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Type-I Heterostructure and Improved Phase Stability of Formamidinium Lead Iodide Perovskite Grown on WS₂

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Abstract: Heterostructures of two-dimensional materials provide an opportunity for the discovery of novel properties and improved material performances. In this work, we demonstrate the chemical vapor deposition growth of two-dimensional perovskite/WS₂ heterostructures. Owing to type-I band alignment, photoluminescence (PL) measurements indicated the photogenerated carrier transfer from the WS₂ to the perovskite layer. In order to investigate the carrier transfer mechanism, power-dependent PL spectra were measured. The PL intensity of the two-dimensional perovskite grown on WS₂ exhibited super-linear dependence to the excitation power. In addition, two-dimensional perovskites grown on WS₂ showed better air stability compared with the pristine perovskite. The improved stability is attributed to strain in the two-dimensional perovskite layer induced by the underlying WS₂. The results presented here offer better understanding of the two-dimensional perovskite based heterostructures and their potential use in practical applications, such as light emitting diodes and lasers.

Keywords: two-dimensional materials; hybrid halide perovskites; heterostructure, WS₂

1. Introduction

Low-dimensional materials, such as nanoparticles, nanotubes, and nanosheets, offer great potential compared to their bulk counterparts¹⁻⁴. In particular, two-dimensional (2D) materials have been extensively studied due to their unique and diverse properties^{5,6}. The most well-known 2D materials are graphene, transition metal dichalcogenides (TMDCs), and hexagonal boron nitride (h-BN)⁷. Recently, 2D hybrid halide perovskites have been reported as a new addition to the 2D materials family⁸. 2D hybrid halide perovskites are a subclass of the hybrid halide perovskite family, which have a chemical formula ABX₃, where A is an organic amine cation, B is a metal cation, and X is a halide anion⁹. Within a decade, these perovskites have shown promising applications in solar cells¹⁰, photodetectors¹¹, and light emitting diodes (LEDs)¹². Compared to their bulk counterparts, 2D hybrid halide perovskites have several advantages, such as better stability, bandgap tuning by thickness engineering, and higher exciton binding energy⁸. In addition, 2D perovskites exhibit novel properties due to strong quantum confinement effect¹³.

Van der Waals heterostructures of 2D materials offer new phenomena in next generation device applications, such as interlayer excitons, valleytronics, and moiré potentials¹⁴⁻¹⁶. Recently, heterostructures of 2D

perovskite with other 2D materials have been reported. These heterostructures exhibited improved performances in device applications and novel properties. Very recently, we demonstrated a perovskite/TMDC heterostructure with type-II band alignment¹⁷. In type-II heterostructures, electrons and holes are separated into different layers due to the staggered alignment of valance and conduction bands of each layer. Type-II heterostructures of 2D materials have been widely studied for charge separation, which is an important phenomenon for solar cells¹⁸. On the other hand, in type-I band alignment electrons and holes are confined in the small bandgap material, which are transferred from the large bandgap material. These confined charge carriers (electrons and holes) in heterostructures with type-I band alignment offer a great potential in optoelectronic applications, such as LEDs¹⁹. However, type-I heterostructures based on 2D materials have been scarce.

In this work, we report a 2D perovskite/tungsten disulfide (WS₂) heterostructure with type-I band alignment. We employed a small bandgap 2D perovskite, namely, formamidinium lead iodide (FAPbI₃). FAPbI₃/WS₂ heterostructures were fabricated by chemical vapor deposition (CVD) methods. The photoluminescence (PL) measurement of the FAPbI₃/WS₂ heterostructure revealed a PL enhancement in the FAPbI₃ emission, while WS₂ peak showed PL

