Interfacial engineering of quasi-2-D formamidinium lead iodide nanosheets for perovskite solar cell by mechanochemical approach

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ABSTRACT

Solvent-free synthetic protocols for the formation of nanoarchitectures continues to attract a great attention among the wide class of synthetic chemists in order to overcome the harsh reaction conditions. In the current work we demonstrate, for the first time, solvent-free synthesis of dodecylammonium formamidinium lead iodide (DDA) 2 (FAPbI 3n ) 2PbI 4 a quasi-two-dimensional (2D) red-light-emitting perovskite nanosheet, where DDA is dodecylammonium, a long chain ammonium cation, and FA is a formamidinium cation. By varying the amount of DDA, we controlled the dual emission of quasi-2D perovskite comprising of both 2D and three-dimensional morphs—trigonal, three dimensional, luminescent, narrow band gap semiconducting black α-phase; and 1-D hexagonal, non-luminescent, yellow insulating non-perovskite δ-phase, which generally forms at room temperature as opposed to the other phase that is stable at elevated temperature [16–19]. As a result of the above, several synthetic protocols have been employed to synthesize stable and pure α-phase FAPbI 3 mostly from wet-chemistry [20–24]. Fu et al. recently confirmed that by functionalizing the surface with large-sized organic molecules, the cubic FAPbI 3 process can be stabilized [25]. They showed that the functionalized surface helps to stabilize the cubic FAPbI 3 process at room temperature by lowering formation energy. However, despite their potential benefits, the use of a mechanochemical method for the synthesis of these types of nanocrystals has not been widely utilized [26–31].

Calabrese et al. [32] reported the first quasi-two-dimensional (2D) perovskite, PEA 2 MAPbI 3, in 1991, and Mitzi et al. [33] explored the layered structure of quasi-2D perovskites (BA) 2 (MA) n–1 Sn nI 3n+1 (n =

1. Introduction

Organic–inorganic halide perovskites have attracted significant attention owing to their impressive optoelectronic and photovoltaic properties, such as high carrier diffusion lengths, tunable bandgaps, and high carrier mobility, among other things [1–4]. The intrinsic properties of this class of materials have sparked a flurry of research, with the goal of better understanding their inorganic–organic structure; fundamental, structural, and motional behavior, and ultimately improving their efficiency for a variety of applications [5–10]. Among the perovskite family, particularly in relation to light harvesting applications, methylammonium lead iodide (MAPbI 3 ) has been much exploited as a photoactive material with its power conversion efficiency being over 20% [11, 12]. However, another variant, formamidinium lead iodide (FAPbI 3 ), has also recently garnered considerable interest by virtue of its peculiar merits, namely, its larger organic formamidinium (FA) cation relative to methyl ammonium (MA), thereby affording a more symmetric crystal structure, smaller optical band gap that enables light absorption to near infra-red region, and elevated decomposition temperature that potentially enhances its thermal stability [13–15]. Moreover, a major setback in the synthesis of FAPbI 3 for use is its phase purity.

During the synthesis, its crystal structure revealed different polymorphs—trigonal, three dimensional, luminescent, narrow band gap semiconducting black α-phase; and 1-D hexagonal, non-luminescent, yellow insulating non-perovskite δ-phase, which generally forms at room temperature as opposed to the other phase that is stable at elevated temperature [16–19]. As a result of the above, several synthetic protocols have been employed to synthesize stable and pure α-phase FAPbI 3 mostly from wet-chemistry [20–24]. Fu et al. recently confirmed that by functionalizing the surface with large-sized organic molecules, the cubic FAPbI 3 process can be stabilized [25]. They showed that the functionalized surface helps to stabilize the cubic FAPbI 3 process at room temperature by lowering formation energy. However, despite their potential benefits, the use of a mechanochemical method for the synthesis of these types of nanocrystals has not been widely utilized [26–31].
Significant efforts have recently been made to obtain high-performance quasi-2D PeLEDs, enabling unparalleled rapid growth. Generally, organic–inorganic halide three-dimensional (3D) perovskites show higher solar cell efficiency as compared to their 2D congener. However, the ambient stability of 2D perovskites is significantly better than that of the 3D perovskites. For practical applications, quasi-2D perovskite, which is a combination of 3D and 2D perovskites, is better than 2D and 3D perovskites. Two-dimensional perovskites contain large-size organic cation, which is hydrophobic in nature. The organic cation protects the perovskite geometry from water and oxygen. Owing to their superior semiconducting properties, quasi-2D perovskites have drawn significant attention and have emerged as one of the most promising materials for next-generation light-emitting diodes (LEDs). Quasi-2D perovskites have exceptional optical properties owing to their structural features. The spectral tunability of quasi-2D perovskites can be modulated by composition and dimensionality engineering. These properties enable continuous wavelength tuning of photoluminescence (PL) from violet to near-infrared (NIR) spectral regions. However, currently, the performance and stability of quasi-2D PeLEDs are currently inadequate to make them commercially viable. Therefore, more research into the optical and electrical properties of these materials is required.
Herein, we report solvent-free mechanochemical synthesis of quasi-2D perovskite \((\text{DDA})_2\{\text{FAPbI}_3\}_{n-1}\text{PbI}_4\). The synthesized products were characterized by XRD, XPS, transmission electron microscopy (TEM), UV, and PL experiments. We used different amounts of DDA to tune the molecular level structural dimensionality and optical properties. With the increasing amount of DDA, the emission from 3D layer diminished whereas the emission from the 2D layer increased. As a proof-of-concept demonstration the materials have been explored in perovskite solar cell.

