Tuning Interlayer Coupling in Large-Area Heterostructures with CVD-Grown MoS$_2$ and WS$_2$ Monolayers

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Supporting Information

ABSTRACT: Band offsets between different monolayer transition metal dichalcogenides are expected to efficiently separate charge carriers or rectify charge flow, offering a mechanism for designing atomically thin devices and probing exotic two-dimensional physics. However, developing such large-area heterostructures has been hampered by challenges in synthesis of monolayers and effectively coupling neighboring layers. Here, we demonstrate large-area (>tens of micrometers) heterostructures of CVD-grown WS$_2$ and MoS$_2$ monolayers, where the interlayer interaction is externally tuned from noncoupling to strong coupling. Following this trend, the luminescence spectrum of the heterostructures evolves from an additive line profile where each layer contributes independently to a new profile that is dictated by charge transfer and band normalization between the WS$_2$ and MoS$_2$ layers. These results and findings open up venues to creating new material systems with rich functionalities and novel physical effects.

KEYWORDS: Monolayer, heterostructure, MoS$_2$/WS$_2$, interlayer coupling, 2D materials

Recently, single unit-cell thick semiconducting transition metal dichalcogenides (sTMDs) attracted much interest owing to their unique physical properties. When isolated to monolayers, sTMDs undergo a crossover from indirect bandgap in the bulk to direct bandgap in two-dimensional (2D) monolayers and absorb and emit light rather efficiently. The band structure renormalization as a function of the number of layers originates mostly from relatively strong interlayer coupling. This results in shifts in the conduction and valence band edges at different rates at various symmetry points in the Brillouin zone. Built on the basis of monolayer sTMDs, vertical sTMD heterostructures formed by stacking up these monolayers offer a rich collection of physics and functionalities. For example, novel, atomically thin charge-separating devices can be envisioned using these heterostructures because of the wide range of bandgaps and band offsets available among these sTMDs. However, forming sTMD heterostructures with mechanically exfoliated monolayer flakes is impractical, while large-area growth of high-quality sTMD monolayers is still under development.

In this work, we report on formation, tuning, and characterization of large-area, 2D heterostructures using chemical vapor deposition (CVD) - grown MoS$_2$ and WS$_2$ monolayers. In these heterostructures, the interlayer coupling can be tuned externally with vacuum annealing, so that the system behaves between the limit of isolated, independent monolayers and the limit of coupled heterobilayers. Our results not only present the first, large-area, bilayer sTMD heterostructures as a material platform to study unusual 2D effects but also offer new venues to control optical properties of sTMDs by externally tuning the interlayer coupling.

WS$_2$/MoS$_2$ heterostructures were prepared from CVD grown monolayers using conventional PDMS stamping method (see Methods and Supporting Information Figure S1). In this notation, the former material, WS$_2$ in this particular case, refers to the top (transferred) monolayer, whereas the latter material (MoS$_2$) is a monolayer directly grown on the substrate. Figure 1a–e shows typical optical image and Raman/photoluminescence (PL) mapping of a WS$_2$/MoS$_2$ heterostructure prepared on SiO$_2$ (300 nm)/Si substrates. Because the vibrational

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frequencies of MoS$_2$ and WS$_2$ are vastly different$^{12,13}$ Raman mapping clearly shows distinct signal from each of the two layers; in contrast, the ground-state (1s) excitonic light emissions from MoS$_2$ and WS$_2$ are relatively close to each other in energy, and mapping at the WS$_2$ PL peak position (2.01 eV)$^{14−17}$ is shadowed by contributions from the PL shoulder of more luminescent (>2−4 times) MoS$_2$ as well as the strong edge luminescence in WS$_2$.$^{14}$ The Raman and PL spectra taken on the as-transferred heterostructure can be described as “additive” (Figure 1f,g), that is, each layer contributes independently to the overall signal irrespective of the other layer. This is in stark contrast to exfoliated bilayer sTMDs where the band structure is significantly renormalized to indirect bandgap from direct bandgap in monolayers owing to strong interlayer coupling, which can be described as a relaxation in quantum confinement along the thickness direction.$^3$ The Raman spectrum of the heterostructure displays in-plane (E$'$) and out-of-plane (A$_1^\text{g}$) modes of MoS$_2$ and WS$_2$ at the same frequencies as in their monolayers;$^{18,19}$ the PL spectrum features two separate emission bands at 1.85 eV from MoS$_2$ ($P_{\text{MoS}_2}$) and 2.01 eV from WS$_2$ ($P_{\text{WS}_2}$) (Figure 1f,g). The lack of band renormalization in as-transferred heterostructures implies that the stacked monolayers behave as if they are isolated from each other and exert negligible amount of influence onto each other. This is observed also in the as-transferred inverse heterostructures, MoS$_2$/WS$_2$ (Supporting Information Figure S2).

