WS₂ Monolayer Integration in a FAPbI₃-based Heterostructure

Jorge Luis Miró-Zárate¹, Felipe Cervantes-Sodi^{*,2}, Milton Carlos Elias-Espinosa¹, Skarleth García-Trujillo², Carolina Janani Diliegros-Godines^{*,3}

¹Instituto Tecnológico y de Estudios Superiores de Monterrey, Campus Santa Fe, School of Engineering and Science, Mexico City 01389, Mexico

²Physics and Mathematics Department, Universidad Iberoamericana Ciudad de México, Prolongación Paseo de la Reforma 880, Mexico City 01219, Mexico

³Instituto de Física, Benemérita Universidad Autónoma de Puebla, Edificio IF1 Ciudad Universitaria, Puebla, Pue, 72750, Mexico

*Corresponding author: felipe.cervantes@ibero.mx and carolina.diliegros@correo.buap.mx

Abstract

Incorporating a monolayer of WS₂ via interface engineering enhances the overall physical properties of a FAPbI₃ perovskite based heterostructure. FAPbI₃/WS₂/TiO₂/ITO and FAPbI₃/TiO₂/ITO heterostructures were analyzed by UV-Vis spectroscopy, X-ray diffraction, scanning electron microscopy and atomic force microscopy. The configuration with WS₂ interlayer presents higher absorption in the visible region with a bandgap of ~1.44 eV. WS₂ also enhances the deposition process of FAPbI₃, resulting in the formation of pure photoactive α -phase without the non-photoactive δ -phase nor residual plumbates. The incorporation of the monolayer improves the crystalline structure of the FAPbI₃, promoting a preferential growth in the [100] direction. The smooth surface of WS₂ favors a homogeneous morphology and an increase of the grain size to ~4.5 µm, the largest reported for similar structures. Furthermore, the work function obtained lets us propose an enhance an adequate energy band alignment between FAPbI₃ and the n-type layers for the electron flux to the cathode. These findings strongly suggest that the interfacial coupling of FAPbI₃/WS₂ could be a promising candidate in photovoltaic applications.

The necessity to enhance the photovoltaic properties of perovskite based heterostructures has prompted the incorporation of new layers and functional materials into its the original architecture. A typical perovskite architecture comprises of HTL/perovskite/ETL/TCO/Glass¹²³, where TCO, ETL, and HTL are the transparent conductive oxide, electron transport layer, and hole transport layer, respectively. The above-mentioned heterostructures are known to be affected by trap states and interfacial defects, resulting in a loss of electronic and optoelectronic properties due to inadequate interfacial charge transfer⁴.

Recently, 2D semiconducting materials, such as transition metal dichalcogenides (TMDs), in particular their monolayers (ML), have been reported to improve the charge separation mechanism, reduce the interfacial recombination and passivate defects, and improve the energy level alignment when incorporated into a heterostructure⁵. H phase WS₂ present an electron mobility of ~28 cm² V⁻¹ s⁻¹ ⁶, a direct energy band gap (E_g) as ML and inherent n-type semiconductor characteristics⁷. It has been studied in 2D van der Waals heterostructures, and in 2D-3D heterostructures with photoactive materials.⁸ Density Functional Theory (DFT) calculations suggests that the incorporation of ML WS₂ in a photoactive structure, as ETL, can improve the performance of power conversion efficiency (PCE) ⁷.

Among photoactive materials, hybrid inorganic-organic perovskite such as FAPbI₃ exhibits outstanding optoelectronic properties and a E_g of 1.42 eV ⁹, optimal for photovoltaic applications. Nevertheless, FAPbI₃ properties depend not only upon the perovskite itself, but also, on its interaction with adjacent layers, their quality, and the interfaces ⁸.

Compact layers of TiO₂ are the most used ETLs in perovskite-based heterostructures¹⁰. However, TiO₂ displays a low electron mobility of 0.11-4.15 cm² V⁻¹ s^{-1 11 12}, and inadequate charge separation with the perovskite layer¹³. Promising approaches for optimization the ETL have been explored to enhance its properties, such as interface engineering, through the incorporation of materials like TMDs at the ETL/perovskite interface¹⁴.

