

Improving the optical quality of MoSe₂ and WS₂ monolayers with complete *h*-BN encapsulation by high temperature annealing

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ABSTRACT

We improved the optical quality and stability of exfoliated monolayer (ML) MoSe₂ and chemical vapor deposition (CVD)-grown WS₂ MLs by encapsulating and sealing them with both top and bottom few-layer *h*-BN, as tested by subsequent high temperature annealing up to 873 K and photoluminescence (PL) measurements. These transition metal dichalcogenide (TMD) MLs remained stable up to this maximum temperature, as seen visually. After the heating/cooling

cycle, the integrated photoluminescence (PL) intensity at 300 K in the MoSe₂ ML was ~4 times larger than that before heating and that from exciton and trion PL in the analogous WS₂ ML sample was ~14 times and ~2.5 times larger at 77 K and the exciton peak was ~9.5 times larger at 300 K. This is attributed to the reduction of impurities, the lateral expulsion of contamination leading to clean and atomically flat surfaces, and the sealing provided by the *h*-BN layers that prevents the diffusion of molecules such as trace O₂ and H₂O to the TMD ML. Stability and optical performance are much improved compared to that in earlier work using top *h*-BN only, in which the WS₂ ML PL intensity decreased even for an optimal gas environment. This complete encapsulation is particularly promising for CVD-grown TMD MLs because they have relatively more charge and other impurities than do exfoliated MLs. These results open a new route for improving the optical properties of TMD MLs and their performance and applications both at room and higher temperatures.

KEYWORDS

MoSe₂ monolayers, WS₂ monolayers, *h*-BN encapsulation, exciton, trion, photoluminescence, high temperature processing

INTRODUCTION

Two-dimensional transition metal dichalcogenides (TMDs) have aroused intense attention due to their exotic physical properties.^{1,2,3} They can be useful for a wide range of applications in optical devices and optoelectronics,^{4,5} such as photodetectors and light emitters.^{6,7,8} All such applications require high optical quality of the TMDs with any disorder removed. There are several types of adsorbed species trapped between the individual layers during transfer in TMD stack fabrication. For graphene, high temperature annealing has proved to be effective in limiting extrinsic disorder and contamination from the external environment.⁹⁻¹² However, the major obstacles in advancing the use of TMDs includes their instability at high temperature. Bulk TMDs are known to be less stable at higher temperature, in oxygen-containing media, in inert gases, and under vacuum.^{13,14}

Photoluminescence (PL) enhancement in TMD MLs has been reported in previous studies that has been attributed to chemical doping,¹⁶⁻¹⁹ plasmonic effects,²⁰ and surface engineering.^{21,22} For example, Nan *et al.* reported the PL enhancement of MoS₂ MLs by defect engineering and oxygen bonding at the defect sites.²² Additionally, Tyurnina *et al.* found that the PL intensity of TMDs can be enhanced by the funneling effect resulting from external strain.²³ In most of these studies the PL increases are not from improving sample optical quality through the reduction of inhomogeneity and impurities, but by introducing defects at the surface and strain.

Improved properties by thermal annealing and better stability at elevated temperatures might be expected by encapsulating the TMD ML by *h*-BN (hexagonal boron nitride), which is known to be thermally stable at high temperature, before heating the TMD.¹⁵ We have previously seen notable improvement in the stability and optical properties, notably PL, of chemical vapor

deposition (CVD)-grown WS₂ monolayers (MLs) after heating/cooling cycles, relative to the bare ML, by first fully covering the WS₂ ML with multi-layer *h*-BN.²⁴ However, though PL was stronger with top layer *h*-BN than without it, the intensity still decreased in these samples. Markedly better improvements in both properties and stability might be expected with the better sealing of the edges of the TMD monolayer expected from full encapsulation of the ML by using top and bottom *h*-BN with larger areas than the TMD, prepared by employing established transfer methods.²⁵ This would be expected to limit molecular diffusion between the TMD and the substrate. **We examine the impact of full encapsulation here, for two light-emitting TMD MLs.** First, we investigate the exfoliated monolayer MoSe₂ in some detail and then more briefly the CVD-grown monolayer WS₂, the latter for a comparison with our previous work with top layer *h*-BN. Moreover, because CVD-grown WS₂ MLs have more charge impurities, unintentional doping and other inhomogeneity and impurities (due the fabrication process) than does exfoliated WS₂,^{26,27,28} any improvements seen here could be significant more widely, when the CVD-growth method is needed to fabricate the TMD ML.

MoSe₂ and WS₂ monolayers completely encapsulated by *h*-BN are seen to remain stable to 873 K here, with their PL greatly increased after cycling to high temperature (873 K) with this encapsulation. In particular, this use of top and bottom *h*-BN greatly improved these properties of the CVD-grown WS₂ ML, both absolutely and relative to WS₂ with only top *h*-BN.

