ENGINEERING HALIDE PEROVSKITE NANOPARTICLES USING REVERSE MICELLE SYNTHESIS FOR ENHANCED STABILITY, UNIFORMITY AND USE IN OPTOELECTRONIC DEVICES

ENGINEERING HALIDE PEROVSKITE NANOPARTICLES USING REVERSE MICELLE SYNTHESIS FOR ENHANCED STABILITY, UNIFORMITY AND USE IN OPTOELECTRONIC DEVICES

BY

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Abstract

In this thesis, we aimed to overcome the limitations of organo-metallic halide perovskites as materials for future optoelectronic applications. Despite having unique optical and electrical properties that make them attractive for various fields, such as energy conversion, photonics, and electronics, perovskites are known to be unstable in the presence of moisture, oxygen, and UV light. To tackle this issue, we employed a reverse micelle synthesis route using an amphiphilic diblock copolymer poly(styrene)block-poly(2vinylpyridine) (PS-b-P2VP) as a nanoreactor, which was dissolved in a non-polar solvent. This approach allowed us to synthesize perovskite nanoparticles, with various A, B, and X site ions, with tunable emission wavelengths between 475 nm and 850 nm. Additionally, exploiting the properties of reverse micelle templating, novel properties were achieved including stable nanoparticles with two distinctly different emission spectra in a single solution, large induced Stokes shifts up to 660 meV and high stability in ambient conditions over 200 days. To further improve the stability and electrical conductivity of perovskite nanoparticles, we created a core-shell structure by growing a suitable conductive shell around the perovskite nanoparticles using a three-step loading mechanism. For this, we opted for metal oxides with type-II band alignment with FAPbBr₃, which allowed the separation of the exciton and improved the stability of the perovskite nanoparticles. We synthesized FAPbBr₃-TiO₂, FAPbBr₃-NiO, and FAPbBr₃-ZnO core-shell nanostructures with various shell thicknesses, which were able to withstand harsh conditions such as oxygen plasma etching. The incorporation of various nanoparticles as optical filters and as electrically active layers in organic solar cell devices resulted in an improvement in the overall performance. To apply the nanoparticles on sensitive surfaces, such as organic thin films, we also developed an indirect mechanical method using graphene transfer printing. This technique allowed us to successfully transfer perovskite and iron oxide nanoparticles without loss of properties.

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List of Publications

* Organo-halide perovskite synthesis by RMD

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- * I am the first author of this article and my role in the paper was data collection, analysis and writing. I synthesized the nanoparticles, collected and analyzed AFM images, I also analyzed the order of dispersion using a Mathematica spatial statistics package, Dislocate. XRD and TEM data was analyzed by me. I also wrote the manuscript in its entirety under the supervision of Dr. Turak, with reviews and edits from the co-authors. Some emission measurements were performed by Markus Clark Scharber, Linz institute of ogranic solar cells, Johannes Kepler University, Linz Austria. Absorption spectrum were collected by Yolanda Salinas at institute of Polymer Chemistry (ICP), Johannes Kepler University, Linz Austria.
- 2. Hui, L. S., Munir, M., Vuong, A., Hilke, M., Wong, V., Fanchini, G., ...

Turak, A. (2020). Universal Transfer Printing of Micelle-Templated Nanoparticles Using Plasma-Functionalized Graphene. ACS Applied Materials & Interfaces, 12(41), 46530-46538. https://doi.org/10.1021/acsami.0c12178

- * I am co-author in this article. The project was inherited from a prior graduate student. My contribution to this study entailed experimental validation of the transfer printing technique by utilizing optically detectable nanoparticles. The order of dispersion was analyzed utilizing the Mathematica spatial statistics package, Dislocate. The portion of the manuscript related to the confirmation of transfer printing was written by myself, while the section of the manuscript pertaining to the graphene study was authored by Lok Shu Hui, both under the supervision of Dr. Turak. Emission measurements were conducted by Markus Clark Scharber and were analyzed by the present me. Scanning near-field optical microscopy was done by Victor Wong. Graphene was provided by An Vuong.
- Munir, M., Arbi, R., Scharber, M. C., Salinas, Y., Sariciftci, N. S., Turak, A. (2020, July). Anionic exchange route to synthesize highly uniform, stable and luminescent MAPBr nanoparticles. In Optical Devices and Materials for Solar Energy and Solid-state Lighting (pp. PvTu3G-5). Optica Publishing Group. https://doi.org/10.1364/PVLED.2020.PvTu3G.5
- * I was the first author of this manuscript. I wrote this article under the supervision of Dr. Turak. The analysis of AFM, absorbance and emission spectroscopy data were analyzed by myself. I would like to acknowledge the contributions of Yolanda Salinas, who collected the absorbance data, Markus Clark Scharber,

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- Hui, L. S., Munir, M., Whiteway, E., Vuong, A., Hilke, M., Wong, V., ... Turak, A. (2020). Tunable Etching of CVD Graphene for Transfer Printing of Nanoparticles Driven by Desorption of Contaminants with Low Temperature Annealing. ECS Journal of Solid State Science and Technology, 9(9), 093006.

10.1149/2162-8777/aba855

- * I contributed to the discussion and review of this article.
- 6. Hui, L. S., Beswick, C., Getachew, A., Heilbrunner, H., Liang, K., Hanta, G.,

Arbi, R., Munir, M. ... Turak, A. (2019). Reverse micelle templating route to ordered monodispersed spherical organo-lead halide perovskite nanoparticles for light emission. ACS Applied Nano Materials, 2(7), 4121-4132.

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* Other nanoparticle and material synthesis

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- * I am the first author of the article, and my role in the paper was the synthesis, data collection, and analysis of optically active nanoparticles. This article was written by me under the supervision of Dr. Turak. Co-authors contributed to the study of optically non-active nanoparticles.
- Munir, M., Habib, M., Khan, S. A., Kim, M. H., Lee, S., Song, T. K., ... Turak, A. (2021). Energy storage and piezoelectric properties of leadfree SrTiO3-modified 0.965 Bi0.5 Na0.5 TiO3-0.035 BaTiO3 ceramics. Journal of Materials Science: Materials in Electronics, 32, 10712-10725. https://doi.org/10.1007/s10854-021-05728-6

- * As the first author of this manuscript, I wrote the manuscript under the supervision of Dr. Turak and Dr. Ali Hussain. I was responsible for conducting the experimentation to prepare the composition. The gathering and analysis of strain, XRD, Raman, and dielectric data was conducted by myself and Habib. Salman assisted in obtaining the polarization data. The scanning electron microscopy (SEM) data was collected by Dr. Ali Hussain. The manuscript was reviewed by the co-authors.
- 9. Lee, S., Munir, M., Arbi, R., Oliveira, P., Lee, S., Lim, J., ... Turak, A. Uncoupling Nanoparticle Geometry from Material Properties for Improved Hole Injection at Submonolayer Nanoparticle Electrode Interlayers in Organic Hole-Only Devices. Available at SSRN 4221673. http://dx.doi.org/10.2139/ssrn.4221673
- * I am contributed in the synthesis of few nanoparticles, AMF characterization, discussion and review of this article.
- Habib, M., Munir, M., Akram, F., Lee, S., Song, T. K., Turak, A., ... Hussain, A. (2021). Structural evolution and electromechanical properties of SrTiO3-modified Bi0. 5Na0. 5TiO3–BaTiO3 ceramics prepared by sol-gel and hydrothermal methods. Materials Chemistry and Physics, 266, 124529.

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* I am a co-author of this article. I was solely responsible for the experimentation of the manuscript. I helped with writing the experimental portion of this article and reviewing the article.

- Lee, S. I., Liang, K., Hui, L. S., Arbi, R., Munir, M., Lee, S. J., ... Turak, A. (2021). Necessity of submonolayer LiF anode interlayers for improved device performance in blue phosphorescent OLEDs. Journal of Materials Science: Materials in Electronics, 32, 1161-1177. https://doi.org/10.1007/s10854-020-04889-0
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 - * I contributed to the discussion and review of this article.
- Lin, N., Verma, D., Saini, N., Arbi, R., Munir, M., Jovic, M., Turak, A. (2021). Antiviral nanoparticles for sanitizing surfaces: A roadmap to self-sterilizing against COVID-19. Nano Today, 40, 101267. https://doi.org/10.1016/j.nantod.2021.101267
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- Saad, A., Shen, H., Cheng, Z., Ju, Q., Guo, H., Munir, M., ... Yang, M. (2020). Three-dimensional mesoporous phosphide-spinel oxide heterojunctions with dual function as catalysts for overall water splitting. ACS Applied Energy Materials, 3(2), 1684-1693. https://doi.org/10.1021/acsaem.9b02155

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Abbreviations and Symbols

Abbreviations

PS-b-P2VP	poly(styrene)-b-poly(2-vinylpyridine)
2VP	2-vinyl pyridine
NCs	Nanocrystals
OA	Oleic acid
OAm	Oleylamine
OMHPs	Organo-metalic halide perovskites
MHPs	Metal halide perovskites
FA	Formamidinium
MA	Methylammonium
$MAPbI_3$	Methylammonium lead iodide
MAPbBr ₃	Methylammonium lead bromide

FAPbI_3	Formamidinium lead iodide
FAPbBr ₃	Formamidinium lead bromide
$PyPbI_3$	Pyrrolidinium lead iodide
$\mathrm{PyPbBr}_{3-x}\mathrm{I}_{x}$	Pyrrolidinium lead mix halide
NPs	Nanoparticles
OPV	Organic Photovoltaics
LED	Light Emitting Diodes
RMD	Reverse Micelle Deposition
RMS	Reverse Micelle Synthesis
UV	Ultraviolet
Vis	Visible
XPS	X-ray Photoelectron Spectroscopy
EDS	Energy Dispersive Spectroscopy
AFM	Atomic Force Microscopy
XRD	X-ray Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy

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ITO	Indium Tin Oxide
PCE	Power Conversion Efficiency
\mathbf{J}_{sc}	Short-circuit current density
Voc	Open-circuit voltage
МО	Metal Oxide
${ m TiO}_2$	Titanium dioxide
NiO	Nickel Oxide
ZnO	Zinc Oxide
номо	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
QNM	Quantitative Nanomechanical Mapping

Chapter 1

Introduction

1.1 Thesis overview

The methodology employed in this study involves the utilization of diblock copolymer reverse micelle deposition (RMD) to produce organo-metalic halide perovskite (OMHP) nanoparticles. The emphasis is on tuning the properties of the perovskite nanoparticles (PNPs), by exploiting the controlled reaction kinetics of RMD. The first chapter of the thesis delves into the potential, accomplishments, and limitations of OMHPs within the field of optoelectronics. Various techniques are being employed to circumvent the challenges associated with perovskites, yet certain limitations remain to be resolved. The utilization of RMD has demonstrated promise in addressing certain issues of MHPs; dealing with the challenges for its practical application to produce PNPs was the key focus of this thesis.

The second chapter examines how reverse micelle synthesis can be employed to tune the bandgap of PNPs by varying the loading time, precursor ratio, and concentration of reverse micelles. Through the use of only MAI and PbBr₂, taking advantage of the slowed-down reaction kinetics of perovskite formation, we were able to tune the bandgap and synthesize two different types of nanoparticles in a single solution, achieving a large induced Stokes shift. The third chapter continues to discuss the synthesis of PNPs extending to using a large five-membered pyrrolidinium ion as an A-site cation for the synthesis of pyrrolidinium-based nanoparticles. A bathochromic shift was observed when iodide was substituted by bromide in these PNPs nanoparticles, generating a large Stokes shift of 660meV (182 nm). Due to their polymer shielding, all of these nanoparticles were successfully used as optical down converters for organic photovoltaic devices with absorption matching the emission wavelengths of the PNPs, showing increased performance.

The fourth chapter focuses on stabilizing FA-based perovskite nanoparticles by capping them with a conductive material. Following the successful synthesis of perovskite nanoparticles, the nanoparticles were capped with TiO_2 with variable shell thickness. With increasing shell thickness, the core-shell structure was clearly visible and the emission spectrum of nanoparticles was quenched. Such capping allowed the PNPs to withstand the harsh oxygen plasma conditions required to remove the polymer templates, allowing them to be incorporated as electrically active layers in solar cells. Used as an interlayer, the nanoparticles improved the efficiency of organic solar cells. In the same way, NiO and ZnO shells were created around FAPbBr₃ nanoparticles and they also enhanced the efficiency of solar cells.

The fifth chapter discusses an indirect mechanical method of transferring nanoparticles to a sensitive substrate on which the nanoparticles cannot be applied directly, using graphene-nanoparticle composites. Using this technique, we also showcased the stability of polymer encapsulated perovskite nanoparticles in water, as this process involves floating in an aqueous etching solution to exfoliate the graphene.

The sixth chapter presents the conclusion of the thesis as well as the future objectives related to this thesis.

1.2 Background and motivation

Halide perovskites are a new generation of optically active materials that have gained a lot of attention due to their potential optical and electrical properties. Since the first research article on photoactive perovskites was published by Konjma et al. in 2009 [1], this group of materials has gained interest and widespread attention. The capability of halide perovskite was further revealed by Snaith et al. in 2013, who reported a solid-state planar perovskite solar cell demonstrating a power conversion efficiency (PCE) of over 15% [2]. In response to these studies, intensive research has been conducted on this class of materials in order to improve their efficiency, tuneability, and stability. [3–7]. These materials have a unique three-dimensional cage-like structure with a chemical formula of ABX₃, where A is a monovalent cation [e.g., methylammonium(MA) $CH_3NH_3^+$, cesium (Cs)⁺, formamidinium (FA) $CH(NH_2)^+$, or boron (B)], B is primarily a divalent transition metal [e.g., lead (Pb^{+2}) , or tin (Sn^{+2})], and X is a halide anion [chlorine(Cl^{-1}), bromine (Br^{-1}), or iodine (I^{-1})] [8–11]. Due to the cage-like structure and the selection of various candidates for various positions, perovskites can be tuned for a wide range of properties. Perovskites have been found to exhibit excellent optoelectronic properties, including high absorption coefficients [12], long carrier lifetimes. [13], low recombination losses [14], and adjustable bandgap [15]. As a result of their unique properties, perovskites have displayed their potential for various applications, such as solar cells [16], light-emitting diodes (LEDs) [17–19], photovoltaics [20,21], lasers [22], down converters [23,24], photodetectors, and singlephoton sources [25,26].

Perovskites cover a wide emission spectrum from 450 nm to 850 nm depending on the halide ion used. As a general rule, chlorine-based perovskites emit ultraviolet light, bromine-dominant perovskites emit green light while iodine-based perovskites emit red light or in near-infrared region [27–29]. This bandgap tunability of perovskites is among their most appealing features. Other qualities of perovskites include their cheap and easy fabrication which starts with mixing inexpensive salts providing suitable conditions and a calculated amount of precursors. Once combined, they crystallize very quickly forming the final product. [25,30,31]. They can also be deposited using vapor deposition at very low temperatures [32–34].

Considering their unique properties, such as high absorption coefficients, high power conversion efficiency (PCE), and low material costs, metal halide perovskites (MHPs) are a strong candidate for green energy production [35]. The efficiency of perovskite solar cells has been rapidly increasing in recent years. In 2009, the first perovskite solar cell was reported with an efficiency of 3.8% [1]. Since then, the efficiency of perovskite solar cells has continuously improved and achieved a record efficiency of 25.7% [36] within only 13 years. The power conversion efficiency (PCE) of perovskite solar cells (PSC) has surpassed those of silicon (non-crystalline) and organic solar cells only after 13 years of research [36]. Currently, PCE of perovskite solar cells has surpassed those of poly-crystalline silicon and is rivaling crystalline Si single junction cells [37], as shown in figure 1.1.



Figure 1.1: A chart depicting the highest confirmed conversion efficiencies of diverse photovoltaic technologies, plotted over a span of time from 1976 to the present (source NERL).

The framework structure of the perovskite provides a broad range of tunable properties, but also imposes restrictions on the selection of ion sizes for the A, B, and X sites due to its cage-like architecture. The stability of the BX₆ octahedron that encloses the A-site cation in a perovskite cage is linked to the octahedral factor (μ). The octahedral factor (μ), expressed as the ratio of the radius of the B-site cation (r_B) and the halide counter ion (r_X), shown in equation 1.2.1, can be used to approximate the stability of the BX₆ octahedra. The binding of the B-site cation is determined by the ionic size restrictions imposed by the X_6 octahedra. When the octahedral factor μ falls within the range of 0.442 to 0.895, the metal halide perovskite exhibits a stable configuration [38–40].

$$u = \frac{\mathbf{r}_{\mathrm{B}}}{\mathbf{r}_{\mathrm{X}}} \tag{1.2.1}$$

The Goldschmidt tolerance factor (t) is a parameter determined using the ionic radii of the constituent A, B, and X ions $(r_A, r_B, and r_X)$, as described by the equation 1.2.2 [41]. This factor is crucial in determining whether different combinations of A, B, and X ions are capable of forming an optically active perovskite structure. The stability and formation of the ABX₃ perovskite structure rely on the dimensions of the cations and anions involved. The literature reports that if the tolerance factor falls between the range of 0.8 to 1.0, an optically active perovskite crystal structure is formed. When the tolerance factor ranges from 0.9 to 1.0, an optically active perovskite with a cubic structure is formed. On the other hand, when the tolerance coefficient lies within the range of 0.80 to 0.89, a distorted perovskite structure with an orthorhombic, tetragonal, or rhombohedral (in order of stability) crystal structure is more likely to emerge. A tolerance factor less than 0.8 indicates that the A-site cation is too small to form an optically active perovskite phase. Furthermore, if the A-site ion is too large, it produces an optically inactive hexagonal perovskite phase with a tolerance factor greater than 1.0. Hence, the size of the A-site ion must lie within the range of approximately 155 pm to 260 pm, as illustrated in Figure 1.2, imposing a constraint on the size of the A-site ion. [40, 42, 43].

$$t = \frac{\mathbf{r}_{\mathrm{A}} + \mathbf{r}_{\mathrm{X}}}{\sqrt{2}(\mathbf{r}_{\mathrm{B}} + \mathbf{r}_{\mathrm{X}})} \tag{1.2.2}$$

Due to the versatility of ions substitutions possible for MHPs without disrupting the perovskite crystal structure, fine-tuning of the properties of the perovskite material is possible to suit a particular application [26]. Such substitutions of the A, B and X site ions have been used to engineer the bandgap, improve material stability, and improve photoluminescence quantum yields (PLQYs) [42–44].As a result of intensive research, materials including Li, Na, K, Ca, Sr, Mg, Mn, Zn, Bi, and Ce are being doped into various perovskites to engineer the most suitable material for a given application [45–47].

The compositional engineering of perovskites has greatly improved their performance, yet a few drawbacks still need to be addressed for widespread commercialization. The fast reaction kinetics involved in halide perovskite formation can limit the stable tailored compositions [25, 30, 31] which leads to defects and phase instability. Controlling the reaction kinetics of the formation of bulk perovskites is challenging, and many groups used annealing after deposition to tune the structure [48,49]. However, after the bulk phase is formed, such modifications will introduce more defects due to re-crystallization [50]. Therefore, for bulk halide perovskite synthesis, the ideal method of obtaining the desired band gap is by adding the raw precursor in extremely precise stoichiometric ratios, which is complicated by the fast kinetics.



Figure 1.2: Effect of A-site cation on tolerance factor and perovskite phase.

On the other hand, low dimensional perovskites which include quantum dots (QDs) and nanoparticles offer additional degrees of freedom over bulk to tune the optoelectronic properties and control the synthesis process [51]. They also have enhanced perovskite capabilities in optics and electronics due to their large surface-to-volume ratio, enhanced optical and electrical properties [52], improved stability, and tuned chemical composition, which allows fine-bandgap tuning [53–55]. Based on the synthesis conditions, a wide range of nanostructures can be obtained due to controllable crystallization [56, 57].

In general, the physical properties of semiconducting nanoparticles are not only tuned by chemical stoichiometry [26] (the ratio of cations to anions yielding different bandgaps) and confined size growth on a dimensional scale [58] (smaller nanoparticles tend to have higher absorption coefficients and larger bandgaps, while larger nanoparticles tend to have lower absorption coefficients and smaller bandgaps) [59] but also by other parameters such as crystallinity [60] (nanoparticles with higher crystallinity tend to have better electronic and optical properties than those with lower crystallinity), temperature and pressure of the formation [61] (high temperature and pressure can improve the crystallinity of the nanoparticles and high pressure can affect the bandgap), the synthesis route [51] (Different synthesis methods can produce nanoparticles with different sizes, shapes, and chemical compositions, which can affect their properties), and surface passivation [62] (surface passivation can improve the recombination lifetime of the carriers and can reduce the non-radiative recombination rate).

