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# Imaging of interlayer coupling in van der Waals heterostructures using a bright-field optical microscope

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## Abstract

Vertically stacked atomic layers from different layered crystals can be held together by van der Waals forces, which can be used for building novel heterostructures, offering a platform for developing a new generation of atomically thin, transparent and flexible

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3 devices. The performance of these devices is critically dependent on the layer thickness  
4 and the interlayer electronic coupling, influencing the hybridisation of the electronic  
5 states as well as charge and energy transfer between the layers. The electronic coupling  
6 is affected by the relative orientation of the layers as well as by the cleanliness of their  
7 interfaces. Here, we demonstrate an efficient method for monitoring interlayer coupling  
8 in heterostructures made from transition metal dichalcogenides using photolumines-  
9 cence imaging in a bright-field optical microscope. The color and brightness in such  
10 images are used here to identify mono- and few-layer crystals, and to track changes in  
11 the interlayer coupling and the emergence of interlayer excitons after thermal anneal-  
12 ing in heterobilayers composed of mechanically exfoliated flakes and as a function of  
13 the twist angle in atomic layers grown by chemical vapour deposition. Material and  
14 crystal thickness sensitivity of the presented imaging technique makes it a powerful  
15 tool for characterisation of van der Waals heterostructures assembled by a wide variety  
16 of methods, using combinations of materials obtained through mechanical or chemical  
17 exfoliation and crystal growth.  
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## 32 33 34 35 Keywords

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37  
38 van der Waals heterostructures, transition metal dichalcogenides, 2D materials, interlayer  
39 coupling, optical imaging, annealing  
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## Introduction

Atomically thin materials offer a new paradigm for control of electronic excitations in the extreme two-dimensional (2D) limit in condensed matter. Recently this concept has been developed further with the creation of 2D heterostructures in which individual atomic layers are held together by van der Waals (vdW) interaction.<sup>1-4</sup> The weak interlayer bonding loosens the lattice matching requirement, allowing a wide range of materials to be used in one device. Such vdW heterostructures combine unique properties of 2D materials with transparency and extreme flexibility, allowing a range of novel electronic and optoelectronic devices to be fabricated. Indeed, a wide variety of such devices has been demonstrated, including field-effect transistors,<sup>3,5-9</sup> light emitting devices,<sup>10-13</sup> vertical tunneling transistors<sup>14-17</sup> and photodetectors.<sup>14,18-24</sup>

Van der Waals heterostructures also open an attractive possibility to access interlayer excitons formed by electrons and holes localized in adjacent materials. This has recently been observed in transition metal dichalcogenide (TMD) heterobilayers with type-II band alignment.<sup>21,25-31</sup> Such excitons have binding energies comparable to those of their intralayer counterparts,<sup>32</sup> however, they can have orders of magnitude longer lifetimes due to the spatial separation of the charge carriers.<sup>28</sup> The long lifetimes in conjunction with valley-dependent optical selection rules have made interlayer excitons a promising platform for valley index manipulation and valleytronic applications.<sup>33,34</sup>

Recent advantages in growth techniques have allowed lateral<sup>35-41</sup> and vertical<sup>29,42,43</sup> vdW heterostructures to be manufactured by direct growth. However, the majority of heterostructures employed in research of electronic and optical properties are still created by stacking of exfoliated or chemical vapour deposition (CVD) grown crystals using polymers (such as PMMA, PC, PDMS etc.) as transfer medium.<sup>44-46</sup> Along with the fast device prototyping, this method offers the ultimate control of the overlap and twist angle between individual layers, enabling control of the degree of the electronic coupling between them. The electronic and mechanical coupling between the layers is also affected by fabrication imperfections

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3 leading to organic residues on the crystal surfaces, which to some degree can be rectified by  
4 thermal annealing.<sup>25,43,47–50</sup> A fast method for monitoring the coupling between the layers  
5 is highly desirable, and will enable rapid assessment of the heterostructure properties and  
6 quality, that is key for fabrication of novel atomically thin optoelectronic devices.  
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11 In this paper, we present a method for rapid monitoring of the interlayer coupling in  
12 vdW heterostructures made from monolayer semiconducting TMDs using a bright-field op-  
13 tical microscope. We show that photoluminescence (PL) images of a large area of exfoliated  
14 or CVD-grown TMD crystals can be obtained using a standard microscope equipped with a  
15 white light source and a set of optical edge-pass filters. Using the color and brightness of the  
16 images, the presented techniques can be utilized for rapid identification of TMD mono- and  
17 few-layers on various substrates, including polymethylmethacrylate (PMMA), polycarbonate  
18 (PC) and polydimethylsiloxane (PDMS) commonly used for vdW heterostructure fabrica-  
19 tion. Furthermore, we use this method to assess the changes in the degree of the electronic  
20 coupling between the adjacent TMD crystals following thermal annealing. The microscope  
21 PL images unambiguously reveal that, while the as-fabricated TMD heterobilayers act as  
22 a set of independent monolayers because of the polymer residue between the layers, signif-  
23 icant improvement of interlayer coupling is observed after the thermal treatment. Using  
24 PL imaging, we also investigate the coupling between individual layers in heterostructures  
25 composed of exfoliated or CVD-grown TMD monolayers with varying the interlayer twist  
26 angles. While all TMD heterobilayers show significant reduction of PL intensity due to in-  
27 tralayer exciton dissociation, the PL quenching is an order of magnitude stronger in samples  
28 with small rotational misalignment. The noticeable change of PL color due to bright inter-  
29 layer exciton emission can be seen in heterobilayers with aligned principal crystal axes. The  
30 sensitivity of the TMD PL emission to the individual layer thickness and coupling between  
31 different layers makes microscope PL imaging demonstrated here an indispensable tool for  
32 vdW heterostructure characterisation with wide ranging applications. Previously a similar  
33 technique employing a microscope equipped with a dedicated UV source and a monochrome  
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camera was used to study blinking in two dimensional semiconductor heterostructures.<sup>51</sup> In our work the imaging relies on the intensity as well as the color of the detected PL, which enables an extended range of experiments on a wide variety of material combinations.

