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Nano Lett., Just Accepted Manuscript • Publication Date (Web): 24 Jun 2019

Downloaded from http://pubs.acs.org on June 24, 2019

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Giant Enhancement of Photoluminescence Emission in WS₂-2D Perovskite Heterostructures

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Keywords: Two dimensional materials; perovskite; transition metal dichalcogenide; heterostructure; interface; photoluminescence

Supporting Information Placeholder

ABSTRACT: Transition metal dichalcogenides (TMDCs) and two-dimensional organic and inorganic hybrid lead halide perovskites (2DPVSKs) have emerged as highly promising materials for ultralight and ultrathin optoelectronics application. They both exhibit tunability of electronic properties such as band structure, and they can form heterostructures with various types of two-dimensional materials for novel physical properties not observed in single components. However, TMDCs exhibit poor emission due to defect states and direct-to-indirect interband transition, and 2DPVSKs suffer from poor stability in ambient atmosphere. Here we report that fabrication of TMDC-on-2DPVSK heterostructures using a solvent-less process, leads to novel optical transitions unique to the heterostructure, which arise from the hybrid interface and exhibit a strong photoluminescence. Moreover a two orders of magnitude enhancement of the photoluminescence as compared to WS₂ emission is observed. The TMDC on top of 2DPVSK also significantly improves the stability as compared to bare 2DPVSK. Enhanced emission can be explained by electronic structure modification of TMDC by novel interfacial interactions between TMDC and 2DPVSK materials, which shows promise of the heterostructure for high efficiency and stable optoelectronic devices.

As two-dimensional (2D) semiconductors, transition metal dichalcogenides (TMDCs) have emerged as highly intriguing materials in the fields of optics¹², electronics¹³,¹⁴, catalysis¹⁵, and mechanics⁶. They also present some unique physical properties at the mono- and bi-layer level, such as valley polarization effects that allows controlling of spin carriers by light polarization, and led to development of the field of valleytronics in information processing. However, many optoelectronic applications of these materials are limited by their low photoluminescence quantum yield (PLQY), especially at multilayer thicknesses.⁷

Another family of 2D materials - organic-inorganic (hybrid) layered perovskite materials have also emerged as serious candidates for optoelectronic and information technologies. In contrast to TMDCs, layered perovskites not only present unique physics at the monolayer level but also preserve these properties in microscopic thin film devices, such as in solar cells⁸,⁹ and light emitting diodes¹¹,¹²,¹³,¹⁴,¹⁵ (LEDs). Notably, hybrid 2D perovskites (2DPVSKs) are able to sustain large density of current¹⁵ (>10 mA/cm²) and yield reasonably high PLQY values of several to twenty percents¹²,¹⁶,¹⁷. However, 2DPVSKs are susceptible to ambient environmental¹⁸ (oxygen, humidity, temperature, etc.) degradation as compared to purely inorganic materials, which has limited the exploration of their fundamental photo-physical properties.

Recent efforts have aimed at exploring their unique physical properties by creating hierarchical stacks of different 2D materials.¹⁹,²⁰ Here, we investigate the physical properties of a new type of vertical heterostructure composed of a few layers of TMDCs and 2DPVSKs. By creating an atomically-thin interface between these two types of materials, we were able to identify a two-order of magnitude enhancement in photoluminescence emission and improved air stability as compared to the TMDC and 2DPVSK, respectively. We also investigated the underlying mechanisms for the enhancement in heterostructure photoluminescence with a combination of time-resolved photoluminescence spectroscopy (TRPL) spectroscopy, ultraviolet photoemission spectroscopy (UPS), and materials...
modeling, where plausible mechanisms for this enhancement is discussed. The giant enhancement of photoluminescence combined with good air stability makes this heterostructure highly promising for ultrathin and ultralight optoelectronic devices. We believe that by creating a functional heterostructure platform combining inorganic and hybrid materials such as TMDCs and 2DPVSKs, this work presents a unique opportunity to quantitatively understand and tailor the interfacial coupling and electronic structure of such dissimilar hierarchical assemblies by tuning the chemical composition, structure and thickness of each of the materials under external stimuli such as light, electric field and strain.15–26

