Preserving the Emission Lifetime and Efficiency of a Monolayer Semiconductor upon Transfer

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Monolayer transition metal dichalcogenides (TMDs) are promising semiconductors for nanoscale photonics and optoelectronics due to their strong interactions with light. However, processes that integrate TMDs into nanophotonic and optoelectronic devices can introduce defects in the monolayers, resulting in lower emission efficiency. Quality control is therefore needed to process monolayer semiconductors effectively. Through micro-photoluminescence and fluorescence lifetime imaging measurements, this work investigates the effects of encapsulation on the optical properties of TMD monolayers, focusing on the impact of different processing techniques and different dielectric environments. Spin coating a polymer layer on top of a TMD monolayer is shown to significantly reduce its emission lifetime and efficiency. In contrast, the soft transfer of a monolayer deposited on a polymer substrate can preserve its intrinsic emission properties almost perfectly in various dielectric environments. This approach can be widely applied to integrate TMDs into devices and heterostructures while protecting sample quality, and demonstrates that intrinsic quantum efficiency and photoluminescence lifetimes of TMDs can be preserved upon transfer to different dielectric substrates.

1. Introduction

Monolayer transition metal dichalcogenides (TMDs) such as MoS₂ or WS₂ exhibit optoelectronic properties that are exceptionally different compared to their bulk crystals.[1–7] TMDs display a direct band gap and high quantum efficiency of emission when they are thinned down from the bulk to the monolayer.[1,2] These atomically thin semiconductors are promising sources for highly efficient emission[8–10] and lasing.[11,12] The lack of inversion symmetry and strong spin–orbit coupling in monolayers allows circularly polarized light to populate excitons in a given valley with a defined momentum direction.[13–16] Such valley polarization enables the storage of information in the valley degree of freedom and the development of valleytronics.[6,17] Despite being atomically thin, monolayer TMDs show strong absorption in the visible and near-infrared regimes, with absorption coefficients as high as ≈15%.[18] Such strong interactions with light make TMDs ideal for applications in integrated photonics, photodetectors, and other nanoscale devices.[8,19]

Further enhancement[20–23] and tuning[24–27] of light–matter interaction is still possible through the integration of monolayers into nanophotonic architectures. In structures such as microcavities[20–22] or metal nanoantennas,[23,25,26,28,29] dielectric layers are frequently placed on top of the TMD monolayer to tune optical resonances, to protect the samples from degradation, or as spacers to avoid charge transfer. In this way, TMD monolayers may be surrounded by a dielectric environment that could modify their absorption and emission, which if controllable, is desirable for engineering properties such as the optical density of states or dielectric screening.[30–32] Furthermore, variations in fabrication methods and processing techniques of these configurations can also lead to the uncontrolled modification in emission efficiency and photoluminescence (PL) lifetime of the monolayers.[33] Additionally, the effect of dielectric substrates on excitonic resonances and binding energy of TMD monolayers has been under discussion.[34–39] The extent of the modification of emission efficiency and lifetime caused by the dielectric environment and the possibility of preserving the emission properties of high-quality monolayers is particularly important for integrating TMDs into viable devices and heterostructures.

Here, we clarify the impact that transferring TMD monolayers to different dielectric environments has on their photoluminescent properties. We use micro-PL imaging and fluorescence lifetime imaging (FLIM) to characterize the PL emission intensity and lifetime of monolayers, respectively. Firstly, we investigate differences arising from encapsulation methods and employ two different processing techniques, spin coating and soft transfer, to encapsulate exfoliated WS₂ monolayers.
in several dielectrics. Then, we examine the effects that the dielectric environments themselves have on the PL properties.

We show that the PL efficiency and lifetime of monolayers decrease significantly upon spin-coating polymer layers on top. On the other hand, by carefully soft-transferring samples onto new substrates, we can preserve the emission properties, demonstrating that the addition of protective dielectric layers leaves the underlying exciton dynamics in these structures almost unaffected. Due to the significant variations in PL for similarly exfoliated samples, we suggest that comparative studies that correlate the effect of any substrate parameter must evaluate any observed changes by comparing each individual monolayer before and after transfer. These results underline that particular attention must be paid to the method used to encapsulate monolayers when fabricating TMD-based devices,[29] and that the combination of the soft-transfer method with PL lifetime measurements provides a reliable method to produce controlled quality samples.

