vacuum at 110°C overnight and acquired a dark red tone. The as-prepared solution was stored under nitrogen.

Synthesis of \(\mathrm{Cs}_2\mathrm{TiBr}_6:\mathrm{I}_x\) nanocrystals. 120 mg of cesium acetate (0.625 mmol) and 60 mg of 3-(N,N-dimethyloctadecylammonio)propanesulfonate (≥99.0%) and acetonitrile (≥99.5%) were purchased from Sigma-Aldrich. Cesium acetate (CsAc, 97%) was purchased from Aldrich. Toluene (anhydrous, 99.8%) was purchased from TCI (Tokyo Chemical Industry Co. Ltd., Japan). TMSBr was obtained from Sigma-Aldrich.

Chemicals. Cesium acetate (CsAc 99.9% trace metals basis), titanium (IV) isopropoxide (Ti(O-i-Pr)\(_4\), ≥97.0%), oleic acid (Ols, technical grade 90%), bromomethylisilane (TMSBr, 97%), 3-(N,N-dimethyloctadecylammonio)propanesulfonate (≥99.0%) and acetonitrile (≥99.5%) were purchased from Sigma-Aldrich. Toluene (TMSI, 97%) was purchased from Fischer Scientific. Toluene (anhydrous, 99.8%) was purchased from Scharlabor. 1-octadecene (90%) was purchased from Alfa Aesar. All chemicals were used without any further purification.

X-ray Diffraction (XRD) characterization. XRD patterns were collected using a Rigaku SmartLab diffractometer in Bragg-Brentano \(\theta/2\theta\) geometry, Cu ka radiation (wavelength=1.5406 Å) and a D/teX Ultra 250 silicon strip detector. The NCs samples were prepared by drop casting the nanocrystals’ solutions on the top of a silicon wafer. All the samples were measured inside an air-sensitive sample holder, which was loaded in the glovebox to avoid any contact with air.

Transmission Electron Microscopy (TEM) characterization and elemental analysis. TEM measurements were performed at the
Scientific and Technological Centres of the University of Barcelona (CCIT-UB). HRTEM images were acquired in a JEOL J2010F TEM microscope, equipped with a field emission electron gun (FEG). EDXS experiments were carried out in a JEOL J2100 TEM microscope, equipped with a LaB6 thermionic filament, and using an Oxford Instruments INCA X-sight spectrometer with Si (Li) detector. Both microscopes were operated at an accelerating voltage of 200 kV. Samples for TEM characterization were prepared in the glovebox by drop-casting diluted toluene solutions (50 μL of NCs solution in 1 ml of toluene) onto 200 mesh carbon-coated copper grids. Elemental analysis of the samples was carried out using an inductively coupled plasma optical emission spectroscopy (ICP-OES) PerkinElmer, model Optima 3200RL, in standard conditions. UV-vis Absorption and PL measurements. Optical absorption spectra were collected using a Varian Cary-5000 UV-vis-NIR spectrophotometer. Photoluminescence (PL) measurements were performed using a Horiba Jobin Yvon iHR550 Fluorolog system, with a OXXUS 405 nm continuous wave laser as the source. The PL spectra were corrected for the system response function.

Associated content
Supporting information. Additional XRD data, TEM images with size distribution and symmetry analyses, STEM-EDS maps, Tauc Plots of Cs₂TiBr₆:Na NCs solutions and pictures for visual comparisons of different treatments.

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Conflicts of interest
There are no conflicts to declare”.

Acknowledgement
The authors acknowledge financial support from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement no. 725165) as well as from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 713729. This project has received funding also from the Spanish State Research Agency, through the “Severo Ochoa” Center of Excellence CEX2019-000910-S, the CERCA Programme / Generalitat de Catalunya and Fundació Mir-Puig. We also acknowledge Funding by the Fundació Joan Ribas Araquàstain (FJRA). This project was funded also by EQC2019-005797-P (AEI/FEDER UE).

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