2. Experimental section

2.1. Materials

Lead (II) iodide \([\text{PbI}_2]\), formamidinium acetate (HN=CHNH2-CH2COOH, 99%), dodecylamine hydrogen iodide (DDA) \((\text{C}_{12}\text{H}_{25}\text{NH}_2\cdot\text{HI})\), toluene \((\text{C}_6\text{H}_5\text{CH}_3\), anhydrous, 99.8%) were purchased from sigma-Aldrich and used without any further purification.

2.2. Solid state synthesis of \(\alpha\)-phase FAPbI$_3$ NSs

In a typical synthesis of 1, lead iodide \((0.2 \text{ mmol, 0.92 mg})\) and formamidinium acetate \((0.2 \text{ mmol, 0.21 mg})\) were grinded by mortar and pestle for 30 s to obtain yellow colored powder. Dodecylamine, hydrogen iodide \((0.14 \text{ mmol, 0.44 mg})\) was added to the above powder and grinded. The powder turns from yellow-reddish yellow after 60 s of grinding to form an intermediate. The continuation of grinding for another 60 s afforded deep red colored \(\alpha\)-phase FAPbI$_3$. The product was washed with ethyl acetate \((10 \text{ ml})\) and dried at 60 °C for overnight.

For the preparation of compounds 2, 3, 4 and 5, we used different amounts of dodecylamine hydrogen iodide \((\text{DDA.HI})\) such as 22 mg, 11 mg, 5.5 mg and 3 mg, respectively, in each case. The amounts of lead iodide \((0.2 \text{ mmol, 0.92 mg})\) and formamidinium acetate \((0.2 \text{ mmol, 0.21 mg})\) were the same for syntheses of 2-5. The molar ratios used in the synthetic protocol are tabulated in Table S1.

![Fig. 2. XRD analysis of \((\text{DDA})_2\{\text{FAPbI}_3\}_{n-1}\text{PbI}_4\).](image)

![Fig. 3. XPS analysis of \((\text{DDA})_2\{\text{FAPbI}_3\}_{n-1}\text{PbI}_4\): (a) Pb 4f, (b) I 3d, (c) C1s, and (d) N1s.](image)
2.3. Characterization methods

The powder X-ray diffraction (XRD) was performed on D/MAX2500V/PC diffractometer, Rigaku using Cu-rotating anode x-ray. During the measurement, the Bragg’s diffraction angle (2θ) range was set to 10–50° and scan rate was 2°/min. The X-ray photoelectron spectroscopy (XPS) was performed in K-alpha (ThermoFisher) to analyze the chemical compositions. The morphology, shape, and composition of the catalysts were studied via field emission scanning microscopy (FESEM; MIRA II KMH-TESCAN, Brno, Czech Republic). Energy Dispersive X-Ray Spectroscopy (EDS) was done to characterize the elements of the samples. The transmission electron microscopy (TEM) is performed on FEI-Tecnai 20 G2, at 25 keV. JASCO V-770 UV–VIS spectrophotometer is used for measuring the absorbance spectra of the solid materials. All the photoluminescence (PL) spectra were taken in Cary Eclipse fluorometer, (Varian) in solid-state.

The J-V characteristics were recorded with a solar simulator LA850 (McScience). The power conversion efficiency (PCE) spectrum was measured using a McScience Spectral IPCE Measurement System with monochromatic light from a Xenon lamp. Light intensity (I) dependence of J-V was recorded with the solar simulator by varying the sun intensity from 10–100 mW cm–2.