Photoluminescence imaging of few-layer TMD samples

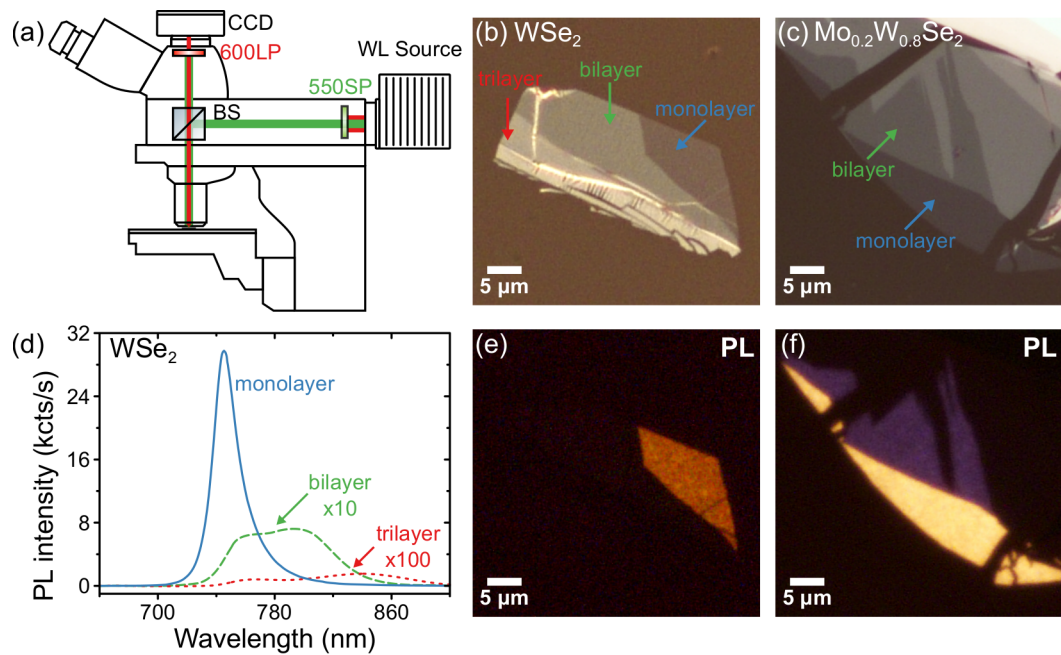


Figure 1: **Photoluminescence imaging of TMD monolayers and bilayers using a bright-field optical microscope.** (a) Schematic representation of the PL imaging set-up based on the optical microscope. (b)-(c) Bright-field images of mechanically exfoliated few-atomic-layer crystals on PDMS substrates: WSe<sub>2</sub> in (b) and Mo<sub>0.2</sub>W<sub>0.8</sub>Se<sub>2</sub> in (c). (d) PL spectra recorded in monolayer (blue), bilayer (green) and trilayer (red) regions of the WSe<sub>2</sub> sample shown in (b). (e) PL image of the WSe<sub>2</sub> sample acquired with 1 s acquisition time and 9.6x analog gain on the camera, showing PL from the monolayer region only. (f) PL image of the Mo<sub>0.2</sub>W<sub>0.8</sub>Se<sub>2</sub> sample shown in (c) with clearly identifiable regions of a monolayer (yellow) and a bilayer (purple). Image recorded with 1 s acquisition time and 3.4x analog gain.

The PL imaging set-up used in this study is schematically shown in Figure 1 (a) and described in more detail in the Methods section below. Figure 1 (b) shows a bright-field image of a WSe<sub>2</sub> flake exfoliated onto a PDMS substrate. The most translucent area in the top right corner of the flake corresponds to the monolayer region. The PL image of the

