Observation of Room-Temperature Dark Exciton Emission in Nanopatch-Decorated Monolayer WSe$_2$ on Metal Substrate

Mahfujur Rahaman,* Oleksandr Selyshchev, Yang Pan, Rico Schwartz, Ilya Milekhin, Apoorva Sharma, Georgeta Salvan, Sibylle Gemming, Tobias Korn, and Dietrich R. T. Zahn

The presence of strong spin–orbit coupling in the valence band and weak spin-splitting in the conduction band result in the lowest energy exciton in WX$_2$ (X = S, Se) being spin forbidden and optically dark. Because of their long lifetimes, dark excitons are highly attractive for quantum optics and optoelectronic applications. To date, studying dark excitonic emissions is limited to cryogenic temperatures or requires very complex experimental configurations to observe them at room temperature (RT). Here, the radiative decay of dark exciton related emission in WSe$_2$ monolayers is studied using both conventional and tip-enhanced photoluminescence (TEPL) at RT. Monolayer WSe$_2$ flakes are sandwiched between noble metal substrates and polydimethylsiloxane nanopatches providing a strong local electrostatic out-of-plane dipole moment with respect to the 2D plane resulting in the observation of dark excitonic emission at RT. The spatial distribution of this dark exciton related emission is studied by TEPL with a spatial resolution of <10 nm confirming the confinement of these excitons within the polydimethylsiloxane nanopatches. The tip-enhanced Raman scattering (TERS) investigation excludes any local strain induced effects and reveals a direct correlation between dark excitons and defects in WSe$_2$. Finally, removal of the nanopatches led to the recovery of bright excitonic emission in WSe$_2$.

1. Introduction

Beyond graphene, transition metal dichalcogenides (TMDCs) are currently at the heart of 2D material research owing to their extraordinary fundamental physical properties. Among all TMDCs, molybdenum (Mo)- and tungsten (W)-based chalcogenides (S, Se, and Te) are the most widely studied materials. When thinned down to monolayer thickness, new properties emerge from these materials, including an indirect to direct band gap transition in the visible region situated at the K point of the Brillouin zone.[5] Despite being atomically thin, TMDC monolayers can absorb up to 15% of light in the visible range due to the strong light–matter interaction and are therefore highly promising for applications in optoelectronics.[2] Moreover, the loss of the inversion center in the monolayers offers great potential for spintronics[3] and higher harmonic generation[4] applications. The dramatically reduced dielectric screening due to the strong confinement in the out-of-plane direction combined with large electron and hole effective masses creates strongly bound excitons. The exciton binding energies are in the range of a few hundreds of meV.[5] Therefore, the optical response is strongly dominated by excitons and hence provides an ideal platform for studying excitonic or many-body physics at room temperature (RT).[6]

One important feature of TMDC monolayers is the broken inversion symmetry related to spin–orbit coupling (SOC). This leads to valley-spin locking and valley (and spin) polarized optical absorptions/emissions.[7] SOC in TMDCs creates spin splitting in both the valence band (VB) and the conduction band (CB) with opposite spins at K and K’ band edges.[8,9] The contribution of d$_{xz}$ – d$_{yz}$ and d$_{xy}$ orbitals of transition metals generates a large splitting (of the order of few hundreds meV) in the VB, leading to well separated optically allowed transitions from each sub-band known as A and B excitons.[10] However, the CB states stem predominantly from d$_{yz}$ orbitals. Therefore, the second order perturbation of transition metal (d$_{xz}$ and d$_{yz}$ orbitals) and chalcogen (p$_x$ and p$_y$) atoms leads to a modest spin splitting (of the order of tens of meV).[10] The conduction band spin splitting leads to both bright (optically active) and dark (optically
inactive) excitonic states for both A and B excitons; the lowest energy excitons are bright (dark) in Mo (W) based TMDC monolayers. An exciton is optically bright (dark) when the VB and CB states have the same (opposite) spin projections in the same valley for electrons. One key advantage of dark excitons is the long lifetime limited by nonradiative decay channels and spin-flip processes. This distinct feature offers great potential in the field of applications like Bose–Einstein condensation (BEC) or quantum computing. The lowest energy dark excitons limit the photoluminescence (PL) quantum yield via energy relaxation from bright exciton states, particularly at low temperatures. However, dark states can also become bright, e.g., via many body effects. When dark states are coupled to strain-localized point defects, they can assist the funneling of excitons to these defects, leading to single photon emission in TMDC monolayers. Additionally, when localized charged defects capture dark states, they can brighten the dark excitons in the form of charged impurity states. Thus, the variety of spin, valleys, and the number of complexes that can form well-resolved optically active bound states results in rich light–matter interactions and can offer plenty of useful tools for accessing information on the quantized valley pseudospin. Therefore, it is of critical importance to induce radiative emission of dark excitons in TMDC monolayers for valley and spin transport and optical manipulation.