All of the above-mentioned parameters vary with the fabrication technique. Recently, a number of synthesis methods have been used to synthesize PNPs, including solvent-induced re-precipitation, ligand-assisted re-precipitation (LARP), microemulsion, hot injection, and template-assisted synthesis [62–69]. It is worth noting that each synthesis method has its own advantages and drawbacks. For example, without any shielding around them, nanoparticles degrade under ambient environmental conditions such as UV light illumination, heat, and moisture, even faster than bulk MHPs. Using the LARP technique, PNPs are obtained by regulating solvent volumes and concentrations. A supersaturated solution is created by dissolving the precursors in a suitable solvent and then transferring them to a poor solvent, where ligands (oleic acid (OA) and oleylamine (OAm)) are used to precipitate PNPs. However, reprecipitation causes high polydispersity. Additionally, the proton exchange between OA and OAm can lead to the loss of ligands from PNP surfaces during the purification process or storage period, reducing their stability [70].

Other processes require high temperatures, which lead to polydispersity and agglomeration [51, 53, 62, 71, 72]. Therefore, a synthesis process that allows the controllable size and emission wavelength, enables easy incorporation of the PNPs into electronic devices, and prevents water-induced degradation and halide ion migration would be highly advantageous to commercialize them. MHPs exhibit structural degradation under ambient conditions and moisture, leading to a substantial decrease in device performance and even device failure [73]. The sensitivity of perovskite materials to moisture is due to the vulnerability of their ionic bonding, which renders them susceptible to water penetration and ion migration [38].



Figure 1.3: The figure presents a schematic representation of the Type I, inverse-type I, inverse-type II, and type II core-shell configurations

In recent years, efforts have been made to passivate perovskite NPs to overcome their stability limitations. A well-established classical technique for tackling surface defects and improving nanoparticle stability is encapsulating the nanoparticles with

a strong and stable material with a band gap larger or smaller than that of the nanoparticle. According to a photo-generated charge distribution, core-shell band alignment can be designed [74]. The band alignments of core-shell semiconductors can be divided into three types based on their characteristics: type-I, inverse type I, type II, and inverse-type II [75, 76]. The type-I band alignment refers to a situation where the capping material possesses a larger energy bandgap than the optically active core. As a consequence, the conduction band edge and valence band edge of the core material lie within the shell band gap, thereby resulting in the confinement of electrons and holes to the shell. This configuration leads to enhanced stability of NCs [77,78]. Conversely, in the inverse-type I band alignment, the band gap of the core material is larger than that of the shell material [78]. The type-II band alignment is characterized by either an overlapping or a small offset between the conduction bands of the core and shell, while the valence band of the core and shell has a relatively large offset. In such a heterostructure, electrons can be transferred over the heterostructure while holes with low energies remain in the core. The type-II band alignment not only improves the stability of nanoparticles but also enhances the efficiency of photonic devices by improving charge extraction [79,80]. In contrast, the inverse-type II band alignment is characterized by a situation where the valence band edge of the shell either overlaps with the valence band of the core material or has a small offset, while the conduction band of the core and shell has a relatively large offset. As a result, holes are delocalized over the core-shell heterojunction, whereas electrons with low energy remain in the core. This type of band alignment also improves the stability of active material and helps in efficient charge extraction [81,82]. schematic of core-shell heterostructures is shown in Figure 1.3. Creating core-shell heterojunctions is an ideal way to overcome stability issues of perovskite nanoparticles. Various successful attempts have been made to fabricate core-shell structures, mainly using cesium-based perovskites as cores. Through various synthesis techniques, various shells, including metal oxides, polymers, metal chalcogenides, perovskites, inorganic layers, and organic layers, have been explored to improve stability and charge transport [78, 80]. During core-shell synthesis, one of the major problems is the difficulty in controlling the thickness of the shell due to the fast reaction kinetics of perovskites. By controlling the thickness of the shell material, we will be able to partially delocalize the charge carriers over the shell, allowing tuning of the emission spectrum and improving charge extraction. A further concern observed during typical core-shell synthesis was that the perovskite NCs were homogeneously incorporated into one shell, reducing optoelectronic efficiency. Furthermore, efficient techniques that would allow growth of various types of shells without changing experimental techniques and conditions would be highly desirable for future up-scaling for mass production of devices. It is therefore necessary to evaluate the reaction mechanisms and side reactions, as well as to carefully design the surface engineering of the nanoparticles, for rational design of smart core-shell structures.

To address the above-mentioned issue of perovskites, this research project uses diblock copolymer reverse micelle template-assisted synthesis to fabricate perovskite nanoparticles. The template-assisted synthesis of nanoparticles has had widespread use in producing size-controlled, ordered nanoparticle arrays of a variety of nanoparticles under ambient conditions with maximum control over the tuning parameters [23, 67, 83–91]



Figure 1.4: This figure illustrates the process of creating perovskite nanoparticles through reverse micelle synthesis

The process begins with the dissolution of an amphiphilic diblock copolymer in a selective polar solvent to form nanoreactors. Following the formation of the nanoreactors, reactive precursors are added to the nanoreactor solution and stirred to facilitate infiltration of the precursors into the core. This method has also been used to produce well-dispersed perovskite nanoparticles with low polydispersity and fine control over size as the nanoparticles are produced inside the nanoreactors [66, 68, 69, 92]. From previous research conducted in the Turak group, it is known that in PS-b-P2VP diblock copolymer systems, pyridine acts as a monodentate ligand for transition metals and halogen ions [92, 93]. The diblock polymer comes in a variety of PS-to-P2VP ratios that define different sizes of nanoreactors and provide varying levels of protection from the environment [94]. Diblock copolymers with heavier molecular weights create stiffer nanoreactors that offer high levels of protection to the nanoparticles formed inside, avoid aggregation, and exhibit uniform sizes, but only allow selective salts to infiltrate. In contrast, PS-b-P2VP co-polymer with a lower molecular weight forms crew-cut nanoreactors. The crew-cut nanoreactors enable the infiltration of almost any salt but do not provide a high level of protection, which leads to polydispersity and agglomeration [94]. This template-assisted synthesis route provides the advantage of loading the precursors into the micelles step by step, slowing down the reaction kinetics to achieve phases that are difficult to obtain by other synthesis routes [23]. Although the micelle encapsulation provides shielding and external stability, the insulating nature of polystyrene in corona prevents it from being used directly in optoelectronic devices. Traditionally O_2 plasma etching is used to remove the PS-bP2VP diblock copolymer shielding from around the nanoparticles [83, 95]. While plasma etching is effective at removing the polymer coating from nanoparticles surfaces without affecting the particle size or distribution, the harsh plasma atmosphere would also degrade the perovskite nanoparticles, decomposing it back to PbI₂ [67]. The development of a core-shell structure is the key to allowing these particles to be used for applications that require electrical conduction.

1.3 General overview of the research project

1.3.1 Typical synthesis procedure to achieve perovskite nanoparticles

The diblock copolymer reverse micelle templating process begins with the dissolution of the amphiphilic diblock copolymer polystyrene-b-poly(2-vinylpyridine) (PSb-P2VP) in a selective non-polar solvent. That mixture is allowed to stir for 24 hours, resulting in the formation of nanoreactors. When dispersed in a non-polar solvent, the monomers of this diblock copolymer arrange themselves in a pattern in which the hydrophobic polystyrene extends outward to form the corona of the nanoreactor while the hydrophilic poly(2-vinylpyridine) forms its core. Following the formation of the nanoreactors, perovskite precursors dissolved in DMF or IPA are added to the nanoreactor solution with a 24-hour gap and allowed to stir for a further 24 hours to facilitate infiltration of the precursors into the core to allow the formation of desired perovskite nanoparticles. Finally, the solution is centrifuged to remove any unloaded precursors. Such polymer shielded nanoparticles are utilized for their emission properties, either in solution or after deposition onto a planar substrate. Typically to examine the size of the nanoparticles, and to use them in applications where electrical conduction is required, the polymer templates are removed after deposition using O_2 plasma etching for 30-40 mins.

1.3.2 Overview of research project

Initially, in the Turak lab, we were only capable of producing MAPbI₃ and FAPbI₃ nanoparticles in dense core PS-b-P2VP nanoreactors, as described in Hui et al. in ACS Applied Nanomaterials [92]. Through the course of the project, to generate perovskite nanoparticles of different compositions, and different emission properties with tunable bandgaps, I conducted research on multiple parameters such as micelle concentration, loading time, and precursor ratio. Figure 1.5 illustrates the emission spectra of the diverse nanoparticles that were successfully synthesized throughout the course of this project, covering an emission range from 475 nm to 860 nm.



Figure 1.5: (a) Depiction of the emission spectrum of perovskite nanoparticles with diverse band gaps synthesized via the reverse micelle synthesis method during my research for this thesis.

Although the loading step facilitates tuning of the bandgap through control over the reaction kinetics, the precursor could also dissociate the nanoreactor if it interacts strongly with the core, leading to reverse micelle flipping [92]. This limits the precursors that can be used and the sequence of loading. It is for this reason that bromine and chlorine-based nanoparticles could not be produced using conventional precursors such MABr + PbBr₂ or MACl + PbCl₂ in dense core nanoreactors, even though these are desirable for perovskite NPs synthesis. To overcome these problems, I explored various combinations of precursors, and developed new two and three step synthesis routes to achieve the various compositions of interest, as described in the following chapters.



Figure 1.6: The figure depicts the photoluminescence emission spectra of perovskite nanoparticles under different conditions: (a) following immersion in water. (b) Comparing the spectra of freshly synthesized nanoparticles, those aged for 250 days, and particles that underwent a two-minute oxygen plasma etching process. The nanoparticles were synthesized via the reverse micelle synthesis route.

As the nanoparticles encapsulated in the micelle have a polymer shielding around them, we have observed that they can survive when immersed in water for over 5 hours, as shown in Figure 1.6(a) and under ambient conditions for over 250 days shown in Figure 1.6(b). We took advantage of this increased stability to incorporate the perovskite nanoparticles into graphene composites, where the graphene was exfoliated from Cu using an immersion technique, without loss of emission properties, as described in chapter 5.

Although the micelle encapsulation provides shielding and external stability, the insulating nature of polystyrene in the corona prevents it from being used directly in optoelectronic devices. By using plasma etching, the PS-bP2VP diblock copolymer shielding is easily removed from RMD synthesized nanoparticles without affecting the

size or distribution of nanoparticles [83,95]. However, the harsh plasma atmosphere also degrades the perovskite nanoparticles, rendering them optically inactive as shown in figure 1.6(b).



Figure 1.7: A schematic illustration of the three-step reverse micelle synthesis approach utilized to produce perovskite core-shell nanoparticles.

To stabilize perovskite nanoparticles for use as electrically conductive layers in optoelectronic devices, I developed a three-step loading technique that allowed the formation of core-shell nanoparticles, with a metal oxide shell formed surrounding a perovskite core. Figure 1.7 demonstrates the three-step loading process for FAPbBr₃metal oxide (Mo) nanoparticles. This approach enabled control over the shell thickness surrounding the nanoparticles, by tuning the third precursor addition. By employing this method, we were able to develop a controllable shell of TiO₂, NiO, and ZnO around $FAPbBr_3$ nanoparticles as described further in chapter 4. These particles exhibited enhanced stability towards oxygen plasma, UV, and humidity and were implemented as electrically conductive interlayers in optoelectronic devices.

Chapter 2

Enhanced Stokes shift and phase stability by co-synthesizing perovskites nanoparticles (MAPbI₃/MAPbBr₃) in a single solution

The findings of this research were published in the journal "Advanced Photonics Research".

Abstract

Herein, diblock-copolymer reverse micelle templating was used to control the reaction kinetics of metal halide hybrid perovskites formation to fabricate systems showing dual phase emission. Through control of the reaction kinetics of perovskite formation with micelle templating, desired compositions can be engineered which show high phase stability of mixtures of perovskite nanoparticles through micellar shielding and stabilizing of the cage structure. Additionally, a Stokes shift of around 150nm, one of the largest reported for perovskite systems, can be obtained with careful control over the synthesis kinetics. Using an unconventional approach i.e. mixing methylammonium iodide (MAI) and lead bromide PbBr₂, systems consisting of both green and red emitting nanoparticles (NPs) were fabricated by a two-step reaction process using reverse micelle templating. By obtaining two stable phases in a single solution, the NP system can absorb in the ultraviolet region and emit in the red region, making them excellent candidates for down-conversion to improve solar cells efficiency, as shown for two polymer active layers in organic bulk heretojunction solar cells. Exploiting the phase stabilizing effect of the micelles, the reaction kinetics of perovskite formation can be tuned for various halide substitutions, opening up new avenues for co-existing perovskite phases for photovoltaic and light emitting applications.

2.1 Introduction

In recent decades, the family of metal halide hybrid perovskites have attracted attention owing to record-breaking achievements in fields such as photovoltaics (PV), light-emitting diodes (LEDs), lasers, sensors, and many other electronic devices [5– 7,96–99]. Perovskites, with the generic chemical formula ABX₃, owe these properties to their flexible cage crystal structure where the A-site is occupied by a monovalent cation which could either be an organic molecule such as methylammonium (CH₃NH₃⁺) (MA) or formamidinium (CH(NH₂)₂⁺) (FA), or an inorganic atom, such as cesium (Cs⁺); the B-site accommodates a divalent inorganic cation such as lead (Pb²⁺) or tin (Sn²⁺); and the X position is occupied by a halide group, which could be chloride (Cl⁻), bromide (Br⁻), or iodide (I⁻) [100].

A critical issue hindering the commercialization of perovskite based optoelectronic devices is instability and phase degradation. The desirable α -phase perovskite structure, which is ideal for photoelectric conversion, eventually degrades in ambient conditions into the δ -phase, which is a yellowish non-perovskite phase with an unwanted large bandgap and poor charge transport [7, 19, 101–103]. Various approaches have been attempted to limit such degradation processes. Common is to use encapsulation approaches, including copolymer micellar shielding [67, 69, 104], core-shell formation [68, 104], polymer co-precipitation [105], solid polymer composite formation [83, 106–108], incorporation into metal-organic frameworks (MOFs) [109], or in-situ stabilization in mesoporous templates [110]. Another approach is through substitution of suitable ions which stabilize the cage symmetry of optically active perovskites [6, 111, 112]. Importantly, the substitution of ions also induces changes in the emission and absorption spectrum of the parent composition, resulting in a tunable band gap by tailoring of the ionic composition [113]. Substitution of halides in particular can be leveraged to tune the emission maxima of the perovskite between $400 \leq \lambda \leq 800$ nm [114–116]. Therefore, halide substitution offers the best avenue for improving the stability of ABX₃ perovskites, while simultaneously allowing bandgap tunability.

Phase purity or achieving a desired composition can be complicated, however, by incomplete substitution and lack of control over the formation of the final product. All such substitution attempts either involve the addition of a third or forth precursor in precise stoichiometric amounts or require extra steps after perovskite formation to incorporate the desired halides in the already formed perovskite. It can be difficult to achieve and maintain the desired synthesis, due the very fast reaction kinetics of perovskite formation [25, 31, 117]. Chauhan et al. monitored the absorption and emission spectra during the formation of MAPbI₃ during a two-step synthesis process, where they concluded that it took only 14 seconds (including the deposition time) for the precursors to form the final perovskite product [118]. The fast reaction kinetics using conventional approaches do not typically allow for the introduction of additional ions once the reaction is started, making the precise tuning of composition very challenging. Fast halide reaction kinetics inside the perovskite cage and its phase instability leads to an inclusion even in the absence of a parent halide source. Nedelcu et al. demonstrated that for the first 30 seconds of mixing pre-fabricated cesium lead iodide $(CsPbI_3)$ and cesium lead bromide $(CsPbBr_3)$, two distinct peaks (one for iodide based perovskite and one for bromide based perovskite) were visible; however, with further mixing, both the peaks merged into a single peak, resulting in the formation a stable single mixed phase perovskite [103].

These issues are exacerbated for nanoparticle systems, where the large surface area to volume ratio often leads to high phase instability. However, perovskite nanostructures are highly desirable because of their high photoluminescence quantum yield at room temperature, approaching almost 100% [119]; easy optical tunability [120]; long photoluminescence lifetime [121]; and a high tolerance for defects [7].

In this work, we have successfully controlled the reaction kinetics and slowed down the rate of perovskite formation using diblock copolymer reverse micelle templating (RMD). The slowed reaction allows the use of an unconventional approach, mixing methylammonium iodide (MAI) and lead bromide (PbBr₂) to produce pure methylammonium lead bromide MAPbBr₃ nanoparticles. This anionic exchange was done without the engagement of any catalysts and at room temperature. This synthesis route also allows for the simultaneous formation of stable and luminescent MAPbI₃-dominant and MAPbBr₃-dominant nanoparticles coexisting within a single solution. As our nanoparticles are fabricated within the core of diblock copolymer micelles, they are shielded by the hydrophobic PS branch of the amphiphilic diblock copolymer which forms the corona of the micelles. Phase degradation is therefore prevented by the micelle, allowing for tuning of the relative abundance of each nanoparticle within the solution. The presence of both iodine and bromine lead to a more stable, non-degradable perovskite phase because the most suitable anion occupies the available positions within the perovskite cage, limiting mixed phase formation. The NPs are also sheltered from the external atmosphere (oxygen and humidity), owing to the shielding offered by the hydrophobic corona. These give rise to interesting properties for the nanoparticles such as a large Stokes shift, resulting from self-trapped exciton state (STE) formation due to co-existence of two halide ions. By tuning the emission characteristics, the nanoparticles synthesized from the same precursors with slightly different deposition conditions can be effectively used to down-convert UV light into useable photons, enhancing the device performance of organic bulk heterojunction solar cells based on both poly(3-hexylthiophene) (P3HT) and poly [[4,8-bis](2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7) bulk heterojunction blends with [6,6]-phenyl C61-butyric acid methylester (PCBM) as active layers, even though they have different absorption regions.

2.2 Results and discussion

Using diblock copolymer templates, we have been able to produce various perovskite nanoparticles using a two-step RMD process [67]. Iodine based perovskite synthesis was relatively straightforward utilizing MAI and PbI₂ loaded sequentially to obtain uniform, well-dispersed MAPbI₃ nanoparticles, from PS-b-P2VP nanoreactors. Infiltration of MAI was found to stabilize the micelle, preventing the destructive interaction of Pb based precursors [67], as shown schematically in **Figure** 2.1(a). **Figure** 2.1(b) shows the photoluminescence PL emission spectrum with inset AFM micrograph from well dispersed $MAPbI_3$ nanoparticles, fabricated using the two step loading process. However, MABr did not produce the same stabilizing effect, and upon adding PbBr₂, no nanoparticles could be obtained as can be seen from **Figure** 2.1(c). Attempts at imaging micelles after addition of both precursors (MABr and $PbBr_2$) revealed non-micellar structures, similar to the structures observed when the lead precursor was added first to the micelle solution. This suggests that the organic ion failed to infiltrate the core; as a result the micelle core was not stabilized and unraveled on the introduction of the lead salt due to the strong affinity between Pb and 2VP units [67].

Typically for NP synthesis and size control, high molecular weight polymers are chosen that form dense-core micelles, where the corona offers tight shielding against the environment [83, 122, 123]. Using lower molecular weight polymers results in the formation of a larger ballooning micelle structure with a looser corona of shorter PS chains, allowing easier infiltration of precursor salts [122] (see supporting information SI-1). However, the downside of such a micellar structure is lowered protection from hydration, as proven by Arbi et al. in the case of different iron oxide phases using different PS-b-P2VP diblock copolymer micelles [122]. The failure of MABr loading in the higher molecular weight PS-b-P2VP micelles result from its failure to infiltrate the densely packed polystyrene brushes in the corona. Using lower molecular weight polymers led to successful synthesis of MAPbBr₃ nanoparticles from MABr and PbBr₂ precursors; however, it also resulted in an uneven size and spatial distribution, as can be seen in **Figure** 2.1(d).



Figure 2.1: (a) Schematic of direct synthesis of $MAPbI_3/MAPbBr_3$ nanoparticles using reverse micelle nanoreactor process. Numbers refer to the order of precursor addition, with the organic cation added 24 hr prior to the halide. If there is no organic cation inside the micelle, the addition of the lead halide leads to micelle destruction and no nanoparticles are formed. Dense crewcut micelles with high molecular weight polymers result in individual nanoparticles, large balloon type micelles with low molecular weight polymers result in multiple particles forming inside the nanoreactor. (b) PL emission spectrum and AFM image of $MAPbI_3$ nanoparticles synthesized with conventional precursors (MAI and PbI), (c) AFM image of unsuccessful attempt to synthesize $MAPbBr_3$ in dense core high molecular weight micelles using direct synthesis route with conventional precursors (d) MAPbBr₃ nanoparticles with wide size distribution obtained using conventional precursors (MABr and PbBr₂) in balloon-like lower molecular weight micelles (e) PL emission spectrum showing a bathochromic shift in pre-synthesized MAPbI₃ nanoparticles after the addition of PbBr and MABr to the micelle solution. (f) PL emission and UV-Vis absorption spectra of MAPbBr₃ nanoparticles synthesized by unconventional route using MAI and PbBr₂ after 24 hours of stirring at room temperature, inset AFM image shows the well ordered nanoparticle formation. The density cloud (FFT) of the nanoparticle dispersion shows strong hexagonal packing of the nanoparticles. (g) XRD spectrum of MAPbBr₃ nanoparticles synthesized with unconventional precursors.