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3 same sample acquired using the experimental set-up is shown in Figure 1 (e). Even with  
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5 1 second acquisition time, the monolayer region is clearly visible in the image due to the  
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7 bright PL emitted by the flake. The PL emission from the WSe<sub>2</sub> bilayer region is two orders  
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9 of magnitude weaker and requires longer acquisition times to be detected.  
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11 The thickness dependence of the PL intensity reflects the changes of the WSe<sub>2</sub> band  
12 structure with increasing numbers of layers.<sup>52</sup> While monolayer WSe<sub>2</sub> is a direct bandgap  
13 semiconductor, the bandgap becomes indirect for bilayers, leading to a strong quenching of  
14 the PL. Figure 1 (d) compares PL spectra recorded in different regions of the flake using a  
15 separate micro-PL set up (see Methods for details). The monolayer region shows bright PL  
16 with emission peak centred at 745 nm (blue line). The direct-to-indirect bandgap transition  
17 in bilayer WSe<sub>2</sub> leads to a shift of the emission maximum to lower energies, as well as two  
18 orders of magnitude reduction of the emission intensity (dashed green line). Further increase  
19 of thickness leads to almost complete disappearance of the PL signal (dotted red line).  
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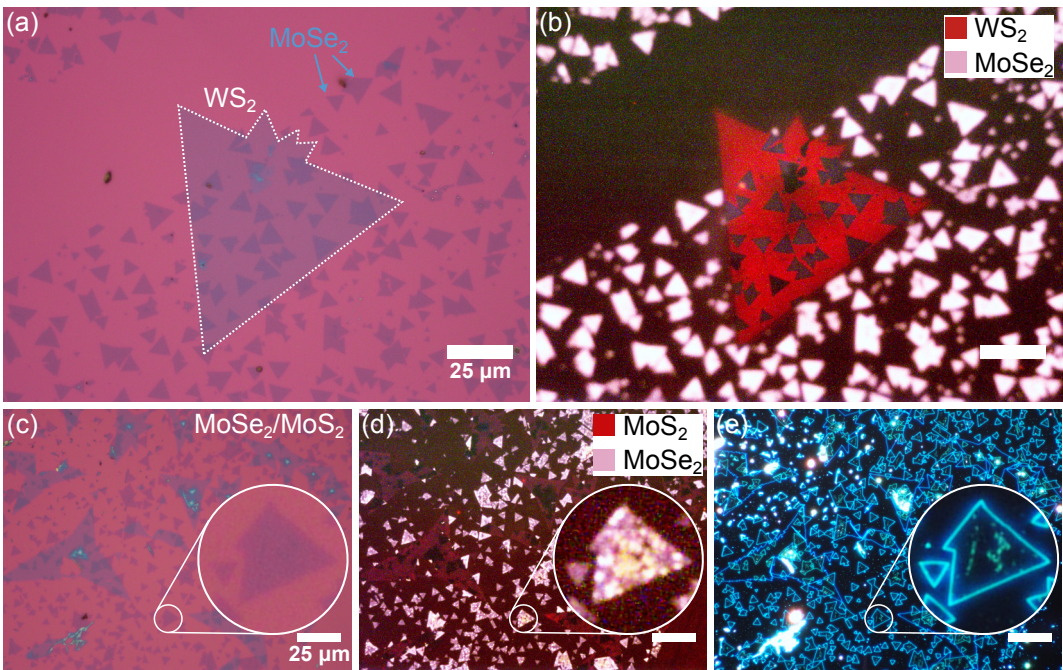
30 The abrupt change of the PL characteristics with increasing numbers of layers allows PL  
31 imaging to be used for sample thickness identification. Unlike other methods, such as optical  
32 contrast measurements,<sup>53</sup> it relies on the change of the TMD band structure and therefore  
33 its effectiveness is independent of the type of the substrate used. The exception will be  
34 substrates where PL of the TMD monolayers is strongly quenched (for example, when they  
35 are placed on gold) or the TMD flakes become strongly strained and their band-structure is  
36 modified. For such structures our method provides additional insight in the coupling of the  
37 flake and substrate and will highlight any non-uniformity of such interaction through the  
38 intensity and color of the PL image.  
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48 Figure 1 (c) and (f) compares bright-field and PL images of a Mo<sub>0.2</sub>W<sub>0.8</sub>Se<sub>2</sub> sample ex-  
49 foliated onto a PDMS substrate. Compared to the pure binary compound, the TMD alloy  
50 shows much brighter PL emission, making both monolayer and bilayer regions clearly visible  
51 in the PL image. The difference in the color reflects the variation of emission spectrum with  
52 increasing sample thickness. Similar to WSe<sub>2</sub>, the PL spectrum broadens and shifts to longer  
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wavelengths in the bilayer regions (see Fig. S2 in the Supplementary information). PL at longer wavelengths appears as a false purple color in Fig. 1 (f), a feature related to the transmission efficiency in the near-infrared of the color filter arrays in the digital camera used. The thickness sensitivity of PL imaging makes it a convenient tool for rapid identification of TMD mono- and bilayers on various substrates, including PMMA and PDMS commonly used for vdW heterostructure fabrication (see more image examples in Supplementary information).

### Imaging of interlayer coupling in TMD heterobilayers



**Figure 2: Photoluminescence imaging of CVD-grown TMD samples.** (a) Bright-field image of a MoSe<sub>2</sub>/WS<sub>2</sub> heterostructure on a SiO<sub>2</sub>/Si substrate. (b) PL image of the sample in (a) showing that the two materials have distinctly different colors according to the wavelength of their PL bands: red for WS<sub>2</sub> and a false pink for MoSe<sub>2</sub> emitting in the near infra-red. The PL quenching in the overlap regions indicates efficient electronic coupling between two layers. (c), (d) and (e) Bright-field, PL, and dark-field images of a MoSe<sub>2</sub>/MoS<sub>2</sub> heterobilayer on a SiO<sub>2</sub>/Si substrate. The zoomed-in regions show the same part of the substrate in all three images, with the PL exhibiting a large amount of additional detail compared to the bright- and dark-filed microscopy images. All scale bars in the figure correspond to 25 μm. PL images are recorded with 10 s acquisition time and 9.6x analog gain.