3. Result and discussion

3.1. Synthesis of α-phase FAPbI3 NSs

In a typical synthesis, lead iodide and formamidinium acetate were ground in a mortar using a pestle (Scheme 1). The molar ratios of the precursors used for the green synthetic protocol are summarized in (Table S1). The formation of a yellow product indicated the formation of bulk δ-phase FAPbI3 [34] At room temperature, bulk FAPbI3 tends to settle in the δ-phase, which is thermodynamically more favorable than the α-phase. For practical applications, the α-phase is more important than the δ-phase because α-phase indicates a light-active material whereas the δ-phase indicates a light-inactive material with a high bandgap energy [35]. In our case, DDA.HI, a long-chain alkyl ammonium salt, was added to δ-phase FAPbI3 to stabilize the product in the α-phase, in which the color changed from orange to dark red. Generally, a long-chain surfactant stabilizes the α-phase by reducing the thickness.

![Fig. 4. (a–e) SEM images for (DDA)2 [FAPbI3]n–1PbI4 for compounds 1–5, (f–i) Elemental mapping.](image-url)
or size of the nanocrystals. This kind of phenomenon was previously reported in the case of CsPbI\(_3\) [36] and FAPbI\(_3\) [19]. Interestingly, in our case, the DDA chain was incorporated into the crystal structure, thereby reducing the size of the bulk \(\delta\)-phase and stabilizing it in the \(\alpha\)-phase of quasi-2D-(DDA)\(_2\)[FAPbI\(_3\)]\(_n\)-PbI\(_4\) (Fig. 1).

3.2. Phase analysis by X-ray diffraction (XRD)

The XRD analysis is utilized in order to determine the formation of phase purity of (DDA)\(_2\)[FAPbI\(_3\)]\(_n\)-PbI\(_4\) perovskite nanosheets. DDA-incorporated FAPbI\(_3\) adopts quasi-2D structure as observed in powder X-ray diffraction (PXRD) pattern (Fig. 2). The quasi-2D structure of our synthesized compounds, 1–5, is represented by the planes, \(<111>\), \(<002>\), \(<012>\), and \(<112>\) at 8.23, 10.13, 11.87, and 13.42, respectively [37].

3.3. X-ray photoelectron spectroscopy analysis (XPS)

The XPS spectra are illustrated in Figs. 3 and S2 for 5 are illustrated by Voigt curve fitting by following Shirley background elimination to designate the twin peaks of Pb 4f\(_{7/2}\) and Pb 4f\(_{5/2}\). Four peaks were obtained in the Pb 4f spectra, which reveal that Pb is represented in unique chemical environments. The peaks at 137 and 142 eV are assigned to Pb 4f\(_{7/2}\) and Pb 4f\(_{5/2}\). The spin-orbit split between the Pb Peaks is 4.84 eV. The small peaks at 137.5 and 142.5 eV are designated to Pb\(^{2+}\). The peaks at 619.5 and 635.5 eV are assigned to I 3d\(_{5/2}\) and I 3d\(_{3/2}\). The spin-orbit split between the I peaks is 11.4 eV. Two N peaks at 400 and 401.5 eV are assigned to FA and surface bound DDHI, respectively. The appearance of peaks for nitrogen manifests the successful formation of (DDA)\(_2\)[FAPbI\(_3\)]\(_n\)-PbI\(_4\).

3.4. Morphology studies (SEM and TEM analysis)

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies were employed to understand the surface morphology of (DDA)\(_2\)[FAPbI\(_3\)]\(_n\)-PbI\(_4\). The SEM images for compound 1–5 are shown in Fig. 4(a–e) indicating the formation of nanosheets (NSs) with few micrometers during the mechanochemical synthesis of quasi-2D perovskites. In addition, the formation of (DDA)\(_2\)[FAPbI\(_3\)]\(_n\)-PbI\(_4\) hybrid structure was further confirmed by energy-dispersive X-ray mappings, as illustrated in Fig. 3(f–i), revealing the presence of the Pb, I, C and N atoms in the sample. The SEM images of the (DDA)\(_2\)[FAPbI\(_3\)]\(_n\)-PbI\(_4\) hybrid structure with low magnification are also provided in the Fig. S2. The presence of the N atom further indicates that the \(\alpha\)-FAPbI\(_3\) NSs are stabilized by the addition of DDHI. The TEM images for compound 5 are illustrated in Fig. 5(a–d) indicating nanocrystalline morphology of the nanosheets. High-resolution TEM images of compound 5 exhibited a fringe spacing value (d) = 0.261 nm and 0.32 nm corresponding to the (121) and (222) planes, respectively [38].