2. PL Lifetime Microscopy of Exfoliated WS\(_2\) Monolayers

We use WS\(_2\) monolayers due to their high PL quantum yield (QY) (measured QY ≈ 20%, see below). We obtain the flakes via mechanical exfoliation of a bulk crystal, then transferred to a flexible polydimethylsiloxane (PDMS) substrate; a wide-field reflection microscope image of such samples is shown in Figure 1a. Their micro-PL displays a pronounced emission from monolayer regions only (Figure 1b). After exfoliation, we acquire a pixel-by-pixel lifetime image of the sample (Figure 1c) with a beam-scanning confocal microscope that synchronizes a time-correlated single-photon counting (TCSPC) system using an avalanche photodiode detector with a pulsed laser (Figure S1, Supporting Information). In FLIM images, only the monolayer areas show notable mean lifetime (\(\tau\)) signals. The powerful FLIM technique allows deeper analysis of the emission properties of each sample, as it maps both PL lifetimes and intensities in space. For example, PL lifetime quenching can be observed at the edges and the interfaces between a monolayer and multilayer, and the homogeneity of PL lifetime across monolayers can be assessed (Figure 1c). We plot the average PL decay curve over a region of interest within a monolayer with homogenous lifetime in Figure 1d (black curve). Next, we combine micro-PL imaging and FLIM to characterize the quality of monolayer samples and quality changes after different fabrication processes.

To ensure the reproducibility of our measurements, we first studied the variations in the optical properties of simultaneously exfoliated WS\(_2\) monolayers before any additional processing. The absorption, PL spectra, and decay curves of two typical samples are shown in Figure 2. The absorption

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Figure 1. Emission lifetime microscopy of monolayer WS\(_2\). a) White-light reflection and b) micro-PL images of a WS\(_2\) flake. The monolayer regions correspond to the bright red emission in (b). c) Fluorescence lifetime image (FLIM) of the sample; the color scale represents the mean lifetime (\(\tau\)) of the emission detected at each pixel. d) PL decay curves extracted from the FLIM data for the monolayer region that is encompassed by the dashed black curves in (c) and the instrument response function (IRF) of the FLIM setup. Scale bar in (a–c) is 5 \(\mu\)m.
spectra exhibit three main peaks. These correspond to exciton transitions between the upper (A excitons) and lower (B excitons) valence bands and the lowest conduction band at the \(K/K'\) points of the Brillouin zone. The A and B transitions arise from energy splitting in the valence band due to spin–orbit coupling, and the C exciton absorption corresponds to the optical transitions from the energetic states near the \(\Gamma\) points in the valence band to \(\Lambda\) points in the conduction band.\[40\] The absorption band of A excitons in the two monolayers (\(\lambda_1 = 613\) nm, \(\lambda_2 = 617.6\) nm) differs by 4.6 nm (15 meV) (Figure 2b). The A transition in monolayer #2 presents a higher absorption peak (abs. = 14%) and sharper linewidth (\(\gamma_A = 25\) meV) compared to those of monolayer #1 (abs. = 10%, \(\gamma_A = 32\) meV).

We obtain the PL QY of the two samples, \(QY_1 = (1.8 \pm 0.5)\%\) and \(QY_2 = (21 \pm 3)\%\) by comparing the emission of the sample (see the Experimental Section). We obtain the PL decay curves (Figure 2d), and after deconvolution with the instrument response function, fit the curves with a stretched exponential function\[41\]

\[
I(t) = I_0 \exp\left(-t/\tau_{1/e}\right)^\beta
\]

where \(I(t)\) is the exponentially decaying PL intensity with initial value \(I_0\) dropping to \(1/e\) at the decay time \(\tau_{1/e}\). \(0 < \beta \leq 1\) is the stretching exponent, which describes the distribution of relaxation rates involved in the PL decay process, with a smaller \(\beta\) corresponding to a broader distribution.\[41\] The PL decay of monolayer #2 is nearly single exponential with \(\beta = 0.95 \pm 0.05\), and \(\tau_{1/e} = 1.82\) ns, whereas monolayer #1 shows a smaller value of \(\beta = 0.5 \pm 0.02\) and \(\tau_{1/e} = 0.11\) ns.

We obtain the average lifetime of A excitons, \(\langle \tau \rangle = 0.22 \pm 0.03\) ns and \(\langle \tau \rangle = 1.87 \pm 0.05\) ns, respectively, from the fitted parameters and the gamma function.\[41\]

\[
\langle \tau \rangle = \frac{\tau_{1/e}}{\beta} \Gamma\left(\frac{1}{\beta}\right)
\]

By studying additional samples with similar behaviors, we conclude that monolayers with longer lifetimes display higher emission efficiency. These results indicate that FLIM measurements can provide a quick direct measure of the quality of samples after exfoliation. The variability between similarly exfoliated samples shows the importance of evaluating changes monolayer properties relative to the initial performance of a particular sample before correlating observations to studied...
parameters, and of choosing monolayers exhibiting the same initial properties. Hence, we choose only monolayers with PL lifetimes around 2 ns for the systematic study below.

