

Proceeding Paper

Effective Surface Washing of All Inorganic Perovskite Nanocrystals to Enhance Optoelectronic Properties [†]

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Abstract: All inorganic perovskite colloidal nano crystals are an emerging class of optoelectronic materials. However, their colloidal and structural stability during isolation and washing are major hurdles for their commercial application. Their intrinsic chemical instability and optical stability are directly related to the bonding nature of the nanocrystals' surface and organic capping agents that passivate the surface of nanocrystals. We studied the surface ligand properties of CsPbBr₃ prepared by the conventional hot injection method and their washing with varying polarity antisolvent. We observed changes in electrical and optical properties through experimental studies. The study was mainly done by optical and electronic measurements. We determined a facile nanocrystal washing protocol and observed a considerable improvement in the optoelectronic properties of the all-inorganic perovskite colloidal nanocrystals.

Keywords: nanocrystals; hot injection; inorganic perovskite; surface ligands; NC washing



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1. Introduction

AMX₃-type hybrid organic perovskite (HOP) materials have attracted rushing interest of the scientific community due to their exceptional optoelectronic properties. However, they have faced challenges due to structural instability in ambient atmospheres [1]. CsPbX₃ is one of the best substitutes for its organic counterpart, having all inorganic components. All inorganic Perovskite Nanocrystals (AIP NCs) show greater stability and better defect tolerance than HOP, as well as large diffusion lengths and high charge carrier densities [2]. Due to these exceptional properties, AIP is a future candidate for promising applications in PV cells, LEDs, lasers, and photodetectors. To make them commercially feasible devices, significant work is ongoing to improve the optoelectronic properties of AIP NCs.

Surface-passivated colloidal hot injection (HI) synthesis of AIP NCs was first reported by Kovalenko et.al in 2015 [3]. The composition, morphology, and size are crucial parameters for the AIP functionality index and can be influenced by surface capping ligands [4]. To make AIP NCs colloidally stable, the surface is passivated by capping agents. Conventionally, long-chained organic molecules like oleic acid (OA) and oleylamine (OLAM) are used as capping agents for the preparation of CsPbX₃ [4], as shown in Figure 1a.

Long-chain organic capping agents create an electrically insulating layer on NCs, which significantly hinders charge carrier mobility and makes NCs hydrophobic in nature [5]. All these findings encourage us to investigate surface interactions/chemistry of NCs and control of surface capping agents to optimize optical and electrical properties for solar cell applications.

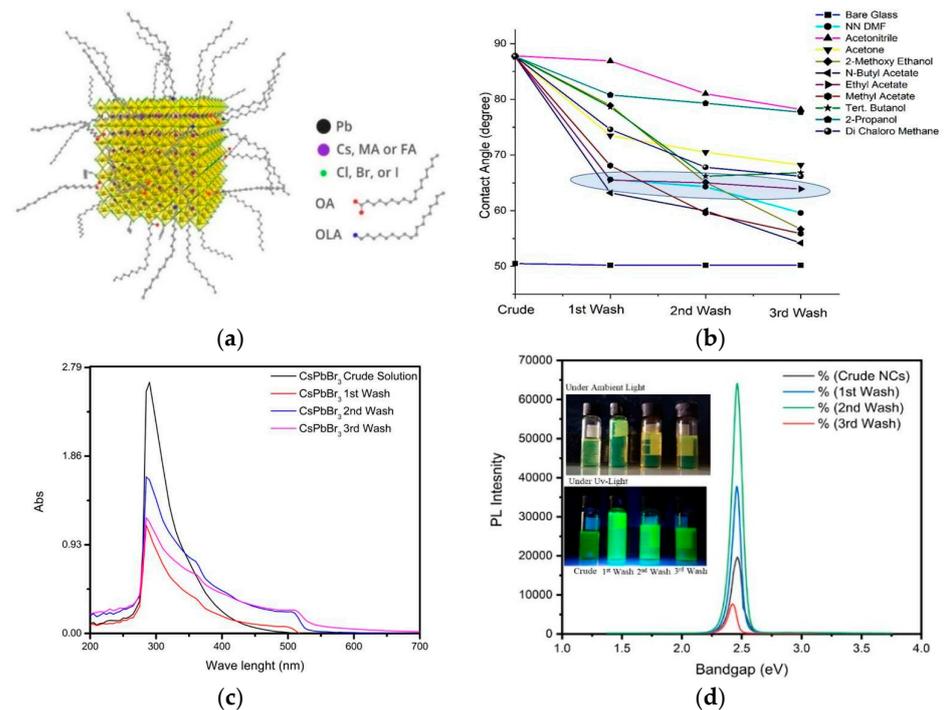


Figure 1. (a) Schematic of typical surfactant-capped AIP NCs. (b) Contact angle studies of perovskite NCs. (c) UV-Vis absorbance spectra. (d) PL spectra. The inset figure shows ambient light and UV light images of various washing cycle AIP NCs.

Binding of surface ligands to NCs' surface can be conventionally described, as per the covalent bond classification (CBC) theory. There are three basic interactions present between inorganic–organic ligands, Z (Lewis Acid), X (Radical), and L (Lewis base), which correspond to 0-electron, 1-electron, and 2-electron interactions. As NCs' surface has a lot of halide vacancies [6], NCs' surface is rich in metal cation and is proved to be coordinated by X-type ligands such as carboxylates and L type ligands such as amines [7].