Several approaches were demonstrated in recent low temperature photoluminescence studies to induce the radiative decay of dark excitons in TMDC monolayers. Some studies involved applying a strong in-plane magnetic field (≥14 T) to tilt the electron spin direction. This approach induces a weakly allowed in-plane optical transition via the Zeeman effect. In another attempt, the out-of-plane surface plasmon polariton was coupled to the dark excitons inducing a spin-flip, thus causing radiative emission. Alternatively one can also detect the dark optical transition using an objective of high numerical aperture (NA) from the sample edges or couple their emission to suitable waveguide structures. It is important to note that the weak nature of the dark-exciton related emissions limited all the above mentioned studies to be performed at cryogenic temperatures, since otherwise the small energy difference between the bright and dark emission (<50 meV) leads to an overwhelming thermal population in the bright exciton channel. More recently, Park et al. demonstrated radiative emission of dark excitons at room temperature by coupling the out-of-plane transition dipole moment to a scanning probe nanooptical antenna. The nanogap between the tip and the substrate creates a strongly confined out-of-plane optical dipole moment (oscillatory dipole moment), which facilitates the probing of dark excitons. However, in that work a complex experimental geometry was required to detect dark excitons at room temperature.

Here, we demonstrate a novel approach to induce radiative emission from dark excitons in a TMDC monolayer at room temperature, which can be detected via conventional PL spectroscopy. As the material to be probed, we chose WSe$_2$ for two specific reasons: first, for its high bright-dark energy splitting, and secondly, for a straightforward comparison with previous works. A scheme of the investigated system is presented in Figure 1a. The monolayer WSe$_2$ is sandwiched between an Au (or Ag) substrate and PDMS nanotapes. The combination of metal and PDMS induces a strong out-of-plane electrostatic dipole gradient in WSe$_2$ serving as a local gate as shown in Figure 1b. PDMS is known to have a large dipole moment along its polar Si-O bonds, which can alter the local structure or dynamics of physisorbed probe molecules. This particular phenomenon inspired us to test the possibility of modifying the transition dipole moment of dark excitons so that radiative recombination of e–h pairs can be detected. Both conventional and tip-enhanced photoluminescence (TEPL) spectroscopy at room temperature are employed in this study. Interestingly, the use of PDMS nanotapes or Au (or Ag) substrates alone cannot induce a brightening of dark excitons as manifested in our experiments. TEPL mapping with a spatial resolution of <10 nm on several samples reveals a spatial distribution of dark excitonic emissions confined within PDMS nanotapes when Au or Ag are used as substrates. We have multiple experimental evidence to support our claim that these excitonic features stem from dark excitons and not from localized strain.

2. Sample Preparation

Monolayer WSe$_2$ (exfoliated from a bulk WSe$_2$ crystal purchased from HQ Graphene) flakes are transferred on the desired substrate using a conventional deterministic dry transfer method, a commonly adopted technique for 2D monolayers and their heterostack preparation. At first, a monolayer WSe$_2$ is exfoliated on both homemade (preparation details are discussed in the Supporting Information) and commercially available PDMS (Gel-Film PF-40-X4 sold by Gel-Pak) film using Nitto Blue tape.
After confirming the monolayer thickness of WSe$_2$ using micro PL measurements (see Figure S1 in the Supporting Information), the PDMS stamps supported by microscopic glass slides are aligned on top of the desired substrate. In total 24 monolayer samples on Au (or Ag) (thermally evaporated 100 nm films on Si substrate) and four on 300 nm SiO$_2$ substrates are prepared. Among them, fifteen samples are made with homemade PDMS and the remaining nine samples are prepared using commercial PDMS. All transfer processes are monitored under an optical microscope with a 10× objective. It is generally known that 2D samples prepared by this process contain hydrocarbons including PDMS residuals on the flake surface. Therefore, annealing at high temperature is a common practice to clean the 2D surface since these residuals can be mobilized and often segregated into isolated pockets. After the transfer, all samples are annealed at 150 °C for 2 hours in an inert atmosphere (N$_2$ chamber, O$_2$ and H$_2$O < 1 ppm). Figure 2a displays the atomic force microscopy (AFM) topography images (optical micrographs can be found in Figure S2 in the Supporting Information) of one representative sample on Au substrate before and after annealing. As can be seen, before annealing PDMS is hardly visible on the flake since it is distributed rather homogeneously as a thin film on top. However, the phase and the surface potential (SP) images (see Figure S2 in the Supporting Information) taken simultaneously on this sample reveal a more heterogeneous surface, which better indicates the PDMS coverage on the sample. Moreover, comparing the thickness of the flake before and after annealing, it is also evident that the monolayer flake has a higher thickness before the annealing, which most likely originates from residual PDMS and water layers between the flake and the gold substrate. After annealing, a drastic change in the topography is observed, revealing nanopatch formation on the monolayer flake. This is also visible in the corresponding phase and SP images taken simultaneously (Figure S2, Supporting Information). The dynamics of the formation of such nanopatches after annealing is most likely related to inherent defects within the WSe$_2$ film. It is well known that TMDCs contain intrinsic defects in the form of chalcogen vacancies. The density of the chalcogen vacancies can further be increased during exfoliation and transfer of the flakes. Since PDMS has a polar chain of Si–O bonds, it is reasonable to assume that during the annealing process PDMS will agglomerate around intrinsic chalcogen vacancies or at grain boundaries. To verify that the nanopatches are formed on top of WSe$_2$ and not agglomerated underneath or originating from the nanobubbles at the WSe$_2$–substrate interface, we also acquired spatially resolved current maps of our samples using an Au tip in I-Top AFM mode (see the Experimental Section and Figure S3 in the Supporting Information for details). As can be seen from the current maps (see Figure S3 in the Supporting Information), the areas covered by the nanopatches have current values at the noise level (pA) at a bias of 0.05 V; whereas, the clean WSe$_2$ surface show a very good conductivity (~4500 pA).