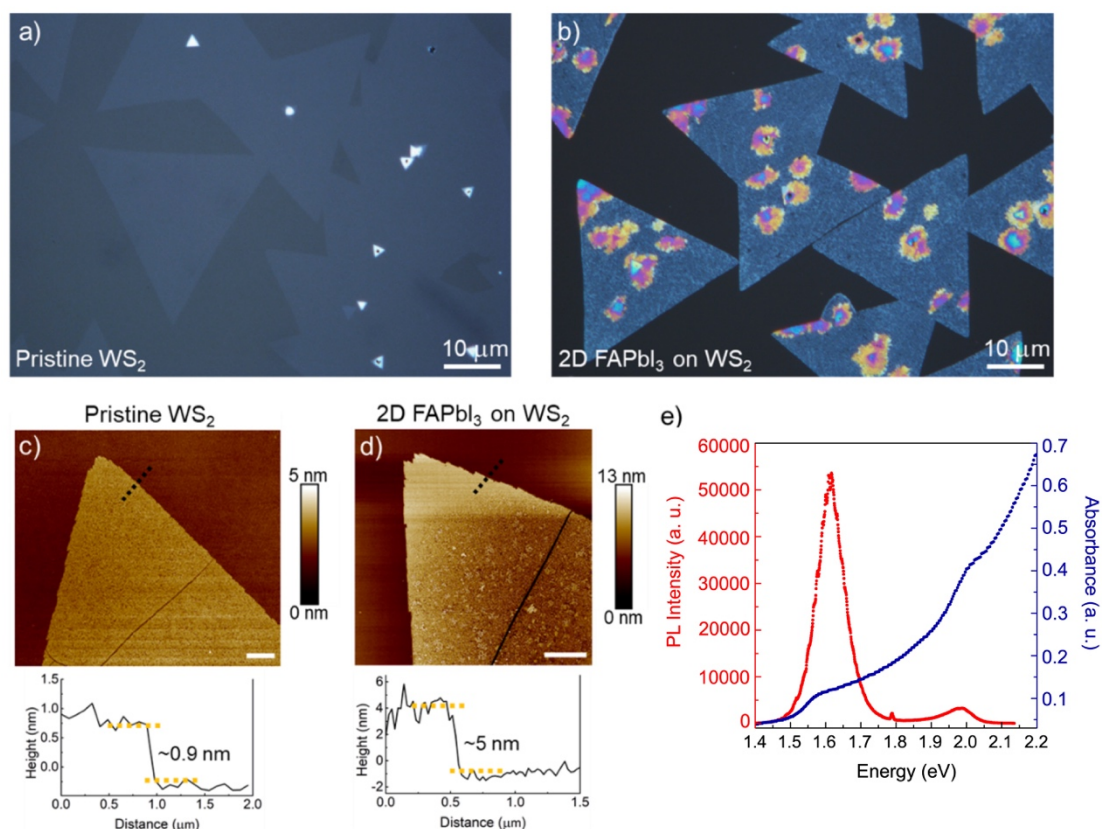


Fig. 1: Optical images of (a) as-grown WS₂ grain with a triangular shape and same grain after the deposition of a 2D FAPbI₃ (b). AFM images of pristine WS₂ (c), and FAPbI₃/WS₂ heterostructure (d). Scale bars are 2 μ m. Lower panels of AFM images are the height profiles measured along the black dashed lines shown in the corresponding AFM images. (d) PL (red data) and absorption (blue data) spectra of the FAPbI₃/WS₂ heterostructure.

quenching. This is attributed to the transfer of photogenerated carriers from the WS₂ layer to FAPbI₃ because of type-I band alignment. Power dependent PL measurement also supported the transfer of both electrons and holes from WS₂ to FAPbI₃. In addition, the FAPbI₃ grown on WS₂ showed higher stability over long time compared to FAPbI₃ only sample. We discuss the origin of this improved stability in detail.

2. Experimental

2.1 CVD growth of FAPbI₃/WS₂

First, monolayer WS₂ was synthesized by CVD on c-plane sapphire, as reported previously from our group²⁰. WO₃ and sulfur powders were placed in a three-zone furnace. The WO₃, sulfur, and substrates were heated at 1065 °C, 165 °C, and 925 °C, respectively. This as-grown WS₂/sapphire substrate was subjected to the following two-step process¹⁷ to synthesize FAPbI₃ perovskite layer on the WS₂ surface. First step was the vapor-deposition of PbI₂ on WS₂. For this, PbI₂ powder was placed at the center of a CVD furnace, and as-grown WS₂/sapphire substrate was put at the downstream. While flowing 50 ccm of Ar gas, the furnace temperature was gradually increased to 360 °C and kept at this temperature for 15 min to deposit PbI₂ on WS₂. PbI₂ was then converted to perovskite (FAPbI₃) by intercalating formamidinium

iodide at 150 °C for 20 min under a constant Ar flow.

2.2 Characterizations

Optical images were taken by an optical microscope (Nikon Eclipse ME600). Atomic force microscope (AFM) images were obtained using a Nanoscope V (Bruker). PL spectra were collected with a Raman spectroscope (Tokyo Instruments Nanofinder 30) using a 532 nm laser. UV-vis absorption spectra were measured by using a UV-3600 (Shimadzu) spectrophotometer.