EXPERIMENTAL SECTION

An exfoliated MoSe₂ ML (~5-10 μm largest lateral dimension) and several-layer *h*-BN (~20-30 μm) flakes were exfoliated onto two different 285 nm SiO₂/Si substrates. **(See the**

Supporting Information Section S1 for details about exfoliation.) The MoSe₂ ML was characterized by optical microscopy and the thickness and uniformity of the *h*-BN flakes were determined by atomic force microscopy (AFM) (20-40 nm). Stacks were prepared by using a dry transfer method with a polycaprolactone/polydimethylsiloxane slide (polycaprolactone (PCL), polydimethylsiloxane (PDMS)).²⁵ The top *h*-BN was picked up with PCL, and then this top *h*-BN was used to pick up the MoSe₂ ML and for transfer onto the bottom *h*-BN, so that on the periphery of the MoSe₂ ML, the *h*-BN flakes, which were both much larger than the MoSe₂, were in contact. The samples were placed in a Linkam cell (LINKAM THMS 600) which enabled the *in-situ* control of temperature and environment (Figure 1a, see Supporting Figure S1). $\lambda = 514.5$ nm CW laser light produced by an argon-ion laser illuminated the sample, in the presence of 25 sccm N₂ flowing during a heating/cooling cycle during which the temperature was increased from 77 K to 873 K and then back down to 77 K. The focused laser was kept at specific set-points for ~10 min during which *in-situ* PL was captured by a cryogenically-cooled silicon CCD detector array (Princeton Instruments Spec-10:400B). (See Supporting Figure S2 for the optical setup.)

The left part of Figure 1c shows the optical image of an *h*-BN/MoSe₂/*h*-BN stack on the SiO₂/Si substrate at room temperature before temperature cycling. It also indicates the region outside the MoSe₂ ML where the top and bottom *h*-BN overlap. The left part of this figure gives the optical image of this same sample after the heating/cooling cycle. The area enclosed by the dashed line is the *h*-BN/MoSe₂/*h*-BN region. With complete encapsulation, optical imaging suggests the MoSe₂ ML is stable during this cycle. In contrast, without the *h*-BN encapsulation, even many-layer (bulk) MoSe₂ started to decompose above 773 K and the entire bulk MoSe₂ sample was no longer present at 873 K (Figure 1b, right side). In all optical comparisons, the

optical images were taken at the same spot before and after the cycle. An *h*-BN flake was used as an alignment mark in Figure 1b. This shows that with this complete encapsulation, MoSe₂ MLs are stable to higher temperatures than without it.

Figure 1d shows the PL spectra of monolayer MoSe₂ in this *h*-BN/MoSe₂/*h*-BN stack during the heating and cooling cycles, taken while the sample was at the indicated temperature for 10 min. PL at selected temperatures is shown. Data from all PL measurements are given in Figure S3 in the Supporting Information. The PL spectra generally follow similar trends at corresponding temperatures within the heating and cooling cycles, but the peak PL intensities are larger during the cooling cycle, as detailed below and in [Supporting Figure S3](#).

Then we spatially mapped the peak PL intensity across a second monolayer MoSe₂ sandwich stack (Figure 2), which was prepared in the same way as the one used for Figures 1b and 1c, in the ambient environment by using a 532 nm CW laser (frequency-doubled Nd³⁺:YAG) for excitation. After mapping this stack at ambient temperature (Figure 2a), it was placed in the Linkam cell for a 300 K to 873 K to 300 K heating/cooling cycle, and then it was mapped again (Figure 2b). The maps have three distinctive features. First, the PL intensity after heating is larger than before it, as noted before. Second, both the line shapes and integrated area profiles of the PL patterns are largely unchanged after heating, indicating that the MoSe₂ flake does not decompose or become damaged during heating and that it is well protected by the complete *h*-BN encapsulation. Third, the PL intensity changes from before to after heating are uniformly distributed across the entire sample, which means the PL changes are not due to localized defects generated by O₂ or other molecules penetrating beneath the overlayer, as in Ref. 22. (Figure 2a,b)

Figure 2c presents the AFM trace of this same MoSe₂ stack before the heating/cooling cycle. There are several large bubbles on the MoSe₂ flake that likely correspond to adsorbents and contamination formed during the transfer process. Figure 2d is the AFM image of the same sample taken after the heating cycle. Figure 2b shows that after heating there are fewer bubbles and they are larger, suggesting they have coalesced, and they are now at the lateral edges of the MoSe₂ flake, and seem to have migrated there. The locations of the bubbles match the respective lower PL intensity regions in Figures 2a and b. In particular, there is a large bubble on the bottom right of the sample in Figure 2c that corresponds to the large low-PL-intensity area in Figure 2a. Moreover, the boundaries of the MoSe₂ ML in the encapsulated *h*-BN/MoSe₂/*h*-BN stack are clearer and sharper in the AFM images after heating (Figure 2d), which indicates that the vertical separations between the MoSe₂ and the *h*-BN layers have decreased (Figures 2c,d).