Indeed, atomic force microscopy (AFM) line scans confirm that these as-transferred heterostructures have an interlayer separation significantly higher than their expected equilibrium value. For example, tapping mode line scans typically yield thickness (step height) around 0.8 nm for monolayers and multiples of 0.8 nm for additional layers.$^8,20−22$ On the contrary, the stamped WS$_2$ monolayer has a step height of ∼1.6 nm (Figure 2a) measured from the MoS$_2$ bottom layer. The large step height can be attributed to unintentional residues trapped between the WS$_2$ and MoS$_2$ monolayers during the transfer process. We found that the step height can be reduced from 1.6 nm toward the expected 0.8 nm by mild
vacuum annealing (<0.133 Pa, 120 °C, 6 h) as shown in Figure 2a–c. This is consistent with the possibility that such annealing is able to drive out trapped residual molecules, such as water.\(^{23}\)

From tight-binding theory or quantum tunneling model, the interlayer interaction is expected to be exponentially sensitive to the interlayer distance. As a result, the vibrational modes may stiffen due to increased restoring forces acting onto the layers. However, comparison between the as-transferred and annealed WS\(_2/\)MoS\(_2\) heterostructures reveals that only the out-of-plane (A\(_{\text{2g}}\)) mode of the top layer (transferred WS\(_2\)) stiffens (by a small amount on the order of 4–5 cm\(^{-1}\)), while all the other peaks (A\(_{\text{1g}}\)\(^{\text{MoS2}}\), E\(^{\text{MoS2}}\), and E\(^{\text{WS2}}\)) remain at the same position (Figure 2d top panel). The bottom monolayer MoS\(_2\) is CVD-grown on the substrate, therefore, its vibration is mostly dominated by strong interaction with the substrate, and its A\(_{\text{2g}}\)\(^{\text{MoS2}}\) peak is thus insensitive to the much weaker interlayer coupling with the top WS\(_2\) layer. In-plane modes (E\(^{\text{MoS2}}\) and E\(^{\text{WS2}}\)) are typically less susceptible to changes in the interlayer coupling\(^2\) and indeed do not display any notable shift after the annealing. The stiffening of the out-of-plane mode of the top WS\(_2\) layer is thus an indication of enhanced interlayer coupling by the annealing. To further test this, we also prepared the inverse heterostructure, MoS\(_2/\)WS\(_2\), where the top layer becomes MoS\(_2\) that is transferred onto the bottom, as-grown WS\(_2\) monolayer. In agreement with the expectation, annealing in vacuum again leads to stiffening of the out-of-plane mode of the top layer (A\(_{\text{2g}}\)\(^{\text{MoS2}}\) peak in this case) (Figure 2d).

Our high-resolution transmission electron microscopy (HRTEM) images (Figure 2e–h) show that the annealing step does not induce any structural defects such as phase change on the heterostructures; based on the fast Fourier transform (FFT) images of the heterostructures (Figure 2i)), there is no evident chemical reaction between the MoS\(_2\) and WS\(_2\) monolayers. In addition, the split spots (inset in Figure 2g,h) confirm the presence of MoS\(_2\) and WS\(_2\) layers. This implies that the observed changes in the optical properties of the heterostructures are attributed to effects arising from changes in interlayer distance by the annealing.

Similar to the observed stiffening in the vibrational spectra, the enhanced interlayer coupling also affects the excitonic light emission of the heterostructures. When the layers are not interacting with each other as in the case of as-transferred heterostructures, the PL is a simple “additive” spectrum with the emission peaks of MoS\(_2\) and WS\(_2\) monolayers independently added together (Figure 3a). Here, we note that the P\(_{\text{MoS2}}\) is typically 5–10 times stronger than P\(_{\text{WS2}}\) possibly due to differences in their radiative/nonradiative recombination times and higher density of defects in WS\(_2\) associated with its higher growth temperatures. After annealing the WS\(_2/\)MoS\(_2\) heterostructures for different duration times, the PL spectrum gradually changes from additive to “renormalized”. After multiple-peak fitting to the measured PL spectra (for fitting details see Supporting Information Figure S3), the overall trend can be summarized as follows (Figure 3b-c).

(1) A new PL peak (P\(_{\text{hetero}}\)) emerges at 1.94 eV, and its integrated intensity grows for prolonged annealing time.

(2) Upon the annealing, P\(_{\text{MoS2}}\) and P\(_{\text{WS2}}\) gradually decrease. After 12 h of annealing, both P\(_{\text{MoS2}}\) and P\(_{\text{WS2}}\) peaks are barely observable as minuscule features appearing at lower and higher-energy shoulders of the P\(_{\text{hetero}}\) peak.

(3) Another weak emission peak (P\(_{\text{indirect}}\)) appears at 1.75 eV, and the peak position rapidly and eventually red-shifts to ~1.5 eV.