Anionic substitution by adding bromide compounds to iodine based perovskites has been previously successfully shown to convert perovskites from one phase to another [103, 124–128]. Therefore, we added MABr and PbBr individually to presynthesized MAPbI₃ nanoparticles solutions. After 24 hr stirring time, a slight hypsochromic shift was observed in the emission spectra of the solution, which can be seen in **Figure 2.1**(e). Both the spectra were blue shifted compared to pristine MAPbI₃ spectrum, with a maxima at 735 nm for MABr addition and at 714 nm for PbBr₂ addition. There was also a broad shoulder artifact with a peak around 550nm, suggesting formation of some MAPbBr₃. This suggests that only fractional anionic substitution occurred inducing a slight blue shift, not forming pristine MAPbBr₃ nanoparticles, even though the solutions were left to stir for times substantially longer than the complete conversion times observed by others [103, 128]. Complete substitution is inhibited both by the micellar shielding and by the covalent character of iodine, which is more than that of bromine; therefore, once a stable MAPbI₃ nanoparticle is formed inside a nanoreactor, all the iodine cannot be replaced fully by halide substitution.

As MAI has been shown to stabilize the PS-P-2VP nanoreactors, and as quaternization with iodine is known to encourage salt interaction with diblock copolymers [129,130], an unconventional route using mixed precursors MAI and PbBr₂ were used to synthesize MAPbBr₃ nanoparticles, as shown in **Figure** 2.1(f). PL-emission and UV absorption spectrum of the nanoparticles confirm formation of MAPbBr₃, with an emission peak at 521nm (FWHM of 30.03nm), and a bandgap of 2.28nm, from a Tauc analysis of the absorption spectra (see supporting information Figure SI-3, green spectrum). The inset shows an AFM micrograph of the dispersion of the synthesized nanoparticles with polydispersity index for the nanoparticle diameters of 0.096 (i.e. i10% variation in size), nearest neighbour distance of roughly 78nm and a quasi-hexagonal array with lattice distortion [131] of only 8.56 (see supporting information Figure SI-4 for full spatial statistics). XRD results, shown in Figure 2.1(g), further confirms the formation of MAPbBr₃. Peaks at 2θ of 17.4, 24.7. 31.4, 35.3, 39.65, 43.62, 50.8, and 54.1correspond to reflection planes 100, 110, 111, 200, 210, 211, 220, and 300 of MAPbBr₃. The XRD results confirm the space group of Pm-3m and cubic symmetry of nanoparticles with lattice parameter of 5.89Å [132]. Inset of Figure 2.1(g) also displays HRTEM images of the formed MAPbBr₃ nanoparticles. The nanoparticles were resolved to be approximately 6.1 nm.

The significant benefit of the reverse micelle route is the ability of the iodide salt to penetrate the dense-core micelles, owing to the strong interaction between the P2VP group of the micelles and the iodide ion. Iodine is well-known for preferentially staining pyridine over polystyrene, and has been utilized to improve contrast in electron microscopy of the diblock copolymer [133]. The addition of the iodide stabilizes the core by quaternization with the P2VP group of the diblock copolymer, while leaving it unchanged in the presence of a more reactive ion [134]. The infiltration of the iodine and the quaternization of the P2VP block of the diblock copolymer seems to trigger a rearrangement of the PS chains in the corona, allowing for a more feasible entry for the second added precursor, PbBr₂.



Figure 2.2: Schematic diagram of $MAPbBr_3$ fabrication utilizing anionic exchange phenomenon with both iodide and bromide precursors

When Pb^{+2} and Br^- infiltrate into the core, they rearrange in the presence of MA^+ and a very stable and highly emissive MAPbBr₃ nanoparticle is formed encapsulated by the di-block copolymer. We also saw similar behaviour using other iodide precursors, such as formadinium iodide, showing the general applicability of the organometallic iodide stabilizing the core (see supporting information Figure SI-5). The schematic of MAPbBr₃ creation inside the dense core diblock copolymer is shown in Figure 2.2, which also illustrates the unraveling of the nanoreactor by the Pb precursor alone. Interestingly despite the presence of both iodide and bromide ions, pure MAPbBr₃ nanoparticles were formed. There are two main justifications for
this preferential formation. On the one hand, the formation rate constant and stability constant for iodine-pyridine complexes is higher than that of bromine-pyridine complexes [134, 135]. Therefore, once complexated, it would not be easy to replace iodine with bromine due to the overlap of the π * orbital of I₂ with the pyridine LUMO [134]. This suggests that the iodine would remain complexated to the polymer preferentially over the bromine, leaving the bromine free to form the perovskite. On the other hand, the formation of MAPbBr₃ in the presence of both I⁻ and Br⁻ ions can also be justified in terms of the Gibbs free energy of formation of MAPbBr₃ and MAPbI₃. The calculated and extracted Gibbs free energy of MAPbBr₃ reported by different researchers, (-12.5, -3.5, and -17.0 kJ.mol⁻¹) from MAX and PbX₂ is always lower than that for MAPbI₃ (-11.3, 22.8 and -7.2 kJ.mol⁻¹) which thermodynamically validates the preferential formation of MAPbBr₃ in such a situation [136–138]. Yet, pure phase formation is typically not observed with mixed precursors due to the extremely fast reaction kinetics during perovskite formation, instead resulting in mixed phases.

It is well understood that metal halide hybrid perovskites form quickly once the precursors are mixed together [139–144]. Chauhan et al. saw final perovskite formation within 14 seconds of adding the precursors [118]; Nedelcu et al. showed that mixed phases form after only 30 seconds [103]. Such fast reaction kinetics using conventional approaches do not allow for the introduction of additional ions once the reaction is started. To examine the mechanisms of this reaction in the presence of the micelles, PL emission spectroscopy as a function of time was performed and tracked over 24 hr after the addition of precursors to observe the kinetics of this unconventional approach. The formation of MAPbBr₃ nanoparticles with stirring time can

be observed from Figure 2.3(a), with increasing PL intensity with time of stirring. After 2 min, we can observe conversion of the organic salt into MAPbBr₃ with sharp emission at 532 nm starting to emerge. This emission continues to sharpen with time, becoming more and more intense, and becoming clearly visible as a sharp peak approximately 10 min after the addition of the second precursor. A slight red shift in emission suggests that the particles are also starting to grow in size over a short time. The emission from unreacted MAI forming the background extending to beyond 750nm is still visible after 20 min reaction time. The intensity of the emission peak steadily increases until a maximum was reached after stirring for 24 hr, with no visible background emission and no further change observed. There is a slight blue shift to 526nm after this stirring time, potentially suggesting that there maybe a mixture of I/Br in the initially formed crystals, but they become more bromine dominant (more MAPbBr₃ like) after prolonged stirring.



Figure 2.3: (a) PL of MAPbBr₃ nanoparticles formation through unconventional anionic exchange route with MAI and PbBr₂ as a function of time. (b) PL emission spectrum of MAI and PbBr₂, mixed in o-xylene as a function of time (c) PL emission spectrum of MAPBbr₃ nanoparticles fabricated using LARP synthesis route with conventional precursors (MAI and PbBr₂) (Green) and unconventional precursors (Maroon)) (d) PL emission spectra of nanoparticles after (green line) and before (black line) interaction with water.

The micellar environment is critical to the formation of these nanoparticles, providing a stabilized environment for the reaction. To verify how MAI and PbBr₂ interact in the absence of the nanoreactors, both the precursors were added to o-xylene directly in the same concentration as that added to the reverse micelle solution in o-xylene. As soon as the second precursor was added (in milliseconds), a very broad peak of MAPbI₃ appeared and the spectrum maxima kept shifting within a range of 20 to 25 nm, as shown in **Figure** 2.3(b). There was also significant crystallization and visible precipitation of the precursors immediately, and when the supernatant solution was characterized after 4 hr, no emission spectrum could be observed. This illustrates the instability of the produced perovskite phase in the presence of o-xylene and bromide ions without reverse micelles, where fast reaction kinetics prevent the formation of MAPbBr₃.

This was further compared to a standard method of nanoparticle growth, ligandassisted re-precipitation (LARP), using oleic acid and oleylamine. Unlike MABr and PbBr₂, which resulted in bright and luminescent nanoparticle films as shown in **Figure** 2.3(c) (green spectrum), MAI and PbBr₂ showed almost no emission (**Figure** 2.3(c) (Maroon spectrum)). The inset optical micrographs show the contrast between centrifugally cast samples of LARP-MAI+PbBr₂ and MABr+PbBr₂ under UV illumination. Unlike the reverse micelle templating approach, where the micelles provide a shielded nanoreactor for uniform and luminescent MAPbBr₃ nanoparticles, in LARP, the ligands typically rapidly detach and reattach as precursor molecules encounter the forming crystal, resulting in inhomogenous elongated crystals rather than true 0D nanoparticles [97, 117, 145, 146]. The slower reaction kinetics from reverse micelle templating and the interaction of the iodine with the P2VP in the micelle core allows the formation of the thermodynamically stable MAPBr₃ dominated nanoparticles which were suppressed in the fast reaction kinetics of ligand assisted approaches.

The stabilizing environment provided by the micelle also enhances the stability of the nanoparticles with exposure to other precursors or to humidity. To verify the stability of our synthesized nanoparticles in solution, we added PbI_2 to the centrifuged solution of FAPbBr₃ nanoparticles produced from FAI and PbBr₂, and stirred them for 24 hr (see supporting information Figure SI-5). No shift was noticed in the emission spectrum suggesting that no anionic substitution occurs with additional precursor, making the nanoparticles more stable than conventional nanoparticles where reversible mixed phases are formed [7, 116, 126, 147].

Micellar environments are also known to increase the stability of perovskite nanoparticles in the ambient environment [67, 68, 104, 148]. We also confirmed the stability of our produced nanoparticles in the presence of moisture by letting a spin-coated sample float over water in 100% humidity for 4 hr, followed by immersion in water for 10 min. The PL emission spectra before and after water immersion can be seen from **Figure** 2.3(d). A slight change in the intensity of the PL emission spectrum was noticed, which could be attributed to characterization of two different spots for the pre and post-treated sample. Strong emission despite the interaction of nanoparticles with water validates that the micelle not only protects the nanoparticles from the ambient atmosphere but also protects them from direct water interaction.

We can take advantage of the slower kinetics involved in this synthesis approach, as well as the presence of both bromine and iodine, to engineer the nanoparticle solution by controlling different factors throughout the synthesis process, such as the infiltration time, amount of precursors or number of nanoreactors to achieve various novel phases.

First, we increased the concentration of nanoreactors by increasing the amount of PS-b-P2VP diblock copolymer dissolved in the solvent by a factor of 4, to 12 g/L. This has been known to increase the density of particles as well as decrease the size and spacing of particles [149]. As the concentration increases, residual solvent is

excluded and the structure is more compact. To maintain the salt to P2VP ratio, we increased the amount of precursor to 10 μ l of MAI and PbBr₂ to account for the increasing diblock copolymer blocks per unit volume. The loading was then performed, with a 24 hour loading time between precursor additions. By varying the polymer concentration and the precursor amount, a different PL emission spectrum emerged dominated by MAPbBr₃, as expected, but with some intensity suggestive of MAPbI₃ centred at 725nm, as shown in **Figure** 2.4(a) (brown spectrum). The Tauc plot derived from the UV absorption data ((see supporting information Figure SI-3, brown spectrum), indicates a slight decrease in the band gap of the bromide dominant nanoparticles. As expected with an increased concentration of reverse micelle nanoreactors, the particles have a 3x higher density, with nearest neighbour distance decreasing to 27.7nm ((see supporting information Figure SI-4, (b)). There is also the emergence of some smaller particles, of an average size of around 4.7 ± 0.9 nm; however, most of the particles have a size of 8.0 ± 1.4 nm. A slight hypsochromic shift from 521 nm for pure MAPbBr₃ phase to 518 nm is observed in **Figure** 2.4(a) (brown spectrum) for the higher polymer concentration samples, which might be attributed to the change of size of the nanoparticles due to the increased density of the nanoreactors [150]. Note also that the iodide dominant emission peak was broad (FWHM of 73.12 nm) compared to pure $MAPbI_3$ (FWHM of 50.9 nm) formation without PbBr₂; possible reasons could also be a difference in nanoparticle sizes, with some smaller particles emerging or the existence of mixed-halide structures causing a blue-shift in the MAPbI₃ emission [151, 152].

The formation of both iodide and bromide perovskite simultaneously suggests an uneven loading of the iodide ion into the micelles after 24hr for this larger amount of available nanoreactors. Cores where an excess of iodide was loaded resulted in $MAPbI_3$ -dominant particles while those with a scarcity of iodide led to $MAPbBr_3$ -dominant particles upon the introduction of the second precursor.

Therefore, we increased the infiltration time by a factor of 3 before the addition of the second precursor to allow for maximum loading of MAI to the core. Previously, we had established that infiltration can be quantified by an increasing Young's modulus as measured by quantitative nanomechanical mapping (QNM) across the micelle core compared to an unloaded nanoreactor [67, 153]. As shown in supporting information Figure SI-6, the infiltration increases with stirring time and plateaus after 50 hr. This plateau is thought to be due to the maximum salt infiltration and interaction with the polymer [153]. To ensure maximum infiltration, the second precursor $PbBr_2$, slightly in excess of the MAI, was added after 72 hr stirring. As can be seen from the PL emission spectrum in **Figure** 2.4(a) (red spectrum), the MAPbI₃ emission peak dominates the spectrum. The MAPbBr₃ emission is almost not visible, with a broad enhancement observed between 470 and 540 nm. This spectra is similar to that observed in **Figure** 2.1(e) for conversion of fully formed MAPI with Br salt addition (see supporting information Figure SI-7). This suggests a higher number of $MAPbI_3$ (iodide dominant) nanoparticles and a lower number of $MAPbBr_3$ (bromide dominant) nanoparticles were synthesized, or that formed MAPbI₃ were incompletely substituted with Br. This is likely due to an excess of iodide ions in the core, from the longer loading time beyond the maximum infiltration. Due to the very strong affinity between Pb and N in 2VP (0.17eV) [69], lead (Pb) would be expected to infiltrate first, followed by the infiltration of Br^{-} . In the excess of iodide, potentially free iodine is available in the core, not interacting with the polymer, resulting in the preferential formation of MAPbI₃ with respect to MAPbBr₃. As also seen in **Figure** 2.1(e) for conventionally produced MAPbI₃, once a stable MAPbI₃ nanoparticle is formed inside a nanoreactor, all the iodine cannot be replaced fully by halide substitution.

The loading results suggests that with a lower concentration of MAI, and shorter loading times, a scarcity of iodide ions in the core result in a MAPbBr₃-dominant perovskite cage. The MAPbBr₃ nanoparticles formed using the unconventional route are not halide-substituted MAPbI₃; they seem to be formed through the infiltration of Br^- ions which occupy the halide sites, causing perovskite (MAPbBr₃) formation, and stabilizing the symmetry of the perovskite cage. Subsequently, by changing parameters that affects the amount of iodide in the core, we can synthesize stable iodide or bromide dominant solutions.

The presence of both iodide and bromide dominant nanoparticles in a single solution showcases the phase stability and shielding effect resulting from the use of micelle templates. Neither nanoparticle degrades into an intermediate phase, unlike that observed for ligand assisted systems [103]. Interestingly due to the mixture of phases in the nanoparticles, our dual phase system shows an extremely large Stokes shift, with over 150nm gap between the emission and absorption spectra.

In general, the Stokes shift is a spectral difference between the maximum peaks of absorption and emission spectra in the same transition. In some materials such as semiconductor quantum dots (QDs) [154] and perovskites [103], it is hard to determine the maximum absorption peak in the UV-Vis spectra. In addition, for broad absorption such as observed for perovskites generally, the possibility of self-absorption



Figure 2.4: (a) UV-Vis absorption and PL emission spectrum of solutions for MAPbBr₃ with 24 hr infiltration of MAI before addition of PbBr, and 3g/L diblock copolymer micelle concentration (green spectrum), dual phase emission from a mixture of particles with 24 hr infiltration and 12g/L micelle concentration (brown spectrum), dominant red emission after 72 hr infiltration of MAI, with 12g/L micelle concentration (red spectrum). Note the large Stokes shift for the iodide dominated solution. (b) Schematic of self-trapped exciton state (STE) formation due to co-existence of two halide ions. J-V characteristics of organic photovoltaic devices under a high-intensity UV light source. (c) P3HT:PCBM and (d) PTB7:PCBM organic solar cell before (black) and after (red) addition of **bromine** dominant nanoparticles (emission maxima at 505 nm). (e) P3HT:PCBM and (f) PTB7:PCBM organic solar cell before (black) and after (red) addition of **iodine** dominant nanoparticles (emission maxima at 706 nm). Each J-V image includes a reference performance without perovskites nanoparticles and the best performance of devices with perovskite NPs. Note that the device performance under the UV light has not been optimized.

is high, and the pure absorption of a downconverter could be low even the universal Stokes shift is high. In this case, using the generalized concept of Stokes shift can result in an error in determining the validity of the downconverter. Thus, it is common to use the gap from the absorption edge to the highest peak of the photoluminescent region as the definition of the Stokes shift, as a criterion to judge whether the downconverter would be efficient taking into account the pure absorption of the downconverter [103, 154, 155].

In our case, the dual phase solution in which MAI was allowed for maximum infiltration followed by PbBr₂, the Stokes shift is caused by the formation of mixed halide octahedrons due to both iodide and bromide incorporation. Merging of both iodide and bromide creates self-trapped exciton state (STE) [156, 157], which is an established mechanism for Stokes shifts in 0-dimensional (0D) perovskites. STE refers to trapped bound exciton that acts as a polaron due to photoexcitation in an altered lattice because of the presence of mixed halides [158]. Once this low energy state is developed because with multiple halides, the electrons are first excited to the high energy excited state and consequently, shifted to the lower excited energy state [159, 160, resulting in broad emission with a large Stokes shift. This is exactly the case shown in Figure 2.4(a) where the red spectrum has a broad emission (FWHM of 73.12 nm) far from the absorption edge. A schematic diagram of the band splitting indicating the states is shown in Figure 2.4(b). This STE mechanism is also supported by the slight bathochromic shift in the absorption spectrum edge, which is slightly red-shifted ($\Delta \lambda = 35$ nm) compared to the absorption edge of pure MAPbBr₃ and blue-shifted ($\Delta \lambda = -175 \text{ nm}$) compared to that of pure MAPbI₃ with a bandgap of 2.14 eV, (see supporting information Figure SI-3, (red spectrum) for the Tauc plot). This behaviour was also observed for the emission maximas, which was higher than pure MAPbBr₃ but lower than pure MAPbI₃, displayed in **Figure** 2.4(a) (red spectrum). As shown schematically in **Figure** 2.4(b), a small amount of energy is released when the excited electron is shifted from a higher energy excited state to a lower energy state followed by a transition to the ground state, due to mixed halide octahedrons, generating the observed Stokes shift.

Using this principle of establishing the Stokes shift from the absorption edge to the highest emission peak, the synthesized nanoparticles were used for down-conversion and UV filtering in organic bulk heterojunction solar cells. Though there has been some interest in using metal halide perovskites for down-conversion [161, 162], typically perovskites have a small Stokes shift compared with other common downconversion materials such as organic dyes [163]. This typically results in significant parasitic absorption (PA) by the perovskite down converter material. In such a case, device performance may actually decrease as the emitted visible light could be absorbed by the down conversion materials before going into and being used in the active layer [155]. As a rule of thumb, a Stokes shift of above 100 nm is required for increased performance and zero re-absorption by downconverters. As we observed a Stokes shift of 150nm with the iodine dominant nanoparticle system, we believed this system could be a suitable downconverter. To show the efficacy of the nanoparticles, different active materials were used to match the absorption of the device with the emission of the nanoparticles. P3HT:PCBM shows an absorbance region between 350 and 620 nm [164] with optimal absorption (as defined by the highest absorption coefficient or the highest measured external quantum efficiency as shown in **supporting** information table SI-3) between 500-620 nm would be expected to show enhancement with bromine dominant (green emitting) nanoparticles under UV illumination, but none with the iodine dominant (red emitting) nanoparticles. PTB7:PCBM, with optimal absorbance between 600 and 700 nm [165], on the other hand should be enhanced with the iodine dominant (red emitting) nanoparticles. As seen in **Figure** 2.4(c)-(f), this was the behaviour observed for OPVs under UV illumination conditions. Figure 2.4(c) shows the current density-voltage characterization curves of the P3HT:PCBM device under UV illumination. The black and red curve shows the results before and after the deposition of green emitting nanoparticles (brown curve in Figure 2.4(c)) respectively. The increase in short circuit current indicates that the bromide dominant ($\lambda_{\text{major emission}} = 508 \text{ nm}$) nanoparticles acted as downconverters for P3HT:PCBM devices. The same dual phase solution when used with PTB7:PCBM showed only a minor increase in the short circuit current. This improvement could be attributed to the presence of some red emission ($\lambda_{\text{minor emission}} = 704 \text{ nm}$), which can be seen in the emission spectrum as well, or due to the weaker absorption of PTB7 around 500nm (see supporting information Table SI-3). The improvement can be seen in **Figure** 2.4(d), which is negligible when compared to the P3HT:PCBM device with the same nanoparticles.