Electrical gating is an effective way to control the carrier concentration level in ML TMDs.^{29,30} To this end, we first performed gate-dependent PL measurements (514.5 nm) with an *h*-BN/MoSe₂/*h*-BN field effect transistor at 77 K under vacuum ($\sim 10^{-6}$ Torr) with gate voltage biasing using a Keithley 2400 source meter. Then a stack, prepared as were the two samples used in Figures 1 and 2, underwent a heating/cooling cycle in a separate oven (300 K to 873 K to 300 K), with a flow of 25 sccm N₂ gas. Gate-dependent PL was then re-examined at 77 K. Figure 3a presents a color map of the PL intensity of this stack of completely encapsulated MoSe₂ at a fixed pump laser power (~ 0.3 mW, with ~ 1 μ m spot size) as a function of gate voltage from -10 V to 10 V, before the heating/cooling cycle. There are two optical transition peaks at each gate voltage. The PL peak nearest 0 V is due to excitons (X^0). The second, lower energy emission peak at large magnitude gate biases corresponds to either the negative trion (X^-) (for positive V) or the positive trion (X^+) (negative V). Figure 3b presents a color map of the PL intensity as a

function of gate voltage over the same voltage range for this same sample after the heating/cooling cycle. Figure 3c plots the integrated PL intensities of the exciton and trion peaks before and after the heating cycle.

Completely encapsulated *h*-BN/CVD-grown WS₂/*h*-BN stacks were fabricated by first growing WS₂ ML triangles (~5 μm largest lateral dimension) by CVD on one 285 nm SiO₂/Si substrate, as in Ref. 31. Then, *h*-BN flakes were exfoliated on a second 285 nm SiO₂/Si substrate; AFM determined their thickness and uniformity (with lateral dimension and thickness as before). Stacks were then prepared by spin coating a poly(propylene) carbonate (PPC) layer and then two cellulose acetate butyrate (CAB) layers on the substrate with the WS₂ flakes.³² The SiO₂ layer on the Si was etched with potassium hydroxide (KOH) solution, leaving the PPC/CAB layers with several WS₂ ML flakes at the surface of this solution. One WS₂ ML flake (with the PPC/CAB) was transferred onto the *h*-BN flake serving as the bottom *h*-BN by using a glass slide with PDMS and PPC, and then the CAB layer was removed with the slide. The *h*-BN flake serving as the top *h*-BN layer was picked up with a PPC/PDMS glass slide and transferred onto the WS₂/bottom *h*-BN assembly to form the completely encapsulated WS₂ stack.

Figure 4 shows the PL spectra of this WS₂ stack at 77 K before (blue) and after (red) the 77 K to 873 K to 77 K heating/cooling cycle. The two optical transition peaks in each spectrum again correspond to the exciton peak at higher energy and the trion peaks at lower energy.

RESULTS AND DISCUSSION

Both TMD ML stacks seem to be structurally stable during the heating cycle, with no changes in material structure. The WS₂ ML stack appears to be stable because the Raman

spectrum is the same before and after (Supporting Figure S4). Because the stability of this CVD-grown ML is thought to be worse than that for a corresponding exfoliated ML^{26,27,28}, the MoSe₂ ML stack is also expected to be stable, as is confirmed by the optical microscopy image of the first MoSe₂ ML stack, in Figure 1c, and the AFM images of the second stack, in Figure 2c before heating and Figure 2d after heating. The heating cycle narrows the PL widths (Figure 1d), further confirming the stability of this stack. Also, the decrease in the PL widths suggests fewer defects and that there are no new PL peaks after annealing, suggests that there are no new defects.

As seen in Figure 1d, the integrated MoSe₂ PL intensity at 300 K from the stack is $\sim 4\times$ larger after the heating/cooling cycle than before it. Both have PL peaks located at ~ 1.57 eV, but there is small red shift of 4 meV after the cycle, which is likely due to a reduction in strain during the heating process.^{33,34,35} This corresponds to an increase in the biaxial in-plane tensile strain of $\sim 0.12\%$ if all of it were due to strain.³⁶ Because MoSe₂ monolayers have a larger thermal expansion coefficient than does Si but is similar to that of *h*-BN,^{37,38,39} an increase in this strain during the cooling cycle is expected with adhesion between MoSe₂ and the substrate (of $\sim 0.26\%$).

The peak width is 40.5 meV (FWHM) before the cycle and 36.1 meV after it. This narrowing could mean that the exciton lifetime is longer after the cycle, there are fewer impurities, and/or there is a reduction in inhomogeneity (some of which may have been introduced during sample preparation).^{26,27,28} At room temperature, the decay time is usually not only dominated by radiative recombination processes but by nonradiative recombination processes.

The inset in Figure 1d shows the PL spectra at 77 K of the same MoSe₂ stack at the start (blue) and end (red) of the heating/cooling cycle. There are two peaks in each spectrum,

corresponding to the exciton peaks (the larger, higher-energy peaks) and trion peaks (the smaller, lower-energy peaks). (The trion peak is very small at the end of the cycle.) As at 300 K, at 77 K the integrated PL intensity is larger after the cycle (now by ~ 4 times). The exciton emission energy after the heating/cooling cycle has a slight red shift (7 meV) at 77 K compared to the peak position before the cycle, again which is likely due to a reduction in strain during heating.^{33,34,35} This corresponds to an increase in the biaxial in-plane tensile strain of $\sim 0.21\%$ if it were all due to strain,³⁶ as noted above. Also, the peak widths of the exciton peaks are ~ 5 meV, and they are a bit smaller after the cycle, by ~ 0.4 meV.

As noted above, Figure 2 suggests that adsorbents and contamination formed during the transfer process diffuse and aggregate into bubbles. During heating, these bubbles are laterally expelled from the interfaces between the TMD and the upper and lower *h*-BN, and coalesce into larger bubbles, and this leaves much of these interfaces clean and atomically flat. This adsorbent and contamination diffusion can contribute to PL enhancement and the reduction of inhomogeneity could contribute to the PL line shape narrowing. At the same time, the MoSe₂ flakes are well protected by the *h*-BN encapsulation layer during the high temperature annealing.