To confirm the source of these nanopatches conventional and imaging X-ray photoemission spectroscopy (XPS) are performed on one of the samples prepared on Au. The results are presented in Figure S4 (Supporting Information). In the narrow-scan XPS spectra apart from tungsten and selenium of WSe$_2$, carbon, oxygen, and silicon are detected stemming from PDMS. One can see from the Si2s imaging spectra (Figure S4a, Supporting Information) that the silicon signal in particular coincides with the areas covered by WSe$_2$ flakes. The XPS sampling depth with the Al Kα X-ray source is less than 10 nm.
Since the thickness of the Au film is about 100 nm, contributions of Si from the substrate can be completely excluded. Therefore, the only source of Si in our experiments comes from the PDMS residuals.

3. Results and Discussions

3.1. Radiative Emission of Dark Excitons

Figure 2b,c displays the spatial maps of PL intensity and peak position of the monolayer WSe₂ sample shown in Figure 2a obtained in a micro-PL configuration at room temperature. The PL spectra were acquired using a 100×, 0.9 NA objective, and 2.33 eV continuous wave (CW) laser excitation with a power of 100 μW measured at the sample surface. For the ease of presentation the results obtained for Au substrates are discussed here, while results obtained for the Ag substrates are presented in the Supporting Information. Before annealing, both the PL intensity and the peak position maps show a homogeneous distribution over the whole flake. Interestingly, after annealing this spatial homogeneity as well as the spectral behavior alter drastically. As shown in Figure 2d, before annealing WSe₂ has a single feature centered at 750 nm (equivalent to 1.65 eV) characteristic for the emission from the neutral A exciton (bright, X₀ emission) in the monolayer. However, once the sample is annealed, the PL intensity decreases dramatically. More importantly, new features appear in the spectra. One of the reasons for the drastic reduction of the PL intensity can be due to a stronger WSe₂–Au interaction after annealing. In order to get more spectral information, a series of spectra was taken along the dots shown in Figure 2c and is presented in Figure 2e. It is evident from Figure 2e that the spectral weights of the spectra are divergent from each other with at least four distinctive features of different intensity ratios. The first two features can be attributed to the neutral A exciton and trion (X₀ and X¹) from the upper branch of the CB as shown in Figure 1c separated by ~30 meV from each other. The remaining features stem from dark excitons and are the main focus of our discussion in this work. It is important to note that the total of twenty-four samples prepared on Au and Ag as mentioned above show consistent results. Additionally, we also observed a shift of all the features up to 20 nm (equivalent to 44 meV) from substrate to substrate. We attributed this effect to the local dielectric disorder originating from the substrate morphology and cleanliness.

In order to confirm that none of these PL features stem from local strain induced excitons as reported recently, we also tested monolayer MoS₂ following the same sample preparation procedures. The PL results are presented in Figure S5 (Supporting Information). If there is any local strain formed due to the presence of PDMS nanopatches or by nanobubbles, which results in multiple excitonic features in monolayer WSe₂ as observed in the present study, then monolayer MoS₂ should exhibit a similar behavior. However, both micro-PL and TEPL hyperspectral maps of monolayer MoS₂ before and after annealing shown in Figure S5 (Supporting Information) contain a single peak homogeneously distributed over the whole flake regardless of nanopatches or clean gold areas. This confirms that the multiple features observed in PL spectra of monolayer WSe₂ in the presence of PDMS nanopatches do not stem from local strain.

We also studied the influence of longer annealing time. For this purpose, two samples were annealed a second time for another two hours in the same inert atmosphere at 150 °C. The PL results are presented in Figure S6 (Supporting Information). We did not observe any notable difference after the additional time annealing. It can be seen in Figure S6 (Supporting Information) that the radiative emission from dark excitons is still present after the second annealing, meaning that the annealing time has only little influence in brightening the dark excitons as long as nanopatches are formed on top of the monolayer WSe₂.