Before we discuss these trends with the density functional theory (DFT) calculations, excitonic interactions, and charge transfer processes, we provide a phenomenological explanation. When monolayers are well separated from each other (as-transferred heterostructures), each layer emits light that is specific to itself, MoS\(_2\) (P\(_{\text{MoS2}}\)) or WS\(_2\) (P\(_{\text{WS2}}\)). After the annealing, the two monolayers start to electronically couple to each other, and their band structure gradually changes from the isolated limit toward the true heterostructure, bilayer limit. This is manifested in the PL spectrum as a gradual reduction in P\(_{\text{MoS2}}\) and P\(_{\text{WS2}}\) and appearance of the P\(_{\text{hetero}}\) and P\(_{\text{indirect}}\) peaks.

Because the P\(_{\text{indirect}}\) peak position changes rapidly with the degree of coupling (annealing time), we attribute this to phonon-assisted, indirect bandgap transition, which involves the valence band maximum (VBM) at the Γ-point and the conduction band minimum (CBM) at the K-point.\(^3\) To test this scenario, we also transfer CVD monolayer MoS\(_2\) onto MoS\(_2\), forming MoS\(_2/\)MoS\(_2\) homostructures (see Supporting Information Figure S4). These as-transferred MoS\(_2\) homostructures only display emission at P\(_{\text{MoS2}}\). Upon annealing, a new, weak PL peak develops at lower energies and shifts to a position in agreement with the indirect-bandgap, Γ → K transition often observed in exfoliated bilayer MoS\(_2/\)MoS\(_2\).\(^1\) Indeed, this is consistent with the evolution in the PL spectrum of exfoliated sTMDS from monolayers to multilayers,\(^1,2,13,14\) where a new, indirect-bandgap emission line emerges for increasing number of layers.

To provide an insight on the observed phenomena, we have carried out DFT calculations on the heterostructures by including the spin–orbit coupling (SOC) interactions. The latter effect is known to be large for monolayer sTMDS and splits the VBM level at the K-symmetry point by 0.15 and 0.4
between dfl and uence the optical bandgap significantly (Supporting Information Figure S5). Such contrast between graphene and graphitic materials. However, DFT calculations show that once the MX2 heterostructure reaches the equilibrium distance, different interlayer registry configurations change the VBM at Γ point only by ∼50 meV, and do not influence the optical bandgap significantly (Supporting Information Figure S6). Such contrast between graphene and sTMDs heterostructures stems from the fact that the band structure of covalently bonded graphene is exponentially sensitive to the coupling between p orbitals. In contrast, in sTMDs, the VBM and CBM at K-point is dictated by in-plane metal-chalcogen bonding, and the VBM at Γ-point is relatively insensitive to orientation angle at the equilibrium distance as a result of weak interaction between d and p orbitals with low charge densities. Consistent with these discussions, 2D heterostructures with randomly different orientation angles do not exhibit detectably different PL spectrum.

To elucidate the $P_{\text{hetero}}$ emission, we consider excitonic effects and ultrafast charge relaxation across the heterostructure. On the basis of DFT calculations, the VBM and CBM at K-point is dictated by in-plane metal-chalcogen bonding, and the VBM at Γ-point is relatively insensitive to orientation angle at the equilibrium distance as a result of weak interaction between d and p orbitals with low charge densities. Consistent with these discussions, 2D heterostructures with randomly different orientation angles do not exhibit detectably different PL spectrum.

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negatively (positively) charged exciton, namely, eeh or X⁻ trion (ehh or X' trion), as such, the trion recombination emission intensity would grow at the cost of the neutral exciton (eh) recombination emission intensity. The trion peak is redshifted from the neutral exciton by an amount given by the binding energy of the extra free carrier to the neutral exciton, ranging from 30 to 60 meV at room temperature depending on the Fermi level.\(^{25}\)

On the basis of this analysis, we attribute the \(P_{\text{hetero}}\) peak to \(X_{\text{WS}}\). in the heavily hole-accumulated WS\(_2\) monolayer, which is approximately 60 meV below the original \(P_{\text{WS}}\) peak \((X_{\text{WS}})\). However, this model equally considers MoS\(_2\) and WS\(_2\); therefore, it does not explain the different behavior of MoS\(_2\) in the heterostructure, that is, the gradual disappearance of the \(P_{\text{MoS}}\) peak but in absence of a trion peak, \(X_{\text{MoS}}\) emitted from the electron accumulated MoS\(_2\) monolayer.