In Figure 3a, before the heating/cooling cycle the charge-neutrality point (with the maximum exciton density and with equal electron and hole densities) is highlighted by the dashed line at ~ 2.01 V. This means that initially it is p-type. With more positive gate voltage, there are additional free electrons added in the sample and the exciton (X^0) population decreases and negative trions (X^-) are more likely to be formed, and the material shows more n-type doping. In contrast, when negative voltage is applied, additional holes are added and it becomes more p type, and now the X^0 peak decreases as the positive trion X^+ peak appears, the more so at larger negative voltages.⁴⁰ From the peak separation of exciton and trion, the trion binding

energy is ~ 33 meV. For the same (magnitude of the) gate voltage relative to its respective offset, the X^+ peaks are shifted from the X^0 peak by $\sim 1-3$ meV more than the corresponding X^- peaks, mainly due to Coulomb interactions, as has been observed in other work.²⁹

In Figure 3b, the trion binding energy after the heating/cooling cycle is the same as that before it (Figure 3a). Also, all peaks undergo an ~ 10 meV red shift due to this cycle, which is likely due to a reduction in strain during the heating.^{33,34,35} This corresponds to an increase in the biaxial in-plane tensile strain of $\sim 0.3\%$ if it were all due to strain,³⁶ as noted above.

After the heating/cooling cycle the charge-neutrality point of the MoSe₂ ML PL is at the dashed line, ~ 0.01 V, in Figure 3b, which is shifted by ~ -2 V compared to that in Figure 3a before the cycle. This shows the intrinsic carrier concentration has changed. The MoSe₂ monolayer became less p-type doped, with the hole carrier density changing by $\Delta n \approx -1.1 \times 10^{12} \text{ cm}^{-2}$ (Supporting Information Section S5). This intrinsic carrier concentration change leads to the observed PL enhancement, due to the passivation of non-radiative recombination centers in the sample.⁴⁰ In addition to charge impurities, two other possible disorder sources could contribute to p-type doping in the sample before heating. One is the contamination trapped between the MoSe₂/*h*-BN interfaces during the stacking process. The contamination trapped at these interfaces is mostly due to hydrocarbon molecules, causing the p-type dopants that shift the charge neutrality gate voltage to positive voltages.⁴¹ The other sources of contamination are the residual O₂ and H₂O molecules trapped at these interfaces, which also introduce p-type doping.²² Our work shows that bubbles, presumably of these molecules, are formed and move during heating to the periphery, leading to atomically flat and clean graphene and *h*-BN interfaces, as others have also seen,^{10,11,12} and, moreover, we see that this leads to enhanced PL. Adsorbents and contamination formed during the transfer diffuse and are laterally expelled from the

interfaces so these interfaces are mostly clean and atomically flat. Unintentionally trapped charges are also removed, which results in switching the dominant PL from excitons and trions to mostly that from excitons, as has also been done by others by using chemically doping.⁴²

After first extracting the gate-voltage dependent exciton and trion peaks from both Figures 3a and 3b, in Figure 3c we plot the integrated exciton and trion intensities vs. gate voltage shifted so the charge-neutrality points of each is 0 V. This enables comparison of the PL intensities at the same doping density. These plots clearly show that the integrated MoSe₂ PL from the stack after the heating/cooling cycle is larger for both excitons and trions than before it. This PL intensity increase is expected to be due to not only the doping level reduction see here.⁴² Because these data specifically compare PL intensities at a fixed doping density (Figure 3c), they indicate the suppression of non-radiative decay due to the reduction of the impurities that arise from ML preparation and handling. These latter impurities are being removed, as seen in the formation of clean and atomic flat interfaces in Figures 2c and 2d.

Complete *h*-BN encapsulation and annealing might improve the stability and optical properties of other TMD MLs as well by also reducing doping levels via removing unintentionally-trapped charges at the interfaces and by making them atomically flat and clear (Figure 2). In particular, it may be very promising to do this for CVD-grown ML samples, because they usually have even more unintentional doping than samples exfoliated from crystals,^{26,27,28} as well as other impurities and defects from sample fabrication and preparation⁴¹, and so CVD-grown materials are less stable than exfoliated samples. The degradation and decomposition of TMDs result from oxygen dissociating into individual atoms and adsorbing on the surfaces of the TMD flakes. The TMD can be stable because decomposition is limited by the large energy barrier for O₂ dissociation and chemisorption.⁴³ However, defects can dramatically

lower this barrier and make decomposition possible at lower temperatures, and even at room temperature.^{43,44}

Figure 4 shows the PL spectra of the completely encapsulated WS₂ stack at 77 K before (blue) and after (red) the 77 K to 873 K to 77 K heating/cooling cycle. The two main optical transition peaks in each spectrum again correspond to the exciton peak at higher energy and the trion peak at lower energy. Whereas the exciton and trion PL peaks for the MoSe₂ stack are fit well with a Lorentzian line shape, those peaks in CVD-grown WS₂ are well fit this way only after heating. Those before heating are severely and asymmetrically broadened by inhomogeneities, so these two peaks were fit with a Gaussian distribution.