3. Comparison of Sample Encapsulation Methods

Firstly, we study the effect of spin coating a thin film on a monolayer. Spin coating is a processing technique widely used to encapsulate TMD samples with polymers, for instance to tune the optical resonances of nanophotonic architectures or as lithography resists for patterning (e.g., electrical contacts). After depositing the monolayer sample onto a quartz substrate through the dry-transfer method, we measured the optical spectra and PL lifetime of the same sample before and after coating a 100 nm thick layer of poly(methylmethacrylate) (PMMA) on top (see details in the Experimental Section). The emission peak of A excitons shows a slight blue shift of 1.3 nm (see Figure 3b), which is consistent with the absorption measurement (Figure 3a). Interestingly, the absorption of the indirect C excitons shows a decrease of 2.6 percentage points, i.e., more than that of the A excitons (1.7 percentage points). The decrease of the absorption (α) of the excitons could be due to the higher refractive index (n) of the dielectric environment of the monolayers and the screened transition probabilities \( M_{\text{exc}} \) from valence bands to conduction bands, i.e., \( \alpha \approx |M_{\text{exc}}|/n^{2} \). The C excitonic transitions are due to an admixture of nonbonding tungsten d-orbitals and sulfide p-orbitals. Therefore, C excitons are more sensitive to the environment compared to bonding tungsten d-orbital transitions of A or B excitons at K/K\' points.

The absorption measurements characterize optical transitions between different points in the valence and conduction bands, whereas the PL decay of WS\(_{2}\) monolayers only records the recombination processes of the lowest excited states, i.e., direct A excitons. The PL lifetime before coating (black curve in Figure 3c) drops significantly after coating (red curve). The stretched exponential fits of the PL decay curves show that the average lifetime of the monolayer before coating decreases from 3.24 ± 0.05 to 0.67 ± 0.03 ns after coating, although both curves are well fitted with a single exponential (\( \beta = 1 \)). The emission intensity of the sample is reduced by ≈74%, as determined through the PL spectra (Figure 3b). Therefore, the QY decreases by ≈73% after coating, correcting the absorption change at the excitation wavelength. The shorter PL lifetime is consistent with the reduction of PL intensity and QY obtained after coating. The lower QY might be attributed to either a reduced radiative recombination rate due to the decreased transition dipole moments of A excitons, or to an increased nonradiative rate due to an increased density of defect states created during the spin-coating process. Besides PMMA, we repeated the measurements with another transparent polymer, polyvinyl alcohol (PVA). We observe a similar reduction in PL lifetime and QY after spin coating (Figure 1, Supporting Information).

To exclude the contribution of the encapsulation method itself on the PL lifetime and to determine more accurately the effect of the dielectric environment, we repeat our analysis for samples produced using a soft-transfer approach (Figure 4a), more details in the Experimental Section). In this method, a flexible PDMS superstrate with a monolayer was carefully placed on top of a PMMA film on a quartz substrate, with the PDMS physically adsorbing to the substrate through van der Waals forces. In this way, we minimize any strain and chemical residue that could significantly modify PL. By leaving the PDMS on the sample, a protective dielectric superstrate is obtained without introducing cracks in the monolayer. The absorption and PL spectra (Figure 4b,d) exhibit very similar changes to that of the sample before and after spin coating, which confirms good contact between the monolayer with the PMMA substrate. However, the degradation of the PL lifetime seen in monolayers after spin coating is not observed here. Instead, the similarity between the time-resolved curves (Figure 4d) and the emission intensity (Figure 4c) obtained before and after transfer illustrates that the effective radiative lifetime of excitons does not significantly change after PMMA encapsulation. These results indicate that while the presence of the dielectric environment screens the optical absorption, it does not significantly affect the emission lifetime of monolayers. Therefore, we attribute the reduction of emission after spin coating mostly to the increased nonradiative recombination due to defect creation. This is an important result that limits the use of the spin coating for the fabrication of high performance optical devices based on monolayer semiconductors.