For the iodine dominant red-emitting dual-phase nanoparticles ($\lambda_{\text{major emission}} = 710 \text{ nm}$, $\lambda_{\text{minor emission}} = 515 \text{ nm}$), the P3HT:PCBM device showed no obvious changes in the J-V characteristics (as shown in **Figure** 2.4(e)), demonstrating that there was no significant down-conversion observed. This is likely a result of the absorption region of the device (350nm to 620nm) not overlapping with the major emission wavelength of the red emitters (\sim 700nm). On the other hand, when the same redemitting nanoparticles were applied to the PTB7:PCBM device, a huge increase in the short circuit was observed. This confirms that the red-emitting solution absorbs in the UV region and emits mainly in the red wavelengths, making them excellent candidates as active UV filters. The drastic difference between the improved short circuit current shown in **Figure** 2.4(f) for PTB7 devices with the red emitting particles compared to the more limited improvement for P3HT with the green emitting particles also confirms the extremely large Stokes shift in the case of the red particles. In the green emitting particles, where there is a negligible Stokes shift, parasitic absorption might be limiting the efficiency of the down-conversion. Our dual phase red emitting system generates one of the largest Stokes shifts so far reported for a perovskite system, making them excellent candidates for down-conversion for UV sensitive materials.

2.3 Conclusion

By taking advantage of the slower reaction kinetics resulting from the use of diblock copolymer micelles, we have used an unconventional approach i.e. mixing MAI and PbBr₂ to produce monodispersed, uniform, stable, and highly luminescent MAPbBr₃ nanoparticles, as well as co-emitting solutions made up of both MAPbBr₃ and MAPbI₃ simultaneously. The unconventionally formed MAPbBr₃ nanoparticles are not halide-substituted MAPbI₃; they are formed through the infiltration of Br⁻ ions which then occupy the halide sites, stabilizing the symmetry of the perovskite cage. Varying the concentration of iodine, by increasing infiltration time, amount of precursors and concentration of nanoreactors in the presence of both iodine and bromine ions, we were also able to synthesize both perovskite nanoparticles in a single solution with different concentrations of MAPbI₃ dominant and MAPbBr₃ dominant nanoparticles. It was even possible to extend this to other A site organic cations, such as FAI, to form FAPbBr₃ and FAPBI₃ mixtures and pure phases. The micelle environment provided shielding for the perovskite leading to phase stability, allowing the coexistence of multiple simultaneously emitting perovskite phases, in addition to providing environmental stability. The presence of both bromine and iodine dominant particles resulted in the emergence of a large Stokes shift for the dual phase systems due to self-trapped exciton formation. This allowed such particles to be used as efficient down-converters for OPVs without significant reabsorption. Down-conversion for both P3HT:PCBM and PTB7:PCBM bulk heterojunction devices were obtained from the same precursors purely by changing the synthesis conditions during nanoparticle formation. Exploiting the phase stabilizing effect of the micelles, the reaction kinectics of perovskite formation can be tuned to allow for the various halide substitutions, opening up new avenues for co-existing perovskite phases for photovoltaic and light emitting applications.

2.4 Experimental

Perovskites precursor solution preparation

0.5M precursor solutions were made by adding organic salts (methylammonium iodide (MAI), formadinium iodide (FAI), methylammonium bromide), Sigma-Aldrich) to isopropanol (IPA) (Caledon, reagent grade) and the inorganic salts (lead(II) iodide (PbI₂, Alfa Aesar, 99.9985%) and lead(II) bromide (PbBr₂, Sigma-Aldrich 99.99%)) to N,N-dimethylformamide (DMF) (Sigma Aldrich, 99.8%).

Nanoparticles Synthesis

Reverse micelles were prepared by dissolving poly(styrene-b-2-vinyl pyridine) di-block copolymers (Polymer Source) (Molecular weight 75.0-b-66.5, or 28.0-b-36.0 kDa), in reagent grade non-polar solvent o-xylene, with concentration of 3 g/L under continuous stirring. For some experiments the polymer to solvent ratio was changed to 12 g/L. After confirmation of reverse micelles formation by atomic force microscopy (AFM), precursor salts and reactants were added to the reverse micelles solutions, with a time interval of 24 hr to allow thorough infiltration of each precursor. Pure methylammonium lead bromide $(MAPbBr_3)$ was formed by mixing 0.5M precursor solutions of MAI in IPA and PbBr₂ in DMF sequentially in the micelle solution. To obtain mixed MAPbI₃/MAPbBr₃ phases, conditions and parameters were changed slightly. For a mixed phase solution with more $MAPbBr_3$ and less $MAPbI_3$, 12 g/L of the diblock co-polymer was dissolved in o-xylene. After the formation of the nanoreactors 10 μ l of MAI was added to the solution to penetrate into the core of the nanoreactor, followed by the addition of 10 μ l of PbBr₂. For a solution with more MAPbI₃ and less MAPbBr₃, 10 μ l of MAI in IPA was added to the 12 g/L reverse micelle solution and was left to stir for 72 hr to allow maximum infiltration, followed by the addition of PbBr₂. The final loaded reverse micelles solutions were centrifuged to clear out the unloaded excess salt and stirred further to prevent coagulation. 4 μ l of solution was spin coated on silicon (1x1) cm slab for AFM characterization.

For LARP synthesis, 12.5 mg (0.034 mmol, 1 equiv.) of $PbBr_2$ was weighed into a vial to which 6.0 mg (0.37 mmol, 1.1 equiv.) of MAI or MABr was added. Furthermore, oleic acid (0.320 mmol, 9.4 equiv.) along with oleylamine (0.027 mmol, 0.8 equiv.) were added to the vial. DMF was added to the mixture of precursors to reach 1.25mL. In order to precipitate the nanoparticles, 12.5 mL of previously dried toluene (molecular sieve, 3 Å) are cooled in an ice bath to approximately 5 while stirring, and 75 μ L from the mixed precursors vial was added to the chilled toluene, and stirred for 2 minutes. To deposit the synthesized nanoparticles on a substrate, a thoroughly cleaned glass slide (0.9x0.9 cm) was plasma treated and placed at the bottom of a centrifugation tube. The colloidal solution along with 37 mL EtOAc was gently added to the centrifugation tube, and centrifuged at 5000 rpm for 5 minutes, resulting in the deposition of the NPs on the glass slide. Using a Pasteur pipette, the supernatant was carefully removed, and the film was placed in a vial and dried under a toluene atmosphere. After the nanoparticle thin film dried, it is placed on a hot plate at 120. As soon as the colour change is visible (approximately 10 seconds), the film is removed and stored in a glass vial under ambient conditions.

Organic solar cell fabrication

The organic solar cells were based on a convention standard structure of ITO/PEDOT:PSS/bulk heterojunction/aluminum (Al). Active layers consisted of poly(3-hexylthiophene) (P3HT) or poly [[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7) blended with [6,6]phenyl C61-butyric acid methylester (PCBM).

The ITO substrates were cleaned by acetone and 2-propanol (IPA) for 15 min respectively in an ultrasonic cleaner to obtain a dust-free substrate and were etched for 5 min in oxygen plasma to remove residual chemicals. Then, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) mixed with 50% of IPA was spin-coated on ITO at 3000rpm for 30s and annealed at 150 for 10min in the glovebox (inert atmosphere). For PTB7:PCBM, 25mg/ml PTB7:PCBM (weight ratio: 1:1.5) in chlorobenzene was deposited on the top of PEDOT:PSS subsequently at 2000rpm for 30s before drying the substrate overnight. Regarding the P3HT:PCBM deposition, 15mg/ml P3HT:PCBM(weight ratio: 1:1) in chlorobenzene was used, following by substrate annealing at 120 for 10min. After that, Al electrodes were deposited by thermal evaporation with a mask to limit the active area in 0.06 cm² under low pressure of 10^{-6} mbar. The encapsulated device was post annealed at 150 for 10min in ambient environment to enhance the self-conjugation of the organic blend. To investigate the UV conversion of perovskite nanoparticles, a small amount of perovskite layered on the bottom of ITO-coated glass by spin coating at 2000rpm for 20s. The characterization of solar cells was under a UV light source with a strong intensity at around 395nm in ambient environment. Note that under UV illumination, the device with perovskite nanoparticles were removed before the device was measured again under the same illumination conditions.

Characterization

Atomic force microscopy (AFM) images were collected using an Asylum MFP-3D instrument (Oxford Instruments Asylum Research) in the alternating current (AC) mode under ambient environment. AFM probes (Nanotools, EBD-FMR) with spring constant of 2.8 N/m and resonant frequency at 75 kHz was engaged in tapping mode for topography scan. WSxM 5.0 was used for AFM image processing. All AFM samples were prepared by spin coating 4 μ l of solution at 2000 rpm for 45 seconds on (1x1) cm silicon slab.

PL measurements were performed using a 405 nm diode laser with laser power in the range of 11 mW (spot diameter 1-2mm). The sample emission is collected with a lens and guided to the detection unit with an optical fiber. A long-pass filter (550 nm) removes the excitation light before the collected radiation is fed into a monochromator (Andor, Shamrock 303i, grating 500 nm blaze, 150 lines/mm) and detected with an intensified charge-coupled device (Andor, iStar A-DH320T-18U-73). The sample was introduced to the laser with an exposure time of 0.0237 sec and a slit opening of 50 μ m. The detection range is from 500 to 900 nm. The measurement was taken in a darkened environment to prevent stray light.

UV-Vis spectra measurements were performed to characterize the optical properties of the materials using a Lambda 35 UV-Visible spectrometer (PerkinElmer). The samples were prepared at concentrations 0.1 mg/mL, using o-xylene as dispersant, measured in a 1x1 cm quartz cuvette.

2.5 Supporting information figures



Figure 2.5: (*SI-1*)Quantitative nanomechanical mapping of the polymer micelles showing simultaneously collected topography and the corresponding elastic modulus (a) AFM topography of the higher molecular weight micelles (b) AFM topography of the lower molecular micelles (c) Young's modulus micrograph of higher molecular weight micelles (d) Young's modulus micrograph of lower molecular micelles (e) Line profiles for the higher molecular micelles (f) Line profiles for the lower molecular micelles



Figure 2.6: (SI-2)Quantitative nanomechanical mapping of the polymer micelles showing simultaneously collected topography and the corresponding elastic modulus (a) AFM topography of the higher molecular weight micelles (b) AFM topography of the lower molecular micelles (c) Young's modulus micrograph of higher molecular weight micelles (d) Young's modulus micrograph of lower molecular micelles (e) Line profiles for the higher molecular micelles (f) Line profiles for the lower molecular micelles



Figure 2.7: (SI-3)Tauc plot of the UV-Vis absorption spectra data to extract the optical band gap for MAPbBr₃ nanoparticles with 24 hr infiltration of MAI before addition of PbBr, and 3g/L diblock copolymer micelle concentration (green spectrum), dual phase emission from a mixture of particles with 24 hr infiltration and 12g/L micelle concentration (brown spectrum), dominant red emission after 72 hr infiltration of MAI, with 12g/L micelle concentration (red spectrum).



Figure 2.8: (SI-4)AFM micrographs of perovskite nanoparticles formed within PS-b-P2VP micelles from (a) MAPbBr₃ with 24 hr infiltration of MAI before addition of PbBr, and 3g/L diblock copolymer micelle concentration (b) a mixture of particles with 24 hr infiltration and 12g/L micelle concentration, (c) dominant MAPbI₂ with 72 hr infiltration of MAI, with 12g/L micelle concentration (d, e, f) Pair correlation functions with the nearest fit hexatic lattice shown in grey. Nearest neighbour distances and the lattice disorder parameter [131] are given in the graph. (g, h, i) Voronoi tesselation of the particle distribution from AFM images arranged by color corresponding to deviation from the expected hexagonal lattice Voronoi area, as shown in (j, k, l) the histogram of the number of Voronoi cells against the



Figure 2.9: (SI-5)FAPbBr₃ nanoparticles produced with unconventional route show no change in emission spectrum in presence of competing iodide ion from PbI₂, after 24hr stirring.



Figure 2.10: (*SI-6*)QNM characterization of loading of MAI into the nanoreactor core with respect to time, inset are the Young's modulus map of MAI loaded micelles at different times



Figure 2.11: (SI-7)Normalized PL emission spectrum showing a bathochromic shift in pre-synthesized MAPbI₃ nanoparticles after the addition of PbBr and MABr to the micelle solution, and with MAI + PbBr₂ with excess of MAI loading. All three show evidence of some conversion of iodide based perovskites into bromides, as well as some bromine doping.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

adpr202100372-sup-0001-SuppData-S1.pdf

Chapter 3

Anomalous behavior of pyrrolidinium perovskite nanoparticles induced by bromine substitutions; bathochromic shift with large Stokes shift

The findings of this study have been submitted to the "ACS Applied Nano Materials" journal.

Abstract

Using the reverse micelle synthesis route polystyrene-b-2vinylpyridine (PS-b-P2VP) diblock copolymers are used to synthesize hybrid perovskite nanoparticles with re-58 cently introduced organic 5-membered heterocycles of pyrrolidinium (C₄H₈NH). Uniform, well-dispersed, and highly luminescent nanoparticles were fabricated with high stability due to the presence of hydrophobic pyrrolidinium and polymer encapsulation. By substituting bromine for iodine, a bathochromic shift was observed, resulting in a Stokes shift of 660 meV (182 nm) for mixed halide phase nanoparticles rather than the hypsochromic shift expected with the bromine doping. This feature of pyrrolidiniumbased perovskites is uncommon, making it a viable candidate for down-conversion in low bandgap organic solar cells. With Py-based perovskites as down-conversion layers, extensive improvements were observed in the short circuit current of bulk heterojunction cells well matched to the nanoparticle emission spectrum.

3.1 Introduction

Since their emergence, hybrid organic-inorganic halide perovskites (MHP) have led to record-breaking achievements in photovoltaics [6,98], light-emitting diodes [17,19], lasers [7,166], and as down converters [23,24]. Among their interesting characteristics are their high optical absorption coefficients, [98,167] tunable bandgaps [117], defect tolerance [168], and long carrier lifetimes [169,170].

Perovskite nanoparticles have been reported to possess better photoluminescence (PL) properties than bulk perovskites and other quantum dot materials including high quantum yield, broad emission tunability, and the multi-dimensional structural flexibility with the same chemical formulae [17,171,172]. Most defects act as shallow trap states rather than non-radiative deep traps [168], yielding longer photoluminescence lifetimes and higher efficiency.

Significant progress has been made with compositional tuning with respect to efficiency, thermal stability, and band alignment [173], due to their compositional and structural flexibility. However, organic cation-based perovskites are typically unstable when exposed to moisture or oxygen [73, 174]. One approach to combat degradation is incorporating a large 5-membered heterocycle pyrrolidinium ring in place of the methylammonium ion [175, 176]. The larger hydrophobic ring has successfully stabilized single crystals in the presence of water for 4 months, [176] showing that bulk PyPbI₃ is stable compared to methylammonium and formamidinium-based perovskites.

However, MHPs are very sensitive to the A-site cation size, which can lead to reorganization of their cage structures. Due to their soft ionic nature, strain can occur when different cations are added, which can be used to engineer the band gap and cage stability [177, 178]. A compressive strain typically produces a red shift in absorbance and emission with a narrower band gap, while a tensile strain results in a blue-shift with a wider band gap [178]. Computationally the bandgap range of CsPbI₃ perovskite is shown to be tunable between 1.03 eV and 2.14 eV by adjusting the strain from -5% to 5% [179].

The optical properties of 0D perovskites are determined by their isolated metal halide octahedra, stemming from the lack of electronic coupling [180]. This generates broadband emission resulting in large Stokes shift in perovskites nanoparticles, [157, 181] which are not observed in the bulk [156]. Stokes shift in this context refers to a spectral difference between the emission and absorbance band maxima. Materials with a large Stokes shift, typically <100 nm, are good candidates for optical applications due to the decreased possibility of photon self-absorption [182, 183]. Stokes shift in MHPs have been attributed to either the nanoparticle size or the creation of self-trapped exciton states [156, 180, 184]. Already well known for colloidal quantum dots, [185] size dependent Stokes shifts in perovskites were observed by Brennan et al. [184] for 13 to 4 nm CsPbBr₃ nanoparticles showing Stokes shifts of 20 to 82 meV, respectively. Introducing mixed halides also changes the cage structure and lattice parameters, affecting the optical properties [186]. Using mixed halides (CsPbBr_xI_{1-x}), Zhao et al [187] reported larger Stokes shift compared to pure CsPbX₃ (X=I, Br). Meinardi et al. [188] reported that a Stokes shift of approximately 200nm could be achieved by doping 4% Mn²⁺, with the emission spectra broadened with a slightly red-shifted maxima [188].

Here, we have investigated the properties of pyrrolidinium (Py) based perovskite nanoparticles. We fabricated our nanoparticles by leveraging the properties of diblockcopolymer reverse micelles to achieve nanoparticle structures that were not possible in the bulk. Moreover, our nanoreactors slow down the reaction kinetics of nanoparticle formation, resulting in high uniformity and thermodynamically stable stoichiometry. In producing such nanoparticles, we have observed an anomalous bathochromic shift in emission with bromine doping resulting in a large Stokes shift. Taking advantage of the optical properties, we successfully incorporated Py-based perovskites as down converters for low bandgap organic solar cells, improving short circuit currents.

3.2 Results and discussion

Using PS-b-P2VP copolymer micelles templates, we previously developed a recipe for producing ordered MA and FA-based MHPs with a low polydispersity index (PDI) at room temperature [23, 67]. Micelle templated nanoparticles had better surface coverage and a longer photoluminescence lifetime than nanoparticles made by methods such as ligand-assisted synthesis [23, 178]. Due to the separate loading step, we are able to control the reaction kinetics allowing better tunability over doping or ionic substitution. Furthermore, in the presence of competing ions, a thermodynamically stable phase forms preferentially due to the slowed-down reaction kinetics [23]. We implemented this approach to produce pyrrolidinium based perovskite nanoparticles, as shown schematically in Figure 3.1(a).



Figure 3.1: (a) Schematic of the two step reverse micelle fabrication process of PyPbI₃ nanoparticles. Numbers refer to the order of precursor addition. (b) PL emission and UV-Vis absorption spectrum of PyPbI₃ nanoparticles showing a 250 meV Stokes shift (highlighted box). (c) XRD spectra of PS-b-P2VP encapsulated PyPbI₃ nanoparticles; inset displays a high resolution TEM image. (d) Predicted ideal hexagonal unit cell of bulk PyPbI₃.

The PL emission and absorption spectrum of the PyPbI₃ nanoparticles is shown

in Figure 3.1(b). The emission spectrum was broad with maxima at 540 nm, similar to that of bulk PyPbI₃. [176] The nanoparticles, however, had a blue shift in the absorption edge when compared to bulk, from 750 nm down to 500nm. This results in a change in the band gap from 1.8 eV in the bulk [176] to 2.4 eV for the nanoparticles. This shift could be the result of quantum confinement, as the particles were \sim 6nm in size, which should increase exciton binding energy through band splitting [10, 171]. As the absorption threshold undergoes a blue shift, with emission spectrum identical to the bulk, a larger Stokes shift is observed in the PyPbI₃ nanoparticles (with a large overlap in the emission and absorption characteristics). Previous studies have also observed more pronounced Stokes shift in 0D perovskites compared to bulk perovskites [23, 189].

The formation of a hexagonal crystal structure was verified by X-ray diffraction (XRD) (Figure 3.1(c)) of nanoparticles encapsulated in the PS-b-P2VP di-block copolymer. The inset shows a high resolution TEM image of a representative nanoparticle. The data revealed hexagonal perovskites phase with a = b = 9.3117 and c = 8.180nm lattice cell parameters, in good agreement with bulk measurements [175]. Peaks were also observed corresponding to the [005] and [105] planes of lead iodide, indicating the presence of un-reacted precursor.

