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Approaching the Intrinsic Properties of Moiré Structures Using Atomic Force Microscopy Ironing

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moiré effects and reducing disorder. This is crucial for the investigation of TMD heterostructure physics, which currently suffers from low reproducibility.

KEYWORDS: transition metal dichalcogenides, atomic force microscopy, heterostructures, interlayer exciton, photoluminescence

V an der Waals (vdW) crystals are considered key enablers of the next-generation electronic and optoelectronic devices with improved performance.¹⁻⁶ The absence of lattice matching constraints enables new paradigms of material engineering, in which semiconductors, metals, superconductors, insulators, or topological insulators can be seamlessly combined.⁷

Fabricating vdW stacks has revolutionized the investigation of graphene⁸⁻¹⁰ and transition metal dichalcogenides (TMDs).¹¹ Encapsulating these stacks with hexagonal boron nitride (hBN)^{8,11-13} has provided access to their intrinsic properties, which are otherwise hidden by charged impurities and dielectric disorder.^{11,13} Simultaneously, the precise control relative twist angle in bilayer graphene or TMDs led to the discovery of new phenomena such as superconductivity¹⁴ or long-lived interlayer optical transitions with controllable selection rules.^{15,16}

In this perspective, the quality of the interfaces between the layers in the stack is of utmost importance to unveil their intrinsic properties, which are highly sensitive to their surroundings.¹⁷ Moreover, the mechanical exfoliation of bulk crystals¹⁸ unavoidably entails some form of interface disorder, which include charged impurities, traps,¹⁹ wrinkles, or bubbles.^{20–23} These localized strain gradients impact profoundly the electronic properties of layered materials^{24–26} and are considered to be one of the main sources of disorder in

high-quality samples.²⁷ Providing long-range homogeneity of the interface represents an ongoing challenge, and the lack thereof explains the considerable variations of the optoelectronic properties of nominally identical heterostructures.^{15,16,28} Reports on the interlayer exciton in TMD heterobilayers show significant variation in the number of peaks and their energy, with a range of up to 110 meV.^{28–31} Even in high-quality monolayers, the energy of the exciton transition can vary as much as 10 meV.¹¹

Various preparation techniques such as transfer in inert atmosphere³² and annealing³³ have been effective in minimizing defects in layered materials. Lately, AFM ironing^{21,23,34,35} has proven to further reduce these defects and enhance optical properties by enabling the observation of interlayer exciton at room temperature,²¹ bilayer Raman peaks,²⁸ and moiré pattern reconstructions.³⁶ However, systematic studies of the impact of AFM ironing on the optical properties of the interlayer excitons are needed.

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Figure 1. Topographic atomic force microscopy (AFM) images in the dynamic mode of the (a) as-prepared samples and after ironing with (b) 5 and (c) 70 nN, demonstrating the impact of incremental ironing forces on the sample. (d) Root-mean-square (RMS) values as a function of the ironing forces exerted on the region of interest $(1 \mu m^2)$ indicated by the square in (a). (e) Height profile of the bubble of interest (dotted circle in (a)) taken along the black dash line cross-section, scanned in dynamic mode, before and after ironing with 120 nN. (f) Volume and (g) height of the bubble of interest as a function of the applied force during ironing.

Here, we demonstrate that AFM ironing improves the interface quality and, as a consequence, the optical properties of hBN-encapsulated $MoS_2/MoSe_2$ heterostructure.^{37–39}

We probe the quality of the interface by optical methods, focusing on the interlayer exciton transitions,^{15,16,29,40-42} which are highly sensitive to the interlayer distance. We demonstrate that ironing improves the layer coupling, enhancing moiré effects and reducing disorder. We begin our investigation by ironing a MoS₂ monolayer deposited on an hBN substrate and partially capped with another hBN flake (see Table S1 in the Supporting Information (SI)). With an AFM, we perform an ironing procedure by scanning selected areas with the tip in contact mode using different pressing forces. We study the evolution of the surface morphology as a function of the applied force. We then investigate, using optical spectroscopy, three hBN-encapsulated MoS₂/MoSe₂ heterobilayers: samples A and B with a nominal twist angle of 60° and sample C with 0° alignment, which facilitates strong interlayer exciton emission^{16,43} (see Table S1 in the SI for sample details). Within the ironed areas, the surface homogeneity can be greatly enhanced, with a reduction in the root-mean-square (RMS) roughness compared to the nonironed regions. The increased interface quality of the heterostructure gives rise to a more uniform PL spectrum from the ironed parts, whose properties correlate with the applied ironing force. The high reproducibility of the properties of van der Waals stacks we demonstrate here qualifies AFM ironing as a strategy for the post-fabrication treatment of van der Waals heterostructures, providing access to their intrinsic properties.