In this work, the structural and optoelectronic properties of FAPbI₃/TiO₂/ITO/Glass and FAPbI₃/WS₂/TiO₂/ITO/Glass heterostructures are presented. A polystyrene (PS) assisted transfer methodology was employed to incorporate the WS₂, grown initially on sapphire, into the TiO₂ layer for its subsequent use in a perovskite-based heterostructure by depositing the FAPbI₃ photoactive layer on top of the WS₂. All the experiments were performed under an ambient air

atmosphere. It was demonstrated that the incorporation of WS₂ as an interlayer promotes the α -phase of FAPbI₃, with no trace of the δ -phase of the FAPbI₃ nor PbI₂. The effect of the WS₂ MLs in FAPbI₃ surface, results in homogeneous morphology and free-pin holes surface with grain size of ~4.5 µm, enhancing the absorption in the visible range. Work function (Φ) measurements performed by atomic force microscopy (AFM) prove that the WS₂ interlayer enables appropriate band energy alignment for electron flux from the FAPbI₃ layer to the ITO. This work reports the potential of the WS₂ as an interlayer into a perovskite solar cell (PSC) to achieve highly efficient devices.

A modified chemical vapor deposition (CVD) method¹⁵ was used to grow WS₂ on C-plane sapphire substrates. 30 ml of 0.02M solution of Na₂WO₃ was spin coated on 0.8x0.8 cm² substrates at 3.5krpm for 1 minute and loaded in the center of a 1in quartz tube that was positioned through a tubular furnace. 100mg of S powder was placed inside the tube, 20cm upstream of the substrates. A 15-minute 200sccm Ar purge preceded the growth process in the S and W precursors, which were heated to 220°C and 825 °C with an Ar flux of 100sccm. At these temperatures, 10sccm H₂ flux was added for 5 minutes, and then the system was allowed to cool down to room temperature.

A wet transfer method was employed to delaminate the WS₂ films on sapphire¹⁶. An aqueous PS solution was prepared and spin-coated at 3.5krpm, followed by an annealed treatment at 85°C. A water droplet method was employed to form pathways to penetrate the WS₂/sapphire interface. The detached film was then slightly lifted off from the sapphire and transferred to the TiO₂/ITO/Glass, followed by thermal treatment. PS was removed by dissolving in toluene. The TiO₂ film was grown following the methodology reported in reference¹⁷.

FAPbI₃ films were obtained from a modified methodology previously reported by the authors¹⁸. 1 M precursor solution of PbI₂ and NH₄SCN were mixed in DMF and spin-coated on the TiO₂/ITO/Glass and WS₂/TiO₂/ITO/Glass substrate. Then, the PbI₂-coated substrates were immersed in a solution of CH₅IN₂ with isopropyl alcohol for 90s, followed by an annealed treatment at 170°C.

A representative scheme of the heterostructure fabrication is presented in Figure 1(a) and the schematic diagram of the resulting FAPbI₃ heterostructure is displayed in Figure 1(b).

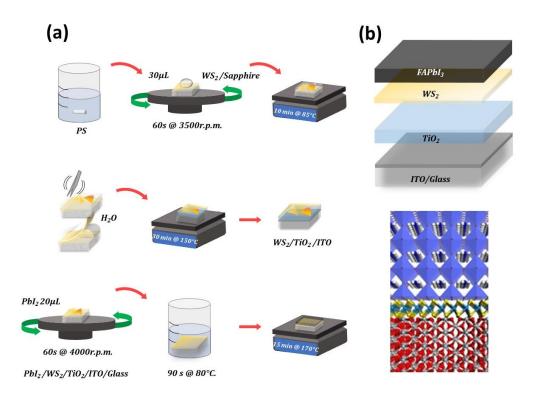


Figure 1. (a) Schematic diagram of the wet transfer method of WS₂ from a sapphire substrate into the TiO₂/ITO/Glass structure, followed by the deposition of FAPbI₃ on the heterostructure. (b) Illustration of the FAPbI₃/WS₂/TiO₂/ITO/Glass heterostructure (top) with an atomistic diagram of the FAPbI₃/WS₂/TiO₂ (bottom).

