

# Substrate-Dependent Exciton Diffusion and Annihilation in Chemically Treated MoS<sub>2</sub> and WS<sub>2</sub>

Published as part of The Journal of Physical Chemistry virtual special issue "Time-Resolved Microscopy".

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**Cite This:** *J. Phys. Chem. C* 2020, 124, 12175–12184

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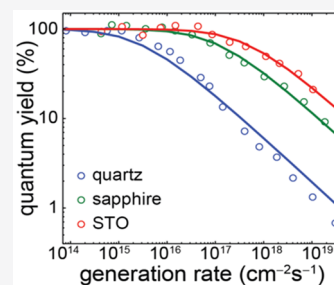
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**ABSTRACT:** Atomically thin semiconductors such as monolayer MoS<sub>2</sub> and WS<sub>2</sub> exhibit nonlinear exciton–exciton annihilation at notably low excitation densities (below  $\sim 10$  excitons/ $\mu\text{m}^2$  in exfoliated MoS<sub>2</sub>). Here, we show that the density threshold at which annihilation occurs can be tuned by changing the underlying substrate. When the supporting substrate is changed from SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> or SrTiO<sub>3</sub>, the rate constant for second-order exciton–exciton annihilation,  $k_{\text{XX}}$  [ $\text{cm}^2/\text{s}$ ], is reduced by 1 or 2 orders of magnitude, respectively. Using transient photoluminescence microscopy, we measure the effective room-temperature exciton diffusion coefficient in bis(trifluoromethane)sulfonimide-treated MoS<sub>2</sub> to be in the range  $D = 0.03\text{--}0.06$   $\text{cm}^2/\text{s}$ , corresponding to a diffusion length of  $L_D = 350$  nm for an exciton lifetime of  $\tau = 18$  ns, which does not depend strongly on the substrate. We discuss possible mechanisms for the observed behavior, including substrate permittivity, long-range exciton–exciton or exciton–charge interactions, defect-mediated Auger recombination, and spatially inhomogeneous exciton populations arising from substrate-induced disorder. Exciton annihilation limits the overall efficiency of 2D semiconductor devices operating at high exciton densities; the ability to tune these interactions via the underlying substrate is an important step toward more efficient optoelectronic technologies featuring atomically thin materials.



## INTRODUCTION

Since the discovery<sup>1</sup> of monolayer and atomically thin transition metal dichalcogenides (TMDs), the diverse physics of strongly bound and highly absorbing excitons in TMD monolayers has attracted interest in these materials. The dielectric environment resulting from atomically thin high index media produces anomalous Coulomb interactions<sup>2–4</sup> resulting in stable excitons, trions,<sup>5,6</sup> and biexcitons.<sup>7</sup> Simultaneously, atomically thin optoelectronic devices such as transistors,<sup>8</sup> phototransistors,<sup>9</sup> and LEDs<sup>9,10</sup> have been fabricated. Heterostructures composed of multiple TMDs<sup>11–14</sup> as well as TMDs paired with other complementary nanostructures<sup>4,15,16</sup> have been explored. Of particular importance for light-emitting applications is the photoluminescence quantum yield (QY). QY values less than unity indicate the presence of nonradiative recombination channels that act to reduce the charge carrier lifetime and limit the brightness of optoelectronic devices. In recent years, a variety of chemical and electrical approaches have been developed that can increase the QY of TMDs.<sup>17–22</sup> These treatments can increase QY at low excitation density, but exciton–exciton annihilation still often limits brightness at device-relevant exciton densities.

Exciton transport and annihilation in TMDs has previously been characterized using a variety of steady state and time-