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**Figure 3.** Reduction in PL and lifetime after spin coating. a) Absorption spectra, b) PL spectra, and c) PL decay curves of a WS\(_{2}\) monolayer before (black curve) and after (red curve) a 100 nm thick layer of PMMA was spin coated on top of the sample. The blue and green curves in (c) are the corresponding fits to a stretched exponential function.
4. Effect of Changing Dielectric Environment

To elucidate the effect of different dielectric substrates, we investigate additional WS$_2$ monolayers transferred to hydrophobic polystyrene, hydrophilic fused silica, and alumina/silica. We chose these substrates due to their extended use in nanophotonic applications.[20,28,29,43] We plot the normalized time-resolved PL decay measurements of monolayer WS$_2$, obtained via FLIM, before and after soft-transfer encapsulation in these dielectric substrates in Figure S3 (Supporting Information). In Table 1, we summarize the static dielectric constants ($\varepsilon_0$) and the dielectric constant at optical frequencies ($\varepsilon_\infty$) of each substrate, as well as the emission decay parameters of the monolayers before and after transfer, considering that both $\varepsilon_0$ and $\varepsilon_\infty$ can affect the electric (i.e., dielectric screening)[39,44] and optical properties of the excitons.[30,32]

To identify the different substrates, we plot the ratio of the average PL lifetimes upon transfer ($\langle \tau \rangle/\langle \tau \rangle^0$) as a function of the change of the static dielectric constant of the environment ($\Delta \varepsilon_0$) as black squares in Figure 5a. The black circle in this figure represents the spin-coated sample. There is no clear correlation between changes in PL lifetime and the effective static dielectric constant of the surroundings. Additionally, the resonance wavelength and linewidth of the excitons do not change pronouncedly when the monolayers are transferred onto PMMA (Figure 4b,c) or alumina film (Figure S2b,c, Supporting Information) at room temperature. These results suggest that the electric properties of the excitons, including the optical bandgap and binding energies, are not affected through varying $\varepsilon_0$.[19,44] We focus next on the modification of the radiative lifetime $\tau_{\text{rad}}$ of monolayer emitters by varying $\varepsilon_\infty$.

To compare with theoretical predictions using only optical considerations, we calculate the radiative rate enhancement relative to free space by a reciprocity method (details in the Supporting Information). We plot the change in the radiative lifetime in Figure 5a (blue triangles) when varying the surrounding $\varepsilon_\infty$ of the emitters. The calculated ratio of a radiative lifetime $\tau_{\text{rad}}/\tau_{\text{rad}}^0$ follows the trend of the measured PL lifetime $\langle \tau \rangle/\langle \tau \rangle^0$. However, the measured PL lifetime of monolayers is an effective value that couples the decay of bright states (i.e., direct A excitons) and spin- or momentum-forbidden dark states,[45,46] shown in Figure 5b,c, while the calculated radiative rate is only a fraction of the recombination rate $k_b$ of bright states. Considering the ultrafast scattering ($\approx$ps) between bright states and dark states at room temperature,[45,47] we solve the two coupled rate equations

$$\frac{dn_b}{dt} = -k_b n_b - k_{\text{rad}} n_b + k_{\text{dark}} n_d$$

$$\frac{dn_d}{dt} = k_{\text{rad}} n_b - k_{\text{dark}} n_d - k_d n_d$$

The transition probability $k_{\text{rad}}$ is determined by the matrix elements of the dipole operator $\mathbf{D}$ and the photon density $n_b$. The detailed calculations are presented in the Supporting Information.
The bright excitons are generated by the direct optical transitions from the ground states $|g\rangle$ to the bright excited states $|e\rangle$ with a stretched exponential function.

$$\tau(t) = \tau_0 \exp(-k_{\text{bd}} t)$$

where $\tau_0$ and $\tau(t)$ are the bright and dark exciton numbers at time $t$ after optical excitation, respectively. $k_{\text{bd}}$ is the scattering rate from bright states $|e\rangle$ into the dark states $|d\rangle$, $k_{\text{ub}}$ the population rate of dark states into bright states, and $k_{\text{d}}$ the recombination rate of dark states. We obtain that both the bright and dark states decay as the superposition of two effective (eigenvalue) exponential components, $\exp(-k_1 t)$ and $\exp(-k_2 t)$, where $k_1$ and $k_2$ are

$$k_1 = k_{\text{ub}} + k_{\text{bd}},$$

$$k_2 = k_{\text{bd}}/(k_{\text{ub}} + k_{\text{bd}})$$

under the approximation $k_{\text{ub}} \gg k_{\text{bd}}$.