3.5. UV–visible and PL studies

Several absorption peaks at 566 nm, 510 nm, 444 nm, 390 nm, and 308 nm were observed in the absorption spectra of compounds 1–5 due to different-sized nanosheets produced during the solid-state synthesis as shown in Fig. 6(a). The Tauc’s plot (Fig. 6(c)) shows that the first absorption bandgap energy increased marginally from 2.02 to 2.05 eV in compounds 1–5 (Table S2). The increased amount of surface-passivating ligand, DDA, is thought to reduce the thickness of the nanosheets, thereby resulting in an increase in the bandgap (Fig. 6(d)). Compound 1 exhibits a photoluminescence (PL) peak at 610 nm, while compounds 1–4 exhibit a tail peak as well as a PL peak at 600 nm, as shown in Fig. 6(b). The dual emission peaks are observed due to the formation of 2D and 3D layers of quasi-2D perovskite [19].
of the 2D perovskite layer dominates over the 3D perovskite layer in compound 1. This is due to the large amount of DDA, which is ideal for the formation of 2D perovskite. All the synthesized compounds dissolved in toluene showed red light when exposed to UV light, as shown in Fig. 7. The various synthetic conditions, precursor salts, and solvents used for the synthesis of α-FAPbI₃ NCs are listed in Table S1. In comparison to the other methods of preparation reported in the literature [38–41] the proposed route of synthesis is easy and ultrafast for producing α-FAPbI₃ NCs at room temperature using a mortar and a pestle. The progress of advances in surface passivation of perovskites using organic halide salts for efficient and stable solar cells is recently reported [42].

### 3.6. Photovoltaic device properties

The FTO substrates were cleaned with detergent, distilled water, ethanol, and acetone using sonication. Then, the substrates were transferred to oven at 70 °C for 2 h. The substrates are treated with UV-ozone for 30 min before coating ETL. The cleaned substrates were then spin-coated with a 0.15 M solution of TiO₂ precursor at 4000 rpm for 20 s to form a compact TiO₂ layer and annealed at 500 °C for 25 min. TiO₂ is a very well-known and widely used electron transport layer for high-efficiency perovskite solar cells. We have fabricated PSCs with n-i-p architecture using: FTO/TiO₂/Perovskite/Spiro-OMeTAD/Au device structure. The optimized thickness of TiO₂ layer is 50 nm. If we keep on increasing the thickness of ETL, it will increase the series resistance in
Fig. 8. Photocurrent density-voltage (J-V) curve for (DDA)$_2$ [FAPbI$_3$]$_n$.PbI$_4$ under 1 sun illumination condition.

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
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</thead>
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<tr>
<td>1</td>
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<td>61.02</td>
<td>12.70</td>
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<tr>
<td>3</td>
<td>0.954</td>
<td>22.97</td>
<td>64.69</td>
<td>14.18</td>
</tr>
<tr>
<td>5</td>
<td>0.961</td>
<td>23.41</td>
<td>67.61</td>
<td>15.23</td>
</tr>
</tbody>
</table>

... solar cells and affects the FF and hinders the efficient charge collection. The (DDA)$_2$ [FAPbI$_3$]$_n$.PbI$_4$ (5) perovskite, 56 mg dissolved in 0.1 mL anhydrous DMF:DMSO (4:1) and deposited via spin coating the precursor solution on the top of TiO$_2$ layer at 5000 rpm for 50 s with 0.5 mL of chlorobenzene dropped on substrate 20 s before the end. The coated films were then annealed at 170 °C for 45 min. Then the hole transport layer (HTL) is coated at 4000 rpm for 40 s by using spiroOMeTAD (73% vacuum of 10$^{-7}$ Torr) and the deposition rate was 4 Å/s Fig. 8 shows the photocurrent density-voltage (J-V) curve of Pervoskite solarcell.

The PCE can be calculated using the following equation:

$$\text{PCE} = J_{SC} \times V_{OC} \times FF / P_{in}$$

Here, $P_{in}$ is the input power of the cell, FF is the fill factor, and $J_{SC}$ and $V_{OC}$ are the short-circuit current density and open-circuit voltage, respectively.

The device showed the open-circuit voltage ($V_{OC}$) of 0.961 V, short-circuit current density ($J_{SC}$) of 23.41 mA cm$^{-2}$, and PCE of 15.23% under one-sun illumination conditions. Further progress in the device architecture is currently underway in our laboratory.

Declaration of Competing Interest

We declare no conflict of interest.

Acknowledgment

This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No. 20194030202320), and the Mid-career Researcher Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (No. 2019R1A2C2086747). A.A. Ghfar is grateful to the Researchers Supporting Project number (RSP-2021/407), King Saud University, Riyadh, Saudi Arabia for the financial support.

Supplementary materials


References