Optical characterization of the heterostructure was performed by ultraviolet-visible-near infrared (UV-Vis-NIR) spectroscopy (Varian Agilent Cary 5000). Structural characterization was conducted by X-ray diffraction (XRD) (D8 Advanced Eco) with CuK α line (1.5418 Å) as X-ray source. Morphology studies were conducted by scanning electron microscopy (SEM) (Hitachi SU 3500) with an accelerating voltage of 5.0 kV.

The work function (Φ) of the individual layers of WS₂, TiO₂, and FAPbI₃ were measured with frequency modulation Kelvin probe force microscopy (KPFM) using sideband configuration following the methodology reported in reference¹⁹. The probe used was a Multi75-G with a resonance frequency of ~75kHz and a force constant of 3N/m. WS₂ individual topography was characterized by AFM NanoSurf model NaioAFM in static mode with a cantilever Stat0.2LAuD.

XRD patterns of the heterostructures are shown in Figure 2 (a). Both heterostructures reveal the characteristic peaks of α -FAPbI₃ at 13.9°, 19.8°, 24.3°, 28.1°, 31.5°, 34.5°, 40.2°, 42.8°, 49.7°²⁰. Also, ITO peaks are present as expected at 30.4° and 35.3°. Diffraction peaks at 14.2° and 28.8° correspond to the WS₂ (JCPDS Card No. 98-003-9096) are only observed for the heterostructure with WS₂ interlayer. Remarkably, when the WS₂ is incorporated into the heterostructure a preferential growth α -FAPbI₃ in the [100] direction is highly promoted.

During the synthesis of FAPbI₃ at different conditions, some plumbates could be present due to an incomplete conversion of the precursor PbI₂ to the α -phase. The direct growth of FAPbI₃ on TiO₂ shows a diminished presence of those compared with our previous work¹⁸, where the perovskite was grown directly on glass. Here, the signal of the PbI₂ (001) plane at 12.6° disappears when FAPbI₃ is grown on WS₂. The disappearance of plumbates was also confirmed with SEM images as shown in what follows. Pure α -phase of the FAPbI₃ perovskite is grown in both substrates, with and without WS₂, which means that both, TiO₂ and WS₂/TiO₂ are appropriate substrates to avoid the formation of the photoinactive δ -phase.

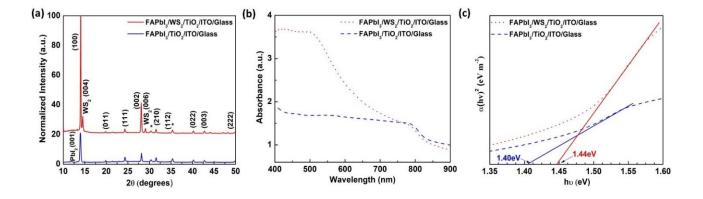


Figure 2. (a) XRD patterns of FAPbI₃/TiO₂/ITO/Glass (bottom) and FAPbI₃/WS₂/TiO₂/ITO/Glass (top) heterostructures, (b) absorbance spectra of heterostructures with and without the WS₂ interlayer. (c) Tauc-Plot used to calculate an E_g of 1.44 eV and 1.40 eV with and without WS₂, respectively.

The absorption spectra of both heterostructures are shown in Figure 2(b), presenting the characteristic absorption edge of the α -FAPbI₃ near to ~800 nm²¹. It is important to point out that the absorption edge of the heterostructure is very similar with and without the WS₂ interlayer, indicating that the WS₂ does not induce a significative change in the excitation absorption edge. This suggests a type-II band alignment in the FAPbI₃/WS₂ interface⁸. The presence of the WS₂ interlayer slightly increases the absorbance in the visible region, which has been reported when a WS₂ layer is used in a CH₃NH₃PbI₃-perovskite based heterostructure²². The heterostructure with WS₂ shows a flat profile from ~400 to ~500 nm, indicative of fewer structural defects and the presence of single crystalline phases on the FAPbI₃ film²³, and promoting the α over the δ phase.

 E_g calculations by the Tauc Plot method, as shown in Figure 2(c), provide values of 1.40 and 1.44 eV without and with WS₂, respectively. The E_g shows a 2.9% increase with the WS₂ interlayer. A widening of the E_g can be explained by the atomic thickness of WS₂ and a strong dipole-dipole repulsion in the FAPbI₃/WS₂ interface²⁴. E_g of the individual layers were also obtained with the same methodology, with values of 3.04, 1.86, and 1.42 eV for TiO₂, WS₂, and FAPbI₃, respectively, which agrees with the reported in the literature²⁵.