Traditionally, polar anti-solvents are used for isolation and washing of NCs' collection, which can cause a phase revision from cubic to orthorhombic or dissolution of ionic NCs [8].

In this study, we used a variety of anti-solvents from higher polarity (NNDMF) to lower polarity (DCM) and shortlisted them as a function of changes in contact angle and further characterized AIP NCs and observed changes in optoelectronic properties as a function of washing cycles.

2. Materials and Methods

The AIP NCs studied in this work were synthesized via the hot injection method, as per previously reported method and protocols [9].

3. Results and Discussion

The surface of NCs is passivated by OA and OLAM, and both are hydrophobic organic long-chain molecules, so the concentration of surface ligands can be quantified by measuring surface hydrophobic properties. The perovskite NCs were washed with various washing agents (Figure 1b) in descending order of dipole movement. The removal of surfactants OA and OLAM is a function of solvent dipole movement. We must maintain a reasonable balance of surface ligands because if excessive ligands are removed, then NCs can agglomerate and can lose optoelectrical properties. Additionally, excessive presence of surfactants can also cause decreases in conductivity between NCs.

As per our study, ethyl acetate (Figure 1b) shows reasonable results for NCs' surface washing. With each washing cycle, a reasonable amount of surface ligands is removed

from the NCs' surface, making it suitable to remove surfactants from NCs via a controllable way, which is evident by the decrease in the contact angle of AIP NCs' film.

UV-Vis absorption spectra (Figure 1c) have shown high absorbance in the visible region, and changes in the absorbance spectra clearly show influence by washing cycles.

It is clearly shown from the PL intensity profile (Figure 1d) that with each washing cycle, PL intensity decreases, possibly due to increased agglomeration resulting from decreases in surfactants, which cause agglomeration in NCs.

The presence of long-chain organic ligands can also be quantified by FTIR studies. As OA is a 12-carboxylic group-containing ligand and OLAM is an amine group-containing ligand, the presence of both group peaks can quantify the presence of surface ligands on NCs. It is evident from FTIR results (Figure 2) that O-H stretch (2900 cm^{-1}), O-H bend (1500 cm^{-1}), C-N stretch (1250 cm^{-1}), and supporting peaks shrink with each washing step.

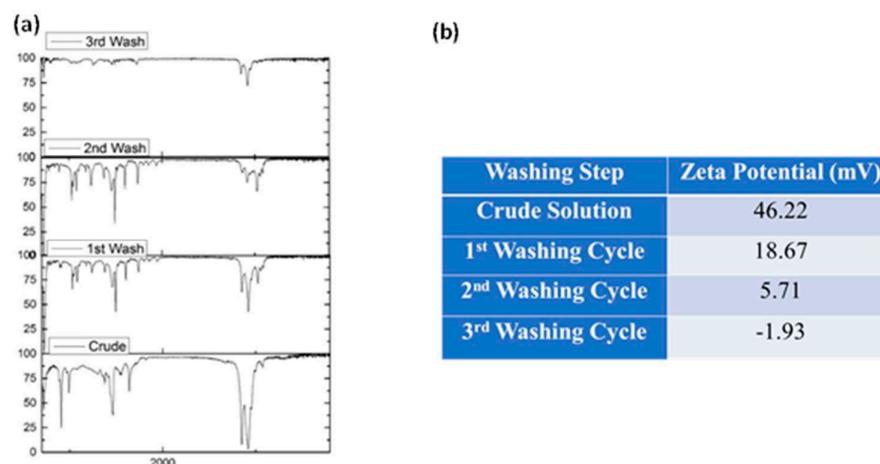


Figure 2. (a) FTIR analysis of AIP NCs. (b) Zeta potential of AIP NCs.

Charge carrier dynamics were studied via Hall effect measurements (Table 1). The results show that sheet resistance decreases considerably with an increase in the wash cycle of perovskite NCs, which support our argument that non-conducting surface ligands are efficiently removed from the surface with each washing cycle, hence increasing charge carrier mobility and decreasing sheet resistance.

Table 1. Hall effect measurements for various washing cycles of AIP NCs.

Parameters	Crude	1st Wash	2nd Wash	3rd Wash
Resistivity (Ohm.cm)	6.909×10^3	6.0200×10^3	5.637×10^3	5.074×10^3
Charge Carrier Mobility cm^2/Vs	9.137×10^{-2}	2.826×10^{-2}	1.860×10^{-1}	1.511
Bulk Concentration ($/\text{cm}^3$)	-9.888×10^{15}	-3.370×10^{16}	-5.953×10^{15}	-8.143×10^{14}

4. Conclusions

In conclusion, this study aimed to explore the effect of washing cycles on the optoelectronic properties of AIP NCs, which are crucial properties for the practical application of AIP NCs in solar cells and other optoelectronic devices. All inorganic perovskite (AIP) CsP-bBr₃ NCs were successfully synthesized. As explained, we assessed charge carrier mobility and optical properties of AIP NCs using suitable solvents and showed the effect of washing cycles directly on the optical and electrical properties of nanocrystals.

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Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available upon request.

Conflicts of Interest: The authors have no conflicts of interest to declare.

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