We investigate the effects of the AFM ironing by examining a MoS_2 monolayer exfoliated on an hBN substrate and only partially capped by another hBN flake. In Figure 1(a), we show the AFM image of the as-fabricated sample measured in dynamic mode, prior to any AFM treatment. The area we selected straddles the edge of the top hBN flake, highlighted by the blue dashed line visible in Figure 1(a-c). A large number of bubbles and wrinkles can be noted, resulting from the

stamping process of the exfoliated flakes.²⁰⁻²³ We then scan an area of $10 \,\mu\text{m} \times 10 \,\mu\text{m}$ in contact mode, by applying subsequently increasing forces ranging from 5 nN to 120 nN. After each scan, the initial area $(12 \,\mu\text{m} \times 12 \,\mu\text{m})$ was imaged in dynamic mode, to verify the effects of the scans in contact mode. Based on the effects on both the surface morphology and the concentration of bubbles, we identify two ranges of forces. In the low force limit (applied force smaller than 20 nN), the debris and adsorbates present on the surfaces are initially moved and clustered, forming ripple-like features on the surface of the sample in the direction parallel to the fast scan, before being completely swept away from the scanned area by the AFM tip. An example of adsorbate clusters is visible in Figure 1(b), where oblique bright lines can be seen in the scanned area, and is highlighted in Figure S1 of the SI. This, in turn, induced an increase of the roughness in the low force limit, which we report in Figure 1(d). Despite the observed changes, it is important to note that the larger defects, including bubbles and wrinkles, remain unaffected, and no other discernible alterations to the surface morphology are apparent. Their number, shape, and size do not change as long as the applied force is small enough. However, when the applied force is larger than 30 nN, significantly large areas are cleared of bubbles and wrinkles. This is visible both on the capped and uncapped MoS_2 of Figure 1(c). Notably, it is easier to achieve bubble sweeping in the non-covered MoS₂ region. Previous studies have reported that the presence of a top hBN layer increases the critical force required to sweep bubbles away with an AFM tip.^{21,23,34} In particular, bubbles larger than 1 μ m in size tend to remain in their position, even for forces in the micronewton regime.³⁴ Reaching these high forces more likely rips apart the bubbles damaging the heterostructure.³⁴ This can be appreciated in the movie available in the SI for the same sample as in Figure 1, showing the topographic evolution during the ironing process for forces up to 200 nN.

While the cleaning effect is apparent at low forces when comparing Figure 1(a) and (b), and is primarily attributed to the removal of residuals from the top surface, it is not



Figure 2. (a) Optical micrograph of sample A, highlighting MOS_2 and $MOSe_2$ flakes (red and green outlines, respectively) and the heterostructure region (black outline). (b) Photoluminescence and reflectance spectra obtained at 4.5 K, featuring inter- and intralayer exciton resonances (indicated). (c) Topographic AFM scan in dynamic mode revealing regions ironed with varying forces, with a close-up view of the ironed area (80 nN) in the inset.

anticipated to significantly affect the optical properties of the heterostructure, as has been shown to be the case for transport characteristics in similar systems.³⁴ To obtain more insight on the cleaning capabilities in the higher force regime, we conducted a quantitative analysis of the evolution of roughness and bubble morphology in the capped region of Figure 1, for gradually increasing applied forces. Despite the fact that large bubbles were not entirely removed, their shape underwent a noticeable transformation, as depicted in Figure 1(e), where profiles taken prior to and after the AFM treatment are compared for the selected bubble (dotted circle in Figure 1(a)) Moreover, both the height and volume evolution as a function of the applied force can be plotted as illustrated in Figure 1(f) and (g). We note that upon ironing both the height and volume of analyzed bubbles increase (see also Figure S2 in the SI). This can be explained by the fact that at these forces, small bubbles can be displaced and adhere to the larger ones, flattening small corrugations at the heterointerface in areas between the blisters. This impacts the quality of the interfaces between the layers composing the heterostructures in the areas cleansed of the smallest bubbles, promoting a more intimate contact between the layers. This is expected to enhance the optical quality of the sample, similar to the improved transport characteristics demonstrated in prior work.³⁴

To prove that, we investigate now a series of three $MOS_2/MOSe_2$ heterostructures. In Figure 2(a), we present the optical image of sample A (for sample B and sample C see SI). It consists of MOS_2 and $MOSe_2$ monolayers sandwiched between hBN layers (for structural data see Table S1 in the SI). The twist angle between monolayers for all structures is determined by second harmonic generation measurements (SI Figure S5). The results for both tilt angles (0° and 60°) are qualitatively the same unless otherwise stated. In the main text, we focus mainly on samples A and B (for sample C see the SI).