To get deeper insight in the origin of the features, one of the PL spectra is deconvoluted using Voigt functions. The deconvoluted spectrum is presented in Figure 2f. Four distinctive peaks are used to fit the spectra using constraints according to the literature. From the fitting we can assign these four peaks to the bright exciton X₀ at 1.63 eV, the bright trion X⁺ at 1.60 eV, the dark exciton X₀ at 1.58 eV, and the dark trion XDT at 1.56 eV. The energy difference between X₀ and X¹ is 50 meV and between X⁺ and XDT 40 meV. This is in very good agreement with values reported in literature. In addition to these four peaks, we also observe a relatively weak feature in the PL spectra (see Figure 2e) appearing around 50 meV below the dark exciton. The origin of this peak is not clear at the moment. However, we expect that this peak can be assigned to an extrinsic charged defect bound dark excitonic state. The argument behind our assignment is that when a dark exciton is captured by a localized electron or hole, it becomes bright via valley mixing in the conduction band. Moreover, the binding energy of this particular band is too large (≈100 meV) to stem from four or five particle complexes or from phonon replica of the dark exciton as reported in the literature.

We also performed low temperature PL measurements at 4.2 K to resolve these excitonic species better. It should be noted that due to the out-of-plane optical transition dipole selection rules the dark excitons are forbidden in conventional optical measurements. Therefore, the goal of the low-T PL measurements with a small numerical aperture was to confirm whether the PDMS nanopatches actually activated dark excitons, which we are able to observe at RT. Figure 3a shows one of the representative PL spectra of WSe₂/Au system acquired under 2.33 eV excitation. Both X₀ and XDT are now clearly visible in the PL spectra. One notable characteristic of dark excitons is their narrow linewidth compared to the bright excitons. As can be seen, the full width at half maximum (FWHM) of both features is narrower than those of X₀ and X¹ in agreement with literature. It is important to note that we observed inhomogeneous PL distribution at 4 K with multiple lower energy species (<XDT) with different intensity ratios. The origin of this low energy species remains an open question and beyond the scope of this work. Importantly, regardless of the spatial position, together with these inhomogeneous low energy features we could clearly observe both bright and dark exciton and trion emissions consistently at 4.2 K PL measurements. The energy difference between X₀ and X₀ is measured to be 45.8 meV; while between X⁺ and XDT it is determined to be 32.6 meV. Both values are in good agreement with the RT PL data.
Next, we turned our attention to study the photoexcitation power dependent behavior of dark excitons. Since the intensity of both bright and dark excitons should obey a linear dependence as a function of incident power, the power dependence therefore is a very good indicator for dark excitons. Figure 3b presents one typical double-logarithmic plot of the photoexcitation power dependent PL intensity of \(X^0\) and \(X^D\) emissions measured at 4.2 K based on curve fitting the PL spectra. From the fit to the slope, the linear power dependent factor is determined to be approximately 1 for both excitons. The linear power dependence of the dark exciton emission also excludes any possibility of emission by multiparticle complexes, which should follow a superlinear excitation power dependence.

From the micro-PL measurements, it is evident that we observe PL emission from dark excitons and trions at room temperature. Our hypothesis behind this observation is that PDMS nanopatches formed during the annealing process “brighten” the dark excitons. In order to verify this hypothesis, we performed TEPL on our samples with a spatial resolution of \(<10\) nm. Figure 4 displays one typical TEPL result. More TEPL data can be found in Figures S9 and S10 (Supporting Information). The experimental configuration of our TEPL setup is shown schematically in Figure 4a. All TEPL measurements were performed with the tip in contact with the sample. It is important to note that all TEPL experiments were carried out at room temperature. As can be seen in the AFM topography image (Figure 4b) nanopatches are randomly distributed on the sample with a typical size from tens to a couple of hundreds of nanometers. The corresponding TEPL map (Figure 4c) has a clear correlation with the AFM image with higher PL intensities coming from the areas covered by nanopatches. The TEPL spectra of a monolayer WSe\(_2\) on clean Au (see Figure 4d top) shows a strong feature around 1.6 eV and two shoulders at the high energy side around 1.63 and 1.65 eV. Comparing these spectra with our micro-PL results (see Figure 2), the two higher energy features are due to \(X^0\) and \(X^T\), while the peak around 1.6 eV stems from radiative emission of \(X^D\). This is not surprising since we induce an out-of-plane optical dipole moment in our TEPL configuration. Therefore, the out-of-plane transition dipole of dark excitons couples to the optical field created at the tip-sample sub-nanogap and enhances the radiative emission of dark excitons. This is in very good agreement with recent \(X^D\) observations facilitated by a TEPL geometry at room temperature.