The exciton and trion peak widths at 77 K are 14.2 meV and 56.4 meV (FWHM), respectively, before the heating/cooling cycle, and 12.6 meV and 20.7 meV after it. The peak PL intensity was larger after the annealing cycle, by ~14 times for the exciton and ~2.5 times for the trion. (The dark exciton effect lowers the overall PL intensity.^{45,46,47}) After the heating cycle the peaks are red shifted relative to those before, by 4.6 meV for the trion peak and 26.9 meV for the exciton.^{33,34,35} These exciton peak red shifts correspond to an increase in the biaxial in-plane tensile strain of ~0.04-0.26% if it were all due to strain,^{24,48} as noted above. Also, the trion peak red shift ~22 meV more indicating the reduction of trion binding energy. As is shown in Figure 2d, after heating, the decreasing of vertical separations in Van der Waals heterostructures between the MoSe₂ and the *h*-BN layers results in changes of surrounding dielectric environment. This change can heavily reduce the trion binding energy. By the calculation from Florian et al, a 5 Å interlayer gap between *h*-BN-MoSe₂-*h*-BN can cause ~15-20 meV trion binding energy difference.⁴⁹

In our earlier paper, Ref. 24, a CVD-grown WS₂ ML was seen to be more stable and had larger integrated PL at 300 K after a 300 K to 873 K to 300 K heating/cooling cycle with top *h*-BN than without it and with nitrogen flow, rather than in ambient air or with flowing forming gas. However, the PL was still smaller than before the cycle, by ~47%. Therefore, top *h*-BN helped stability some, but improvement was still needed. As seen in Figure 4, now with complete encapsulation, after a 77 K to 873 K to 77 K cycle the WS₂ ML PL peak and integrated intensities no longer decrease but increase. Measured at 300 K, during cooling ramp-down, it is ~9.5× larger than that at 300 K before the heating ramp-up, with purging N₂.

One reason for this marked improvement with full encapsulation is that with top-layer *h*-BN and no bottom-layer *h*-BN, trace residual molecules such as O₂ and H₂O, present with nitrogen flow, still diffuse between the WS₂ ML and the SiO₂ substrate, due to its roughness and dangling bonds; this leads to some degradation in PL during heating, though the sample does not decompose. This diffusion does not occur with complete the encapsulation and sealing of the *h*-BN sandwich. Other reasons for this improvement are noted above. Because the PL intensity exhibits a dramatic enhancement for this CVD-grown ML with complete encapsulation, this technique is expected to be especially useful for other CVD-grown samples as well, whose performance is also hurt by the known higher levels of impurities introduced by CVD.

The increases in PL intensities for both ML stacks that result from the heating cycle are thought to be due to decreased impurities, as detailed above. One other potential factor could be the changes in strain of the TMD MLs. Lloyd *et al.* measured the integrated PL intensity change of MoS₂ as function of biaxial in-plane tensile strain⁵⁰ and using this as a guide for both TMD studied here, there is an estimated increase in biaxial in-plane tensile strain of ~0.21% for the MoSe₂ ML and ~0.26% for the WS₂ ML; this corresponds to a decrease in PL integrated

intensity of ~20% for the MoSe₂ ML and ~25% for the WS₂ ML. However, we observed PL enhancement by a factor of 4 for the MoSe₂ stack and by 9.5 for the WS₂ stack. The observed PL shifts are consistent with strain changes due to thermal expansion, but the increases in the PL intensities do not appear to originate from the changes in strain. Another possible cause for the PL increases is dielectric screening effects due to the changes in bubbles in the heating cycle, as seen above in the MoSe₂ stack in Figure 2. Fu *et al.* showed that dielectric screening of *h*-BN leads to a peak PL intensity increase of ~60% (in that case for a WS₂ ML) and a much smaller integrated PL intensity increase than this (and which was not given) because the PL width was then much smaller.⁵¹ The increase in integrated PL from the bubble regions would be expected to be locally weaker due to less optical dielectric screening, and this is seen. The integrated PL intensity is weaker from the three bubbles seen in Figure 2a than that from the flat regions by ~16%, 21%, and 38% for the bubbles with diameters the ~0.3 μm, 0.14 μm, and 1.1 μm, respectively. Therefore, the motion and changes in the bubbles due to heating do not contribute to the increases seen in the PL intensity.

CONCLUSIONS

Sealing MoSe₂ and WS₂ MLs with top and bottom *h*-BN encapsulation flakes improves their thermal stability at high temperature, as tested in a heating/cooling cycle, and increases their PL. The increased PL likely occurs because impurities are laterally expelled from the TMD stack during heating (and so the TMD ML interfaces also become flatter). The increased PL also occurs, along with material stability, because other impurities, such as of trace residual molecules such as O₂ and H₂O present with say nitrogen flow, cannot enter during heating since the TMD MLs are sealed at the edges. The reduction of impurities is particularly important for

CVD-grown ML samples, such as for the WS₂ ML here. Encapsulation by only top *h*-BN is not sufficient to achieve these improvements. These improvements are generally expected for TMD MLs and these methods can be applied in applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at xxxx.

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The paper was written through contributions of all authors. All authors have given approval to the final version of the paper.