Figures 1a and 1b depict the layered structure of, respectively, the WS2 TMDC and the Ruddlesden-Popper BA\textsubscript{2}MA\textsubscript{3}Pb\textsubscript{11}I\textsubscript{23} hybrid 2D perovskite (abbreviated as either 2DPVSK or n=4 in the rest of the text) which are investigated here. The thickness of a single WS\2 and single perovskite layer are 0.315 nm and 2.51 nm, respectively. For both, strong carrier confinement effects in the layer plane, which is manifested by a strong anisotropy in optoelectronic and mechanical properties,10,21 as well as unique photophysics17,22 such as quantum confinement effects and large exciton binding energies.23,24 The main difference in the structure of these two materials is that the WS\2 layers are electronically coupled across layers while the layers of perovskites are separated from one another by a thin (~0.7 nm) layer of organic materials (butylammonium BA) and maintains electronic properties of individual layers. The heterostructure (Fig.1c) was constructed by exfoliating 2DPVSK and dry viscoelastic stamping WS\2 on a silicon substrate (Si with a top 285 nm layer of SiO\textsubscript{2}); these processes took place under inert atmosphere to prevent contamination of the interface and degradation of the 2DPVSK (Supplementary Fig. 1). The sample was identified under an optical microscope. Optical image of the sample demonstrates the presence of three regions-- bare WS\2, bare n=4 2DPVSK, and heterostructure (Fig. 1d). From the image optical contrast and Raman spectroscopy (Fig. 1e) we conclude that the WS\2 flake is two layers thick and the n=4 2DPVSK about three layers thick.25 The bare WS\2 flake yields Raman resonances at 351 and 418 cm\textsuperscript{-1}, corresponding to E\textsubscript{2g} and A\textsubscript{1g} vibration modes, respectively. The 67 cm\textsuperscript{-1} separation between the two WS\2 Raman peaks indicates that the WS\2 is double layer (2L).27 The A\textsubscript{1g} mode is related to out-of-plane vibration of sulfur atoms and is sensitive to doping levels,26,27 while the E\textsubscript{2g} mode is associated with the in-plane vibration of tungsten and sulfur atoms and is sensitive to strain.28 The heterostructure presents the same Raman spectrum almost identical to the bare WS\2 flake within the resolution of our instrument (Fig. 1e). These data indicate the doping level is not significantly altered to be observed in Raman spectra (i.e. a doping of more than 6*10\textsuperscript{12}/cm\textsuperscript{2} is needed to register a Raman shift surpassing the instrumental noise), and strain in the WS\2 layers in the heterostructure are unchanged as compared to the WS\2 by itself.29 Based on our fabrication methods, the termination of the 2DPVSK at the interface can take one of several configurations: i) a single layer of BA molecules (the length of BA is about 0.6 nm) with half the density of that in a BA organic interlayer found in the 2DPVSK, ii) a layer of iodine atoms with a negative surface charge, which we can reasonably exclude from the lack of doping observed in the Raman data, or iii) a missing iodine atom in PbI\textsubscript{2} surface exposing a Pb\textsuperscript{2+} bond.30 It is also reasonable to expect a non-homogeneous spatial distribution of the different types of termination enumerated above. The WS\2 is terminated with a layer of S atoms. Depending on the type of termination in the 2DPVSK, the WS\2/2DPVSK interface thickness could vary and display a various degrees of hybridization between the WS\2 and 2DPVSK orbitals at their interface.30,33 Although the lattice constant of the sulfur atom slab is about half the periodic arrangement of the organic BA molecules and perovskite octahedra (Fig. 1a,b), the Raman measurements does not indicate any appreciable strain in the WS\2. This is most likely due to the soft nature of the perovskite and organic layers, as well as the transfer process, which alleviates any significant strain at the interface.34,35

Room temperature photoluminescence (PL) yield significant enhancement of the PL in the heterostructure as compared to
the bare WS$_2$ and 2DPVSK (Fig. 1f). While at first the heterostructure shows a 20-fold enhancement in the PL integrated intensity as compared to the bare 2L WS$_2$, we found that after “interface curing” using laser annealing (with a 532 nm laser at a few kW/cm$^2$ in air for a few minutes) the PL enhancement reaches about 150 times. After degradation of the sample the PL intensity decreases by more than 50 times.