Interestingly, when we probe the area on the nanopatches with the Au tip of the TEPL system, the TEPL spectra change dramatically (Figure 4d bottom) with respect to the spectra recorded on top of nanopatch free WSe\(_2\). First, we can now resolve the dark excitonic emissions much better and secondly the overall intensity increases by 6 to 10 times. The PL quantum yield (QY) in the low excitation limit for a certain exciton population within the light cone depends on the relative spectral distance between dark and bright exciton states. Being the lowest state of the spin split CB in WSe\(_2\), the PL QY of dark excitons in this system therefore depends on the thermal population of the spectrally higher bright states and secondly the radiative emission efficiency of dark excitonic states. This picture can be well understood by the temperature dependent PL QY study in TMDCs since at 0 K all excitons occupy the lowest CB state.

In our system, we observe increased QY on top of nanopatches due to both thermal population to the bright states (less efficient due to large separation \(\approx 45\) meV) and brightening of dark excitons. Hence, we can resolve the \(X^D\) related states much better on top of nanopatches. It is important to note that, in our TEPL measurement, we observed \(X^0\) and \(X^{0T}\) binding energies varying from (45–52) meV and (33–38) meV, respectively. The variation in binding energies from nanopatch to nanopatch most likely indicates the variation of the local dielectric environment on the same sample originating from dielectric disorder as discussed in a previous report.

Figure 4e presents excitation power dependent TEPL spectra taken from three different nanopatches as shown in the TEPL map in Figure 4c. As can be seen the intensity of all spectral features changes in similar proportion excluding any
biexciton or multiparticle complexes formation. This is in good agreement with the excitation power dependent low-T PL in Figure 3b. Interestingly, the spectral weight of each feature in these three spectra is different. This is also true for other nanopatches investigated in this work (see Figure S9 in the Supporting Information). The heterogeneity in the spectral weight of these features indicates local doping processes varying from patch to patch.

Since Raman spectroscopy is a powerful technique for investigating local heterogeneities[40] we also recorded tip-enhanced Raman scattering (TERS) spectra. Figure 5a displays a TEPL map of 1L-WSe₂ on Au. The corresponding AFM topography image is shown in Figure S9 (Supporting Information). Two representative TEPL spectra—one on top of bare WSe₂ (marked by a circle) and one on top of nanopatch (marked by a rectangle) are presented in Figure 5b. As can be seen, the TEPL spectrum on top of the nanopatch shows more features compared to the spectrum on the nanopatch free region. The corresponding TERS spectra of the two regions are displayed in Figure 5c (top panel). More TERS spectra together with corresponding TEPL are shown in Figures S11 and S12 (Supporting Information). Comparing the TERS spectra recorded on a nanopatch to those on bare WSe₂ one can see that the overall spectral weight taken on a nanopatch is shifted to higher wavenumber. In order to get more information, we deconvoluted both spectra (Figure 5c middle and bottom panel) using Lorentz functions. Details of the fitting procedure can be found in the Supporting Information. Since bulk WSe₂ belongs to the D₆h point group (monolayer belongs to D₃h), it has two prominent first order Raman modes with E₀g and A₁g symmetries (in monolayer E' and A'). Even though these two Raman modes are well separated in bulk, owing to opposite layer dependent shifts they become very close to each other in a monolayer as denoted by E(Γ) + A(Γ) in Figure 5c.[41,42] Due to quasi-resonant excitation by the 638 nm laser we can also observe features involving second order phonons below and above the first order Raman modes.[41] The feature around 235 cm⁻¹ involves in-plane phonons located at the M point of the Brillouin zone (E(M)). The modes located at 255 and 260 cm⁻¹ are overtones of the LA phonon at the M point of the Brillouin zone, i.e., 2LA(M), and a phonon having A symmetry at the M point, i.e., A(M). Since E(Γ) and A(Γ) overlap in monolayer, monitoring these modes for possible local strain or doping effects is a challenging task. However, the A(M) mode is in particular sensitive to disorder (in particular defects) similar to graphene.[41,43] Therefore, comparing the intensity ratio \( IR = A(M)/A(Γ) \) can provide a hint of local relative defect density. In our spectra the intensity ratio on bare WSe₂, \( IR_{Au} \) is determined to be 0.8. The value is homogeneous throughout the scanned area with a standard deviation of 0.09. When measured on a nanopatch, the intensity ratio, \( IR_{np} \) is determined to be 1.12, which also varies from patch to patch (see Figure S13 in the Supporting Information). The intensity ratio, IR on top of bare WSe₂ and nanopatches is a clear indication that there are more defects of WSe₂ under PDMS nanopatches than on bare WSe₂. This also supports our hypothesis that PDMS nanopatches are formed around defect sites in WSe₂ during annealing. Note that E(M) is also sensitive to structural disorder. However, due to the weak sensitivity of in-plane modes in the TERS configuration we could not resolve another in-plane mode E(K), which is in the proximity of E(M) (see micro-Raman spectra in Figure S11c in the Supporting Information). Hence, the deconvoluted spectral weight of E(M) most likely has a contribution from E(K) as well. Therefore, we did not monitor this peak for defect concentration in this study.