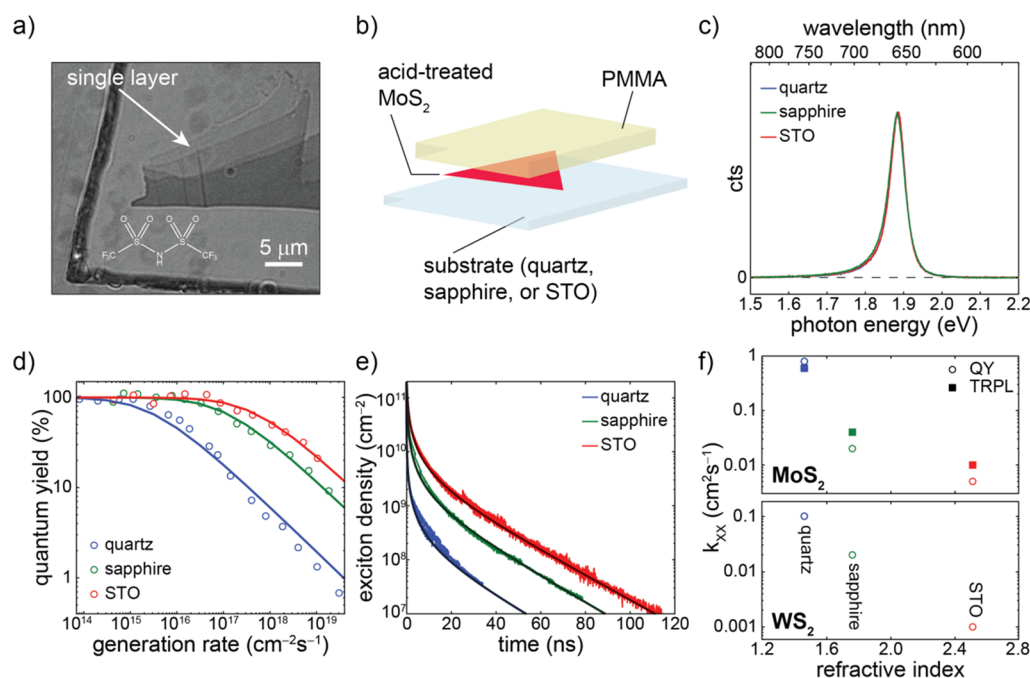
resolved techniques.<sup>23–36</sup> Transient absorption microscopy<sup>27,37–41</sup> and transient photoluminescence microscopy<sup>29,30,32,36,42</sup> have been particularly powerful approaches, since these techniques allow the spatial extent of the exciton population to be directly visualized. Exciton diffusivities have been reported in the range  $\sim 0.1\text{--}10$   $\text{cm}^2/\text{s}$  in exfoliated MoS<sub>2</sub>, WSe<sub>2</sub>, and WS<sub>2</sub>.<sup>27–29,32</sup> However, recent studies on TMDs encapsulated with hexagonal boronitride (hBN)<sup>23,31,33,36</sup> suggest that contributions from the supporting substrate and/or surrounding dielectric environment are responsible for the large spread in reported numbers. Moreover, authors speculate that defects dominate many experimental observations<sup>27,28,36</sup> and the interplay between exciton diffusivity, defect states, and exciton–exciton interactions is not clear.

Here, we use time- and spatially-resolved photoluminescence spectroscopy to measure exciton transport and annihilation in bis(trifluoromethane)sulfonimide (TFSI)-treated MoS<sub>2</sub> and WS<sub>2</sub> supported on quartz, sapphire, and

**Received:** May 5, 2020

**Published:** May 21, 2020





**Figure 1.** Effect of substrate on photoluminescence. (a) Transmission optical micrograph of exfoliated MoS<sub>2</sub> with monolayer region indicated. The inset depicts the chemical structure of the TFSI used in the treatment. The dark thick line is the border of the polymer capping layer on top of the MoS<sub>2</sub> flake. (b) Schematic of the substrate/MoS<sub>2</sub>/polymer stack. (c) Photoluminescence spectra of treated MoS<sub>2</sub> on quartz (blue), sapphire (green), and STO (red). (d) Steady-state QY measured as a function of exciton generation rate. Data were recorded for MoS<sub>2</sub> supported on quartz (blue trace), sapphire (green trace), and strontium titanate (red trace). (e) Time-resolved photoluminescence traces. The traces were globally fit to extract  $k_X$  and  $k_{XX}$  as described in the text. (f) Exciton–exciton annihilation rate constants,  $k_{XX}$ , inferred from steady-state QY measurements (open circles) and time-resolved photoluminescence measurements (filled squares).  $k_{XX}$  values for MoS<sub>2</sub> on quartz (blue), sapphire (green), and strontium titanate (red) are plotted against the supporting substrates' refractive indices (top). Analogous data for WS<sub>2</sub> samples are shown in the bottom panel.