The wide-field nature of the PL imaging makes it especially useful for characterisation



of samples produced by CVD growth, allowing large areas of a sample to be investigated at the same time. Figure 2 (a) show a bright-field image of a MoSe<sub>2</sub>/WS<sub>2</sub> sample on a SiO<sub>2</sub>/Si substrate composed of CVD-grown monolayers. Large triangle in the centre of the image corresponds to single layer WS<sub>2</sub> while smaller flakes around it are MoSe<sub>2</sub> monolayers.

Although both materials have similar appearance in the bright-field image, they can be easily distinguished by their emission color in the PL image (Fig. 2 (b)). Room-temperature PL emission of WS<sub>2</sub> is centred at 630 nm and appears dark red in the PL image, whereas MoSe<sub>2</sub> PL peaks at 790 nm and has pale pink color. Here, the MoSe<sub>2</sub> monolayers have a slightly blurry appearance due to the chromatic aberration, caused by the difference in their PL peak wavelength.

The bright and uniform PL in the WS<sub>2</sub> flake indicates high crystalline quality of the sample. In comparison, the CVD-grown MoS<sub>2</sub> flakes in a MoSe<sub>2</sub>/MoS<sub>2</sub> sample demonstrate much weaker PL and significant variation of the emission intensity both within individual crystals and across the substrate (Fig. 2 (d)). The MoSe<sub>2</sub> monolayers in the same sample also show strongly non-uniform PL emission. The observed 'grainy' structure in PL is likely caused by organic residues left from the transfer process that are trapped between the flakes or the flakes and the substrate. Although the variation of emission intensity within the grainy pattern is clearly visible in the PL image, it shows little correlation with the features visible in the dark-field image (Fig. 2 (e)) and is completely invisible in the bright-field image (Fig. 2 (c)).

The heterobilayer regions in both samples demonstrate strong quenching of the intralayer exciton PL, indicating the efficient coupling between the layers. For the semiconducting group VI TMDs, a heterostructure formed by monolayers of two different materials will have type-II band alignment with the edges of valence and conduction bands located in different materials.<sup>54,55</sup> The staggered gap in TMD heterobilayers facilitates ultrafast charge separation between the two layers that acts as a dominant decay channel for optically excited intralayer excitons, significantly quenching their PL.<sup>49,56,57</sup>

The overall decrease in the PL intensity is related to the non-radiative decay of electron-hole pairs. The intralayer exciton radiative lifetime is of the order of 1 ps,<sup>58,59</sup> while the interlayer excitons radiative decay time exceeds 1 ns.<sup>28</sup> The non-radiative processes are extremely fast in TMDs,<sup>60</sup> competing with the intralayer exciton radiative decay, so when the excitons are dissociated due to the charge transfer in the heterostructures, the overall PL intensity is significantly reduced. This process is further enhanced in heterostructures made of misaligned heterobilayers, where the radiative decay of interlayer excitons is suppressed due to the momentum mismatch between the electron and hole localized in different monolayers.<sup>61,62</sup>

The efficient interlayer coupling in TMD heterostructures requires the interface between adjacent layers to be clean of any contamination. As the van der Waals heterostructure fabrication through mechanical stacking relies on the use of a polymer (PMMA, PC, PDMS etc) as the transfer medium, it often results in the presence of organic residues between the atomic planes. Figure 3 (a) shows an optical image of MoSe<sub>2</sub>/WSe<sub>2</sub> heterostructure mechanically assembled on a SiO<sub>2</sub>/Si substrate. The 2D flakes exfoliated from bulk crystals onto a PDMS substrate were consecutively transferred onto the SiO<sub>2</sub>/Si substrate using viscoelastic stamping<sup>45</sup> with no intermediate cleaning steps. As it can be seen from the PL image in Fig. 3 (b), the PL emitted by the heterobilayer region consists of the sum of MoSe<sub>2</sub> and WSe<sub>2</sub> emission and shows no signs of PL quenching. The unperturbed intralayer emission in the heterostructure region indicates that the interlayer coupling is suppressed by the polymer residues trapped between the layers.<sup>25,43</sup>

## Tuning of interlayer coupling through thermal annealing observed in PL imaging

Thermal annealing in vacuum or inert atmosphere is commonly used to remove organic residues from the surface of 2D crystals.<sup>25,43,47–50</sup> Here we utilize this method to improve interlayer coupling in the existing heterostructure. Figure 3 compares bright-field microscope