The black dashed triangle in Figure 2(a) denotes the heterostructure region, where the two monolayers overlap. A typical low-temperature (T = 4.5 K) photoluminescence (PL) spectrum from the heterostructure region is presented in Figure 2(b). We can distinguish features related to MoSe₂ and MoS₂ intralayer excitons at ~1.62 eV and ~1.9 eV,¹¹ respectively. These transitions are also visible in the reflectance spectrum of the heterostructure, where we also note an additional feature, corresponding to the MoSe₂ B-exciton transition.⁴⁴ On the low-energy side, a strong PL peak, visible

only in the heterostructure region, corresponds to the interlayer exciton 37,38,45,46 (see also SI Figures S3 and S4).

As shown in Figure 2(c), we ironed three square-shaped areas, using an AFM tip in contact mode with 30, 60, and 80 nN pressing force (for the other samples see SI Table S1, Figure S3, and Figure S4), resulting in an applied pressure of approximately 4–6 GPa (Sec. II of the SI). The ironing procedure considerably improves the flatness of the hetero-structure as evident in the inset of Figure 2(c) which shows a close-up view of the corner of the ironed area of the heterostructure. The surface of the ironed part shows the removal of small bubbles and surface adsorbates, and local flattening in between the large bubbles. The presence of bubbles in the non-ironed part of the sample affected the optical response as their in-plane distance was lower than the typical spatial resolution of a μ PL setup.

Figure 3(a) presents the spatial dependence of the interlayer exciton PL integrated intensity in the heterostructure area. We observe that, within the ironed regions indicated by the white squares, the PL intensity is enhanced compared with the nonironed part of the heterostructure. This is especially visible when taking a cross-section through all three ironed regions along the white dotted line, shown in Figure 3(b). The integrated PL intensity exhibits local maxima on the ironed parts (shaded areas). In between the ironed regions, the peak intensity drops. Apart from the enhanced intensity, with increasing ironing force the interlayer transition redshifts and broadens and its lineshape changes. PL spectra from nonironed parts exhibit a low-energy tail while in the ironed parts lineshape is more symmetric with increasing ironing force, and for the highest forces employed, a new feature develops on the high-energy side, as illustrated in Figure 3(c), where representative spectra taken along the cross-section are presented.

To corroborate these observations and to provide a deeper insight into the evolution of interlayer exciton characteristics, we have performed a statistical analysis of the PL spectrum measured at different spots on the heterostructure. The histograms in Figure 4(a–f) show the distribution of the PL peak energy, line width, and intensity for the different forces employed to iron the heterostructure. The ironing results in a redshift of the interlayer exciton transition, as visible in Figure 4(a,b,g). This redshift is roughly proportional to the ironing force, with a coefficient of $-286 \pm 225 \,\mu\text{eV/nN}$. The average broadening of the emission line increases with a coefficient of



Figure 3. (a) PL intensity map for the interlayer exciton, showing higher intensity hotspots for the ironed regions. (b) The evolution of the PL intensity along the cross-section is indicated by the white dashed line. A clear enhancement of the PL intensity in ironed part (indicated by the shaded area) is visible. (c) Representative PL spectra along the cross-section show the change of the PL line shape in ironed part. Gray spectra are from the non-ironed region along the cross-section.

0.26 \pm 0.07 $\mu eV/nN$, as we discuss more in detail below. Finally, on average the PL intensity in the ironed part increases by about 15% compared to non-ironed areas. These results are explained if we consider the more intimate contact between the layers in the heterostructures, due to the reduced density of bubbles we obtain after the AFM treatment. Quantitative estimation of this effect is however complicated by the absence of more detailed structural information, available with transmission microscopy techniques. Moreover, in a MoS₂/MoSe₂ heterostructure, the interlayer exciton transition is

predominantly a strongly hybridized, momentum-indirect exciton,^{47,48} which makes the quantitative analysis of the impact of the interlayer distance very challenging.

Most importantly, the distributions of all three parameters of interest are narrower after ironing, as evident from the direct comparison between Figure 4(a,c,e) and Figure 4(b,d,f), which represent the non-ironed and ironed distributions, respectively. The standard deviation of all the parameters decreases after ironing as shown in Figure 4(j), where we show the dependence of the standard deviation σ of a quantity measured in the ironed area normalized by the standard deviation of the same quantity σ_0 estimated in non-ironed areas as a function of the ironing force. Our analysis demonstrates that the decreased RMS roughness of the ironed areas and the reduced density of bubbles and wrinkles are accompanied by a considerable narrowing (50% decrease of σ/σ_0) of the statistical distribution of the interlayer exciton energy, line width, and intensity along with a general increase of the PL intensity when forces of 60-80 nN are used to iron the heterostructure. This demonstrates that reducing the interface roughness and locally improving the quality of the interface of the heterostructure are key to achieving spatially uniform optical spectra.