Funding Sources

This work was supported by the IGERT program of the National Science Foundation (DGE-1069240).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by the IGERT program of the National Science Foundation (DGE-1069240). K.W. and T.T. acknowledge support from the Elemental Strategy Initiative conducted by the MEXT, Japan (Grant Number JPMXP0112101001) and JSPS KAKENHI (Grant Numbers JP19H05790 and JP20H00354).

FIGURE CAPTIONS

Figure 1. (a) Schematic of the h -BN/TMD ML/ h -BN stack sample in a Linkam cell in which the temperature and gas environment are controlled. The argon-ion laser is focused by an Olympus 50 \times long working distance objective, through the 22-mm thick glass window. LNP95 is the liquid nitrogen cooling pump system and T95 is the temperature system controller working with platinum temperature sensor (not shown). (The water circulator system is not shown in the figure.) (b) The optical image at room temperature of bulk MoSe₂ on a SiO₂/Si substrate (without h -BN encapsulation) (left) before and (right) after heating to 873 K, showing the decomposition after heating. (c) The optical image at room temperature of the h -BN/MoSe₂/ h -BN stack (left) before and (right) after heating to 873 K. (d) *in situ* PL of the MoSe₂ stack at selected temperatures during heating from 77 K to 873 K (dotted curves) and cooling from 873 K to 77 K (solid curves). Very weak PL was seen at 873 K (not shown), but the sample was intact. Half the intensity is plotted for both 77 K spectra (in blue). Inset: PL spectra at 77 K, replotted.

Figure 2. Spatially mapped peak PL intensity of the MoSe₂ monolayer sandwiched by h -BN at 300 K, taken (a) before and (b) after the heating/cooling cycle from 77 K to 873 K to 77 K. The AFM topography of this sample at 300 K is shown in (c) before and (d) after this temperature cycling.

Figure 3. Gate-dependent photoluminescence of the MoSe₂ stack at 77 K plotted as PL intensity, with color indicating this intensity, vs gate voltage (a) before the heating/cooling cycle (taken in ~ 0.11 V steps) and (b) after this cycle (~ 0.09 V steps). The dashed lines represent the charge neutrality points. There are two optical transition peaks at different gate voltage regions. The peak nearest 0 V is due to the exciton (X^0) and the lower-energy peak is either the negative trion (X^-) (at positive gate voltages) and the positive trion (X^+) (negative voltages). (c) The trion and exciton integrated intensities extracted from (a) and (b) vs. the gate voltage difference from the charge neutrality point.

Figure 4. PL spectra of the CVD-grown monolayer WS₂ sandwiched by several-layer top and bottom h -BN, at 77 K (514.5 nm excitation), before and after the heating/cooling cycle.