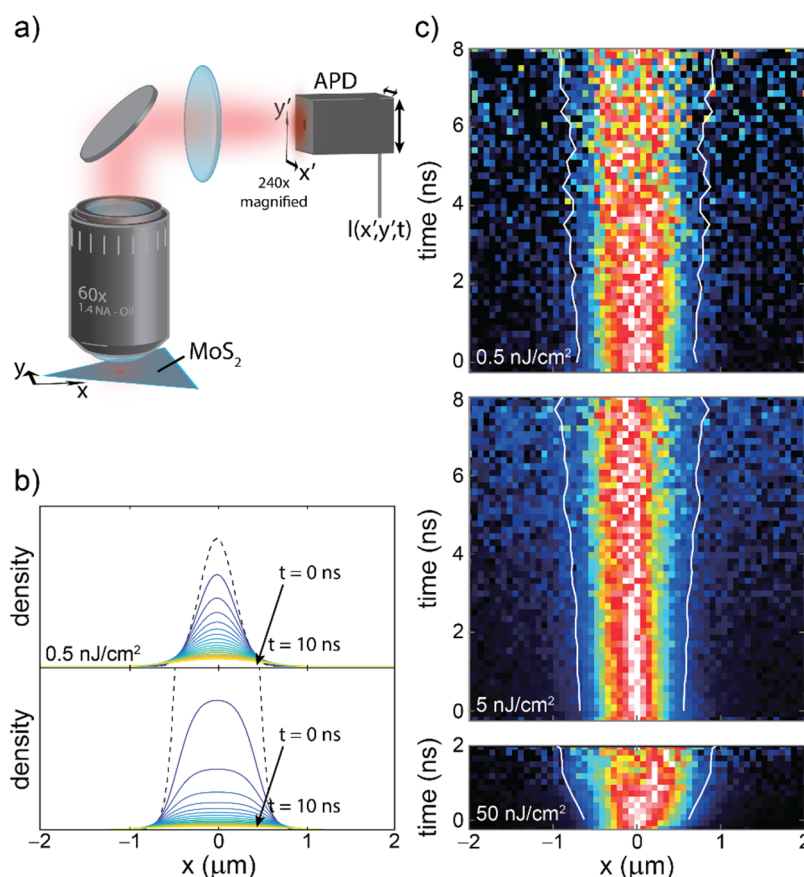
strontium titanate (STO). We show that the exciton–exciton annihilation rate constant,  $k_{XX}$ , decreases by nearly 2 orders of magnitude when the substrate is changed from quartz to STO. We directly measure the exciton diffusivity,  $D$ , to be  $0.06 \pm 0.01 \text{ cm}^2 \text{ s}^{-1}$  in TFSI-treated MoS<sub>2</sub> using transient PL microscopy and show that this value does not depend strongly on the substrate. We discuss possible explanations for these contrasting observations and emphasize the importance of suppressing exciton annihilation in optoelectronic devices operating at high exciton densities, including high brightness LEDs, lasers, and polaritonic devices.

## METHODS

MoS<sub>2</sub> and WS<sub>2</sub> monolayers were mechanically exfoliated from bulk single crystals onto SiO<sub>2</sub>/Si substrates. The samples were transferred to quartz (amorphous SiO<sub>2</sub>;  $n = 1.45$ ,  $\epsilon_r = 3.8$ ), sapphire (crystalline Al<sub>2</sub>O<sub>3</sub>;  $n = 1.76$ ,  $\epsilon_r = 8$ ), or strontium titanate (“STO” = crystalline SrTiO<sub>3</sub>;  $n = 2.50$ ,  $\epsilon_r = 320$  at  $<10^{12} \text{ Hz}$ ),<sup>43</sup> substrates chosen for their varied dielectric constant at frequencies relevant to exciton dynamics,  $\sim 10^9$ – $10^{12} \text{ Hz}$ . MoS<sub>2</sub> samples were then encapsulated with a poly(methyl methacrylate) (PMMA) capping layer and treated according to the TFSI treatment detailed by Amani et al.<sup>17,44</sup> The PMMA encapsulation mimics a similar strategy described in the literature by Kim et al. that uses fluoropolymer encapsulation to stabilize the TFSI treatment against solvent washing and vacuum exposure.<sup>45</sup> An optical transmission micrograph of an exemplar flake is shown in Figure 1a and the corresponding substrate/sample/polymer stack is illustrated in Figure 1b.