Before interface curing the heterostructure yields a single broad emission peak at about 1.9 eV. The bare WS$_2$ and the heterostructure after interface curing exhibit a broad peak at 1.69 eV and a side feature at higher energy (Fig. 1f). The n=4 2DPVSK emits at around 1.9 eV with a low energy shoulder below 1.8 eV. The side feature in WS$_2$ is also around 1.9 eV, whereas the heterostructure side feature peaks at about 1.95 eV and the main peak in the heterostructure is broader than the bare WS$_2$. Again, the main difference between these samples is that the total PL of the heterostructure is enhanced up to 150 times as compared to the bare WS$_2$. We also note that the center region of the heterostructure still showed strong emission even after 7 months of storage under nitrogen atmosphere and intermittent exposure to air, whereas luminescence emission from the bare 2DPVSK was not detectable due to sample degradation (Supplementary Fig. 2).$^{18,36}$ After degradation we observe a definite decrease in the PL intensity as shown in Fig. 1f. More significant decrease of intensity of lower energy peak comparing to the 1.9eV peak indicates that this degradation compromises interfacial interaction achieved through interface curing and is not reversible through further curing process. Our results indicate that WS$_2$ effectively encapsulates and stabilizes the 2DPVSK underneath it as discussed in the case of boron nitrite.$^{18}$

To show that this observation is not limited to the heterostructure in Fig. 1 we also investigated the 1L WS$_2$/n=3 2DPVSK heterostructure (Supplementary Fig. 3). The 1L WS$_2$/n=3 heterostructure yielded PL enhancements of about 25 times and 80 times before and after interface curing, respectively. It is important to note that after interface curing, the heterostructure PL spectrum is dominated by a broad feature at about 1.7 eV (Supplementary Fig. 3c), which is almost identical to the one observed for the 2L WS$_2$/n=4 heterostructure in Fig. 1f. Therefore, we infer that the PL feature at ~1.7 eV in the heterostructure of type WS$_2$/2DPVSK originates from states located at the heterostructure interface that are strongly activated via interface curing. These PL measurements demonstrate that combining WS$_2$ and 2DPVSK in an artificial heterostructure we have obtained materials with enhanced and more stable PL emission at room temperature.

In order to investigate the mechanism of PL enhancement and understand the features observed at room temperature we carried out measurements at low temperature (7K). Differential reflection spectra (defined as $I_{\text{sample}}/I_{\text{substrate}}$ shown in Fig. 2a) exhibit absorption resonances corresponding to the A, B and C excitons for the bare WS$_2$, and the main exciton for the n=4 2DPVSK.$^{18,23}$ Additional peak between 1.85 and 1.95 eV emerging in the bare WS$_2$ were assigned to the defect states. The bare n=4 2DPVSK exhibits absorption features around 1.95 eV, corresponding to exciton states and higher energy transitions as reported previously.$^{23}$ As illustrated in Fig. 2a, the reflection spectrum of the heterostructure is not the result of a simple sum of the component WS$_2$ and 2DPVSK layers, which is confirmed by the optical constants derived from the differential reflection data (Supplementary Fig. 4). Precisely, the lowest absorption resonance H$_1$ in the heterostructure is at the same energy (1.895 eV) as the perovskite exciton peak but with larger amplitude. On the other hand, resonances H$_2$ (1.945 eV) and H$_3$ (2.067 eV) are at about the same energy as the absorption peaks W$_2$ (also corresponding to n=4 exciton excited states) and A in WS$_2$ but with reduced amplitude. Similarly, higher energy transitions at 2.5eV and 2.7eV corresponding to n=4 features yield enhanced or similar absorption amplitude as compared to the bare n=4 2DPVSK. The B and C excitons in the 2L WS$_2$ are damped in the heterostructure (Supplementary Fig. 4). Additionally, we observe a strong resonance peak H$_2$ at 2.1 eV, which is not clearly present in either of the bare materials, except for a small feature in the bare 2DPVSK spectrum. This new feature was clearly measured using PL excitation (PLE) (Fig. 2b). All H$_4$, H$_5$, and H$_6$ appear as strong absorption peak from the PLE data. The most notable observation from the PLE data is the 25-fold enhancement in the heterostructure as compared to the bare WS$_2$ and n=4 2DPVSK. Overall these results can be summarized as following: the heterostructure absorbs about 25 times more than n=4 2DPVSK and 2L WS$_2$. This is also accompanied (Supplementary Figure 4) by an overall decrease (resp. increase) of the refractive index as compared to the bare WS$_2$ (resp. n=4 2DPVSK).