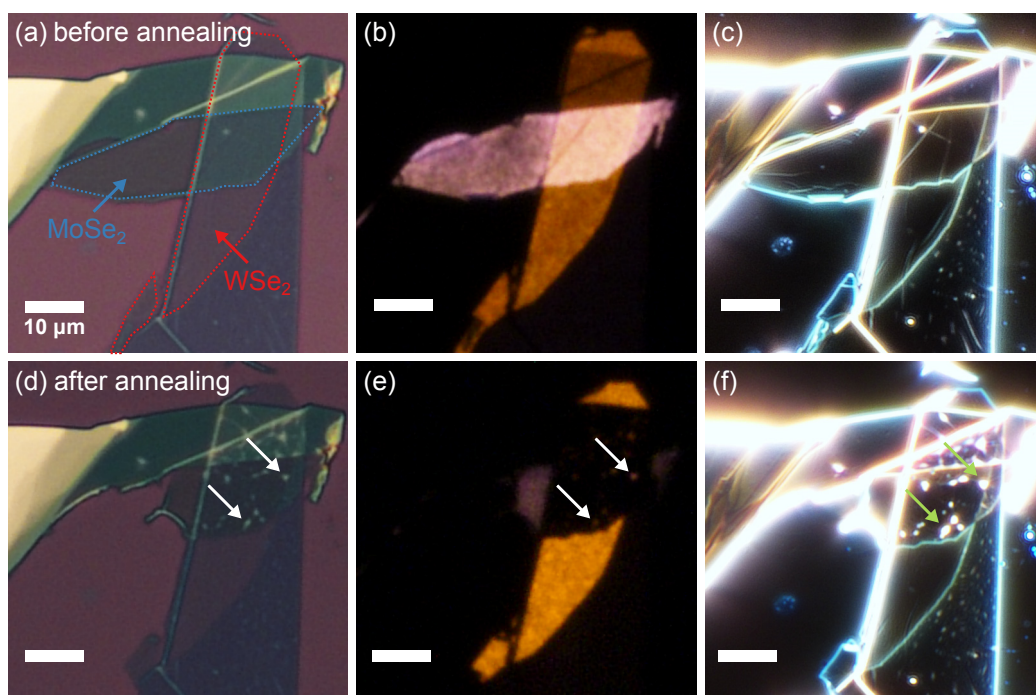


Figure 3: **Monitoring changes in the interlayer coupling introduced by thermal annealing.** (a), (b), (c) Bright-field, PL, and dark-field images of a MoSe<sub>2</sub>/WSe<sub>2</sub> heterostructure fabricated on a SiO<sub>2</sub>/Si substrate by PDMS-assisted transfer of mechanically exfoliated crystals. (d), (e), (f) Bright-field, PL, and dark-field images of the same structure after annealing in high vacuum at 120° C for 2 hours. Arrows show examples of contamination pockets observed in all three types of images. All scale bars in the figure correspond to 10  $\mu$ m. PL images are recorded with 1 s acquisition time and 9.6x analog gain.

images of the sample before (a) and after (d) annealing in high vacuum at 120° C for 2 hours. While a part of the isolated MoSe<sub>2</sub> monolayer was damaged during the thermal treatment, both isolated WSe<sub>2</sub> and heterostructure regions remain mostly intact.

Although the thermal treatment could not completely remove the organic residues trapped between the layers, it has caused their aggregation into small contamination pockets that can be clearly seen in both bright- and dark-field images (shown with arrows in Fig. 3(d),(f)). The pockets formation is caused by the strong attraction between the two layers.<sup>63</sup> Comparing the dark-field images acquired before and after annealing (Fig. 3 (c) and (f), respectively), it is apparent that the contamination pockets have formed only in the areas where the two crystals overlap. The formation of contamination pockets after annealing is similar to the self-cleansing observed in vdW heterostructures<sup>4,64</sup> and results in atomically clean interfaces

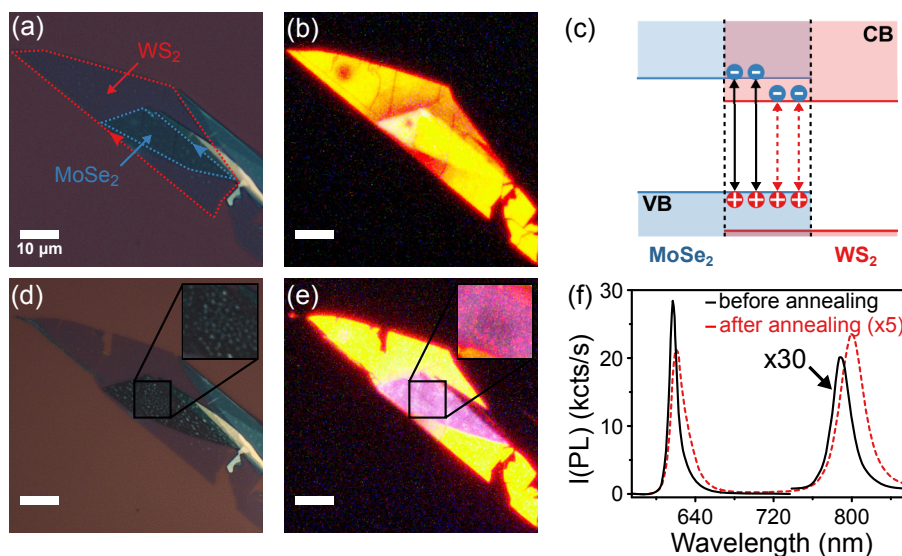
in the contamination-free regions.

The effects of the thermal treatment can be clearly seen in the PL image of the sample in Fig. 3 (e). Substantial increase of the emission intensity has occurred in the WSe<sub>2</sub> monolayer,<sup>50,65</sup> possibly due to removal of the polymer residues from its surface. The strongest change of the PL intensity can be seen in the layer overlap region, where both MoSe<sub>2</sub> and WSe<sub>2</sub> emission has almost completely disappeared after annealing. The strong quenching of the intralayer PL due to ultrafast charge separation indicates significant improvement of interlayer coupling.<sup>28,34</sup> While the WSe<sub>2</sub> emission intensity is significantly reduced in all areas covered by MoSe<sub>2</sub>, bright PL can still be observed in the parts of the heterostructure around the contamination pockets (shown in Fig. 3 (e)). The positions of these bright spots fully correlate with the pockets seen in Fig. 3 (d) and (f)). However, the absence of the electronic coupling in these regions can only be revealed in the PL image in Fig. 3 (e).