3. Results and discussion

Figure 1a and b shows the optical images of monolayer WS₂ before and after the deposition of a 2D FAPbI₃ layer, respectively. As-grown WS₂ grains have triangular shapes, with some of the grains merging with each other. White contrast seen at the center of some grains is multilayer WS₂ which acted as nucleation site. As can be seen in Fig. 1b, FAPbI₃ perovskite layer selectively grew on the WS₂. Previously, we reported this unique selective growth behavior for MAPbI₃ perovskite/WS₂ heterostructures.¹⁷

Our analyses revealed that the higher surface energy of

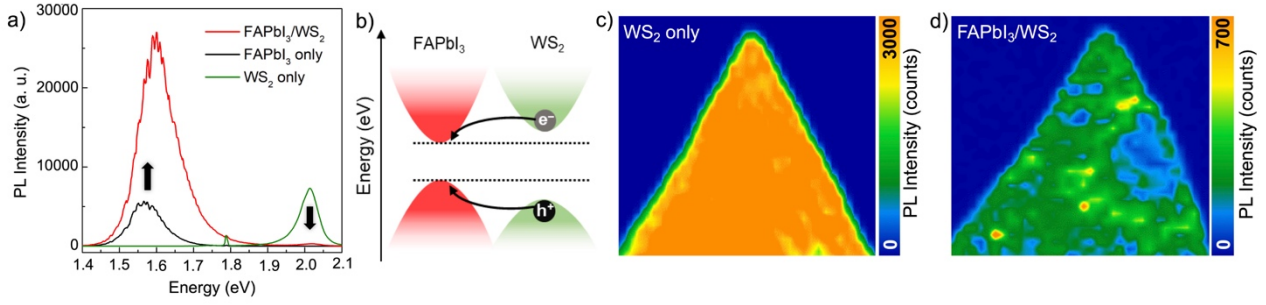


Fig. 2: (a) PL spectra of the heterostructure (red line), FAPbI₃ only (black line), and WS₂ only samples (green line). (b) Band diagrams of FAPbI₃ and WS₂, showing the type-I band alignment. PL intensity mappings for WS₂ peak (2 eV) for WS₂ only (c), and FAPbI₃/WS₂ (d).

WS₂ compared to c-plane sapphire assists the growth of 2D perovskite layer¹⁷. As the selective growth takes place during the deposition of the PbI₂ layer, we observe a similar growth behavior in FAPbI₃. Here, the higher surface energy of WS₂ compensates the energy barrier required for the nucleation of PbI₂. In Fig. 1b, the red and yellow colored areas correspond to thick perovskite layers that grew around the nucleation centers of WS₂ grains. The AFM images of the WS₂ and FAPbI₃/WS₂ heterostructure are shown in Fig. 1c and d, respectively. Pristine WS₂ has a thickness around 0.9 nm, which agrees well with the reported value²¹. In the case of the heterostructure (Fig. 1d), total thickness increased to ~5 nm, indicating that FAPbI₃ thickness is around 4 nm. These results confirm the deposition of a 2D thin layer of FAPbI₃ on WS₂. To further verify the formation of the heterostructure, PL and absorption spectra were also measured (see Fig. 1e). PL spectrum of the heterostructure (red data in Fig. 1e) consists of two distinct PL peaks. The PL peak at 1.61 eV is originated in the 2D FAPbI₃, while the peak at 2 eV is the emission from WS₂ layer²⁰. For bulk FAPbI₃ perovskites optical bandgap is around 1.55 eV²². However, in our case the bandgap increased to 1.61 eV as can be seen in the blue shifted PL emission. This blue shift can be explained by the quantum confinement effect in 2D FAPbI₃ due to the reduced thickness^{17,23}. Absorption spectrum of the heterostructure (blue data in Fig. 1e) agrees well with the PL spectrum. A sharp absorption edge at ~1.58 eV arises from FAPbI₃, while additional absorption edge at ~2 eV is from the WS₂ layer.

To further elaborate the optical properties, PL spectra of isolated FAPbI₃ and WS₂ were compared with that of the heterostructure in Fig. 2a. As expected, the pristine FAPbI₃ and the pristine WS₂ showed PL emission at 1.58 eV and 2 eV, respectively. Interestingly, in the case of the heterostructure, the PL intensity of FAPbI₃ considerably increased. In contrast, the PL from WS₂ was strongly quenched. According to the band structure calculations, the heterostructure of FAPbI₃ and WS₂ possesses type-I band alignment^{17,24–26}. The type-I band alignment is displayed in Fig. 2b. In this type-I alignment, photogenerated charge carriers (both electrons and holes) transfer from the large bandgap material (WS₂) to the small bandgap material (FAPbI₃). Therefore, the

increased PL intensity of FAPbI₃ in the heterostructure can be explained by energy transfer from the WS₂ layer to the FAPbI₃ layer upon photoexcitation¹⁹. PL peak intensity mappings for WS₂ peak measured before and after FAPbI₃ deposition are shown in Fig. 2c and d, respectively. It is clear that after the FAPbI₃ deposition, the PL intensity of the WS₂ decreased on the whole grain. We note that deposition of another material can cause a decrease in the PL intensity by preventing the laser penetration. However, considering the optical absorption coefficient of FAPbI₃ (up to 10⁵ cm⁻¹)²⁷, penetration depth for a 532 nm laser is around 100 nm. Therefore, we excluded the screening effect by FAPbI₃ on the PL quenching of WS₂ peak.