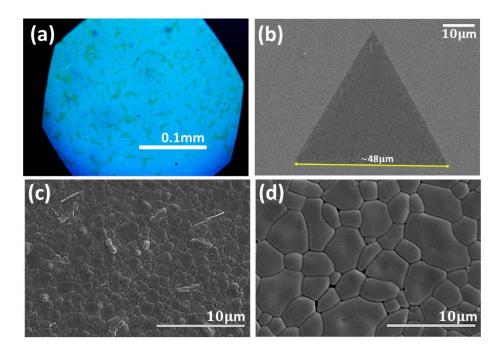


Figure 3. (a) Optical image of as grown ML WS₂ on sapphire. (b) SEM image of an isolated WS₂ ML transferred to TiO₂. (c, d) SEM images of FAPbI₃ film grown on TiO₂/ITO/Glass and WS₂/TiO₂/ITO/Glass, respectively.

In Figure 3(a), it can be observed the high coverage (> 90%) of WS₂ ML, mostly with triangular and hexagonal shapes. The transfer process of WS₂ from sapphire to TiO₂/ITO/Glass allows an almost perfect WS₂ on the ETL, with clean MLs and no PS residues, as can be seen with in a SEM image of an isolated triangular WS₂ ML (area ~1000 μ m²) transferred to TiO₂, shown in Figure 3(b). The high coverage of WS₂ on the TiO₂ surface results in enhanced FAPbI₃ homogeneous morphology and a surface free of pin-holes. Similar to what happens here for FAPbI₃, Ma, *et al.* observed that the atomically smooth surface of WS₂ promotes high crystallinity of a MAPbI₃ film²⁶.

Figure 3(c) shows that the FAPbI₃ perovskite film deposited directly on TiO₂ consists of irregular grains of \sim 1.2µm. The brighter species and irregular shape morphologies over the FAPbI₃ surface correspond to multiplumbates generated by an incomplete conversion of PbI₂ to FAPbI₃; which has been previously reported by the authors¹⁸. The presence of the multiplumbates was also observed in the XRD patterns, along with the existence of the PbI₂ diffraction peak.

The incorporation of WS₂ interlayer promotes the growth of larger grains of ~4.5 μ m of α -FAPbI₃ without any multiplumbates on the film's surface, as illustrated in Figure 3(d). The size of grains in this work are two orders of magnitude larger than other perovskite grains grown on TMDs²⁷. Also, a pin-hole free surface can be observed, which can indicate a reduction of trap densities at the material surface ²⁸.

The surface topography height map of WS₂ and FAPbI₃ and the work function of the WS₂, TiO₂, FAPbI₃ are shown in Figure 4(a-e); all were measured under the same experimental conditions. The surface of the FAPbI₃ films is homogeneous, and Φ is almost constant over the surface with $\Phi \sim 4.7 \text{eV}$, similar to the value obtained by DFT²⁹. The WS₂ ML shows a homogeneous surface with roughness ~0.5 nm and thickness > 1 nm. The smooth surface of ML WS₂ acts as base for nucleation and growth of large grains for FAPbI₃ as previously discussed. Wang, *et al.*, also observed an increase in the grain size of FASnI₃ perovskite grown on MoS₂, WS₂ and WSe₂³⁰. However, the value of Φ presents some variation across the WS₂ surface. Φ increases in the center of the WS₂ triangle, showing a defect heterogeneity formation, also reported in the literature³¹. The charge transfer in perovskite-based heterostructures is regulated by the properties of the interfaces of the perovskite with ETL and HTL, the electrochemical reaction during bonding of charged complexes that compensate surface charging, and irreversible material decomposition³². However,

it is also well known that matching of the Fermi energy (E_F) between layers in a device could play a key role in electron recollection. For the heterostructures reported in this work, a smooth match between the TCO and perovskite layer will be reflected in a better device efficiency. Since Φ is the E_F position with respect to the vacuum level, a comparative energy diagram, based on measured Φ and E_g values, is proposed in Figure 4(f). The E_F is pictured as a horizontal dotted line for each film. The E_F for the n-type ETL, ITO and WS₂ are shifted to the conduction band³³. While the FAPbI₃ film is located at the center of the gap.