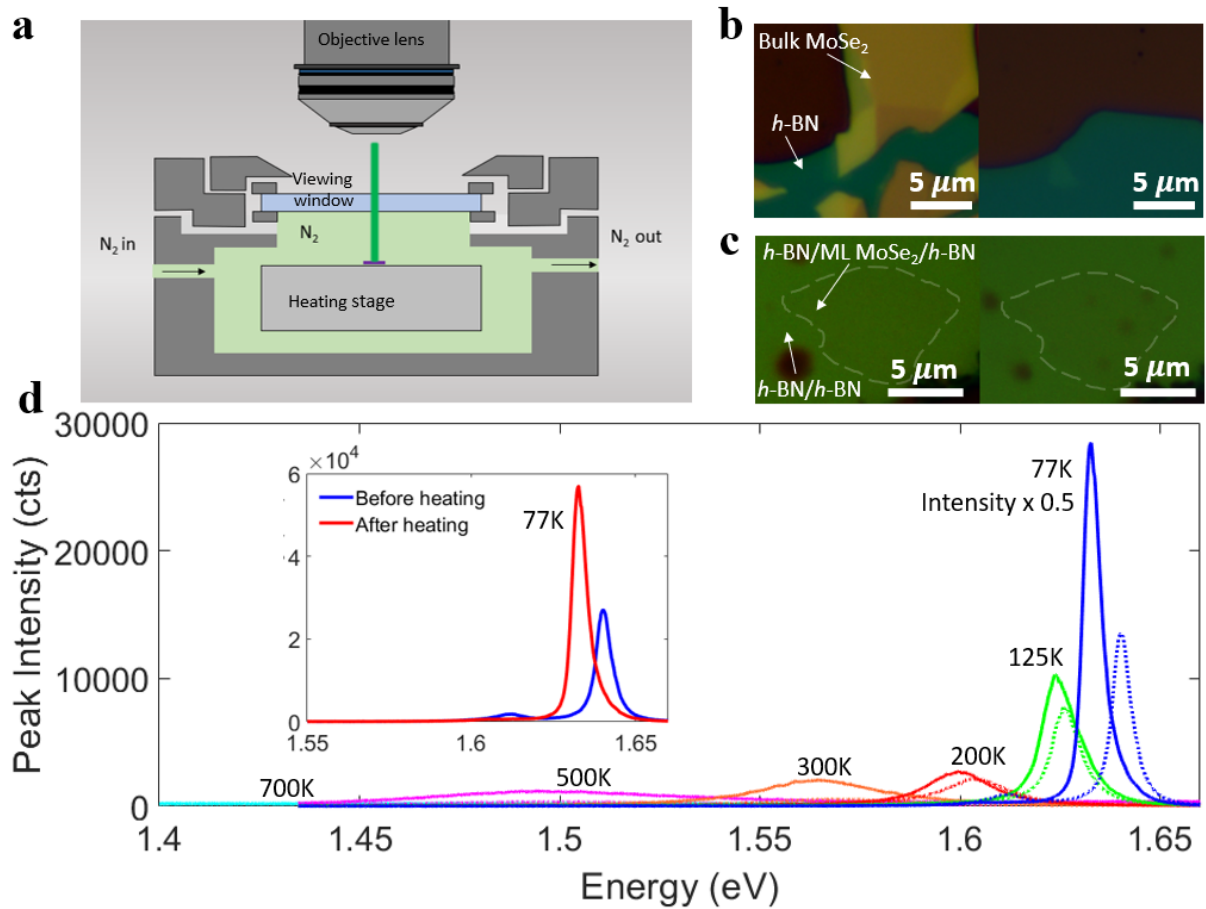


Figure 1. (a) Schematic of the *h*-BN/TMD ML/*h*-BN stack sample in a Linkam cell in which the temperature and gas environment are controlled. The argon-ion laser is focused by an Olympus 50× long working distance objective, through the 22-mm thick glass window. LNP95 is the liquid nitrogen cooling pump system and T95 is the temperature system controller working with platinum temperature sensor (not shown). (The water circulator system is not shown in the figure.) (b) The optical image at room temperature of bulk MoSe₂ on a SiO₂/Si substrate (without *h*-BN encapsulation) (left) before and (right) after heating to 873 K, showing the decomposition after heating. (c) The optical image at room temperature of the *h*-BN/MoSe₂/*h*-BN stack (left) before and (right) after heating to 873 K. (d) *in situ* PL of the MoSe₂ stack at selected temperatures during heating from 77 K to 873 K (dotted curves) and cooling from 873 K to 77 K (solid curves). Very weak PL was seen at 873 K (not shown), but the sample was intact. Half the intensity is plotted for both 77 K spectra (in blue). Inset: PL spectra at 77 K, replotted.

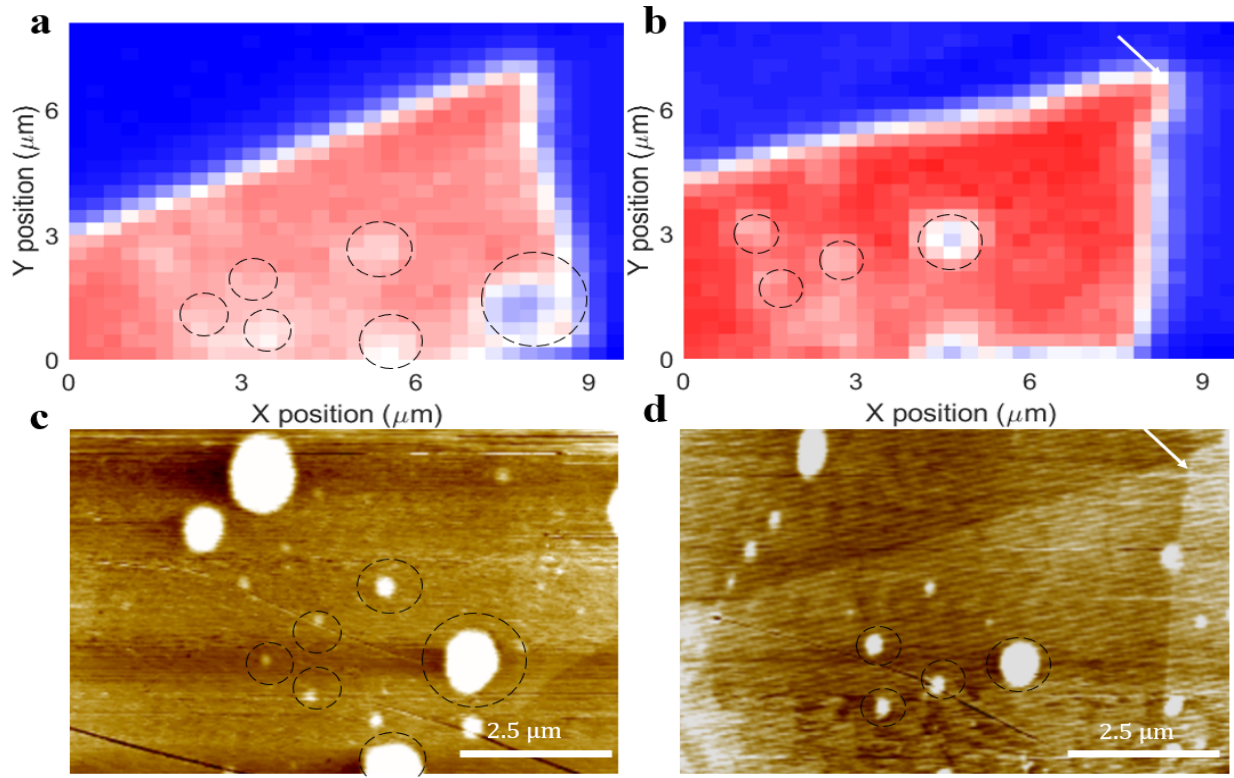


Figure 2. Spatially mapped peak PL intensity of the MoSe₂ monolayer sandwiched by *h*-BN at 300 K, taken (a) before and (b) after the heating/cooling cycle from 77 K to 873 to 77 K. The AFM topography of this sample at 300 K is shown in (c) before and (d) after this temperature cycling.