**Sample Preparation.** Mineral MoS<sub>2</sub> (SPI) was exfoliated on SiO<sub>2</sub>/Si substrates and then transferred to other substrates including quartz, sapphire or STO substrates by a dry transfer technique via a poly(methyl methacrylate) (PMMA) membrane as a transfer media. The transferred MoS<sub>2</sub> was treated by the following procedure: 20 mg of (bis(trifluoromethane)-sulfonimide) (TFSI) was dissolved in 5 mL of 1,2-dichloroethane and then diluted with 45 mL of 1,2-dichlorobenzene to make a TFSI solution. The transferred MoS<sub>2</sub> with PMMA was then immersed in the TFSI solution for 30 s in room temperature. The sample was blow dried with nitrogen. Note that the enhancement is depending on the initial quality of the sample and only a portion of sample can reach >95% QY.

**Transient PL.** Samples were excited using a 405 nm pulsed laser diode (Picoquant, LDH-D-C-405M, 40 MHz repetition rate, 0.4 ns pulse duration) with fluences as indicated in the main text. The laser was focused to a nearly diffraction-limited spot (Nikon, CFI S Plan Fluor ELWD, 40 $\times$ , 0.6 NA). Fluorescence was collected with the same objective and passed through a dichroic mirror and a 600–700 nm bandpass filter before being focused onto a Si avalanche photodiode (Micro Photon Devices, PDM50, 50 ps resolution at the detection wavelength). The detector was connected to a counting board for TCSPC (Picoquant, PicoHarp 300). Exciton densities were estimated by relating the photoluminescence rate at time zero with the number of excitons generated by an excitation laser pulse assuming linear absorption and the measured TMD absorption coefficient. The photoluminescence rate was assumed to be proportional to the exciton density (and the radiative rate constant  $k_X$ ).



**Figure 2.** Time- and spatially-resolved emission microscopy. (a) Schematic diagram of the optical apparatus used to resolve exciton diffusion in space and time. (b) Top: simulation of the photoluminescence intensity along a line cut of the radially symmetric exciton population as a function of time. With an incident fluence of 0.5 nJ/cm<sup>2</sup>, almost all excitons decay radiatively and the spot broadens due to diffusion. Bottom: same as top panel, but with an incident fluence of 50 nJ/cm<sup>2</sup>, many excitons decay due to annihilation. This results in artificial broadening of the density profile; excitons decay most rapidly in the center of the spot where exciton density is highest. (c) Experimentally observed broadening of the exciton population with time at 0.5, 5, and 50 nJ/cm<sup>2</sup> incident fluences in the top, middle, and bottom panels, respectively. White lines indicate the evolution of the standard deviation with time.

**Quantum Yield Measurement.** The calibrated PL QY measurement has been previously described in detail. Briefly, the 514.5 nm line of an Ar ion laser (Lexel 95) was focused to the sample using a 60× ultralong working distance objective (NA = 0.7). PL was collected by the same objective, filtered and dispersed by a spectrograph. The emission was detected by a Si CCD camera (Andor, iDus BEX2DD). The excitation power and optical system spectral sensitivity were externally calibrated. The instrument function was cross-calibrated using rhodamine 6G (QY close to 100%) and Spectralon as reference samples. The measured PL spectra were integrated and converted into external quantum efficiencies and corresponding QYs. The exciton generation rate was estimated using the measured excitation power, laser spot size, and absorption coefficient at the excitation wavelength.

**Transient PL Microscopy.** The 570 nm wavelength laser pulses from a synchronously pumped optical parametric oscillator (Coherent, PP automatic, 76 MHz, <1 ps) were spatially filtered by a single-mode optical fiber and used to excite the sample. The laser was focused to a diffraction-limited spot (Nikon, CFI Plan Apo Lambda, 60× oil, 1.4 NA). Fluorescence was collected by the same objective and filtered by a dichroic mirror and 600–700 nm bandpass filter. The APD detector was placed in the 360× magnified image plane outside the microscope. The detector position in the image

plane was controlled by two orthogonal motorized actuators (Thorlabs, ZFS25B). The evolution of the photoluminescence spatial profile with time was acquired by scanning the detector across the magnified emission profile and collecting a photoluminescence decay histogram at each position.

**PL Spectroscopy, Low Temperature.** A 532 nm continuous wave laser (Coherent, Sapphire SF 532–20 CW) was focused at the sample (Nikon, CFI S Plan Fluor ELWD, 40×, 0.6 NA). Fluorescence was collected by the same objective and filtered by a dichroic mirror before being dispersed by a spectrograph (Princeton Instruments, Acton SP2500) and imaged on a cooled CCD camera (Princeton Instruments, Pixis PIX100BR). Low-temperature data were collected under vacuum in a microscope-mounted cryostat (Janis, ST-500-P).