Remarkably, we can also tune the excitonic features via electrostatic gating.[23,24,26] Figure 5d presents local gate voltage

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**Figure 4.** Probing radiative emission of dark excitons in TEPL configuration. a) Sketch of the experimental TEPL configuration. b) AFM topography and c) corresponding TEPL spatial map of 1L-WSe₂ covered by PDMS nanopatches on Au. The TEPL image was created within the spectral range of 740–820 nm with a step size 10 nm. The excitation energy was 1.94 eV (638 nm). More TEPL results including those for Ag substrates are presented in Figures S9 and S10 (Supporting Information). d) TEPL spectra of monolayer WSe₂ on Au (top) and on PDMS nanopatches (bottom) as highlighted in the TEPL map. e) Photoexcitation power dependent TEPL spectra.
dependent TEPL of 1L-WSe2 on Au. The experimental configuration of the measurement is shown in the inset of Figure 5d. We use a Au tip and the PDMS nanopatches as gate electrode and gate dielectric, respectively. A positive bias is applied to the sample. The illumination/collection geometry of light is the same as stated above for the TEPL measurements. The TEPL spectrum at zero bias shows multiple features including XT, XD, XDT, and other features at longer wavelength as discussed above. As the bias increases (hole doping) the intensity of these features decreases gradually. Among them XT (negative bright trion) shows the strongest tunability and the features at the longer wavelength show negligible sensitivity. The intensities of both XD and XDT also decrease with increasing bias but at a slower rate compared to XT. Interestingly, X0 remains unchanged within the bias voltage range applied. At a sample bias of 1.0 V we can clearly observe all the bright and dark neutral and charged species. This gate dependence agrees well with recent results [23,24,26].

As the final part of exploration, we clean the PDMS nanopatches off WSe2 by scanning over it with a Au tip under illumination and performed TEPL to observe X0 emission from the very same spot. Figure 6 shows a series of AFM scans plus TEPL maps of an area on the sample. After the first scan we can identify four nanopatches within this scanning area as shown in the corresponding AFM topography. Five TEPL spectra—one on bare WSe2 and four on nanopatches (see TEPL map in Figure 6) are presented for comparison. After the first scan, we can observe stronger dark excitonic emissions on four nanopatches and weaker X0 contribution on bare WSe2. After the second scan one of the nanopatches (nanopatch II in Figure 6) disappears. The corresponding TEPL spectra show no evidence of dark excitonic peaks at the lower energy side and match well to the PL on bare WSe2 (see both TEPL map and spectra in the second column in Figure 6). After the third and fourth scan, nanopatches III and IV are washed off (third and fourth columns in Figure 6). The corresponding TEPL spectra similar to the case of nanopatch II do not show dark excitonic shoulders at the lower energy side anymore and become symmetric as the PL on bare WSe2. The results clearly indicate that the brightening of dark states originates from the presence of PDMS nanopatches. More importantly, it also demonstrates a simple path to switch dark excitonic emissions in these systems, which will open the door for exploring the rich physics of spin dynamics and possible quantum device applications.

Up to now we demonstrated radiative emission from dark excitonic states in WSe2 monolayers using micro-PL and TEPL at room temperature. From the experimental results it is evident that the brightening of dark excitons is solely confined within the area of PDMS nanopatches created during annealing on the WSe2 monolayer deposited on metallic substrates. Therefore, it is important to ask whether a similar behavior can be observed on other substrates, especially on insulators. To investigate this phenomenon, we prepared four monolayer WSe2 samples on 300 nm SiO2 oxide on Si substrates. Figure 7a,b
displays micro-PL intensity and peak position maps of one of the samples prepared on SiO$_2$ substrates before and after annealing. The corresponding PL spectra before and after annealing are shown in Figure 7c. AFM topographies before and after annealing are presented in Figure S14 (Supporting Information). PL intensity maps before and after annealing show a homogeneous distribution over the whole sample. However, we observe a shift of 7 nm (15 meV) in some areas of the flake in the peak position map before annealing. We attribute this effect to inhomogeneous Coulomb screening due to nonuniform van der Waals coupling between WSe$_2$ and the oxide surface. This is also confirmed by the peak position map after annealing, in which a homogeneous interface is created. Interestingly, both intensity and peak position maps after annealing show homogeneity over the whole flake with the PL peak centered at 750 nm (1.65 eV). This is a sharp contrast to what we observed on Au or Ag substrates. To investigate this in more detail, we performed TEPL on this sample as shown in Figure 7d,e. Like in the case of the metal substrates (see Figure 4), we observe an increase (though not as efficient) in PL intensity when probed over the nanopatches (Figure 7d). The corresponding TEPL spectra on top of nanopatches and on SiO$_2$ are presented in Figure 7e. As can be seen, the TEPL spectra on top of the nanopatches also result in, aside from the enhancement, a small red shift of the peak position (∼6 nm or 13 meV). More importantly, there is hardly any evidence of dark excitonic emission. The results obtained on SiO$_2$ substrates suggest that the out-of-plane electrostatic field exerted by the PDMS nanopatches on WSe$_2$ alone is not strong enough to observe brightening of dark excitons at room temperature.