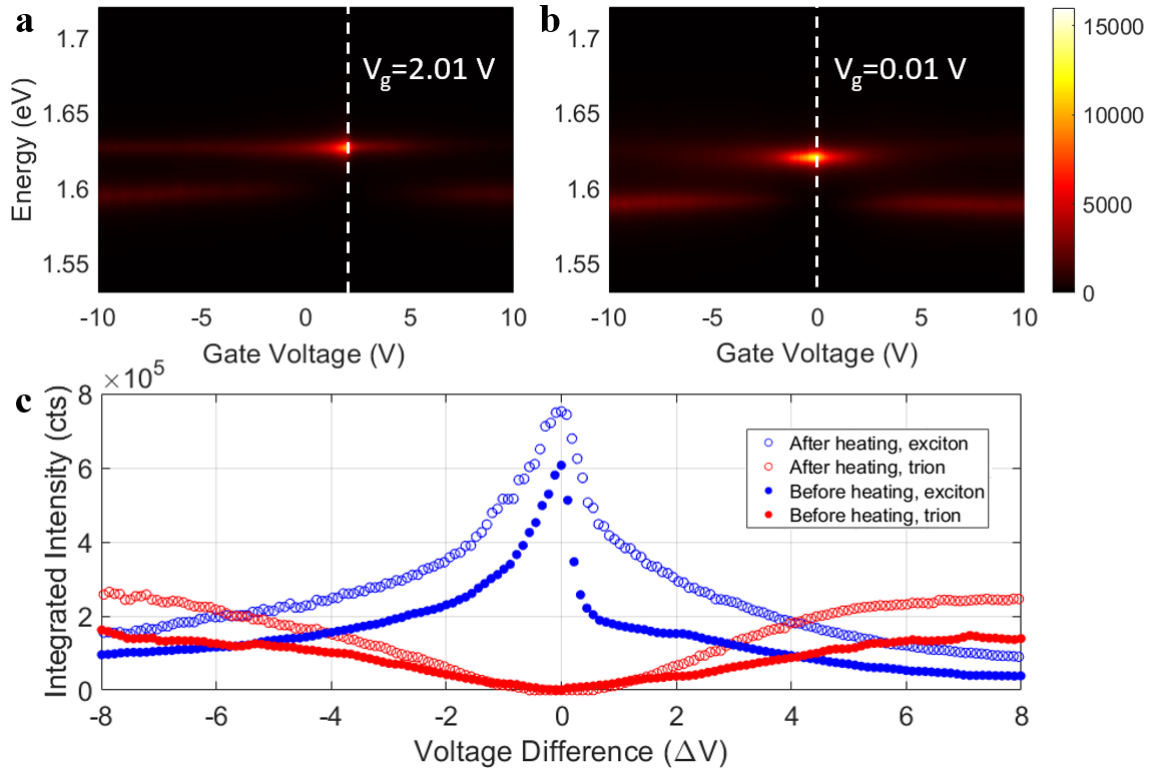


Figure 3. Gate-dependent photoluminescence of the MoSe₂ stack at 77 K plotted as PL intensity, with color indicating this intensity, vs gate voltage (a) before the heating/cooling cycle (taken in ~ 0.11 V steps) and (b) after this cycle (~ 0.09 V steps). The dashed lines represent the charge neutrality points. There are two optical transition peaks at different gate voltage regions. The peak nearest 0 V is due to the exciton (X^0) and the lower-energy peak is either the negative trion (X^-) (at positive gate voltages) and the positive trion (X^+) (negative voltages). (c) The trion and exciton integrated intensities extracted from (a) and (b) vs. the gate voltage difference from the charge neutrality point.

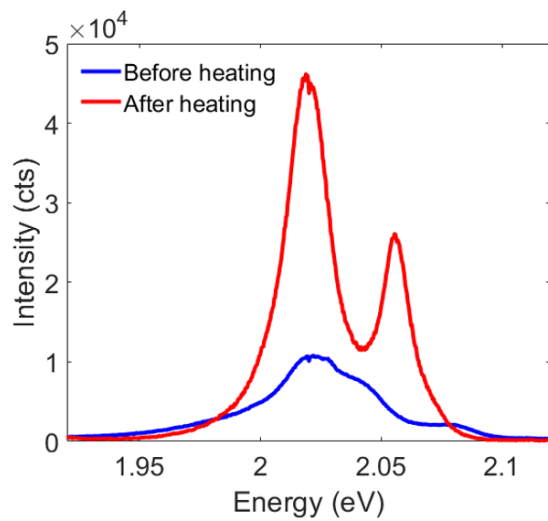


Figure 4. PL spectra of the CVD-grown monolayer WS₂ sandwiched by several-layer top and bottom *h*-BN, at 77 K (514.5 nm excitation), before and after the heating/cooling cycle.

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