**Numerical Simulation.** Exciton dynamics were simulated with a fixed time step Monte Carlo algorithm. Excitons were initialized to the band edge according to a spatial profile matching the excitation laser intensity profile. At each time step free excitons hopped a fixed distance in a random direction. Excitons trapped with unit probability if the center position of the exciton was within 0.4 nm of the center of an empty trap. Upon moving within 2R nm of an occupied trap, the exciton annihilated and was removed from the simulation. Annihilation between pairs of free excitons were rare due to



the low population of detrapped excitons and were thus neglected. Trapped excitons detrapped probabilistically as described in the main text. Detailed procedures and parameter values are included in the [Supporting Information](#).

## RESULTS

**Exciton Annihilation Rate.** After the TFSI treatment, the PL of the MoS<sub>2</sub> monolayers supported on quartz, sapphire, and STO were markedly enhanced (normalized PL spectra are shown in [Figure 1c](#), where the peak energies and profiles are identical; corresponding absorption spectra are shown in the [Supporting Information](#)). Calibrated PL intensity was measured as a function of the generation rate, allowing the extraction of steady-state QYs, which are plotted in [Figure 1d](#). The QY series for MoS<sub>2</sub> monolayers supported by all three substrates are qualitatively similar; the QY was observed to be near unity at low generation rate and then decreased as the generation rate increased. The QY's dependence on the generation rate can be described by the ratio of the radiative decay rate to the sum of the rates of all decay paths available to the exciton:

$$QY = \frac{k_X N}{k_X N + k_{NR} N + k_{XX} N^2} \quad (1)$$

where  $k_X$  is the radiative decay rate, and  $k_{NR}$  and  $k_{XX}$  are the first-order nonradiative decay rate and the exciton–exciton annihilation rate, respectively. This recombination model successfully captures the PL behavior at high generation rate (i.e., high laser power) where the QY drops precipitously because exciton–exciton annihilation ( $k_{XX} N^2$ ) begins to outpace radiative decay ( $k_X N$ ). Note that the QY was near unity in all samples studied at low generation rate, implying that  $k_{NR}$  is negligibly small. This allows us to extract  $k_{XX} = 0.8, 0.02, 0.005 \text{ cm}^2 \text{ s}^{-1}$  for the samples on quartz, sapphire, and STO, respectively (the dash lines in [Figure 1d](#) are the fits using [eq 1](#)). Notably, we found that the threshold generation rate at which the QY dropped below 50% could be increased by 2 orders of magnitude through changing the substrate; for samples on quartz, sapphire, and STO; those generation rates were  $1.5 \times 10^{16}, 2.1 \times 10^{17},$  and  $1.1 \times 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$ .

The exciton–exciton annihilation rate constant,  $k_{XX}$ , can also be extracted from transient measurements. Time correlated single photon counting (TCSPC) measurements were performed at varied incident laser fluences (corresponding to different initial exciton concentrations,  $N(0)$ ) to reveal recombination dynamics. By stitching together the decay curves with varied  $N(0)$ , a single decay curve with an over 4 decades dynamic range was obtained (individual PL decay curves are provided in the [Supporting Information](#)). The decay curves for treated MoS<sub>2</sub> supported by all three substrates are shown in [Figure 1e](#). The decay curves are multiexponential containing fast components due to annihilation at high exciton density and slower radiative decay at low exciton density. The rates  $k_X$  and  $k_{XX}$  can be extracted by fitting the decay curves to a simple kinetic model, in which the excited exciton density,  $N(t)$ , decays according to the equation

$$\frac{dN(t)}{dt} = -k_X N(t) - k_{XX} N^2(t) \quad (2)$$

The values of  $k_{XX}$  obtained by this fitting for TCSPC are in good agreement with the values extracted from the steady-state QY measurements, as plotted in the top panel of [Figure 1f](#).

Notably, we observed that  $k_{XX}$  varied similarly in WS<sub>2</sub> with changing supporting substrate. The values of  $k_{XX}$  found in WS<sub>2</sub> are shown in the bottom panel of [Figure 1f](#) (detail in [Supporting Information](#)).