The ratio of $k_{\text{ub}}$ and $k_{\text{bd}}$ is given by the Boltzmann relationship:

$$k_{\text{ub}}/k_{\text{bd}} = \exp(-\Delta E/k_B T).$$

$\Delta E$ is the energy gap ($\approx 20$ meV) between bright states and dark states and $k_B T$ is the thermal energy at room temperature ($\approx 26$ meV). We can simplify the solutions (5) and (6) as $k_1 \approx 1.46k_{\text{bd}}$, $k_2 \approx 0.32k_{\text{bd}}$. Considering the time resolution ($\approx 50$ ps) of our setup, the quantity we measure is $k_2$, i.e., the slower of the two decay rates. Therefore, $\approx 10\%$ of radiative lifetime decrease only quenches the measured PL lifetime by $2\%$ after taking into account the QY ($\approx 20\%$) of the monolayer samples, which is consistent with the changes observed in the five soft-transferred monolayer samples. These results demonstrate

### Table 1. Photoluminescence lifetimes of WS$_2$ monolayers in different dielectric environments obtained by fitting time-resolved PL decay measurements with a stretched exponential function.

| Monolayer sample | Before/after transfer | Dielectric constant of the substrate $\varepsilon_0$ | $\varepsilon_\infty$ | Stretched exponential fitting parameters $\tau/\langle \tau \rangle$ | Average lifetime $\langle \tau \rangle$ [ns] |
|------------------|-----------------------|-----------------|-----------------|--------------------------|--------------------------|
| #3 PDMS/air$^a$  | 1                     | 1               | 1.79            | 0.97 ± 0.03              | 1.82 ± 0.03              |
| #4 PDMS/PMMA$^b$ | 1                     | 2.22            | 1.66            | 0.97 ± 0.03              | 1.69 ± 0.03              |
| #5 PDMS/air$^a$  | 1                     | 1               | 1.92            | 0.96 ± 0.04              | 1.96 ± 0.04              |
| #6 PDMS/polystyrene$^b$ | 1 | 2.53            | 1.70            | 0.88 ± 0.05              | 1.81 ± 0.07              |
| #7 PDMS/air$^a$  | 1                     | 1.79            | 1.79            | 0.91 ± 0.02              | 1.87 ± 0.03              |

$^a$The values before soft transfer; $^b$The values after soft transfer; $^c$We take into account only the fused silica substrate below the film when calculating the optical response due to the ALD-deposited alumina, as the latter is extremely thin (3 nm).
that the soft-transfer method can preserve the intrinsic optical properties of monolayer samples and provides a route for producing controlled quality samples when combined with PL lifetime measurements.

5. Conclusions

We present a systematic study of the PL lifetimes of TMD monolayers on different dielectric environments. Our results shed light on the significance that different processing techniques have on the emission efficiency of atomically thin semiconductors, and that changes in these quantities cannot always be correlated to spectral profile changes in absorption or PL. As such, we propose FLIM as a simple, fast, and powerful approach to evaluate and control the quality of exfoliated and transferred 2D semiconductors. Our results illustrate that the soft-transfer method is a convenient alternative to spin coating that effectively suppresses the associated degradation of monolayers during spin coating due to excessive strain or chemical residue. We underline the importance of studying the PL lifetime and quantum yield of each monolayer before and after transfer to a new substrate, which is critical to ensure reliability in comparative studies. Importantly, we observe that changing the dielectric environment via the soft-transfer method almost completely conserves the PL lifetime and efficiency of encapsulated monolayers. Our approach and results will be useful for the optimal integration of TMDs in nanophotonic and optoelectronic devices, and to increase the reproducibility of studies into the unique properties of 2D materials in contact with other 2D or bulk materials.[48]

6. Experimental Section

Sample Fabrication: Atomically thin flakes of WS2 were mechanically exfoliated using softly adhesive tape (SPV 9205, Nitto Denko Co.), onto a flexible, optically transparent PDMS substrate through the repeated cleavage of a single synthetic crystal (H&Q Graphene) under ambient conditions. The monolayers were identified using micro-PL imaging. Polymer thin films were obtained through spin coating: a few drops of the desired solution (either 2.5 wt% PMMA in anisole; 2.0 wt% PVA in H2O; or 2.0 wt% polystyrene in cyclopentanol) were placed on a TMD image represents the mean lifetime (τ) of the emission from the sample defined as

$$\tau = \int f(t) dt / \int f(t) dt$$

where $f(t)$ is the photon emission intensity as a function of time t after photoexcitation. The integration is performed in the time interval $0 < t < 12.5$ ns.

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.

Keywords

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