Though the structure was consistent with the unit cell of $PyPbI_3$, extracted using Vesta software shown in Figure 3.1(d), the peak centers were shifted to higher values relative to the reference spectra, suggesting the development of compressive strain [177]. Using the Scherrer and Cauchy approximation [190, 191], the nanoparticles have a strain of -4.98% relative to a $PyPbI_3$ single crystal.



Figure 3.2: (a) Comparison of PL emission for Py-based perovskite nanoparticles and bulk produced from the same precursor solution. (b) PL emission and UV-Vis absorption spectrum of $PyPbBr_{3-x}I_x$ nanoparticles, highlighted box shows 660 meV Stokes shift. (c) Illustration of the indirect electronic band structure of Py-based nanoparticles, showing exciton self trapping states. (d) Tauc plots, derived from UV-Vis absorption data

Typically, strain relief in MHPs can be achieved by introducing a smaller anion, such as bromine, to the perovskite cage, which would result in relaxing the structure and altering the optical properties [192, 193]. To introduce bromine, $PbBr_2$ was added to PyI-loaded nanoreactors instead of PbI₂ during the two-step process. Energy dispersive spectroscopy (supplementary information Figure SI-1) confirms the presence of both iodine and bromine in the resulting nanoparticles. However, though the resultant XRD spectrum for the mixed-phase PyPbBr_{3-x}I_x again showed hexagonal phase formation (Figure SI-2), there was roughly twice the compressive strain observed compared to the pure PyPbI₃ nanoparticles. An induced strain of -11.3% with respect to bulk PyPbI₃ phase and -11.8% with respect to a theoretical bulk PyPbBr₃ structure was calculated using the Scherrer and Cauchy approximation. It is important to note that there has not yet been reported formation of pure PyPbBr₃ either as bulk or as nanoparticles.

The introduction of small ions into strained structures usually results in strain relaxation [178, 194], but we observed an increase in compressive strain for the mixed halide perovskites. We have similarly observed unusual phase formation in other MHPs produced using the reverse micelle templating approach. Hui et al. [67] showed the room temperature synthesis of the orthorhombic MAPbI₃ phase using reverse micelles synthesis, even though this is usually only observed at very low temperatures (around 160K) [195]. Likewise, FAPbI₃ does not form a perovskite phase at room temperature in the bulk, but was formed through reverse micelle templating [67]. Both the unusual phase formation and the strained nanoparticles likely results from the restricted environment provided by reverse micelle shielding. In reverse micelle synthesis, the nanoparticles are formed inside the core of the micelle, which exert an external pressure on the perovskite cage due to micelle shielding. Figure SI-3 (supplementary information) shows quantitative nanomechanical mapping (QNM) measurements of a mono-layer of empty and loaded micelles show an increasing Young's modulus with increased loading of the micelle core. Typically, when nanoparticle formation is complete inside the micelle, the Young's modulus plateaus at a value higher than that of the empty micelle [153]. The stretching of the reverse micelle caused by particle formation might result in induced strain in the perovskite cage. Induced strain has also been observed for other types of ligated [196, 197] and coreshell [198, 199] nanoparticles.

In fact, the formation of the PyPbBr_{3-x}I_x nanoparticles themselves are unusual, as these structures do not form in the bulk. A comparison of the emission spectrum between PyPbBr_{3-x}I_x and PyPbI₃ nanoparticles and bulk Py-based perovskites is shown in Figure 3.2 (a). Precursor solutions were added to o-xylene in order to precipitate bulk perovskites. The precipitates exhibited a broad emission spectrum resembling the spectrum of PyPbI₃ nanoparticles, but without a prominent emission maxima. We have observed similar ambiguous emissions from unreacted perovskite salts, which could also suggest that the precursors did not react fully. As the nanoparticle emission spectra differs significantly from the bulk emission, we can establish that the nanoreactors lead to the formation of nanophases that cannot be attained under ambient conditions without PS-b-P2VP reverse micelles.

In hybrid perovskites, strain can be used to for bandgap engineering [200] as induction and relaxation of strain will result in a slight change in ion positions and shortening of lattice parameters [201]. This was already observed for the PyPBI₃ nanoparticles, which showed a blue shift in absorption relative to the bulk perovskite phase. Figure 3.2(b) shows the PL emission and UV-Vis absorption of PyPbBr_{3-x}I_x. Even though bromine doping generally introduces a blue shift in absorption edges [19,172], the addition of bromine here results in a red-shift in the absorption spectrum. In addition, $PyPbBr_{3-x}I_x$ nanoparticles exhibited a strong red shift in the emission spectrum with maximum emission at 700 nm. Both phenomena were unusual since bromine doping typically causes a hypsochromic shift in both absorption and emission.

The anomalous optical behavior of Py-based perovskites is likely caused by strain induced by the confined shielding environment of the micellar nanoreactor, in combination with the size of the Py cation. In general, bromine dominant perovskites emit green, while iodine dominant perovskites are red or near-infrared emitters [10]. In contrast, the maximum emission of $PyPbI_3$ was observed at approximately 540 nm, whereas $PyPbBr_{3-x}I_x$ had a maximum emission at around 700 nm. Zhang et al. found that PyMnBr₃ perovskites have maximum emission at 640 nm, suggesting that perovskites with a larger Py cation differ from other MHPs. For PyMnBr₃, however, absorption edges appear at 620 nm, effectively nullifying any Stokes shift [202]. In the case of our mixed phase Py-based perovskites, we were able to achieve a Stokes shift of 660 meV, which is among the largest reported for MHP nanoparticles [171]. The PL properties of most 0D perovskites can be explained by their completely isolated metal halide octahedra or clusters, resulting from a lack of electronic coupling. As opposed to 3D perovskites, which typically show small Stokes shifts and narrow band emission, low-dimensional metal halide perovskites generally show broadband emission with large Stokes shifts, which we have also observed. As both particles had roughly the same size (~ 6 nm), this behaviour is more likely due to self-trapped exciton states (STEs) [181] than any size related effects. The term STE refers to excitons trapped in the excited state by transient local lattice deformations. This phenomenon can easily occur in perovskites with soft lattices and strong electronphonon couplings. STEs lead to broad below-band-gap emission bands, and many researchers have applied STEs models in order to explain the Stokes-shifted broadband emission of 0D perovskites [23, 157]. Figure 3.2(c) shows a schematic of STEs formation. This is also suggested by the Tauc plots of PyPbBr_{3-x}I_x and PyPbI₃ extracted from the absorption data shown in Figure 3.2(d). The Tauc plots shows a clear red shift in the absorption edge of mixed halide phase (PyPbBr_{3-x}I_x) due to strain manipulation. Furthermore, band alignment due to the incorporation of small ions lowers the trapped states, resulting in large Stokes shifts.

AFM images of synthesized PyPbI₃ and PyPbBr_{3-x}I_x nanoparticles after plasma etching to remove the polymer shell are shown in Figure 3.3 (a) and (b). The nanoparticles are uniform in size, dispersed evenly, and have almost equal spacing 39 nm (PyPBI₃) and 40.7 nm PyPbBr_{3-x}I_x between adjacent nanoparticles. Polydispersity index for the nanoparticle diameters are 0.0132 (PyPbI₃), and 0.0125 (PyPbBr_{3-x}I_x), in the range of monodispersity [203]. The quasi-hexagonal array only exhibits a lattice distortion of 2.1 PyPbI₃ for and 0.94 for PyPbBr_{3-x}I_x relative to a perfect hexagonal array, suggesting a high degree of order [131]. Such uniformity and control over the spacing can only be achieved due to the PS-b-P2VP nanoreactors. All of these characteristics are critical in optoelectronics as changes in size can result in changes in emission spectrum and refractive index. Figure 3.3 (b, c, e, f) shows the spatial statistics from Voronoi tessellation of particle positions, which are colored to show the deviation in cell area relative to a perfect hexagonal lattice of similar particle number density. In both cases, more than 70% of the Voronoi cells correspond to less than 10% deviation from hexagonal packing.


Figure 3.3: (a, d) AFM image of RMD PyPbI₃ and PyPbBr_{3-x}I_x nanoparticles. (b, e) Voronoi tessellation diagrams extracted from AFM images, displaying packing of the nanoparticles, color indicating deviation from ideal hexagonal packing. (c, f) Histogram of Voronoi cells volume deviation from hexagonal packing. (g, h) Current density-voltage characteristics of OPVs incorporating Py-based nanoparticles as downconverters under illumination.

As the Py-based nanoparticles exhibit large Stokes shifts, they could be used as

UV downconversion filters in organic solar cells to prevent device degradation and improve efficiency, absorbing UV light and re-emitting in the visible regime. To test this, we deposited a layer of $PyPbBr_{3-x}I_x$ and $PyPbI_3$ nanoparticles on organic solar cells using a PBTZT-stat-BDTT-8:PCBM bulk heterojunction absorber layer.

As evidenced by Figure 3.3 (g) and (h), the introduction of perovskite nanoparticles improved the performance of OPVs under high-intensity illumination. The presence of the PyPbI₃ and the PyPbBr_{3-x}I_x nanoparticles resulted in a 39.8% and 6.6% increase in J_{sc} , respectively (shown in Figure 3.3 (g) and (h)). As shown in Figure SI-4 (supplementary information), the emission spectrum of PyPbI₃ extends from 450 nm to 800 nm and the optimal absorption range of PBTZT-stat-BDTT-8:PCBM lies between 550 nm to 670 nm. Accordingly, most of the absorption of the organic blend overlaps with the emission of PyPbI₃ nanoparticles, while only a very small (\approx 50 nm) overlap occurring with PyPbBr_{3-x}I_x. Therefore, only minimal increase in the J_{sc} for mixed phase nanoparticles was observed. These results show that down-conversion using Py-based perovskites is a promising approach for improving the performance of low-bandgap OPVs by matching emission and absorption profiles.

3.3 Conclusion

In summary, we synthesized PyPbI₃ and PyPbBr_{3-x}I_x nanoparticles with 5-membered heterocycles of pyrrolidinium using reverse micelle synthesis. Using the confined environment of the nanoreactor, we achieved phases that are not possible in the bulk. In addition, we observed compressive strain in the synthesized nanoparticles. The strain increased with bromine doping, indicating that it was caused by a confined environment generated by the micellar coating. Synthesized nanoparticles exhibited a Stokes shift of approximately 250 meV for pristine PyPbI₃ nanoparticles, and 660 meV for bromine doped nanoparticles, among the largest reported for MHP nanoparticles. A significant down conversion was observed when synthesized nanoparticles were applied on an OPV, resulting in an improvement in J_{sc} . Since the absorption of the nanoparticles lies in the UV regime and their emission spectrum lies in green and red, the nanoparticles acted as effective UV filters and down-converters.

3.4 Experimental

3.4.1 Perovskites precursor solution preparation

0.5M precursor solutions were made by adding organic salts (Pyrrolidinium iodide (PYI, Sigma-Aldrich) to isopropanol (IPA) (Caledon, reagent grade) and the inorganic salts (lead(II) iodide (PbI₂, Alfa Aesar, 99.9985%) and lead(II) bromide (PbBr₂, Sigma-Aldrich 99.99%)) to N,N-dimethylformamide (DMF) (Sigma Aldrich, 99.8%).

3.4.2 Nanoparticles Synthesis

Poly(styrene-b-2-vinyl pyridine) diblock copolymer (Polymer Source), was dissolved in reagent grade non-polar solvent o-xylene at a concentration of 3 g/L continuous stirring to form reverse micelles. After confirmation of reverse micelles formation by atomic force microscopy (AFM), precursor salts and reactants were added to the reverse micelles solutions, with a time interval of 24 hours to allow thorough infiltration of each precursor. Pure pyrrolidinium lead iodide (PYPbI₃) was formed by sequentially adding the PYI precursor solution followed by the PbI solution into the reverse micelle solution. To obtain mixed halide phase PYPbBr_{3-x}I_x nanoparticles, a stoichiometric amount of PbBr₂ was added from the 0.5M master solution prepared in DMF. The final loaded reverse micelles solutions were centrifuged to filter out the excess salt and kept stirred to prevent coagulation. 4 μ l of solution was spin coated on silicon (1x1) cm slab for AFM characterization.

3.4.3 Organic solar cell fabrication

A conventional structure for the organic photovoltaic device (OPV) was used which included ITO/lithium fluoride nanoparticles (LiF NPs)/poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)/PBTZT-stat-BDTT-8:PCBM/aluminum (Al). The ITO substrates were ultrasonically cleaned in acetone and IPA for 15 minutes each to obtain dust free substrates and etched in oxygen plasma for 5 minutes to remove residual chemicals. A reverse micelle synthesis route was used to fabricate the LiF nanoparticles as previously described. [204]. LiF nanoparticles were spin-coated at 2000 rpm for 45 seconds on ITO and etched for 45 minutes to remove polymer coatings. Afterwards, PEDOT:PSS purchased from Ossila was spin-coated at 5500 rpm for 30 seconds and annealed at 150° C for 25 minutes in ambient conditions. A 30 mg/ml solution of PBTZT-stat-BDTT-8:PCBM (weight ratio: 1:2) was coated over PEDOT:PSS via spin coating at 1000 rpm for 60 seconds, followed by postannealing at 70°C for 10 minutes in an inert atmosphere. Thermal vapor deposition was used to deposit aluminum over a specific area of 0.03 cm^2 at low pressure utilizing a mask. For enhanced self-conjugation of the organic blend, the encapsulated device was post-annealed at 100°C for 10 minutes in the ambient environment. To investigate the down-conversion of PY-based perovskites, 12 μ l of PY-based perovskite solution was deposited on the bottom of ITO-covered glass by spin coating at 2000

rpm for 45 seconds. A xenon (Xe) light source with high intensity (90 W of output power) was used to investigate the characteristics of the OPV.

3.4.4 Characterization

Atomic force microscopy (AFM)

Atomic force microscopy (AFM) images were collected using an Asylum MFP-3D instrument (Oxford Instruments Asylum Research) in the alternating current (AC) mode under ambient environment. AFM probes (Nanotools, EBD-FMR) with spring constant of 2.8 N/m and resonant frequency at 75 kHz was engaged in tapping mode for topography scan. WSxM 5.0 was used for AFM image processing. All AFM samples were prepared by spin coating 4 μ l of solution at 2000 rpm for 45 seconds on (1x1) cm silicon slab.

Photoluminescence (PL)

PL measurements were performed using a 405 nm diode laser with laser power in the range of 11 mW (spot diameter 1-2 mm). The sample emission is collected with a lens and guided to the detection unit with an optical fiber. A long-pass filter (405 nm) removes the excitation light before the collected radiation is fed into a monochromator (Andor, Shamrock 303i, grating 500 nm blaze, 150 lines/mm) and detected with an intensified charge-coupled device (Andor, iStar A-DH320T-18U-73). The sample was exposed to the laser with an exposure time of 0.0237 sec and a slit opening of 50 μ m. The detection range is from 300 to 900 nm. Measurements were done in a darkened environment to prevent stray light.

UV-Vis Spectroscopy

UV-Vis spectra measurements were performed to characterize the optical properties of the materials using a Lambda 35 UV-Visible spectrometer (PerkinElmer). The samples were prepared at concentrations 0.1 mg/mL, using o-xylene as a dispersant, measured in a 1x1 cm quartz cuvette.

3.5 Supporting information figures



Figure 3.4: (*SI-1*) An EDS spectrum of mixed halide phase perovskites synthesized using the reverse micelles fabrication route.



Figure 3.5: (SI-2) XRD spectrum of mixed halide phasePYPbBr_{3-x}I_x, compared to calculated PYPbBr₃ phase



Figure 3.6: (SI-3) QNM characterization of loading of MAI into the nanoreactor core with respect to time, inset are the Young's modulus map of MAI loaded micelles at different times

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Figure 3.7: (SI-4) Comparison of nanoparticle emission spectrum and the absorption spectrum of the BHJ active layer



Figure 3.8: (SI-5) CIE coordinates for particle emission

Chapter 4

Stabilized perovskite nanoparticles: Optically active $FAPbBr_xCl_{3-x}$ -TiO₂ core-shell structures

The findings of this study have been submitted to the "Nano Energy" journal.

abstract

In recent years, hybrid halide perovskite nanostructures have gained interest for their superior optoelectronic properties. Their application, however, is hindered by moisture, oxygen, and UV radiation instability. In our study, we show formation of an perovskite-TiO₂ core-shell nanoparticle to improve their stability upon exposure to an oxygen plasma, allowing them to be used as an effective interlayer for optoelectronic devices. Taking advantage of the properties of rdiblock copolymer everse micelle templating, core-shell particles with varying shell thickness was achieved. A maximum of ≈ 7 nm TiO₂ shell around a perovskite core was possible with monodispersed, uniformly distributed nanoparticles. Increased shell thickness showed a quenching of the emission properties, resulting in better charge carrier extraction when used as an interlayer. It was found that the nanoparticles improved all aspects of organic solar cells when they were practically incorporated in device. As compared to the standard device with only TiO₂ nanoparticles, J_{sc} , V_{oc} , and PCE showed 15%, 11.2%, and 23.56% improvements for FAPbBr_xCl_{3-x}-TiO₂ core-shell incorporated organic solar cell.

4.1 Introduction

Metal organic lead halide perovskite nanoparticles (PNPs) have attracted significant interest in recent years due to their unique optical properties, low cost, and ease of processing. These PNPs have a range of potential applications, including photovoltaics [205], light-emitting diodes (LEDs) [206], display backlights [207], photodetectors [208], single-photon sources [209], solar cells [210], and down converters [23]. PNPs are a promising class of materials for many applications, but their inherent poor structural stability in the presence of external factors presents a major challenge to their widespread use [211, 212]. Among these external factors, moisture and oxygen are particularly problematic for the stability of PNPs [213] in optoelectronic devices. The presence of water or other polar solvents can cause the PNPs to lose their structural integrity due to hydration or solvation leading to its decomposition [214]. The fast degradation of PNPs when exposed to moisture, oxygen, high temperature, or UV light [215–217] limits their usefulness in real-world applications such as photocatalysis, photoelectric catalysis, and biological detection [218], which are often carried out in aqueous environments. it also makes it difficult to scale-up manufacture for commercial production. Moreover, due to the intrinsic ionic nature of perovskites, halide PNPs easily undergo anionic halide exchange upon mixing, which can result in a homogenized sample with less control over the composition [219, 220]. It is therefore beneficial for PNPs to achieve environmental stability before they can be used in practical applications.

There have been significant efforts over the last decade to overcome limitations associated with the synthesis and stabilization of colloidal nanocrystals [221]. Examples include post-synthesis modifications [222], the design of ligands [223], and doping engineering [224] for enhanced stability and compositional control. Among all the approaches adopted to stabilize PNPs, creating core-shell nanostructures appears to be the most promising [78]. Various approaches have used shells of water-proof organic ligands [225,226], polymer matrices [227] or multidendate polymer micelles [23,67,68], inorganic oxide coatings [228,228–231], and another similar perovskite material [232]. However, such shell materials typically have electrically insulating properties, inhibiting charge transport into and out of PNPs, limiting their application. In our previous studies, we have used PS-b-P2VP diblock copolymer micelles as nano-containers to contain and shield perovskite nanoparticles from ambient and moisture based degradation [23,92,233]. However, due to the polystyrene corona, PS-b-P2VP is insulating, which is an obstacle in the use of the formed nanoparticles in devices. Conventional polymer removal techniques, such as oxygen plasma cannot be used with perovskites as they will rapidly degrade under the harsh conditions [23,92]. An ideal approach to overcome the issue of instability and encourage charge transport would be to construct a heterojunctions structure with a shell material with a suitable band gap alignment with the core perovskite material. This would encourage charge separation in the core, thus reducing the possibility of trapped carriers.

In contrast with the fabrication of traditional semiconductors (II–VI, III–V, and IV–VI) [234, 235], the production of perovskite core-shell PNPs with uniform morphologies, perovskite cores, and desirable conductive shells is difficult, as no one efficient method is available to produce them uniformly or with consistent structures [80]. The soft ionic bonding and low crystal lattice energy of perovskite nanocrystals facilitate fast anionic exchange, causing rapid crystallization, which often leads to nonuniform undesirable structures [78, 80]. For example, using a wet chemical approach, Li et al. [230] reported CsPbBr₃-TiO₂ core-shell PNPs using titanium butoxide (TBOT). However, the shell thickness around the CsPbBr₃ core was not the same on all sides. Additionally, post-synthesis processing to remove excess water resulted in aggregation in the synthesized CsPbBr₃-TiO₂ core-shell PNPs. Though there have been a variety of core-shell structures reported for CsPbBr₃ [68, 226, 228–230], there have also been no reports of methylammonium (MA) and formamidinium (FA)-based perovskites being capped with oxides or metal chalcogenides.