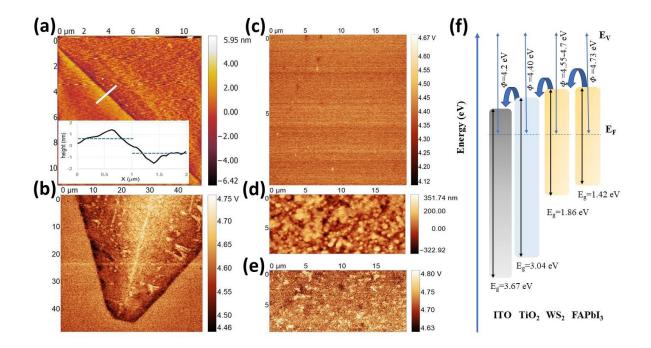


Figure 4. (a) Surface topography by AFM of WS₂ ML. Inset displays the line scan between the interface WS₂/ITO indicated with a white line. Work function values of (b) WS₂, (c) TiO₂, and (e) FAPbI₃. (d) Surface topography of FAPbI₃. (f) Comparative energy diagram of the films included in the heterostructure. The values of E_g and Φ were measured.

In Figure 4 (f) $\Delta\Phi$ between the ITO and ETL is ~0.2 *eV* and then there is another $\Delta\Phi$ ~0.33eV from the ETL to the perovskite. This gives place to a barrier of energy that the free electron needs

to overcome to be recollected. Even when the ETL improves the electron collection the alignment of the E_F observed can provoke charge accumulation and problems of electronic reflux. On the other hand, $\Delta \Phi$ for WS₂ shows a smoother transition even with small Φ variations of WS₂ (4.55 to 4.7 eV), than the observed for structures with only the TiO₂.

The optimization of Φ for the layers that compose a perovskite heterostructure has been studied by other authors. Kang Min Kim *et al.*³⁴ showed that the reduction of Φ for the transparent layer PEDOT:PSS of the PSC ITO/PEDOT:PSS/CH₃NH₃PbI₃/PCBM improves the device performance from 0.07% to 4.02%. Weibo Yan *et al.*³⁵ studied Φ of hole-transporting materials (HTMs) in perovskite solar cells, finding that rationally increasing Φ of HTMs proves beneficial in improving the open circuit voltage of the devices with an ITO/conductive-polymer/CH₃NH₃PbI₃/C₆₀/BCP/Ag structure.

In this work, the incorporation of WS_2 in the heterostructure shows a smoother energy level alignment. This could improve the electron collection, decreasing the recombination process. Therefore, a better performance of the device will be expected, with the improvement of fill factor and short-circuit current density.

In summary, this work presented the experimental incorporation of WS₂ in a FAPbI₃/WS₂/TiO₂/ITO/Glass heterostructure. The presence of WS₂ ML enhances the optical and morphology properties of the FAPbI₃ in the heterostructure. A pure α -phase of the perovskite and the disappearance of plumbates was observed by XRD and confirmed with SEM images for the heterostructures with WS₂. SEM images also show grains of ~4.5 µm of α -FAPbI₃ on WS₂. UV-Vis results suggest a type-II band alignment in the FAPbI₃/WS₂ interface and a widening of 2.9% of the E_g. A smooth energy band alignment was observed by KPFM for the heterostructures with WS₂. Our work presents an experimental analysis of the advantages of the WS₂ as a complementary ETL in perovskites solar cells. Further analysis should be conducted to confirm the improvement of solar efficiency through the incorporation of WS₂.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Conceptualization: JLMZ, FCS, CJDG. Investigation: JLMZ, SGT, FCS, CJDG. Data Curation, Formal Analysis: JLMZ, FCS, CJDG. Funding Acquisition: FCS, CJDG. Resources: FCS, CJDG, MCEE. Supervision: FCS, CJDG. Methodology, Visualization: JLMZ, SGT. Validation: JLMZ, SGT, FCS, CJDG. Writing/Original Draft Preparation: JLMZ. Writing/Review & Editing: JLMZ, FCS, CJDG.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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