FIGURE 2. Optical properties at 7K of the 2L WS$_2$/n=4 2DPVSK heterostructure compared to the bare WS$_2$ and n=4 2DPVSK. (a) Reflection spectra. (b) PL excitation spectra. (c) PL spectra, taken at 7K, at 550 nm laser excitation with intensity 5W/cm$^2$ for the bare n=4 and heterostructure, and 900 W/cm$^2$ for the 2L WS$_2$, and 100 W/cm$^2$ for heterostructure after curing. Intensities are scaled with power and integration time to show relative magnitude. (d) Map of n=4 2DPVSK exciton emission at 900W/cm$^2$ 550 nm laser excitation with 5s integration per point. (e) Map of indirect emission of WS$_2$ at same condition. (color bar in intensity a.u.)
In order to quantify the PL enhancement at low temperature and understand its origin, we analyzed the PL spectra at 7 K. The n=4 2DPVSK exhibits a single PL peak at 1.91 eV with a Stokes shift of about 40 meV (Fig. 2c), which is identified as the exciton ground state. The bilayer WS$_2$ PL spectrum yields two broad optical transitions: a broad emission at 1.75 eV with full width at half maximum (FWHM) = 105 meV, and a narrower emission line at 1.86 eV (FWHM = 19 meV). We also observed a small side feature at about 1.905 eV depending on the location on the sample (Supplementary Fig. 2). Based on previous reports, we attribute the broad emission around 1.75 eV due to defect state emission in bilayer WS$_2$. On the other hand, the heterostructure presents a relatively sharp PL peak at 1.87 eV (FWHM = 16 meV) with a broad shoulder around 1.83 eV, which are identified as H$_1$ and H$_2$, respectively. The main change in the heterostructure PL as compared to the individual constituent materials is a two orders of magnitude enhancement of the overall PL intensity as compared to the bare WS$_2$ with a similar emission spectrum (Fig. 2c). After interface curing the heterostructure PL spectrum is dominated by a broad PL peak at 1.65 eV reminiscent of the 1.7 eV PL feature at room temperature. In this case, the heterostructure is enhanced by about three orders of magnitude compared to the bare WS$_2$ and by 25-fold with respect to the bare n=4 2DPVSK before curing.

We performed the same study at low temperature on the 1L WS$_2$/n=3 2DPVSK. At 7 K, the monolayer WS$_2$ yields two emission features, one broad peak at 1.84 eV and a narrow peak at 1.98 eV (Supplementary Fig. 3d). These two peaks can be attributed to defect emission, since this emission disappears at room temperature in bare WS$_2$. Here, we observe a 130-fold enhancement in the total PL of the heterostructure as compared to the bare 1L WS$_2$ a value on par with the heterostructure 2L WS$_2$/n=4 2DPVSK. The corresponding 50-fold enhancement in the heterostructure PL with respect to the bare n=3 2DPVSK is larger than in the 2L WS$_2$/n=4 2DPVSK heterostructure but could be explained by the beam damage on 2DPVSK due to prior measurements and different effective light intensity at the substrate surface due to interferences in the SiO$_2$. Reflection spectra (Supplementary Fig. 3e) show the presence of A and B exciton resonances of the monolayer WS$_2$ in both the WS$_2$ and the heterostructure. The ground exciton state of the n=3 2DPVSK is observed at about 2.0 eV, at about the same energy as the W$_1$ feature of the 1L WS$_2$. Overall the reflection spectra leads to the conclusion that the absorption of the heterostructure is dominated by the 1L WS$_2$ in the low energy range (< 2.2 eV), and mainly shows 1L WS$_2$ features whereas the features of both the n=3 2DPVSK and 1L WS$_2$ (B exciton) are observed for energies larger than 2.2 eV. This is confirmed in the PLE spectra (Supplementary Fig. 3f). Similar to the 2L WS$_2$/n=4 2DPVSK sample, the PLE spectrum of the 1L WS$_2$/n=3 2DPVSK shows 250 times and 70 times higher PL in heterostructure compared to the bare n=3 PVS and 1L WS$_2$ samples respectively.