Herein, we present a facile room temperature method for growing conductive TiO_2 shells around formamidinium lead bromide (FAPbBr₃) perovskites PNPs that not only increases stability when exposed to oxygen plasma but also improves charge

transport and charge extraction, allowing them to be used as an electrically active interlayer for bulk-heterojunction polymer solar cells. The reverse micelle templating synthesis route adopted in this study enables us to fabricate FAPbBr₃ PNPs under ambient conditions with controlled synthesis and uniform geometry, and subsequently engineer TiO₂ shells of various thicknesses. Importantly, all the synthesis steps were carried out under ambient conditions at room temperature, without the need for any additional post-processing.

4.2 Results and discussion

Previously, we reported the synthesis of uniform and well-dispersed perovskites PNPs based on methylammonium (MA) and formamidinium (FA) using reverse micelle synthesis with poly (styrene)-b-poly(2vinyl pyridine) (PS-b-P2VP) diblock copolymer [23,92]. The polymer encapsulation enhanced the moisture resistance and structural stability of the nanoparticles [233], but it negatively affected charge transport due to the electrically insulating nature of PS-b-P2VP. To address this issue, we developed a three step loading process to coat templated perovskite nanoparticles with a titanium dioxide (TiO₂) shell. TiO₂ is well known as an electron transport layer (ETL) for perovskite solar cells, and is resistant to UV, oxygen and humidity, all factors to which metal hybrid perovskite are vulnerable [236].

As shown schematically Figure 4.1, first FAPbBr₃ nanoparticles were synthesized within diblock copolymer reverse micelle nanoreactors, then titanium tetrachloride (TiCl₄) was added in various concentrations to form a TiO₂ capping layer. The fabrication steps were all completed in ambient atmosphere at room temperature except for the addition of TiCl₄, which was done in a N₂ environment as it is hygroscopic and readily reacts with moisture in the air to form TiO_2 and HCl vapour. Due to its ability to absorb moisture, $TiCl_4$ is an ideal precursor for the formation of TiO_2 shells on perovskite nanoparticles. The formation of FAPbBr₃ nanoparticles before addition of $TiCl_4$ was confirmed by photoluminesence spectroscopy.



Figure 4.1: Schematic illustration of the reverse micelle synthesis route illustrating the formation of reverse micelles using PS-b-P2VP diblock copolymer, the loading of FAPbBr₃ precursors to form nanoparticles, followed by the deposition of TiO_2 shells of varying thicknesses.

Reverse micelle synthesis offers control over size uniformity, dispersion and stoichiometry by separately loading each precursor [23]. Therefore, by changing the amount of precursor added and the infiltration time, we controlled the size and distribution of the core-shell nanoparticles. Figure 4.2(a) shows AFM images of a monolayer of spin-coated FAPbBr₃, TiO₂, and core-shell nanoparticles with different precursor additions. In all cases, uniform nanoparticles with a low polydispersity index are formed. It can also be observed that there is little to no agglomeration of nanostructures. The addition of greater amounts of precursors leads to larger NPs from ≈ 11 nm for the pristine FAPbBr₃ particles to 35 nm with 3 mL addition of TiCl₄, roughly the same size as TiO₂ nanoparticles produced by reverse micelle templating. Figure 4.2(b) shows the nanoparticle density for two spin-coating and plasma etching cycles, showing widely spaced particles, without significant agglomeration that might be detrimental to particle performance. By repeated spin-coating and plasma etching steps, it is possible to increase the particle density of micelle templated nanoparticles without changing the particle dimensions [237, 238].

The addition of precursor salt was correlated to the shell thickness, as confirmed by TEM measurements. Figure 4.2(c) shows clearly the formation of a uniform shell, \approx 7nm thick for 3 ml addition of TiCl₄. At lower concentrations of TiCl₄, the TiO₂ shell was not readily visible, but it is clearly observable at precursor additions of 1 ml and higher. Utilizing the controlled addition of precursor salts, we were able to create shells ranging from 1 nm to 7 nm thick, uniformly around the perovskite core. Further addition of TiCl₄ beyond 3 ml did not result in an increase in the shell thickness, suggesting a maximum infiltration into the micelle. The formation of TiO₂ as the predominant component of the shell around the perovskite was confirmed using electron energy loss spectroscopy (EELS), shown in figure SI-1 (supporting information).



Figure 4.2: (a)(a) AFM images of a monolayer of spin-coated FAPbBr₃, TiO₂ and FAPbBr₃-TiO₂ core-shell nanoparticles, after plasma etching. (b) SEM image of two spin-coated layers of FAPbBr_xCl_{3-x}- 3Ti core-shell nanoparticles, after plasma etching. (c) High resolution TEM image of a single FAPbBr_xCl_{3-x}- 3Ti core-shell nanoparticle showing the measured shell thickness.

To investigate the optical properties of the synthesized core-shell nanoparticles, the photoluminesence emission spectra of the nanoparticles were examined, as shown in Figure 4.3(a). Prior to the addition of $TiCl_4$, FAPbBr₃ nanoparticles exhibited a strong single emission spectra, with a peak of FWHM of ≈ 40 nm, and an emission maxima at 508 nm, consistent with bromine based perovskites [23]. The addition of TiCl₄ resulted in a hypsochromic shift, suggesting the substitution of bromide with chloride ions, as chloride based perovskites tend to emit in the blue region. By virtue of the slowed reaction kinetics, reverse micelle templating allows for the formation of the thermodynamically stable phase even in the presence of multiple halide ions [23]. Consequently, the emission maxima shifted to 430 nm with a subordinate hump observed at 460 nm. This is consistent with chlorine doping of the perovskite, as was also observed by Lingos et al. where 10% doping of Cl⁻ in CsPbBr₃ shifted the emission maxima to 425 nm, with a secondary emission observed around 475 nm [239]. It is likely therefore that adding $TiCl_4$ results in a doped $FAPbBr_xCl_{3-x}$ perovskite cage structure. However, broadening of the emission spectrum suggests multiple doping stoichiometries were achieved in the nanoparticles. With Cl⁻ addition, the total emission intensity is similar up to 1 ml addition of TiCl₄, where emission quenching starts to be observed. This also coincides with the visible formation of a TiO_2 shell around the perovskite nanoparticle under TEM. It is likely therefore that with small amounts of Ti-precursor, doping occurs until sufficient Ti is introduced to form a TiO_2 shell. Further additions of TiCl₄ show further emission quenching, consistent with a thicker shell formation. Such emission quenching typically results from the formation of a junction between the core and the shell, preventing radiative recombination through charge transfer to the shell from the photoexcited charge carriers in the core, if there



is sufficient band alignment between the two components.

Figure 4.3: (a) PL emission spectra of FAPbBr₃, TiO_2 nanoparticles and FAPbBr₃/TiO₂ core/shell nanoparticles of varying shell thickness. (b) Schematic of the core/shell junction, illustrating band overlap and a quasi-type-II band alignment of the core and the shell.

In a type-I band alignment, the conduction and valence band of the core material is confined within the band gap of the shell material [240]. With a small offset with the conduction band of the shell material, while the valence bands are well separated from each other, however, such systems can exhibit quasi-type II behaviour where the electrons can be delocalized over both the core and shell whereas the low-energy holes are confined to the core [241]. As determined by electrochemical methods, the conduction and valance band edges of mixed halide perovskites (FAPbBr_xCl_{3-x}) relative to a normal hydrogen electrode (NHE) were determined by Wang et al to be \approx -1.1 and \approx 1.3 V [242], respectively, whereas the conduction and valance band edges of TiO₂ nanoparticles versus NHE were \approx -0.5 and \approx 2.7 V respectively [243]. In this case, the small offset (\approx 0.6 V) between the conduction bands of the perovskite core and the TiO₂ shell produces a quasi-type-II band alignment which leads to delocalization of the electron, whereas the larger offset (≈ 1.4 V) confines the low energy hole to the perovskite core alone. This proposed band alignment explains the quenching of emission for thicker shells, where radiative recombination is inhibited due to electron transfer at the perovskite-metal oxide junction. Figure 4.3(b) shows a schematic representation of the FAPbBr_xCl_{3-x}-TiO₂ core-shell nanoparticle with energy levels and transitions indicated.



Figure 4.4: (a) Dispersion of FAPbBr₃-TiO₂ core-shell nanoparticles on an electrode surface showing wide spacing between them. (b) Schematic diagram of the organic photovoltaic device that incorporates FAPbBr₃-TiO₂ nano heterojunctions. (c) Measured J-V curves and (d) box plots of the power conversion efficiencies of six organic solar cells constructed using TiO₂ and FAPbBr₃-TiO₂ core-shell nanoparticles. Solar cell IV measurements were done under AM1.5G illumination.

The practical application of $\text{FAPbBr}_x \text{Cl}_{3-x}$ -TiO₂ heterojunctions was explored by incorporating them as charge extraction and transport interlayers in organic solar

Nanoparticle type	J _{sc}	Voc	PEC	FF
	(mA/cm ²	(V)	(%)	(%)
TiO ₂	-17.2	0.71	6.62	52.08
$\operatorname{FAPbBr}_{x}\operatorname{Cl}_{3-x}$ -	-17.5	0.73	6.50	51.00
0.3Ti				
$\operatorname{FAPbBr}_{x}\operatorname{Cl}_{3-x}$ -	-19.1	0.77	7.56	52.70
1Ti				
$FAPbBr_{x}Cl_{3-x}$ -	-18.9	0.79	7.60	52.51
2Ti				
$FAPbBr_{x}Cl_{3-x}$ -	-19.9	0.79	8.18	52.75
3Ti				

Table 4.1: Table showing comparison of the standard TiO_2 device parameters with various FAPbBr_xCl_{3-x}-TiO₂ nano-heterojunctions with various TiO₂ shell thicknesses. All measurements were done under AM1.5G illumination.

cells. As the particles are widely spaced, many deposition and etching cycles are required to achieve full surface coverage [87]. The difficulty of achieving complete surface coverage even after using multiple layers is highlighted by the dispersion of FAPbBr₃-TiO₂ nanoparticles on an electrode surface, as shown in Figure 4.4(a). As each etching step requires 45 mins of exposure to an oxygen plasma to eliminate the PS-b-P2VP polymer shielding, deposition of multiple layers may cause harm or destruction to the electrode surface and/or the nanoparticles. Therefore, only two successive depositions of core-shell particles were deposited in device structures, as shown in Figure 4.2(c). The particles were deposited on the ITO surface between the electrode and a PEDOT:PSS charge transport layer in a PBTZT-stat-BDTT-8:PCBM bulk heterojunction device, as shown in the device schematic illustrated in Figure 4.4(b).

A control device with two layers of just TiO_2 nanoparticles were also made to provide a comparison with the perovskite- TiO_2 core-shell nanoparticles. Figure 4.4(c) shows the JV characteristics of the BHJ device under AM 1.5G illumination with various nanoparticle interlayers. With increasing shell thickness, the \mathbf{J}_{sc} gradually increases, following the trend of quenched emission intensity described previously. The control device with TiO₂ nanoparticles had PCE of 6.62 with J_{sc} of -17.2 mA/cm₂ and V_{oc} of 0.71 V, respectively, as shown in Table 4.1. No significant improvement was observed for $FAPbBr_xCl_{3-x}$ with 0.3 and 0.5 of Ti. As there was also no emission quenching for these samples, it is likely that there was not a sufficient shell to protect the perovskite core from the oxygen plasma etching, rendering it optically inactive and providing no benefit beyond a TiO_2 interlayer. Thicker shell thickness, where significant emission quenching was observed, resulted in both improved short circuit currents and open circuit values, described in Table 4.1. Compared to the reference device, J_{sc} improved 15.23% and V_{oc} improved 11.2% for a maximum TiO₂ shell thickness of \approx 7nm. By improving J_{sc} and V_{oc}, FAPbBr_xCl_{3-x}-3Ti-based solar cells achieved a power conversion efficiency (PCE) of 8.18%, which was an improvement of 23.56% over the control device. The box plot for power conversion efficiency for 6 devices is displayed in Figure 4.4(d).

4.3 Conclusion

In this study, we were able to demonstrate the passivation of formamidinium-based perovskites with a TiO₂ shell. Addition of TiC₄ to micelle templated perovskites resulted initially in Cl⁻ doping, then the formation of a uniform shell of TiO₂, resulting in a hypschromic shift then quenching in the emission characteristics. The conductive TiO₂ shielding allowed the core-shell particles to be used as a charge extracting interlayer in an organic solar cell due to its quasi-type-II band alignment with FAPbBr_xCl_{3-x}. Using the core-shell structures results in improvements in the J_{sc}, V_{oc} and PCE of 15.23%, 11.2%, and 23.56%, respectively, over a device with similarly sized TiO₂ nanoparticles. This suggests that the formation of a heterojunction particle with efficient charge transfer between the core and the shell resulted in more carriers than just found for TiO₂ interlayers. This novel FAPbBr_xCl_{3-x}-TiO₂ nanostructure provides an ideal route to construct stable perovskite nanoparticles with excellent charge transport properties. This provides a new opportunity to enhance the photovoltaic performance and long-term stability of perovskite nanoparticles.

4.4 Generalization to FAPbBr₃-metal oxide coreshell nanoparticles synthesis

Following the successful encapsulation of perovskite nanoparticles with TiO_2 and with control over the shell thickness, other stable charge transport materials were attempted as capping agents. In general, the insolubility of most metal oxides in organic solvents makes them compatible with solution-processing technology for the fabrication of multilayer deviceswang₂₀₁₈ influence. Nickel oxide (NiOx), known for its high carrier mobility, physical and chemical stability, and resistance to humidity and oxygen, is widely used as a hole transport layer in perovskite and organic solar cells [244, 245]. To confirm the generalizability of the reverse micelle templated approach, zinc oxide (ZnO) capping was also attempted.

Using the reverse micelle templated synthesis route, $FAPbBr_3$ nanoparticles were fabricated as previously described. The loading step, which enables the tailoring of various shell thicknesses through the addition of different amounts of capping precursor, was utilized for shell thickness tailoring. Upon the addition of between 0.5 μ l and, 4 μ l of 0.5 M NiCl₂ (referred to as FAPbBr₃-0.5 Ni, -1 Ni, -2 Ni, -3 Ni, and -4 Ni), quenching in the intensity at the emission maxima was observed without a shift in the wavelength, in contrast to observed with TiCl₄, as depicted in Figure 4.4(a). The consistency of the emission wavelength in the case of Ni encapsulation is theorized to be a result of less Cl ion availability with the NiCl₂ precursor, which seems to form a passivation layer without altering the perovskite cage chemistry by doping substitution on the halide sites. By contrast, TiCl₄, an aggressive precursor with 4 chloride ions associated with 1 titanium ion, may generate high osmotic pressure leading to chlorine doping in the perovskite cage [246]. This seems plausible as when titanium isopropoxide is used as a capping agent, similar intensity quenching with no change in the emission maxima was observed, as shown in Figure 4.4(b).



Figure 4.5: (a) Comparison of the emission spectrum of pristine FAPbBr₃ nanoparticles with that of Ni-capped nanoparticles displaying emission quenching. (b) Emission spectrum comparison of FAPbBr₃ with FAPbBr-Ti core-shell nanoparticles capped using titanium isopropoxide precursors. (c) Life study of FAPbBr₃-3Ni nanoparticles, showing emission even after 10 minutes of plasma etching. (d) Comparison of the current-voltage (J-V) characteristics of devices with and without the incorporation of FAPbBr-Ni core-shell nanoparticles.

During this study, it was observed that as the concentration of Ni increased, a decrease in the emission spectrum was observed and the emission fully disappeared at a concentration of 4 Ni. The decrease in emission increased as the concentration of Ni precursor increased, correlated to increasing shell thickness, suggesting that as the shell thickness was increased, the charge extraction was improved. This behaviour seems to be a result of a inverse-Type II band alignment between FAPbBr₃ and NiO, as the valence and conduction band edges of FAPbBr₃ are expected to be -5.5 eV and

-3.5 eV, respectively, whereas those of NiO are -5.4 eV and -1.8 eV versus vacuum electrodes [244]. Assuming an Anderson model of band alignment at semiconductorsemiconductor interfaces, the core and shell band valence bands were approximately at the same level with an offset of only 0.1 eV, while there was a 1.7 eV difference in the conduction bands. In this scenario, when an exciton is generated by the absorption of a photon, the hole is localized at the FAPbBr₃-Ni heterojunction, whereas the electron is confined to the conduction band of Ni [247]. Schematic illustration of the inversetype II band alignment formation is shown in figure 4.6. This band alignment enables efficient hole extraction from the perovskite layer to the semiconductor shell, which acts as a transport layer. Though this was not as effective as a Ti shell in quenching emission, such a nanoparticle should also be expected to improve the performance of organic solar cells. To confirm the practical applicability of the nanoparticles, they were incorporated into organic solar cells, and an improvement in the short circuit current from -15.4 mA/cm^2 to 17.06 mA/cm^2 of the device was observed, confirming that the charge extraction was improved with using the core-shell particles compared to RMD synthesized NiO nanoparticles. The J-V data is shown in Figure 4.4(d). As RMD NiO particles are typically smaller than the core-shell particles, it is unclear if this behaviour is related to the geometric dispersion of the nanoparticles or the material properties and further studies are underway to confirm the mechanism of improvement.



Figure 4.6: Schematic of the FAPbBr₃-NiO core/shell junction, illustrating band overlap and an inverse-type II band alignment of the core (FAPbBr₃) and the shell(NiO)

However, the NiO shell was very effective at stabilizing the perovskite nanoparticles. TheFAPbBr₃-3Ni core-shell nanoparticles were stabilized to such an extent that even after 10 minutes of oxygen plasma etching, the nanoparticles were still emitting, whereas without Ni encapsulation, the nanoparticles were unable to withstand even 1 minute of etching. After 1 year of exposure to ambient, the emission intensity was only reduced by $\approx 2\%$, suggesting an extremely long shelf life for capped nanoparticles. The emission spectrum of FAPbBr₃-3Ni nanoparticles, after 10 minutes of etching, is depicted in Figure 4.4(c). The inset of Figure 4.4(c) shows the glow of the nanoparticles when exposed to a UV laser, as well as an AFM image of the nanoparticles.

To synthesize zinc oxide (ZnO) capped FAPbBr₃ nanoparticles, 0.5 M ZnCl₂ in isopropanol was utilized as the precursor for Zn capping. It was noted that the emission quenched at a slower rate in comparison to TiO₂ and NiO capping. During the

experiment, a maximum of 8 μ L of 0.5 M ZnCl₂ solution was added, yet $\approx 50\%$ of the initial emission intensity was still observed. No shift in the emission maxima wavelength was detected, except for FaPBBr₃-1Zn which showed a ≈ 10 nm blue shift. Figure 4.5(a) displays the emission spectrum of pristine $FAPbBr_3$ and Zn-capped FAPbBr₃. Additionally, the impact of FAPbBr₃-Zn core-shell nanostructures on solar cell performance was analyzed by incorporating them into devices. The results revealed that FAPbBr₃ alone and with lower ratios of Zn addition (i.e. presumed thin shell thickness), the device performance was worse than without ZnO nanoparticles or did not show any improvement. This is consistent with the lack of emission quenching observed, suggesting efficient transfer of electrons between the core and shell were not observed. However, it is also possible that the shell thickness is insufficient to protect the perovskite materials at such thicknesses, as the exposure to O_2 plasma results in degradation of the perovskite to PbBr₂. However, at a higher Zn shell thickness (lowest emission intensity), a slight improvement in J_{sc} and V_{oc} was observed, indicating that the nanoparticles are contributing to the improvement of the solar cell performance when the emission was quenched as expected. However, the improvement does not seem to be consistent with the amount of emission quenching observed in these devices as shown in Figure 4.5(b).



Figure 4.7: (a) A comparison of the emission spectrum of pure FAPbBr₃ nanoparticles and Zn-encapsulated nanoparticles showing a reduction in emission. (b) An evaluation of the current-voltage (J-V) characteristics of devices incorporating only pure FAPbBr₃, only ZnO, and various FAPbBr₃-Zn core-shell nanoparticles.

The study of the effect of Ni and Zn capping on $FAPbBr_3$ nanoparticles is ongoing, and requires further investigation and understanding of the mechanisms of core-shell interaction to understand their application in optoelectronic devices.

4.5 Experimental

4.5.1 Perovskite nanoparticles synthesis

0.5M precursor solutions of formamidinium iodide (FAI, Sigma-Aldrich) in isopropanol (IPA) (Caledon, reagent grade) and lead(II) bromide (PbBr₂, Sigma-Aldrich 99.99%) in N,N-dimethylformamide (DMF) (Sigma Aldrich, 99.8%) were used as precursors to produce perovskite nanoparticles through a two-step loading process into diblock copolymer reverse micelles as described previously [23, 92]. Revere micelles were formed from poly(styrene-b-2-vinyl pyridine) diblock copolymers (Polymer Source) dissolved in reagent grade o-xylene at a concentration of 3 g/L under continuous stirring. Precursors were added to the reverse micelles solutions, with a time interval of 24 hours to allow thorough infiltration of each precursor. Pristine formamidinium lead bromide FAPbBr₃ nanoparticles were formed by sequentially adding FAI precursor solution followed by the PbBr₂ halide solutions. The precursors were allowed to stir for 24 hours together and then centrifuged to wash out the unloaded precursors.