3.2. Mechanism of Radiative Emission of Dark Excitons

The above results point out the importance of a metallic substrate for the observation of the X$^D$ emission in our samples. Dark exciton radiative emission requires unlocking either spins (intravalley) or large momentum across the valley (intervalley). For the latter case, the assistance from a third body, namely phonon, impurity, or another electron or hole is needed since the exciting photon carries a small amount of momentum. Therefore, observing intervalley dark excitonic emission is less probable.

Intravalley excitons require spin flip, which can be achieved by an external in-plane magnetic field. Being a member of D$_{3h}$ point group, selection rules dictate that the intensity of an out-of-plane allowed optical transition (in this case radiative dark exciton) is $\approx 10^{-3}$–$10^{-2}$ times the one of the in-plane optical transition (bright exciton) in WSe$_2$. [44] However, a large magnetic field (>14 T) is required to detect such small radiative dark exciton emission by the Zeeman effect. [21,22] On the contrary, the out-of-plane selection rule is broken by disturbing the reflection symmetry in the surface normal direction. This can be achieved by changing the dielectric environment of the two sides of the flake.
monolayer or applying an electric field perpendicular to the plane. This phenomenon facilitates spin flip by a virtual transition in the CB attributed to the SOC mixing and inducing an out-of-plane transition dipole perturbed by the applied field (also known as Bychkov–Rashba effect).[45] In the case of PDMS nanopatches the methoxy group terminated Si–O bond can induce a point charge based out-of-plane dipole moment of up to 1.2 Debye at a distance of 5 Å. [46,47] The resulting electric field value is comparable to the crude estimate of 0.1 V Å−1 by Slobodeniuk et al. on an insulator with vacuum above.[44] Still, at this electric field the radiative decay rate of the dark exciton is negligible compared to that of bright excitons. This probably explains why we do not observe dark-exciton related emission on SiO2 substrates at room temperature. However, using a metal substrate changes the scenario since Au or Ag can form an induced electrostatic dipole at the interface. In addition, both Au and Ag can take surplus charges from WSe2 created, e.g., by Se vacancies. This can lead to a stronger interaction between the Si–O bond in the nanopatch and W via Se vacancies as shown in Figure 1b. More importantly, as a consequence of the distance between the Si–O bond and W may decrease. Since the point dipole induced by the Si–O bond exponentially increases with decreasing distance to the probing molecule, an enhanced electrostatic field can be exerted on WSe2.[45] Thus, it can act as a local electrostatic gate and induce an increased population of dark excitons at room temperature. Additionally, as shown in Figure 5c and Figures S11 and S12 (Supporting Information) nanopatches are centered at vacancies, which may further facilitate the breaking of the out-of-plane selection rules in pristine WSe2. More importantly, there is a direct correlation between defect density and radiative emission of dark excitons in our samples. This further strengthens our hypothesis that, due to Se vacancies, we can have a large local electrostatic gating effect via the combination of polar Si–O bond in the nanopatches and the metal substrate. However, more experiments and theoretical studies are required to fully understand the physics behind this behavior. Finally, similar to the work by Zhou et al., a surface plasmon polariton on the metal can also induce a local field to enhance the radiative decay of dark excitons in our system.[46]

4. Conclusion

In summary, we demonstrated the radiative emission of dark exciton and trion states in a WSe2 monolayer at room temperature using both micro- and nano-PL measurements. Our approach provides a simple way of detecting and manipulating dark excitons over a wide range of temperatures. While micro-PL measurements indicate dark excitonic emission over the whole flake, nano-PL measurements with spatial resolution <10 nm reveal that this emission originates from monolayer regions covered with PDMS nanopatches on Au or Ag substrates. We attributed this phenomenon to local electrostatic gating via the Si–O bond in the PDMS nanopatch and the metal substrate. Moreover, we also observe a correlation between the defect concentration and X0 emissions in our samples. We could also tune these excitonic features via local electrostatic gating. Finally, by removing the nanopatches from top of WSe2 we were able to tune back the bright excitons. We believe that our results will stimulate more experimental and theoretical work to explore the rich spin physics in the valley.