**Transient Visualization of Exciton Transport.** To probe exciton transport, we followed exciton motion in space and time using transient photoluminescence (PL) microscopy.<sup>46</sup> The optical setup is depicted in [Figure 2a](#). A pulsed laser is focused to a diffraction-limited excitation spot at the sample using an oil-immersion objective, and the epi-fluorescence is collected by the same objective. A 360× magnified image of the fluorescing exciton population is scanned by an APD detector, which is synchronized to the pulsed laser to collect PL decay histograms. A PL decay trace was collected at each detector position in the image plane, allowing time-dependent spatial emission profiles to be reconstructed.

The top panel of [Figure 2b](#) depicts the simulated time evolution of an exciton population initialized with a Gaussian spatial profile, indicated by the dashed black trace, designed to mimic the exciton population instantaneously excited by a 0.5 nJ/cm<sup>2</sup> laser pulse focused to a diffraction limited spot ( $\lambda = 405 \text{ nm}$ ). At this fluence, excitons only decay radiatively. The exciton population decays exponentially as time progresses (coded in the trace colors). Simultaneously, excitons diffuse out of the initial excitation spot, broadening the distribution. We model this decay process in terms of a continuum model in which the exciton density,  $N(\mathbf{r}, t)$ , evolves as a function of space and time according to

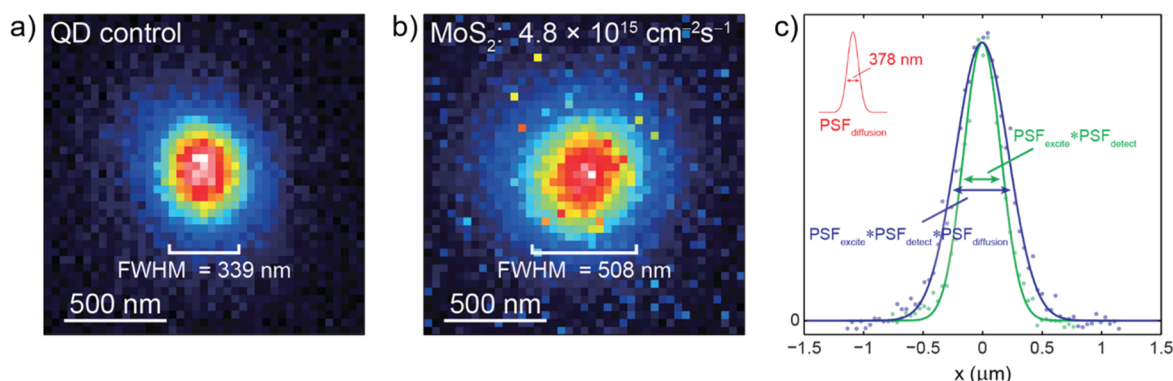
$$\frac{dN}{dt} = D \nabla^2 N - (k_X + k_{NR}) N - k_{XX} N^2 \quad (3)$$

where  $D$  is the exciton diffusivity. The bottom panel of [Figure 2b](#) depicts an analogous simulation performed with a higher excitation fluence. In this regime, the exciton–exciton annihilation term ( $k_{XX} N^2$ ) in [eq 3](#) becomes prominent. Excitons still undergo radiative decay and diffusion but additionally annihilate with a rate that depends nonlinearly on the local exciton density. The nonradiative decay channel increases the overall decay rate of the exciton population and also changes the shape of the distribution. The peak of the excited distribution decays more quickly than the tails, leading to a flattening and broadening that is not due to diffusion.

In [Figure 2c](#) we present the time-resolved spatial broadening of the exciton population measured in quartz-supported monolayer MoS<sub>2</sub> at three different incident laser fluences. The top panel depicts data collected using a  $\lambda = 405 \text{ nm}$  excitation fluence of 0.5 nJ/cm<sup>2</sup>, corresponding to an average density of 1.2 excitons generated per square micron. The white traces track the standard deviation of the distribution with time. For purely diffusive broadening, the change in the distribution variance grows linearly in time:

$$\sigma^2(t) - \sigma^2(0) = 2Dt \quad (4)$$

This behavior is observed at low fluences, and fitting the variance as a function of time allows us to extract a diffusivity  $D_{\text{qtz}} = 0.06 \pm 0.01 \text{ cm}^2/\text{s}$ , corresponding to a diffusion length  $L_D = \sqrt{D\tau} = 350 \text{ nm}$ . In contrast, with higher excitation fluences, the spot appears to broaden more quickly. However, this is due to faster rates of exciton–exciton annihilation in the center of the distribution rather than faster exciton transport. In these cases, the variance of the intensity distribution  $I(x, t)$  grows sublinearly in time. Such details are captured by the data and reproduced by the simulation parametrized by our