4.5.2 Perovskite- metal oxide core-shell nanoparticles synthesis

To produce core-shell nanoparticles, various volumes of TiCl₄ (Sigma-Aldrich 97%), Ti-iso-propoxide, 0.5 M nickel(II) chloride hexahydrate (NiCl₂.6H₂O)) in ethanol or 0.5 M zinc chloride (ZnCl₂) in isopropanol were added to already synthesized FAPbbr₃ nanoparticles. Various shell thicknesses were obtained by varying the volume ratios from 0.3 ml/L to 8 ml/L.The solution was centrifuged after 24 hours to eliminate the excess unloaded precursor and obtain a clear nanoparticle solution of various concentrations: named either FAPbBr_xCl_{3-x} - 0.3Ti,to FAPbBr_xCl_{3-x} - 3Ti for Ti samples or FAPbBr₃- 0.5 - 8 M, where M is Ni or Zn, depending on how many μ L of the precursor was added to the FAPbBr₃ loaded micelle solution. Where indicated, the polymer micelle was removed using O₂ plasma etching (Harrick PDC-001, 29.6 W., 30 sccm) after spin coating the loaded micelle solutions onto various substrates. The plasma chamber was held at a base pressure of 70 mTorr prior to target gas filling.

4.5.3 Device fabrication

A conventional structure for the OPV was used which included ITO/metal oxide or perovskite core-shell nanoparticles/poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)/PBTZT-stat-BDTT-8:PCBM/aluminum (Al). The ITO substrates were ultrasonically cleaned in acetone and IPA for 15 minutes each to obtain dust free substrates and etched in oxygen plasma for 5 minutes to remove residual chemicals. A reverse micelle synthesis route was also used to fabricate the metal oxide nanoparticles, as described previously by adding a specific loading ratio of the precursor salt to reverse micelle solution [83, 153]. Using conditions of 2000 rpm for 45 seconds on ITO, two layers of the nanoparticles were spin-coated sequentially, and each layer was etched for 45 minutes to remove the polymer micelles. Afterwards, PEDOT:PSS (Ossila) was spin-coated at 5500 rpm for 30 seconds and annealed at 150°C for 25 minutes in ambient conditions. A 30 g/L solution of PBTZT-stat-BDTT-8:PCBM (weight ratio: 1:2) was coated over PEDOT:PSS via spin coating at 1000 rpm for 60 seconds, followed by post-annealing at 70°C for 10 minutes in an inert atmosphere. Thermal vapor deposition was used to deposit aluminum through a mask to produce 0.03 cm^2 pixels. The complete devices were encapsulated using UV-cured adhesive with a glass coverslip. The encapsulated device was post-annealed at 100°C for 10 minutes. IV characteristics were measured by an Xtralien X100 SMU attached to an Ossila push fit test board. Devices were illuminated using an AM 1.5G solar simulator.

4.5.4 Characterization

Atomic force microscopy (Asylum MFP-3D instrument) was performed in the alternating current (AC) mode under ambient environment, using AFM probes (Nanotools, EBD-FMR) with a spring constant of 2.8 N/m and resonant frequency at 75 kHz in tapping mode. WSxM 5.0 was used for AFM image processing. All AFM samples were prepared by spin coating 4 μ l of solution at 2000 rpm for 45 seconds on 1x1 cm silicon. PL measurements were performed using a 375 nm diode laser with laser power in the range of 20 mW (spot diameter 1-2 mm). The sample emission was collected with a lens and guided to the detection unit with an optical fiber. A long-pass filter (375 nm) was used to remove the excitation light before the collected radiation is fed into a spectrometer (Ocean optics, USB2000+, grating 31). The samples was exposed to the laser with an exposure time of 2 seconds and a slit opening of 200 nm. The detection range is from 200 to 1050 nm. Measurements were done in a darkened environment to prevent stray light. TEM characterizations were done using Talos 200X (Thermo Scientific) quipped with an X-FEG source and an adjustable high tension between 80 and 200 kV, HRTEM resolution of 0.1 nm, and STEM with a resolution of 0.16 nm.

Chapter 5

Universal transfer printing of micelle templated nanoparticles using plasma functionalized graphene

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abstract

Nanostructure incorporation into devices plays a key role in improving performance, yet processes for preparing 2D arrays of colloidal nanoparticles tend not to be universally suitable, particularly for soft and oxygen sensitive substrates for organic and perovskite based electronics. Here, we show a method of transferring reverse micelle deposited (RMD) nanoparticles (perovskite and metal oxide) on top of an organic layer, using a functionalized graphene carrier layer for transfer printing. As the technique can be applied universally to RMD nanoparticles, we used magnetic $(\gamma$ -Fe₂O₃) and luminescent (methylammonium lead bromide (MAPbBr₃) nanoparticles to validate the transfer printing methodology. The strong photoluminescence from the MAPbBr₃ under UV illumination and high intrinsic field of the γ -Fe₂O₃ as measured by magnetic force microscopy (MFM), coupled with Raman measurements of the graphene layer, confirm that all components survive the transfer printing process with little loss of properties. Such an approach to introducing uniform 2D arrays of nanoparticles onto sensitive substrates opens up new avenues to tune device interfacial properties.

5.1 Introduction

Incorporation of nanostructures into devices have been applied in a variety of advanced technological fields, including organic photovoltaics, displays, sensors, photonics, micromechanical systems, microfluidics and microelectronics. [84,248–251] Nanostructures for nanopatterning used to enhance device performance can be from a wide variety of materials, including noble metals, metal alloys, metal oxides, and dielectric salts. [84,87,249,252,253]

Size monodispersity and control of two dimensional order are particularly important when incorporating nanoparticles in optoelectronic devices, as heterogenity is a key roadblock in the development of nanoparticle based applications [254]. Uniformity is essential particularly in controlling electrical properties such as charge transport and interfacial work function. [84, 87, 249, 253] Reverse micelle templates formed by diblock copolymers offer a high degree of nanoparticle size control with 2D dispersion tuning, for a wide variety of materials [67, 86, 131, 255]. However, processes for preparing such arrays of colloidal nanoparticles tend not to be universally suitable across the variety of substrates used in electronic devices. In particular, there is a need to use an oxygen or inert gas plasma to remove the polymer shell from around the nanoparticle. This poses a challenge for the integration of precise planar arrangements of colloidal nanoparticles into the device fabrication process of organic and perovskite electronics.

Nanotransfer printing methods using elastomer stamps have been successfully applied to move nanoparticles from a donor substrate to an soft target substrate [85,248,256–259]. Successful stamping transfer between substrates depends strongly on the intrinsic surface energy differences between the stamp and the donor substrates [260], surface roughness [261], peeling velocity [262,263], stamp mechanical properties [264], and temperature and humidity [85]. Many approaches suffer from process-specific drawbacks, such as additional chemical treatments [265–268], elevated temperatures [269–271], or functionalization [272] to successfully move nanoscale objects, hence no universal stamp method has yet been identified. Additionally, the introduction of surface discontinuities and/or contamination that can greatly hinder the properties and functions of the transferred materials is common with soft stamping [259]. A related approach is to use a sacrificial carrier layer with high mechanical strength. As defect-free, monolayer graphene is considered to be among the strongest materials tested [273–275], it could be the ideal material for such an approach. Though transfer methods have been used to transfer large area chemical
vapour deposition (CVD) grown graphene for graphene-based organic photovoltaics, field-effect transistors and resonators, [276–282] these approaches also generally suffer from polymer residue contamination from the stamp, as well as tears and wrinkles in the graphene layer limiting their use. [278, 281, 282] Recently, Feng et al. reported a direct transfer method for CVD graphene on Cu using the target organic layer as the holder substrate, which avoids the process of having unnecessary organic contaminants. [283].

In this contribution, we discuss our modification of Feng's approach to successfully transfer RMD nanoparticles using functionalized graphene as a mechanical support. By treating CVD graphene with low temperature annealing, we have created a universal carrier to transfer nanoparticles onto organic surfaces. The reduce graphene oxide (rGO)-like layer that results from plasma etching provides a mechanical and environmental barrier suitable to transfer a variety of nanoparticle types. To validate our transfer printing methodology, two types of nanoparticles were used: magnetic γ -Fe₂O₃ nanoparticles and luminescent perovskite nanoparticles of methylammonium lead bromide (MAPbBr₃). Raman spectroscopy, photoluminescence spectroscopy and MFM confirmed the successful transfer and stabilization of nanoparticles on an organic surface using the modified graphene.

5.2 Results and discussion

Di-block copolymers, due to their amphiphilic nature, spontaneously form core-corona micelles in selective solvents. Using these micelles as "nanoreactors" allows the formation of highly size controllable nanoparticles, with less than 2% deviation in the average particle diameter [67, 83, 87, 249, 284]. The other advantage of reverse micelle deposition (RMD) is the control over the 2D dispersion: highly ordered periodic arrays with varying spacing and organization are achieved with simple tuning of deposition parameters [67, 131]. To produce RMD nanoparticles, poly(styrene-*b*-2-vinyl pyridine) (PS-*b*-P2VP) diblock copolymer reverse micelles are formed in a non-polar solvent. To introduce these nanoparticles on to the organic surface, we utilized a transfer method based on a modified graphene layer acting as a mechanical support.

A schematic flow of the transfer-printing procedure, modified from Feng's study [283], is shown in Figure 5.1. After the CVD graphene on Cu is annealed at 180°C for 60 min, the reverse micelles loaded with precursors are spin-coated onto the graphene. The micelles together with CVD graphene are plasma etched in oxygen to remove the polymeric shell, with the graphene transformed into a reduced graphene oxide (rGO)-like structure, as we have described previously [285–287]. For certain nanoparticles, the plasma is also used to convert the precursor into the desired material (e.g., iron chloride oxidizes to iron oxide). At this point, the target organic layer can be introduced by spin-coating onto the composite layer, with thickness controlled by the spin-coating speed and concentration of the cast polymer.



Figure 5.1: Schematic flow of transfer printing process– direct graphene transfer with nanoparticles using polymer holder. (i) Anneal CVD full graphene on Cu in air at 180°C for 60 min. (ii) Spin-coat nanoparticles-loaded-micelles solutions on the annealed CVD full graphene on Cu. (iii) Plasma etch the whole stack in oxygen for 25 min to expose the nanoparticles from the micelles. (iv) Spin-coat polymer (P3HT or PMMA) on the stack and cure. (v) Float the stack on Cu etchant solution to etch away the Cu layer, mildly agitated by sonication. (vi) Float the stack on DI water for three times to rinse off any Cu etchant residue. Displace water carefully with syringe to avoid tearing of the stack from water surface tension. (vii) Scoop up the stack from the solution by lowering the substrate7(ITO) on top of the stack. (viii) Flip the stack up-side-down and let dry in N₂ environment overnight. Final configuration of stack: Reduced graphene oxide/nanoparticles/polymer/ITO.

After the target organic layer is cured according to the manufacturer instructions, the whole stack of material will be floated onto a Cu etchant solution of 5g/L ammonium peroxydisulfate to dissolve the copper foil. As CVD deposits graphene on both sides of the copper foil, the graphene layer grown at the bottom side of Cu needs to be removed. This happens spontaneously with our process because the etchant will also detach the graphene layer as Cu dissolves. Therefore, only the modified graphene is in contact with the Cu etchant, protecting the rest of the stack, including the organic deposit [283, 288].

The process is followed by displacing the Cu etchant with deionized water so that any Cu etchant residue can be washed away. The stack is subsequently retrieved, by lowering an ITO-coated-glass substrate on top of the stack and allowing the organic layer to attach. Finally, the stack is flipped to achieve the configuration of modified graphene/nanoparticles/organic layer/ITO and is allowed to dry in a N₂ filled glovebox environment. In this way, the nanoparticles should be trapped under the modified graphene layer, and the post-transferred condition of the graphene, nanoparticles and target organic layers are gauged either optically or chemically. As our printing process can be applied universally to nanoparticles produced by RMD, we were able to transfer nanoparticles with properties that could be measured by various analytical techniques to confirm that all components are able to survive.

The reverse micelle deposition (RMD) process requires sustained plasma etching to produce monodisperse nanoparticles with a high degree of two dimensional order, as shown in Figure 5.2. Here MAPbBr₃ nanoparticles are shown, but RMD is able to produce similar nanoparticle dispersions of a wide variety of materials under similar etching conditions [67, 83, 87, 249, 284] (see Figure 5.6 for AFM of γ -Fe₂O₃ nanoparticles produced under similar conditions as MAPbBr₃)

However, this level of etching is typically destructive to organic surfaces (see supporting information Figure 5.7), preventing direct deposition on the organic surface. This same plasma dosage is also typically destructive to graphene [286, 289, 290].

We have recently shown that CVD graphene on Cu behaves very differently under plasma compared to free standing graphene and graphene supported on other substrates [286], forming rGO-like structures under direct oxygen plasma bombardment. Due to the synergistic oxidation mechanism between graphene and the underlying Cu, the degree of oxygen functionalization of the activated graphene can be tuned with the oxygen plasma dose [286].

The high plasma dose required to fully etch the nanoparticles will also completely etch as-deposited CVD graphene [286]. From our mechanistic insight on the interaction between plasma and graphene, we have found that it is possible to prevent the complete destruction of CVD graphene under plasma by pre-annealing at low temperature (180 °C) in order to eliminate volatile surface contaminants [285–287]. A minimum of 4min annealing is sufficient for a monolayer CVD graphene on Cu to withstand 25 min of plasma etching (ET25) [287]. As prolonged low-temperature annealing does not introduce defects on the graphene, but does help to preserve a greater degree of intact sp² hybridization upon plasma exposure [285, 286], we chose an annealing time of 60 min (AT60), as shown in Figure 5.2(a).

Before exposure to plasma, our CVD graphene shows the characteristic G and 2D peaks with the strong 2D signal roughly twice that of the G peak indicating high quality defect free monolayer graphene [291] (see supporting information Table SI-1). The G peak at 1580 cm⁻¹ corresponds to the first order degenerate phonon energy,

 E_{2g} mode, at the G point. The 2D mode at 2690 cm⁻¹ comes from the G mode overtone and is indicative of sp^2 hybridization. After etching (dotted line bottom row Figure 5.2(a)), a defect D mode (at 1354 cm^{-1}) and a broadened G mode with peak maxima at 1603 cm⁻¹ can be identified. The D mode is the defect-activated intervalley two-phonon mode for sp^3 defects [291, 292]. The latter peak, also known as the G_{app} mode resulting from the merging of the G mode and D' mode [293], can be deconvoluted into G at 1590 cm⁻¹ and D' at 1606 cm⁻¹. The D' is a defect activated intravalley one-phonon mode associated with the C-H sp³ hybridization defect and the overtone of the D mode [292]. For defected graphene, the peak position difference of D' to G_{app} can be used to determine the nature of the graphene layer [285,286]. The peak position difference of 3cm^{-1} between G_{app} and D' mode indicates that the CVD graphene is oxygen-doped by the plasma to become rGO-like [286] (see supporting information Figure SI-4 for peak fitting). The 2D mode (at 2790 cm⁻¹) is still visible after this etching step, implying a good degree of sp^2 hybridization [285, 286]. This suggests that the rGO-like layer is quite intact and should be strong enough to transfer nanoparticles onto the target organic layer.



Figure 5.2: (a) Comparison of Raman spectra of annealed graphene, loaded micelles on annealed graphene and transferred loaded micelles on PMMA, showing characteristic peaks for graphene and complexated P2VP. Dotted green lines indicate the expected peak positions for the complexated P2VP peaks. Note that the peaks of graphene are offset from those of the complexated peaks by ~ 10 wavenumbers. A monolayer of $FeCl_3$ loaded micelles on Al, the target PMMA substrate, and annealed graphene exposed to etching (showing both a D and G peak) are also shown for comparison. (b) Atomic force microscopy of images of nanoparticle (MAPbBr₃) dispersion on silicon showing particle uniformity with inset showing the entropic force map of the first neighbour (c) Pair correlation function (pcf) of the dispersion of AFM image in (b) showing hexatic packing of the particles (grey indicates pcf of simulated hexatic packing with lattice disorder parameter to match experimental results). Similar (d) Voronoi of AFM image in (b) coloured to show the number of nearest neighbours. The relatively few defects support the high degree of hexagonal packing.(e) Optical image of modified graphene flakes with γ -Fe₂O₃ nanoparticles transfer printed to PMMA after etching (f) Transmission SNOM image of reduced graphene oxide-like flakes with γ -Fe₂O₃ transfer printed to P3HT: PCBM layer after etching. In both cases, the flake edges are clearly visible and intact.

This can be seen in Figure 5.2(e) and (f) showing films transferred onto poly (methyl methacrylate)(PMMA) and poly(3-hexylthiophene):[6,6]-phenyl C61-butyric acid methylester blend (P3HT:PCBM). As a proof of concept, partially grown CVD graphene on Cu (PG) was used with PMMA, as PG has a refractive index (n=2) which can provide an optical contrast from the background PMMA (n= 1.49). [294, 295]. In such a way, one can optically identify spots where PG is transferred. In Figure 5.2(e), the star shaped rGO-like flakes are clearly visible and intact against the PMMA background. The annealing and plasma processing steps are able to form activated graphene without producing all of the material amorphization associated with conventional wet methods for GO and rGO synthesis.

Ideally nanoparticles should be sandwiched between the activated graphene layer and the target organic using this transfer method; however, as nanoparticles formed by RMD are small, roughly 5-10nm in size for the MAPbBr₃ and γ -Fe₂O₃ discussed here, and beneath the rGO-like structures, they are not optically resolvable. We used SNOM to try to visualize the particles, as it has both spatial and sub-superficial sensitivity [296]. In Figure 5.2(f), the edge of the intact activated graphene flake is also observed in the SNOM micrograph for the transferred stack atop P3HT:PCBM. The SNOM signal in the flake region is modulated by light scattered due to the presence of clusters of nanoparticles beneath the rGO-like layer whereas an rGO layer would be expected to be constant over the flake region, (see supporting information Figure 5.9).

Though the non-uniformity suggests the nanoparticles exist beneath the rGO, it was not possible to spatially resolve the particles. Hence, it is still difficult to confirm successful transfer using a direct imaging technique. As our transfer process can be applied universally to nanoparticles produced by RMD, we were able to transfer nanoparticles with properties that could be measured by various techniques to confirm that all components are able to survive the transfer process intact.

Raman spectroscopy is highly sensitive to graphene, but a monolayer (ML) of nanoparticles or loaded micelles are normally not visible under Raman [285,297]. We have recently observed that FeCl₃ loaded micelles show three distinctive peaks due to the complexation of Fe with the nitrogen in the vinyl pyridine moeities of 2VP [83]. On metal substrates, it is possible due to surface enhancement to observe a monolayer of such micelles.

Figure 5.2(a) shows a ML of FeCl₃ loaded micelles on annealed graphene, showing the expected complexation peaks around 1306 cm⁻¹, 1440 cm⁻¹ and 1591 cm⁻¹ (indicated by the dotted vertical lines and the dotted green spectrum for loaded micelles on Al) [83]. As there is only about a 10 cm⁻¹ difference between the Fe-2VP peak and the G peak of graphene, the graphene peak is buried as a shoulder in the spectrum due to the surface enhancement from the Cu substrate of the complexated micelle peaks (see supporting information Figure 5.8 for peak deconvolution). However, the 2D peak from graphene is visible, showing the coexistence of both micelles and graphene after spin coating.

In order to measure the Raman spectrum of the transferred stack, again PMMA was used as the target organic surface as it contains very few spectral features between 900 and 3000 cm⁻¹, as shown in Figure 5.2(a) (dotted black line), unlike P3HT:PCBM (see supporting information Figure 5.10). Note that in this case, the micelles were not etched prior to transfer printing in order to observe the features from Fe-complexation.