In order to understand the increased PL intensity of FAPbI₃ in the heterostructure, we measured excitation power dependence of the PL spectrum. In Fig. 3,

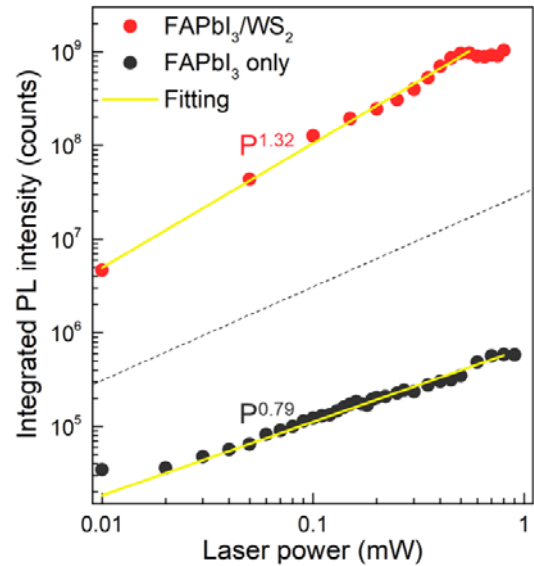


Fig. 3: Log-log plot of laser power dependence of integrated PL intensity for FAPbI₃ peak in the heterostructure (red dots) and in the FAPbI₃ only sample. PL peak intensities are integrated over the range of 1.45–1.75 eV for the FAPbI₃ peak. Yellow lines correspond to the power-law fittings. Black dotted line is the linear power dependence, which is added as a guide for comparing super-linear and sublinear power dependence.

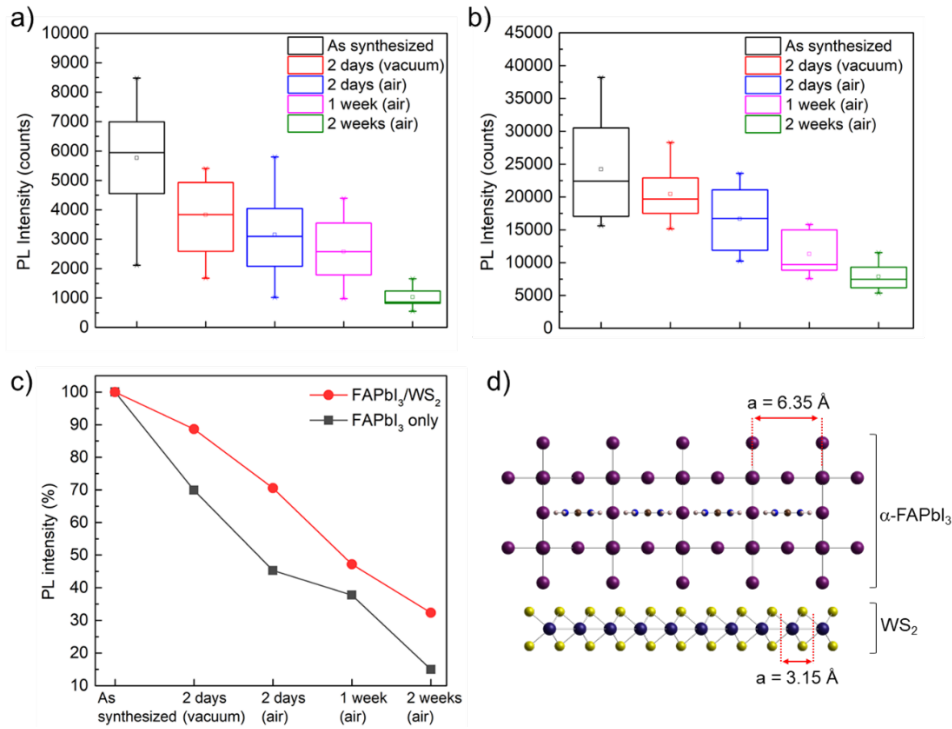


Fig. 4: PL intensity measurements for FAPbI₃ only (a), and FAPbI₃/WS₂ for up to 2 weeks in air. (c) Comparison of intensity decrease in FAPbI₃ PL emission for FAPbI₃ only (black line) and FAPbI₃/WS₂ (red line). (d) An atomic model of FAPbI₃/WS₂ heterostructure.