## Observation of formation of interlayer excitons in TMD heterobilayers using PL imaging

The interlayer charge separation in TMD heterobilayers can lead to the formation of interlayer excitons composed of electrons and holes localized in different materials.<sup>25–31</sup> The lack of observable emission in the overlap region in Fig. 3 (e) is a result of the combination of the suppression of the interlayer exciton emission in MoSe<sub>2</sub>/WSe<sub>2</sub> at room temperature and the relatively low efficiency of the CCD at the wavelengths above 900 nm where the PL of the interlayer exciton is expected. A further important consideration is that the momentum-space alignment of *K* valleys in TMD heterobilayers depends of the relative layer orientation in the real space. In the sample shown in Fig. 3, the crystal axes in the monolayers are not aligned, which allows real- and momentum-space-indirect optical transitions only, which have negligible probability.

In order to investigate the effects of annealing on the formation of interlayer excitons in TMD heterobilayers, we have fabricated a set of heterostructures in which crystal axes



**Figure 4: Emergence of interlayer exciton PL following annealing in MoSe<sub>2</sub>/WS<sub>2</sub> heterobilayers.** (a) and (b) Bright-field and PL images of a MoSe<sub>2</sub>/WS<sub>2</sub> heterostructure fabricated using mechanical exfoliation from bulk crystals on PDMS and consequent transfer on a SiO<sub>2</sub>/Si substrate. The crystallographic axes of the two monolayers are aligned using the the flake edges marked with arrows. (c) Band alignment of a MoSe<sub>2</sub>/WS<sub>2</sub> heterostructure indicating MoSe<sub>2</sub> intralayer (solid black) and MoSe<sub>2</sub>/WS<sub>2</sub> interlayer (dashed red) optical transitions. (d) and (e) Bright-field and PL images of the sample after annealing. (f) PL spectra of the heterostructure before (solid black) and after (dashed red) annealing. The intensity of the low energy peak in the spectrum measured before the annealing is multiplied by 30, whereas the intensity of the whole spectrum measured after the annealing is multiplied by 5. All scale bars in the figure correspond to 10  $\mu\text{m}$ . PL images are recorded with 10 s acquisition time and 9.6x analog gain.

of mechanically exfoliated flakes were aligned using their terminating edges as a guide.<sup>66</sup> Figure 4 shows the bright-field (a) and PL (b) images of a MoSe<sub>2</sub>/WS<sub>2</sub> heterostructure assembled on a SiO<sub>2</sub>/Si substrate using PDMS stamping. Both images were taken before annealing. The PL emission in the overlap region consists mostly of WS<sub>2</sub> PL as at room temperature it is several orders of magnitude stronger than that of MoSe<sub>2</sub>.<sup>30,56</sup>

The improvement of the interlayer coupling after annealing leads to significant changes of the heterostructure emission that can be clearly seen in the PL image in Fig. 4 (e). While isolated monolayer regions of WS<sub>2</sub> show an increase of the PL intensity due to removal of the polymer residues, the heterostructure region demonstrates a prominent change of PL color, indicating a significant shift of its peak PL wavelength.

Figure 4 (f) compares the PL spectra of the heterostructure before (solid black) and after (dashed red) annealing. Prior to the thermal treatment, the WS<sub>2</sub> PL is nearly two orders of magnitude stronger than that of MoSe<sub>2</sub>. Unlike the isolated monolayer regions, WS<sub>2</sub> PL in the heterobilayer region is significantly quenched after annealing due to the efficient interlayer charge separation.<sup>30,56</sup> The slight red-shift of the WS<sub>2</sub> peak is possibly a result of the change in the dielectric environment caused by reduced vertical distance between the layers.<sup>29,50,56,67</sup>

The emergence of a strong peak at 800 nm following the annealing indicates the formation of interlayer excitons. The emission energy of these excitons is defined by conduction and valence band offsets between the two materials (Fig. 4 (c)). Unlike MoSe<sub>2</sub>/WSe<sub>2</sub> heterobilayers, the near-degenerate conduction bands in MoSe<sub>2</sub>/WS<sub>2</sub> heterostructure result in interlayer exciton states having the optical transition just a few tens of meV below the one for MoSe<sub>2</sub>.<sup>30</sup> The regions of the heterostructure containing contamination pockets are visible as spots of a different color in the PL image (magnified in Fig. 4 (e)). The PL in these areas comes from both MoSe<sub>2</sub> and WS<sub>2</sub>, as the aggregated residues prevent efficient coupling between two materials, causing them to act as independent layers.