Photoluminescence maps at peak emission energy for the n=4 2DPVSK and WS$_2$ are shown in Fig. 2d and Fig. 2e, respectively. At the n=4 2DPVSK exciton peak (1.91 eV), strong emission of 2DPVSK is only observed in the bare 2DPVSK region, but not in the heterostructure. In contrast, strong defect state emission is observed in the heterostructure region only (1.81 eV). These maps indicate that 2DPVSK emission is quenched under WS$_2$. Notice that the emission intensities also exhibit spatial variation over the sample, which can be attributed to spatially inhomogeneous layer thickness and coupling between layers (Supplementary Fig. 2).

More insights into the photophysics of the heterostructure were gained by investigating the power dependence of the PL spectra (Fig. 3, and Supplementary Fig. 5 for the 1L WS$_2$/n=3 heterostructure). The integrated PL of the two peaks H$_0$ and H$_2$ yields a close to linear dependence on the light excitation.
intensity, whereas the main PL feature \(H_1\) presents a super-linear intensity dependence with a coefficient of 1.35 (Fig. 3b). Additionally, we observe a ~40 meV blueshift of the energy of the PL peak \(H_0\) with increasing excitation intensity (Fig. 3c) possibly due to state filling. On the other hand, the PL features \(H_1\) undergoes a less than 5 meV redshift over the entire power range and for \(H_2\) we observe a blueshift of less than 2 meV. We also observe no significant broadening of any of the PL features with excitation intensity (Fig. 3d). From these results, we conclude that the feature \(H_0\) corresponds to defect bond exciton,\(^{29}\) which undergoes energy band filling with excitation intensity. Similar to the WS\(_2\) reflection spectra analysis, the main PL emission \(H_1\) is identified as a biexciton state or mixed excitonic - free carrier states. It is confirmed by the super-linear power dependence of PL intensity.\(^{29}\) We suggest this may be a signature of a partial dissociation of the exciton at the interface as reported previously for 2DPVK edge surface or doping at the interface arising from the band alignment and bending. In that case, the redshift with increasing power could be the result of screening effects of the charge interactions at the interface where \(H_1\) state can accumulate, concomitant with the saturation of the \(H_0\) state. In contrast, heterostructure emission after interface curing exhibit slight sublinear power dependence of intensity (coefficient = 0.82), which could be a result of saturation of local states at interface with increasing power. Moreover, its peak position remains unshifted with changing power density, different from defect bound exciton state or indirect transition. This indicates that the PL emission from interface cured heterostructure has different origin than free excitons or band-to-band transition in 2L WS\(_2\).

We observe a more than two order of magnitude increase in PL emission in the heterostructure as compared to the bare WS\(_2\) over the applied range of excitation power density, Fig. 3c shows that this enhancement factor, corresponding the ratio between the integrated PL in the heterostructure and that in the bare WS\(_2\) improves from about 220 at 0.8 kW/cm\(^2\) to 700 at 4.4 kW/cm\(^2\). This improvement is largely attributed to the enhancement of the \(H_1\) state, shown in Fig. 3a.