The observed changes in the interlayer exciton emission properties after ironing are consistent with the enhancement of the moiré effects, 15,49,50 due to the improved proximity of the layers and flattening. The redshift of the interlayer exciton transition upon ironing can be understood as an effect of the increased interlayer exciton binding energy and/or band hybridization, 47 due to a reduction of the interlayer distance. Simultaneously, the improved proximity of the layer together with local flattening deepens the moiré trapping potential ^{15,49,50} which also enhances redshift of the interlayer exciton. The ironing procedure has implications beyond proximity enhancement. Specifically, it is also possible that this procedure serves to mitigate local strain fluctuations and thus increase the moiré effect (see inset of Figure 5).



Figure 4. (a–f) Histograms showing the statistical distribution of PL energy, line width, and intensity for non-ironed (top panels) and ironed (bottom panels) areas of the heterostructure. (g–i) Average values of interlayer exciton transition energy, line width, and PL intensity as a function of ironing force. Dashed lines are linear fits. (j) Interlayer exciton transition energy, line width, and PL intensity standard deviation σ normalized to standard deviation of the corresponding quantity measured on the non-ironed areas σ_0 as a function of the ironing force. Dashed line stands for global linear fit of the relative standard deviation of all the parameters. The fitting procedure in panels (g) and (h) exclude the 0 nN data point, which corresponds to the as-prepared heterostructure, over which we have no control.



Figure 5. Evolution of the difference δE between the maximum of the PL peak and the PL center of mass as a function of ironing force. A positive δE indicates a spectral tail on the low-energy side, while negative δE indicates a high-energy tail. The inset is a schematic illustration of the evolution of the moiré potential and PL spectra upon ironing. The enhanced proximity of the layers in the flattened structure increases the amplitude of the moiré potential, which also becomes more uniform, and on average deeper, therefore it can accommodate more states.

The enhancement of the moiré effect can also explain the surprising, increased broadening of the interlayer exciton PL spectrum with the increasing ironing force. However, at the same time, the line width distribution is narrower. This suggests that the increasing broadening is not related to the disorder, but results from the evolution of the intrinsic properties of the interlayer exciton. This is demonstrated in the evolution of the interlayer exciton PL lineshape upon ironing as shown in Figure 3(c). On the non-ironed part, the PL spectrum exhibits a low-energy tail, which is a typical indication of disorder in semiconductors.^{41,51-54} In the ironed areas, the PL spectrum is more symmetric or, in some cases, a high-energy shoulder appears (see Figure 3(c)). To describe the lineshape evolution quantitatively, we analyze how the difference δE between the maximum of the PL peak (E_{max}) and the center-of-mass energy (i.e., $\delta E = E_{\text{max}} - \frac{\sum E \cdot I(E)}{\sum I(E)}$) changes as a function of the ironing force. δE describes the distribution of the PL intensity with respect to the peak energy. A positive δE indicates a spectral tail at the low-energy side, whereas negative δE is related to the presence of a high-energy shoulder. For non-ironed regions the distribution for δE is centered around ~15 meV (Figure 5). With ironing δE decreases and approaches 0 meV, and, for higher forces, it becomes negative, confirming the change of PL lineshape. Again, we expect that this stems from the enhanced coupling between monolayers building the heterostructure after ironing. This is schematically presented in Figure 5. After ironing, the potential landscape becomes more uniform (as attested by reduced variation of full width half-maximum) and the increased layers coupling deepens the moiré potential. This facilitates the bounding of extra states, which contribute to the emission on the highenergy side of the PL peak.^{15,49} This explains the apparent contradiction of an improved spatial uniformity of the line width, observed in conjunction with a constant (or slightly increasing) average value of line width which does not decrease after ironing.

In conclusion, we have investigated the effect of AFM ironing on the optical quality of TMD heterostructures. We identify two classes of effects. At low forces, the surface roughness of the heterostructure initially increases and then

decreases due to a "sweeping-out" of surface adsorbates. At forces above 30 nN, ironing moves small, more mobile bubbles and merges them into larger bubbles. We show that AFM ironing can significantly improve the optical quality of heterostructures. It improves the homogeneity of the interface (enhancing local flattening and reducing corrugations and strain fluctuations), leading to more uniform optical spectra and enhanced interlayer coupling and moiré pattern impact. Our findings demonstrate that AFM ironing is a promising method to unveil the intrinsic moiré physics in TMD heterostructures, which suffer from low reproducibility and inconsistent results related to low interface and surface quality. Therefore, AFM ironing, in addition to hBN encapsulation, could be a crucial post-stacking step to improve the quality of TMD stacks.

METHODS

A description of sample preparation and AFM and optical spectroscopy setups can be found in the SI.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.2c04765.

Nail-polish fabrication technique used for the fabrication of samples, second harmonic generation measurements and photoluminescence experiments used to characterize the sample, and details of the AFM ironing procedure incorporated (PDF)

Video showcasing the movement and coalescence of bubbles under different ironing forces (AVI)

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Notes

The authors declare no competing financial interest.

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