The Raman spectrum of the transferred stack (black curve Figure 5.2(a)) shows a

clear G mode and a strong 2D mode of the intact graphene, with only a small possible contribution from the $\rm FeCl_3$ loaded micelles. The broad peak around 1400 $\rm cm^{-1}$ is likely a convolution of micelle related peaks and the PMMA background. The broad band at the 1460 cm⁻¹ Raman shift region for PMMA is attributed to the asymmetric C-H stretching mode in the methyl group and methoxy group. [298–300] Though this is clear evidence of the successful transfer of defect free high quality graphene, it is still difficult to confirm the successful transfer of the micelles as the lack of signal from the complexation peaks may be due either to unsuccessful transfer or the loss of the surface enhanced spectrum achievable on a metal substrate. To prove that the micelles are indeed transferred, it might be possible to produce a higher coverage of nanoparticles that is above the Raman detection limit. However, as the thickness of the $FeCl_3$ reverse micelles is increased, the plasma etching required to completely remove the micelles is also increased, beyond that allowing an intact rGO layer. We have also observed that the etching action is escalated with increased micelles such that the graphene is severely damaged even with annealing. [297] Therefore, to prove a single monolayer of particles can be successfully transferred, we have used luminescent organo-halide perovskite (MAPbBr₃) nanoparticles to take advantage of their strong photoluminescence (PL) response under UV illumination.



Figure 5.3: (a) Comparison of normalized photoluminescence spectra of MAPbBr₃ nanoparticles (black line) and MAPbBr₃ nanoparticles transferred onto PMMA (green line), measured with 405 nm laser excitation, showing the expected emission at 525 nm. (b) TEM image with EDX line scan showing evidence of nanoparticle formation, displaying composition of carbon (red line), lead (blue line) and bromine (green line) along the micelle diameter.

Figure 5.3(a) shows a comparison of the PL spectra of MAPbBr₃ nanoparticles deposited on Si and the transferred stack of MAPbBr₃ micelles. There is clearly an intense emission from MAPbBr₃ at around 525nm, as expected. Figure 5.3(b) shows a TEM image of MAPbBr₃ nanoparticles, with the inset EDX line profile showing the presence of C, Pb and Br, confirming the successful formation of MAPbBr₃ nanoparticles by RMD [67].

The transferred nanoparticles also show a strong emission, with a bathochromic shift of 7 nm (from 521 nm to 528 nm). This shift could be due to a slight change in particle size, or it could be the result of some interaction with water during the transfer process. Hydration and dehydration of perovskite nanoparticles has been shown to cause hypsochromic or bathochromic shifts. [301–304]. Lin et al. [288] recently predicted the water permeability of rGO as a function of the oxygen concentration. They found that below 25at% oxygen content, the water permeability was diminished due to the small pore size, with complete impermeability at around 17at% oxygen concentration. [288] The rGO produced through annealing and plasma etching from our earlier study has an oxygen content of 23.1at%, [286] so it is expected to act as a mostly impermeable barrier to water in the ambient glovebox environment.

Though there was some evidence of an emission shift due to hydration and a slight loss in intensity ($\sim 20\%$, see supporting information Figure 5.11), the perovskite particles were not destroyed by the exposure to water. This is also important for the organic active layers such as P3HT:PCBM in organic devices. Figure 5.12 in the supporting information shows the stability of the rGO-nanoparticle stack on P3HT:PCBM, with the topography and optical characteristics unchanged over four months. Moisture is one of the key degradation factors for P3HT [305,306]; the rGOlike layer being able to block the direct contact of P3HT:PCBM with water during the Cu etching process is also an important criteria for its use in viable devices.

Photoluminescence provides strong evidence that the nanoparticles are sandwiched between the rGO-like layer and the polymer, and are able to survive the many steps needed for successful transfer onto an organic surface. However, to preserve the PL, the MAPbBr₃ nanoparticles were not etched prior to transfer (though the graphene layer was etched). To show the coexistence of nanoparticles and modified graphene, we took advantage of the fact that iron oxide nanoparticles formed from FeCl₃ using the RMD method can yield highly magnetic γ -Fe₂O₃ nanoparticles at room temperature [83, 307] (see also supporting information Figure SI-9 for magnetization and structural information on the γ -Fe₂O₃ nanoparticles). Oxygen plasma etching simultaneously removes the polymer shell and converts the precursor into iron oxide.

Successful transfer of γ -Fe₂O₃ nanoparticles to the P3HT: PCBM active layer is confirmed by two-pass tapping-mode MFM, which can be see in Figure 5.4. This shows the amplitude and phase micrographs collected simultaneously at the edge of the transfer printed rGO/Fe₂O₃ nanoparticle layer with and without an applied magnetic field. Before magnetization, there is a clear boundary between the P3HT:PCBM layer and the transfer stack. The topography micrograph shows an intact rGO-like layer on the organic surface, both in amplitude and phase shift, though again the subsurface nanoparticles are not visible. Upon application of a magnetic field (Figure 5.4(c)), the amplitude map changes dramatically. The phase image (Figure 5.4(d)) confirms that there is no change in the real topography; therefore, the apparent change in amplitude must be proportional to the sample magnetization. As P3HT: PCBM and graphene are both non-magnetic, this effect can only be attributed to the intrinsic magnetic field (B_o) of the γ -Fe₂O₃ nanoparticles as shown in the schematic. Therefore, the particles, the rGO layer and the polymer are all able to actively survive the transfer process.



Figure 5.4: Magnetic force microscopy images at the edge of the transfer-printed modified graphene/Fe₂O₃ nanoparticle composite stack. (a) Amplitude and (b) phase images before magnetizing the AFM tip. (c) post magnetizing topographic image (d) post magnetizing phase at the graphene edge, showing a dramatic amplitude shift in correspondence with areas including γ -Fe₂O₃ nanoparticles, while no significant phase shift occurs in the area that is not rGO-Fe₂O₃ coated. This indicates that the nanoparticles have been magnetized, which is an important confirmation of their distribution underneath the activated graphene layer.

5.3 Conclusion

In summary, we show the successful transfer of reverse micelle templated nanoparticles using an rGO-like layer as a mechanical support onto organic surfaces (PMMA, P3HT:PCBM). Though no one technique was able to confirm that all the components of the stack survived the transfer process, various characterization showed the unaffected performance of the stack components. The transfer results of the activated graphene are demonstrated by the post-transfer optical images and Raman measurements. The rGO-like structures transferred onto PMMA and P3HT:PCBM show a high level of intactness, which highlights the importance of pre-conditioning of graphene by low-temperature annealing. Evidence of transferred nanoparticles sandwiched between the modified graphene and the organic layer is provided by the emission PL spectrum of MAPbBr₃ nanoparticles. Intact rGO and active nanoparticles are proven by SNOM and MFM of magnetic iron oxide nanoparticles. By applying our approach to various target organic layers, and using a variety of RMD produced nanoparticles, we show the universality of this transfer approach to introduce uniform nanoparticles onto oxygen sensitive substrates.

5.4 Experimental

5.4.1 Synthesis

Graphene was synthesized by CVD on commercially available 25μ m copper foils (Alfa Aesar). The foils were first chemically treated with acetic acid and annealed for 4 hours at 1078°C under a flow of 8 sccm hydrogen gas to clean the copper surface. Growth temperature was maintained at 1078°C during a 4 minute CVD growth phase where gas flows of 1.2 sccm methane were introduced. In order to ensure the same aging of all samples, the graphene samples were taken from the same master, which was stored in a desiccator in vacuum. Samples were annealed on a hotplate (Barnstead Thermolye Super-Nuova) at 180°C for 60 mins. Samples were allowed to cool before further processing.

Reverse micelles were prepared by dissolving various poly(styrene-b-2-vinyl pyridine) di-block copolymer (Polymer Source), in reagent grade non-polar solvents such as toluene and o-xylene, with concentration of 3 g/L under continuous stirring. After confirmation of reverse micelles formation by atomic force micrograph (AFM), precursor salts and reactants were added to the reverse micelles solutions, with a time interval of 24 hrs to allow thorough infiltration of each precursor. Methylammonium lead bromide (MAPbBr₃) was formed by mixing 0.5M precursor solutions of methylammonium bromide (MABr) in isopropanol (IPA) (Caledon, reagent grade) and PbBr₂ in to N,N-Dimethylformamide (DMF) (Sigma Aldrich, 99.8%) sequentially in the micelle solution. Iron oxide was formed by loading anhydrous FeCl₃ (sublimed grade, 99.9%; Sigma Aldrich) to the micelles, and oxygen plasma etching to form γ -Fe₂O₃ [83]. The final loaded reverse micelles solution was centrifuged to remove excess, non-infiltrated salt and stirred further to prevent coagulation. The solution was spin coated onto annealed graphene samples or cleaned substrates for characterization and transfer.

Poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) solution was prepared by dissolving 0.0281 g of P3HT and 0.0169 g of PCBM in 2.66 cm³ of chlorobenzene to achieve a 1:0.6 weight ratio of P3HT and PCBM. This solution was stirred for 6 hrs at 55°C to achieve a clear solution. 20 μl of the solution was spin-coated on ITO and on top of the nanoparticles/modified graphene/Cu stack and annealed on the hotplate at 120°C for 5 minutes to achieve a uniform P3HT:PCBM spin-coated layer. For PMMA, a10 μl solution of polymethyl methacrylate (PMMA) was spin-coated on the top of nanoparticles/modified graphene stack/Cu.

Plasma etching was performed in a Harrick Plasma PDC-001 plasma cleaner system with 13.56MHz R.F. generator at 29.6W. The plasma chamber was held at a base pressure of 70mTorr prior to target gas filling. During etching, a gas flow rate of 30 sccm was maintained.

5.4.2 Characterization

Raman spectroscopy was performed by a Renishaw inVia spectrometer at 514nm laser excitation. The laser power was set to 1mW to minimize laser heating effects (see supporting information Figure refFigSI41), and a 1800 lines per mm grating was used. The surface was visualized using a 20x objective on the integrated microscope. The baseline of the spectra was created and then subtracted to highlight the peaks of interest if necessary. In addition, the spectra were smoothed by a Savitzky-Golay function in Origin. The spectrum features were deconvoluted using Lorentzian line shape profiles to highlight the characteristic peaks of interest.

Photoluminescence (PL) measurements were performed using a 405 nm diode laser with laser power in the range of 11 mW (spot diameter 1-2mm). The sample emission is collected with a lens and guided to the detection unit with an optical fiber. A long-pass filter (420 nm) removes the excitation light before the collected radiation is fed into a monochromator (Andor, Shamrock 303i, grating 500 nm blaze, 150 lines/mm) and detected with an intensified charge-coupled device (Andor, iStar A-DH320T-18U-73). The sample was exposed to the laser with an exposure time of 0.0237 sec and a slit opening of 50 μ m. The detection range is from 300 to 900 nm. Measurements were done in a darkened environment to prevent stray light.

Scanning electron microscopy (SEM) micrographs were obtained with a FEI VERSA

3D using an accelerating voltage of 5kV and a probe current of 12pA. Atomic force microscopy (AFM) micrographs were collected using an Asylum MFP-3D instrument (Oxford Instruments Asylum Research) in the alternating current (AC) mode under ambient environment. AFM probes (Oxford Instruments Asylum Research) with spring constant of 26N/m and resonant frequency at 300kHz was engaged in tapping mode for topography scan. The dispersion of the nanoparticles were analyzed using the disLocate package in Mathematica [131].

Aperture-type scanning near field optical microscopy (SNOM) measurements were recorded using Witec Alpha 300S to acquire SNOM and AFM topography simultaneously at 532nm excitation. Hollow AFM cantilevers (SNOM-C, NT-MDT Inc.) with 90 nm tip aperture diameter were utilized to scan the sample in transmission mode, and topographical (AFM) and optical SNOM images were acquired simultaneously. The optical signal is collected by an inverted microscope and detected with a photomultiplier tube (Hamamatsu U64000) in photon counting mode.

Two-pass tapping mode magnetic force microscopy (MFM) was acquired using magnetic coated silicon cantilever (budget sensors Multi75M-G). The sample is first scanned with the cantilever demagnetized at the interface of RGO: γ -Fe₂O₃ and bare P3HT:PCBM. After the first scan, the tip is removed and exposed to a external constant magnetic field and scanned over the same area on the sample tor acquire amplitude and phase images for comparison.

5.5 supporting information figures



Figure 5.5: (*SI-1*)Impact of laser irradiation on CVD graphene on Cu with a monolayer of unloaded micelles as a function of accumulation time. Laser power was limited to 20mW to examine any heating effects that might distort the graphene layer. Both the ratio of 2D to G mode peak intensities and the peak positions were unchanged under the accumulation conditions for up to 180 mins of accumulation.



Figure 5.6: (SI-2)(a) Atomic force microscopy of images of nanoparticle $(\gamma$ -Fe₂O₃) dispersion on silicon after 25 mins etching showing particle uniformity with inset showing the entropic force map of the first neighbour (c) Pair correlation function (pcf) of the dispersion of AFM image in (b) showing hexatic packing of the particles (grey indicates pcf of simulated hexatic packing with lattice disorder parameter to match experimental results). Similar (d) Voronoi of AFM image in (b) coloured to show the number of nearest neighbours. (d) histogram of the number of Voroni cells with different nearest neighbours. The relatively few defects support the high degree of hexagonal packing.



Figure 5.7: (*SI-3*)Comparison AFM micrographs of organic surface topography for as-deposited 50nm organic thin films and after oxygen plasma etching for 25 mins (a),(b) pentacene, (c),(d) copper(II) phthalocyanine (CuPc), (e),(f) fullerene (C60), (g),(h) di-indenoperylene (DIP). The organic films are typically completely destroyed after plasma etching.



Figure 5.8: (SI-4) (a) Raman spectrum of a monolayer of FeCl₃ loaded micelles spincoated on CVD graphene on Cu. The spectra consists of a convolution of the Fe-P2VP compexation peaks and the G peak from graphene. Two Fe-P2VP complexation peaks are visible at 1306 cm⁻¹ and 1440 cm⁻¹. The peak around 1600 cm⁻¹ consists of a contribution from Fe-P2VP at 1591 cm⁻¹ and from the graphene G mode at 1580 cm cm⁻¹ (b) Raman spectra of CVD full graphene on Cu annealed for AT60 mins at 180°C and etched for 25 mins (ET25), with deconvolution of G_{app} into G and D' features. The peak position of D' relative to a one peak fit of G_{app} is used to determine the nature of the functionalized graphene (rGO, GO or graphene).



Figure 5.9: (SI-5) Atomic force microscopy (AFM) and transmission mode scanning near-field optical microscopy (SNOM) images obtained simultaneously from 90-nm aperture-type cantilevers coupled with a 532 nm laser source for SNOM. (a) AFM and (b) SNOM at the edge between bare P3HT:PCBM and transfer-printed reduced graphene oxide layer with Fe₂O₃ nanoparticles underneath, where (c) represents an histogram of the SNOM signal. SNOM signal of a flat graphene or rGO layer is expected to be uniform. AFM on graphene is flat. However, because transmission SNOM has sub-superficial sensitivity, the SNOM signal is modulated by light scattered due to the presence of clusters of Fe₂O₃ nanoparticles beneath graphene as shown by the two peaks in the red curve. Variations in topography visible on the rGO/np layer likely due to residual Cu.



Figure 5.10: (*SI-6*) (a) Comparison of Raman spectra of P3HT:PCBM (black line); partial graphene with nanoparticles transferred to P3HT:PCBM (red line); blank spot next to the reduced graphene oxide like flakes on P3HT:PCBM (green line), and Cu on P3HT:PCBM (blue line). Dotted vertical lines indicate the expected peak positions of the G and D mode of graphene. Inset shows the optical image of the transferred star-like flakes with nanoparticles on P3HT:PCBM for Raman measurements.



Figure 5.11: (SI-7)Pl emission spectrum of nanoparticles after (green line) and before (black line) interaction with water



Figure 5.12: (SI-8)UV-vis spectra of (a) P3HT:PCBM acquired at different times after the transfer printing process, with the sample preserved in inert atmosphere except for short measurement times; (b) Contact mode AFM on P3HT: PCBM on the same area immediately after transfer the printing process and (c) 4 months after the transfer process on the same area. The broad peak with a maximum at 520 nm demonstrates the preservation of the $\pi - \pi *$ stacking of the P3HT:PCBM complex. Contact mode AFM concur with UV-vis to show no significant changes in surface morphology of P3HT:PCBM up to four months after the transfer printing process. Significant changes in the sample's UV-vis spectrum are noticeable only after 8 months. Except for the last UV-vis scan in panel (a) all measurements here reported were performed in the first 4 months after sample preparation.

supporting information

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Chapter 6

Conclusion

In this study, the versatility of the reverse micelle templated synthesis method for organo-metallic halide perovskites was demonstrated by successfully producing nanoparticles with emission covering the entire visible range (475 nm to 850 nm), from various A, B, and X site precursors. Pure MAPbBr₃ nanoparticles were synthesized using unconventional precursors (MAI and PbBr₂) by slowing down the reaction kinetics of perovskite formation, and a solution containing both MAPbI₃ and MAPbBr₃ was created with the ability to control their relative concentration by varying the precursor ratio and micelle concentration. These dual-phase nanoparticles induced a 150 nm Stokes shift and were applied as downconverters in devices sensitive to UV radiation. By matching absorption of the organic to the emission of the nanoparticles, noticeable improvement in short-circuit current was observed under UV illumination. The same approach was also used to produce novel pyrrolidinium nanoparticles with an even greater Stokes shift 660 meV (182 nm), which were used as down-converters and UV filters under strong white illumination. A metal oxide shell was created around the

perovskites to form a core-shell heterojunction that also allows them to be electrically conductive. TiO₂, NiO, and ZnO were used as shells due to their known use as charge transport layers, and the thickness of the shells was controlled using the RMD process. All shells were successfully achieved, confirmed spectroscopically by photoluminescence emission quenching due to charge extraction, and visually by TEM images showing the core-shell structure. By incorporating a conductive metal oxide shell, the core-shell nanoparticles could be used as charge transport layers in organic solar cells, improving the efficiency by 23.56% compared to standard polymer bulk heterojunction solar cells with metal oxide nanoparticle interlayers. To further facilitate the use of these nanoparticles on sensitive substrates, a transfer printing technique was developed, allowing for their transfer to a desired sensitive substrate after etching and treatment without affecting the substrate. In this study, the stability of perovskite nanoparticles was established under ambient conditions, direct water exposure, and oxygen plasma etching, using various shielding mechanisms. With polymer encapsulation, the nanoparticles are stable against ambient and moisture degradation, allowing applications that take advantage of the emission properties without requiring electrical conductivity. The addition of a metal oxide shell provided even greater stabilization to the point that particles remained emissive even after 10 minutes of oxygen plasma etching, and its emissivity was retained by 98% even after a year in ambient conditions. With various shell thicknesses, the core-shell particles were able to withstand harsh oxygen plasma etching conditions required to remove the polymer shell, allowing them to be used in as electrically active layers in optoelectronic devices. This enhanced stability positions perovskite nanoparticles towards practical commercial viability even as the active layer if a layer of nanoparticles without insulating polymers and without pinholes can be produced. Additionally, the reverse micelle templating synthesis method provides versatility in the selection of shell materials, thereby offering a universal approach to encase the perovskite nanoparticles with the desired material through minor modifications. Overall, throughout this thesis, I show that the control over the reaction kinetics by splitting the precursor addition steps using reverse micelle templating provides a new paradigm for producing size and property-controlled organo-halide perovskite nanoparticles that are hard to obtain by other methods. Systematically using the reverse micelle templating method allows us to exploit the properties of these emerging materials while overcoming some of the potential limitations to their widespread usage in modern devices.

6.1 Future study

The future objective coming out of this thesis is to further develop and understand the formation of perovskite core-shell nanoparticles, such that they can function as a stand-alone optically active medium in optoelectronic devices. To achieve this, a uniform and pinhole-free layer is required that can serve as both an active layer and a charge transport layer, or should contribute to light harvesting when used with another optically active layers. Although previous attempts to verify the lightharvesting properties of the nanoparticles themselves were inconclusive due to low density, we are optimistic that these properties can be harnessed to make perovskite light emitting and absorbing devices. To improve surface coverage, our group is exploring a range of deposition techniques, including spray coating, dip coating, slot-die coating, and electro-spraying. These techniques offer greater flexibility in engineering surface coverage and can be used in combination to achieve better coverage with fewer depositions. Reduced etching time is another key objective, as etching can damage the substrate and diminish device efficiency and fewer layer deposition will reduce the etching time. This thesis has already demonstrated the efficacy of using various materials to shell around FAPbBr₃ nanoparticles, making the reverse micelle synthesis route a universal approach to producing perovskite core-shell nano heterojunctions. The future study now aims to encapsulate a wider variety of perovskite nanoparticles, including MA/FAPbCl₃, MAPbBr₃, MAPbI₃, FAPbI₃, FASnI₃, and FASnPbI₃. This will enable the creation of materials with various bandgaps, which can be paired with a range of shell materials to optimize light-harvesting capabilities. With different perovskite cores, the nanoparticles can also be used in combination with other light-harvesting materials to produce optoelectronic devices with good band alignment. Additionally, a similar perovskite core-shell nanostructure can be used as an active material in conjunction with the same perovskite bulk counterpart, leading to improved band alignment and high efficiency.

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