To gain a deeper understanding of the PL enhancement in the heterostructures composed of TMDCs and 2DPVSK, we performed TRPL, UPS and transfer matrix calculations (TMM), Fig. 4 and Supplementary Fig. 6. TMM calculations indicate that the PL emission enhancement does not originate from an effect of dielectric environment change. Electric field and generation profiles were calculated for the heterostructure and the bare WS\(_2\) at 550 nm (2.25 eV) and 660 nm (1.88 eV), corresponding to the laser excitation wavelength and for the main emission peak (Figure 4a and 4b). The generation rate per unit length for WS\(_2\) in the heterostructure is higher than from the 2DPVSK in the heterostructure, but is nonetheless lower than that of bare WS\(_2\), indicating the absence of a carrier generation enhancement in WS\(_2\) layer. Calculated absorbance spectra (Fig. 4c).
4a) indicate that the absorbance of the heterostructure is larger than that of individual layers, but smaller than the sum of absorption from both materials confirming our results in Supplementary Fig. 4. Here, A, B, and 2DPVSK exciton peaks observed in reflection measurements (Fig. 2a) are consistent with absorption peaks calculated using transfer matrix method while H cannot be explained. TMM calculation also shows 0.45 and 0.15 absorbance of WS2 A exciton and H2 peaks respectively, which is opposite to the reflectance spectra which shows larger dip in WS2 A exciton, which is likely due to different level of transmission through these two regions and electronic effects. Since transfer matrix calculation do not show either an enhancement of WS2 emission/absorption or a significant reduction of the n=4 2DPVSK emission/absorption in the heterostructure compared to the individual constituents, purely photonic effects, such as changes in the local dielectric environment, can be ruled out as the origin as the giant WS2 PL enhancement. We also confirmed this observation by exfoliating 2L WS2 on hexagonal Boron Nitride (hBN) and BA (Supplementary Figure 7). In both cases we observe little changes in the PL spectra and no significant photoluminescence enhancement. Figure 4e shows the UPS spectra and spectral fits at the high and low kinetic energy cut-off for the n=4 2DPVSK. The valence band energy for the 2DPVSK obtained from these cut-offs is -5.59eV referenced to the vacuum level. Literature values for the 2DPVSK band gap and band positions of WS2,4-42 indicate that they form a Type I band alignment, with an energy level mismatch of about 472 meV and ~100 meV for the conduction band minimum and valence band maximum, respectively (Fig. 4f). We note that the energy difference of the conduction band minima between the 2L WS2 and n=4 2DPVSK is of the order of the difference between the principle exciton energy in these materials and the 2L WS2/n=4 heterostructure PL peak after interface curing.

The relatively good energy correspondence between exciton states in both the 2L WS2 and n=4 2DPVSK might promote dipole-dipole interactions as discussed in ref.43.

TRPL (Fig 4d) measured for the bare 2DPVSK yields a lifetime slightly under the nanosecond time scale, in agreement with a previous report47. On the other hand, the reported lifetime of bilayer WS2 is of the order of tens of picoseconds, attributed to intervalley scattering44. The heterostructure exhibits an intermediate PL decay time between the bare WS2 and n=4 2DPVSK indicative of either a charge transfer and/or dipole-dipole interactions mechanisms at the interface45. This can also be a consequence of the different nature of the photoemitting states at the interface.

The similarities in the results between the two heterostructures support a common mechanism for the origin of the photoluminescence enhancement in TMDCs/2DPVSK heterostructures. We hypothesize that a significant contribution to the PL enhancement in the heterostructures with respect to their bare constituents is due to their interface. Using first-principles calculation, we verified that the 2L WS2/2DPVSK interface modifies electronic structure of 2L WS2 and enables large PL enhancement. Microscopic insights about the heterostructures constructed by TMDCs and 2DPVSK have been obtained by first-principles calculation based on density functional theory (see Supporting information for calculation details). Heterostructures with different thickness of the 2DPVSK and WS2 were systematically calculated. Figure 5(a) and (b) show the side and top view of the 2L WS2/n=4 2DPVSK structures without the organic ligands, respectively. To understand the effect of the heterostructure interface, we first calculated the distribution of the charge transfer between 2L WS2 and n=4 2DPVSK due to the heterostructure formation. As can be seen in Fig. 5(c), a clear charge transfer exists between WS2 and 2DPVSK, where electrons (yellow) and holes (blue) are accumulated at the 2DPVSK and WS2 side, respectively, and most of the transferred charges (electrons and holes) are distributed near the interface. Therefore, electrons are transferred from 2L WS2 to 2DPVSK, resulting in the p-doping of the 2L WS2. Such p-doping effect could compensate possible n-type doping in the as exfoliated WS2 samples, leading to the enhancement of formation of exciton and thus the corresponding PL,48 as observed in the experimental measurements.
On the other hand, due to the charge transfer, an electronic dipole is formed across the heterostructure interface. As can be seen in Fig. 5(d), the difference of plane-averaged potential at the two sides of the heterostructure (black solid line) confirms the formation of the dipole moment. Moreover, the change of the potential profile due to the heterostructure formation (green solid line in Fig. 5(d)) shows that potential drop happens mainly across the interface and extends to the 2L WS$_2$ layers. Such interfacial dipole moment can essentially be considered as an effective electric field (E-field), which is known to alter various properties of 2D layered materials. To understand such effect, we studied the electronic properties of a freestanding bilayer WS$_2$ structure under external E-field. The calculated atom-resolved projected band structures for the two WS$_2$ layers without and with E-field are summarized in Fig. 5(e), which shows that the coupled bilayer is electronically decoupled under E-field, behaving as two non-interacting monolayers. Interestingly, a clear indirect to direct transition is observed due to such E-field induced decoupling effect, which contributes to the enormous PL enhancement, consistent with the experimental observations.