## Twist angle dependence of the interlayer charge transfer

The PL imaging can be directly applied for studying the dependence of the interlayer coupling strength on the relative rotation between the two layers. Figure 5 (a) shows a bright-field image of the MoSe<sub>2</sub>/WS<sub>2</sub> sample composed of CVD-grown monolayers; dashed white line marks the edge of a large triangular WS<sub>2</sub> monolayer. Since terminating edges of triangular TMD monolayers correspond to zigzag directions,<sup>42,68,69</sup> the rotation angle between two layers can be easily identified by comparing the orientation of the WS<sub>2</sub> flake (indicated by dashed white triangles) with MoSe<sub>2</sub> monolayer orientation (colored triangles). Figure 5 (b) shows the PL image of the same region. While isolated monolayer regions of both MoSe<sub>2</sub> and WS<sub>2</sub> show bright PL, the intralayer PL intensity in both materials is significantly lowered in the

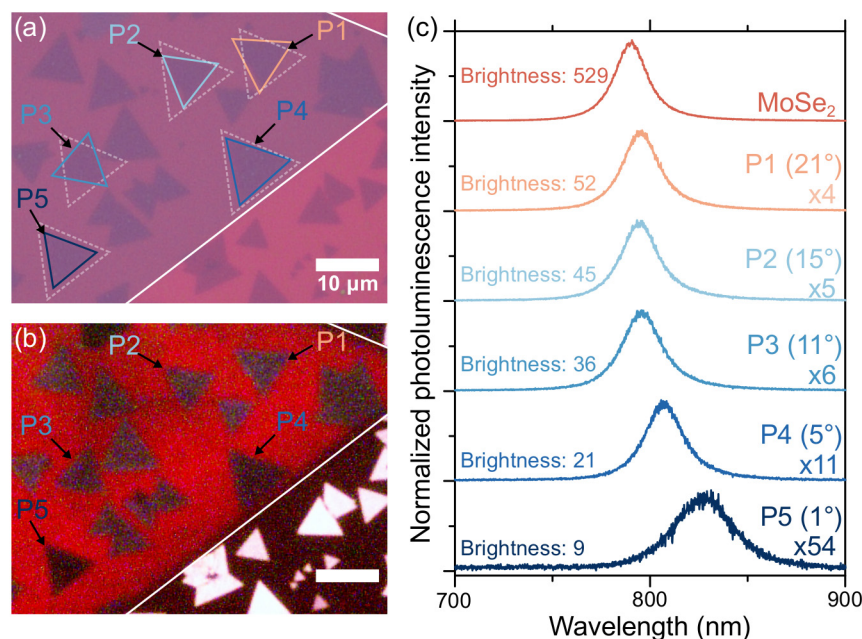


Figure 5: **Twist angle dependence of the interlayer coupling in MoSe<sub>2</sub>/WS<sub>2</sub> heterobilayers.** (a) Bright-field image of a MoSe<sub>2</sub>/WS<sub>2</sub> heterostructure assembled on a SiO<sub>2</sub>/Si substrate from individually CVD-grown layers. Dashed white triangles indicate the orientation of the large triangular WS<sub>2</sub> flake, one visible edge of which is marked by a solid white line. In order to make the relative rotation angles more obvious, the edges of the selected MoSe<sub>2</sub> monolayers were highlighted by lines. (b) PL image of the sample showing varying degrees of the intralayer PL quenching in the overlap regions (see dark triangles); recorded with 10 s acquisition time and 9.6x analog gain. (c) PL spectra measured in the heterobilayer regions with varying twist angles (shown on the right above each spectrum). The spectra are multiplied by the factors shown on the graph (on the right above each spectrum). The brightness indicated above each curve on the left is extracted from the PL image, as explained in text.

overlap regions. The degree of PL quenching shows clear correlation with the interlayer twist angle with well-aligned heterobilayer regions (P4 and P5) appearing darker than regions with strong rotational misalignment (P1-P3). Spectrally-integrated PL intensity can be extracted from the PL images by measuring the average brightness of various regions in the digital image. Here we apply this method for MoSe<sub>2</sub> triangles, both overlapping with the WS<sub>2</sub> monolayer and isolated. The average triangle image brightness is calculated as  $(R + G + B)/3N$ , where  $N$  is the number of pixels in the triangle, and  $R$ ,  $G$  and  $B$  is the intensity in the red, green and blue channels ranging between 0 and 255. The triangle



brightness extracted following this procedure shows that the coherently stacked regions (twist angles of  $\approx 0^\circ$ ) have more than 5 times lower PL intensity compared to rotationally misaligned areas.

In order to establish firmly the correlation between the PL images and detailed spectral properties of the heterobilayer regions, emission spectra were recorded in the areas with different interlayer twist angles using the micro-PL set-up. Figure 5 (c) plots normalized PL spectra collected in the regions P1-P5 of the sample, as well as an isolated MoSe<sub>2</sub> monolayer. Scaling factors as well as emission intensity extracted from the PL image are listed above each curve. Compared to the isolated MoSe<sub>2</sub> (top curve), the heterobilayer regions demonstrate red-shifted PL with significantly lowered intensity, indicating strong interlayer coupling. It is also evident that the PL quenching becomes stronger with the decreasing interlayer twist angle. While the spectral position of the MoSe<sub>2</sub> intralayer exciton peak at 795 nm does not show any clear dependence on the relative orientation of the two layers, for small twist angle the emission peak red-shifts to 830 nm, indicating the change from intralayer to interlayer exciton character. The WS<sub>2</sub> PL shows strong quenching in all heterobilayer regions, however, there is no apparent correlation with the interlayer twist angle (see Fig. S5 in the Supplementary Information).