On the basis of our earlier discussions, we speculate that the thermal annealing gradually drives out liquid residues trapped between the layers, and possibly causes a spatially inhomogeneous 2D heterostructure composed of strongly (Region A) and weakly (Region B) coupled regions (Figure 5a). In Region A, the interlayer distance is close to the equilibrium value \(d_{\text{eq}}\) and the VBM at \(\Gamma\) in Region A becomes higher than MoS\(_2\) VBM at \(K\) in Region B (Figure 4b). As a result, Region A acts as a hole funnel where the holes in the heterostructure are not only swept to WS\(_2\) but also to the VBM of region A (Figure 5b). This process further drains the remaining holes from the MoS\(_2\) layer in addition to the earlier hole transfer from MoS\(_2\) to WS\(_2\), leading to quenching of both eh and eeh emissions in MoS\(_2\) across the entire 2D heterostructure. In contrast, the CBM of Region A stays at the same level as in Region B for both MoS\(_2\) and WS\(_2\) (Figures 4 and 5b), because the CBM energy level at the \(K\) symmetry point is dominated by orbital coupling between in-plane \(d\) orbitals of metal and in-plane \(p\) orbitals of chalcogen atoms, naturally insensitive to the interlayer coupling. As a result and unlike the case of MoS\(_2\) remaining electrons in WS\(_2\) are not funneled to region A, and eeh (trion) emission from the WS\(_2\) layer remains relatively unaffected by the spatially inhomogeneous interlayer coupling. Therefore, the asymmetric behavior in trion emissions from MoS\(_2\) and WS\(_2\) layers originates fundamentally from the different bonding character in the heterostructure.

In summary, we have demonstrated large-area 2D heterostructures formed using CVD-grown monolayer WS\(_2\) and MoS\(_2\) where the interlayer coupling could be tuned by vacuum thermal annealing. As a function of the coupling strength, the light emission evolves gradually from an additive spectrum, that is, MoS\(_2\) and WS\(_2\) monolayers contribute separately to the light emission of the heterostructure, to coupled spectrum where the light emission is dictated by charged exciton recombination and phonon-assisted, indirect-bandgap transition. Our results highlight the significance of interlayer coupling and charge transfer in tuning the light emission and absorption of sTMDs and offer a general route to prepare large-area sTMD tandem structures for fundamental study as well as electronic and photovoltaic applications.

**Methods. Sample Preparation.** The MoS\(_2\) and WS\(_2\) monolayers were grown at by high-pressure CVD technique (see Supporting Information) at 690 °C for 5 min onto SiO\(_2\)/Si substrates.\(^2\) Heterostructures were prepared using PDMS stamping technique as below. PDMS was spin coated on CVD grown monolayer WS\(_2\)/SiO\(_2\)/Si and cured at 120 °C for >3 h. PDMS/WS\(_2\)/SiO\(_2\)/Si sample is baked at 70 °C for 2 h to eliminate air bubbles formed at the monolayer WS\(_2\) and PDMS interface and to increase the adhesion between WS\(_2\)/PDMS. PDMS/WS\(_2\) sample is separated from the SiO\(_2\)/Si substrate by mildly etching SiO\(_2\) in 1 mol/L KOH solution for 0.5–2 h. PDMS/WS\(_2\) sample is transferred to DI water to reduce KOH residue, and then it is transferred onto CVD grown monolayer MoS\(_2\) on SiO\(_2\)/Si substrate for 5 min using long-distance microscope (Stamping process). Afterward, PDMS substrate is peeled off slowly from the SiO\(_2\)/Si substrate, leaving the monolayer WS\(_2\) on top of MoS\(_2\) (see Supporting Information), as shown in Figure 1a.

**Raman/PL Spectroscopy and AFM Measurements.** Heterostructures were measured using commercially available Raman/PL spectrometer (Renishaw Inc.) with 488 nm laser source. Raman and PL measurements were taken on a 5 \(\mu m^2\) laser spot size with 10 \(\mu W\) power. Samples were characterized using commercially available AFM (Veeco Inc.) in contact mode.

**Transmission Electron Microscopy (TEM) Measurements.** HRTEM and TEM-electron energy loss spectroscopy (EELS) measurements were performed on the WS\(_2\)/MoS\(_2\) heterostructures using FEI Titan 80–300 environmental TEM operated at 80 kV. EELS measurements show that W M3 edge is present in the studied region implying that the WS\(_2\)/MoS\(_2\) heterostructure exists (Supporting Information, Figure S7).

**DFT Calculations.** DFT calculations were performed using Vienna ab initio simulation package.\(^2\) The six outer-most electrons for transition-metal and chalcogen atoms were treated as valence electrons. The core–valence interaction was described by the frozen-core project or augmented wave method.\(^3\) The generalized gradient approximation of Perdew–Burke–Ernzerh\(^\dagger\) was adopted for exchange-correlation functional. Energy cutoff for plane-wave expansion was set to 400 eV. Brillouin zone sampling was performed with Monkhorst–Pack special K-point meshes.

**ASSOCIATED CONTENT**

5 Supporting Information
Experimental, Methods, additional DFT calculation and Photo images, and additional measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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