Therefore, we attribute the PL enhancement observed experimentally to these two cooperative effects, i.e., p-doping effect that compensate the n-doping of the as exfoliated WS$_2$ and E-field induced electronic layer-layer decoupling. It is important to mention that similar charge transfer effect is also observed in heterostructures built by WS$_2$ and 2DPVSK with different thickness (Supporting information). The thicker the 2DPVSK the more charge transfer between the WS$_2$ and 2DPVSK, vice versa. Considering the E-field induced decoupling effect is only effective to multilayer systems and stronger charge transfer of the 2L WS$_2$/n=4 2DPVSK, the PL enhancement of the 2L WS$_2$/n=4 2DPVSK is expected to be stronger than that of the 1L WS$_2$/n=3 2DPVSK. This is indeed consistent with the 100 fold and 70 fold PL enhancement of the heterostructures 2L WS$_2$/n=4 2DPVSK and 1L WS$_2$/n=3 2DPVSK, respectively, compared to the WS$_2$. We note the interface curing strongly modify the system, leading to a much larger PL enhancement at a relatively lower energy. The enhancement in PL can be attributed to the reduction in defects, which increases the quantum efficiency of the emission. We anticipate that further theoretical and experimental study will reveal the atomic nature of interfacial structure and interactions between TMDCs and 2DPVSKs.$^{30,33}$

**Conclusion**

TMDCs and 2DPVSKs have emerged as highly promising materials for optoelectronic applications. However, TMDCs exhibit poor emission due to defect states and direct-to-indirect band transition, and 2DPVSKs suffer from poor stability towards ambient atmosphere. By combining these two materials in vertical heterostructures, we observed a significant enhancement of the photoemission with respect to the bare TMDCs and 2DPVSKs, with relatively good stability. The PL enhancement is of the order of two orders of magnitude when we compare the heterostructures to the bare TMDCs. First-principle calculation shows that this PL enhancement can be attributed to charge transfer through the interface that generates dipole moment, which induces increased local effective electrical field, and such field results in in-direct to-

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**FIGURE 5.** DFT calculations of heterostructure of 2L WS$_2$/n=4 2DPVSK. (a) and (b) Side and top view of the heterostructure, respectively. (c) Charge difference distribution of the heterostructure due to the formation of the interface. The yellow and blue color indicate the electrons and holes, respectively. (d) The plane-averaged potential profile of the heterostructure (black), WS$_2$ (red), 2DPVSK (blue), and the difference due to the formation of heterostructure (green), respectively. (e) The layer-resolved projected band structures (black and blue circles for two layers) of 2L freestanding WS$_2$ without and with E-field demonstrate the indirect to direct transition.
direct transition of electronic structure of 2L WS$_2$. Interestingly
the PL emission amplitude and spectral distribution can be altered by
interface curing in air under laser excitation, which induces further
emission enhancement. The giant enhancement in the PL emission
combined with largely improved stability under ambient condition and
laser illumination may open opportunities for practical applications
of the TMD/2DPVSK heterostructures in high efficiency
optoelectronic devices.

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ACKNOWLEDGMENT

This work is part of the Phonons at Thermodynamic Limits’
Energy Frontier Research Center funded by the U.S. Department of
Energy, Office of Science, Office of Basic Energy Sciences under
Award Number DE-SC0019140. We also acknowledge Northrop
Grumman for financial support of instrumentation. A.Y and J.W
acknowledges financial support from a Resnick Institute
Fellowship. A.D.M and J.C.B acknowledge support by DOE-
EEER DE-FOA-0001647 program. We acknowledge support from
the Beckman Institute of the California Institute of Technology
to the Molecular Materials Research Center. We are grateful to Prof.
George R. Rossman for technical help, discussions, and support.
We thank Prof. Jacky Even for useful discussions concerning the
perovskite surface termination.

SUPPORTING INFORMATION

Additional information of experimental details, spatial variation
of photoluminescence, measurement on 1L WS$_2$/hBN and WS$_2$/BA samples,
and details on first-principle calculations are outlined in Supporting
Information.

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