Figure 7. Probing the effect of PDMS nanopatches on excitonic emission in 1L-WSe2 on insulating substrate. a) Micro-PL intensity and b) peak position maps of monolayer WSe2 on 300 nm SiO2 substrate before and after annealing. All experimental parameters are the same as micro-PL measurements on metal substrates stated above. White dotted rectangles in the peak position map are a guide for the eyes of monolayer area. Corresponding AFM topographies of the flake before and after annealing are presented in Figure S14 (Supporting Information). A scale bar is shown in the PL intensity map. c) Representative PL spectra before and after annealing taken form the circles shown in the peak position map. After annealing no sign of X0 is found in the PL spectra. d) TEPL map and corresponding AFM topography acquired simultaneously from the sample. The scale bar is shown in the topography image. e) Three spectra are taken from the TEPL map and compared. We observe an enhancement of PL on top of the nanopatches. However, no X0 emission can be seen.
of the dark exciton landscape. This work is a significant step forward in understanding the physics of dark excitons, which will open the door for the potential application in nanooptics, Qbits, or spintronics.

5. Experimental Section

**Micro-PL Measurements:** All micro-PL measurements were performed using a Horiba Xplora Plus equipped with a spectrometer containing 600 L mm\(^{-1}\) grating and an electron multiplying CCD (EMCCD). A DPSS 532 nm CW laser source was used to excite the samples with an excitation power of 100 μW measured at the sample surface focused by a 100×, 0.9 NA objective. All PL spatial maps were acquired with a step size of 500 × 500 nm\(^2\). All PL spectra were corrected with respect to the EMCCD response curve for accurate identification of all PL spectral band features.

Low-T PL measurements were performed using a self-built optical setup at 4.2 K. The samples were mounted on the cold finger of a small He-flow cryostat. They were excited via a DPSS 2.33 eV laser coupled into an 80×, 0.5 NA objective that was also used to collect the emitted PL. The collected PL was analyzed using a grating spectrometer equipped with a Peltier-cooled CCD.

**Nano-PL Measurements:** TEPL measurements were performed using the Horiba NanoRaman platform consisting of an AFM (SmartSPM) and Xplora Plus spectrometer in side illumination geometry. Excitation and collection of photons were realized in the same optical path using a 100×, 0.7 NA long working distance objective at an angle of 65° from the normal to the 2D plane. A 638 nm solid state laser was used to excite the sample with a laser power of ~100 μW. An Au tip purchased from Horiba Scientific was used in the experiments. In between the measurements the tip was oscillating in intermittent contact (IC) mode while during the measurements the tip was in contact with the sample for a holding time equal to the TEPL acquisition time of 0.2 s.

**TERS Measurements:** The experimental configuration of TERS was the same as for TEPL measurements. The 600 L mm\(^{-1}\) grating was used to disperse the signal onto EMCCD. The spectral resolution of the system in this configuration is 6 cm\(^{-1}\).

**Electric Field Dependent TEPL:** For electric field dependent TEPL measurements, PDMS nanopatches were used as the gate dielectric and the Au tip was used as the top electrode. The TEPL measurement geometry was the same as stated above. The bias was applied to the sample. The measurements started from the zero bias and was then gradually increased to the positive direction. After that, negative biases were applied gradually. At the end a zero bias spectrum was acquired in the same run for comparison for all measurements. In total 10 measurement runs were acquired and the same procedure was followed for all runs.

**SPM Measurements:** All SPM measurements were performed using an AIST-NT SPM setup. AFM images were taken using commercially available Si cantilevers in intermittent contact (IC) mode. KPFM images were acquired using commercially available Pt/Ir tips calibrated against freshly cleaved HOPG substrate. For current images Au coated commercial Si tips with a high force constant (the Au coating was performed by thermal evaporation using home facility) were used. As shown, one can modify the PDMS nanopatches by repeated AFM scanning over the sample in contact mode. Therefore, in order to acquire current images of the sample the system was operated in IC mode while controlling the tip-sample distance during the local current measurements. In this process, the tip was oscillating at the IC frequency while hopping from point to point so that it did not modify or destroy the nanopatches. However, at every measuring point the tip was forced to contact the sample by controlling the set point or nominal force acting on the cantilever. After a few trial and error measurements the optimal force was set on the tip, which confirmed sufficient contact between the tip and the sample for current mapping and at the same time not modifying the nanopatches.

**X-Ray Photoemission (XPS) Measurements:** XPS was performed using a Thermo Scientific ESCALAB 250Xi spectrometer equipped with a monochromatized Al Kα X-ray source (hν = 1486.68 eV). Narrow-scan XPS spectra were acquired form a spot-size of 500 × 500 μm\(^2\) with an array channeltron detector at a pass energy of 40 eV. XPS imaging was performed in a parallel electron optics mode with a 2D detector at a pass energy of 150 eV.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

dark and bright excitons, photoluminescence, TEPL, TERS, transition metal dichalcogenides, valley physics, WSe\(_2\)

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