The angular dependence of the PL intensity can be explained by the relative alignment of the MoSe<sub>2</sub> and WS<sub>2</sub> bands in the momentum space. The edges of the conduction and valence bands in TMD monolayers are located at the six *K* points of the Brillouin zone. Originating from the in-plane orbitals of the transition atoms, these states hybridize very weakly between the layers.<sup>32</sup> The rotational misalignment of the two layers in the real space leads to a rotation of two Brillouin zones in momentum space. Therefore, the interlayer charge transfer in the vicinity of the *K* points in the twisted heterobilayer case is a second order process, which requires phonon or defect scattering to overcome the in-plane momentum mismatch. As the interlayer twist angle decreases, the *K* valleys come into alignment, significantly improving the efficiency of charge transfer between two layers. This leads to further quenching of the

intralayer exciton PL. In coherently stacked heterobilayers, the band-gap at the Brillouin zone edge becomes direct, leading to the emergence of the interlayer exciton PL.<sup>29,31</sup>

## Conclusions

In summary, we have demonstrated that rapid large-area PL imaging of 2D semiconducting TMD samples can be achieved using a standard bright-field optical microscope, rather than a dedicated optical set-up equipped with a spectrometer. The presented technique offers a highly efficient and substrate-material-independent method of flake thickness identification that can be easily combined with flake search in one experimental set-up. Furthermore, we have shown that, due to its sensitivity to interlayer charge transfer, this technique can be used to monitor the electronic coupling between individual layers in vdW heterostructures. We have successfully applied this method to investigate interlayer coupling in vdW heterostructures composed of both exfoliated and CVD-grown TMD monolayers. While the presence of organic residues between the atomic planes in TMD heterobilayers fabricated by viscoelastic stamping prevents efficient coupling between the layers, a significant improvement of the coupling efficiency and the formation of the interlayer excitons can be clearly observed in the microscope PL images of the thermally annealed samples. The presented PL imaging techniques has also been applied to assess the interlayer coupling in TMD heterobilayers having various degrees of the rotational misalignment. We have found that the degree of intralayer exciton PL quenching depends on the relative orientation of the two layers, indicating twist-angle-dependent interlayer charge transfer. The high sensitivity of the PL intensity to the charge transfer efficiency makes the presented method a very sensitive tool for investigating the coupling strength in TMD heterostructures with varying interlayer rotation and vertical separation. The short image acquisition times required makes it possible to investigate changes of the interlayer coupling in real time, allowing for example the microscope PL imaging to be used for in-situ monitoring of sample annealing or surface functionalisation. With increasing industrial and research interest in devices based on

semiconductor vdW heterostructures, the PL imaging developed in this work offers a powerful characterisation method suitable for both exfoliated and CVD-grown samples at various fabrication stages.

## Methods

**Optical microscopy system.** PL imaging of 2D TMD crystals was carried out using a commercial bright-field microscope (LV150N, Nikon). The schematic of the experimental set-up is presented in Figure 1 (a). A 550 nm short-pass filter (FESH0550, Thorlabs) was used to block the near-infrared emission from the white light source. The PL signal produced by the sample was isolated using 600 nm long-pass filter (FELH0600, Thorlabs). The short-pass (long-pass) filters were installed into the polarizer (analyser) slots of the illuminator (LV-UEPI-N, Nikon), allowing quick switching between PL and bright-field imaging modes.

The PL images of the samples were acquired using a color microscope camera (DS-Vi1, Nikon). The hot mirror mounted in front of the sensor was removed in order to enable light detection in the near-infrared range.

**Additional micro-PL characterisation.** Spectrally resolved PL measurements were performed in a custom-built micro-PL set-up. A 532 nm solid state laser (CW532-050, Roithner) was focused onto the sample using 50x objective lens (M Plan Apo 50X, Mitutoyo). The PL signal collected in the backwards direction was isolated using a 550 nm shortpass filter (FES0550, Thorlabs) and detected by a spectrometer (SP-2-500i, Princeton Instruments) with a nitrogen-cooled CCD camera (PyLoN:100BR, Princeton Instruments). All spectrally resolved PL measurements were performed at room temperature and in ambient conditions.

**Sample fabrication.** Monolayer and few-layer TMD crystals were mechanically exfoliated from bulk crystals (provided by HQ Graphene) using wafer backgrinding tape (BT-150E-CM, Nitto). Van der Waals heterostructures were fabricated by exfoliating material onto a PDMS film (PF X4, Gel-Pak) followed by a transfer onto SiO<sub>2</sub>/Si using a viscoelastic stamping method.

CVD WS<sub>2</sub> and MoS<sub>2</sub> crystals were grown directly on a SiO<sub>2</sub>/Si substrate with a 300 nm thick SiO<sub>2</sub> layer. For heterostructure fabrication, MoSe<sub>2</sub> monolayers grown on c-plane sapphire substrates were transferred onto the substrate containing WS<sub>2</sub> and MoS<sub>2</sub> flakes using PMMA-assisted transfer - see the Supplementary Information for more details.

## Supporting Information Available

Optical identification of TMD monolayers and bilayers on various substrates; selective imaging of different materials in a van der Waals heterostructure; PL spectra for mono-, bi- and trilayer Mo<sub>0.2</sub>W<sub>0.8</sub>Se<sub>2</sub>; low-temperature PL spectrum of the MoSe<sub>2</sub>/WS<sub>2</sub> heterostructure before and after annealing; interlayer twist angle dependence of WS<sub>2</sub> emission in a MoSe<sub>2</sub>/WS<sub>2</sub> heterostructures; information on the growth of the CVD MoS<sub>2</sub>, MoSe<sub>2</sub> and WS<sub>2</sub> monolayers and fabrication of heterobilayers. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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## Graphical TOC Entry