integrated PL intensity of the FAPbI₃ peak is plotted as a function of the laser power. Fig. 3 displays the power dependence of the PL intensity measured for FAPbI₃ only peak (black dots) and FAPbI₃ peak in the heterostructures (red dots). The data can be fitted by a power-law function ($I \propto P^k$), where I is the PL intensity, P is the excitation power, and k is the power factor²⁸. Depending on the charge carrier recombination mechanism, different k values can be observed. $k < 1$ is indicative of free-to-bound transitions or Auger process, while $1 < k < 2$ is for excitonic or biexcitonic transitions²⁹. Power factors were calculated based on power-law function fittings shown by yellow lines in Fig. 3. For the perovskite only peak, $k = 0.79$ refers to the recombination of free carrier or Auger recombination³⁰. For the FAPbI₃ peak in the heterostructure, a super-linear power dependence with $k = 1.32$ was observed. This super-linear dependence can be related to recombination of mixed free carrier and excitonic states. This sublinear ($k = 0.79$) to super-linear ($k = 1.32$) transition can be attributed to the disassociation of excitonic species at the FAPbI₃/WS₂ interface as a result of carrier transfer in type-I band alignment^{30,31}. However, the charge carrier dynamics of the FAPbI₃/WS₂ heterostructure need to be further investigated.

Finally, long-term PL stability of the heterostructure was also investigated. In Fig. 4a and b, PL spectra of FAPbI₃ only and FAPbI₃ grown on WS₂ were measured for up to two weeks. In both cases, the PL intensity decreased with increasing the time. It is known that FAPbI₃ undergoes a phase transformation at room temperature²⁰. α -phase of FAPbI₃ is the desired

perovskite structure. However, α -FAPbI₃ is unstable at room temperature and it gradually converts to non-perovskite δ -phase structure^{22,32}. The δ -phase of FAPbI₃ is undesirable as it does not show PL emission. Therefore, the decrease in the PL intensity is a sign of phase transformation of FAPbI₃ into non-perovskite δ -phase. In Fig. 4c, decrease in the PL intensity of FAPbI₃ only (black line) and FAPbI₃ grown on WS₂ (red line) is compared. In the case of FAPbI₃ only sample, PL intensity decreased almost 85% with respect to the initial intensity. For FAPbI₃ grown on WS₂, PL intensity only decreased to ~67%. The better stability of the latter can be attributed to the slower phase transformation of α -FAPbI₃ into δ -FAPbI₃. It is likely that WS₂ layer suppresses the structural transformation of FAPbI₃. Very recently, Chen et al., reported the phase stabilization of FAPbI₃ through strain engineering³³. They claimed that strain is induced by heteroepitaxial growth of FAPbI₃ on lattice mismatched substrates, which stabilizes the α -FAPbI₃ structure. Previously we also reported the epitaxial growth of 2D perovskite on WS₂¹⁷. Therefore, most likely WS₂ may induce a strain on FAPbI₃, which stabilizes the α -phase by preventing the phase transformation. In Fig. 4d, an atomic model of FAPbI₃/WS₂ heterostructure is shown. The α -FAPbI₃ has a larger lattice constant (6.35 Å)³³ compared to WS₂ (3.15 Å)³⁴. Therefore, this large lattice mismatch is expected to cause a compressive strain on the α -FAPbI₃ lattice. As conversion to δ -FAPbI₃ is triggered by the internal tensile strain, the compressive strain caused by WS₂ cancels out the internal tensile strain in α -FAPbI₃.

4. Conclusions

We present the CVD growth of a 2D heterostructure of FAPbI₃ and WS₂. Type-I band alignment in the heterostructure enhanced the PL emission from the FAPbI₃ layer as a result of photogenerated energy transfer from the monolayer WS₂ to the FAPbI₃ layer. The power dependent PL measurements for FAPbI₃ in the heterostructure showed a super-linear dependence, which indicates the excitonic recombination at the FAPbI₃/WS₂ interface. These results hold a promise for realizing type-I device structure based on 2D perovskites. Type-I heterostructures are promising in LED and laser applications due to the enhanced light-matter interactions because of the confined charge carriers. Finally, the heterostructure showed an improved phase stability of α -FAPbI₃, likely due to WS₂-induced strain. As the long-term stability of perovskites is a major concern, we believe that our result would also contribute to the stabilization studies of perovskite structures.

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