**Figure 3.** Static emission microscopy. (a) PL image collected from a thin film of well insulated CdSe/ZnCdS core/shell quantum dots in which exciton diffusion does not occur. The dots were excited with a focused laser ( $\lambda = 520 \text{ nm}$ ,  $\text{NA} = 1.4$ ). (b) PL image collected from MoS<sub>2</sub> with the same imaging system using a sufficiently low fluence to avoid exciton–exciton annihilation. (c) Radial intensity profiles of the images in the left and center panels, revealing quantifiable broadening in the MoS<sub>2</sub> emission due to exciton diffusion.

measured values for  $k_{\text{XX}}$  and  $D$  (see Supporting Information). We performed the same measurement for samples supported on sapphire and STO (see the Supporting Information) and extracted diffusivities  $D_{\text{sapphire}} = 0.04 \pm 0.01 \text{ cm}^2/\text{s}$  and  $D_{\text{STO}} = 0.06 \pm 0.02 \text{ cm}^2/\text{s}$ . The choice of substrate did not appear to significantly affect the exciton diffusivity.

**Static Visualization of Exciton Transport.** To corroborate the time-resolved measurement of exciton diffusivity, we performed a separate measurement of exciton diffusion using steady-state PL microscopy. A  $\lambda = 520 \text{ nm}$  CW laser was focused to a diffraction limited spot at the sample through an oil immersion objective ( $\text{NA} = 1.4$ ) and the emission was collected through the same objective and imaged on a CCD camera. For CW imaging, the measured emission width is a convolution of (1) the excitation point spread function (PSF) (i.e., the Gaussian laser spot size), (2) the collection PSF, and (3) an effective diffusion PSF due to transport during the exciton lifetime. The excitation PSF and collection PSF can be measured independently, allowing the contribution from diffusion to be determined. The collection PSF was assessed by casting a sparse film of isolated CdSe quantum dots (QDs) and imaging their emission ( $\lambda_{\text{emiss}} = 630 \text{ nm}$ ) under wide-field LED illumination. Each point-like emitter appeared as a Gaussian spot with a width representing the collection PSF of the imaging system. To measure the excitation PSF, we imaged a homogeneous emissive film that does not exhibit exciton diffusion. For these experiments, we used a thin film of CdSe QDs coated with a thick (2–3 nm) ZnCdS shell and long-chain oleate ligands that were previously shown to prevent any measurable exciton diffusion.<sup>47</sup>

A PL image of the QD control sample under focused CW laser excitation is shown in Figure 3a. The measured width of the emission pattern ( $\text{fwhm}_{\text{measured}} = 339 \text{ nm}$ ) is close to that predicted for a diffraction-limited optical system ( $\text{fwhm}_{\text{predicted}} = 304 \text{ nm}$ ). In Figure 3b, we show the emission pattern for a TFSI-treated MoS<sub>2</sub> flake on quartz, illuminated with the same focused laser at an excitation rate sufficiently low to avoid exciton annihilation effects ( $4.8 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$ ; see Figure 1d). The MoS<sub>2</sub> emission ( $\text{fwhm}_{\text{measured}} = 508 \text{ nm}$ ) is broadened relative to the QD control due to exciton diffusion in the MoS<sub>2</sub> sample (Figure 3c). From these measurements, we observe that the variance of the MoS<sub>2</sub> exciton distribution is larger by  $0.026 \mu\text{m}^2$ , implying a diffusivity of  $0.03 \pm 0.01 \text{ cm}^2/\text{s}$ , which is consistent with the time-resolved measurements.

## DISCUSSION

**Exciton Diffusion Constant.** The measured low-density exciton diffusivity in TFSI-treated MoS<sub>2</sub>,  $D \approx 0.03\text{--}0.06 \text{ cm}^2/\text{s}$ , which we obtained by two independent methods (transient imaging and CW imaging, Figures 2 and 3), is surprisingly small. Exciton diffusivities as large as  $\sim 2 \text{ cm}^2/\text{s}$  have been measured in exfoliated WSe<sub>2</sub><sup>42</sup> and WS<sub>2</sub><sup>27</sup> under much higher laser excitation intensities. The most comparable study is that of Kulig et al., who used transient PL imaging to measure the density-dependent exciton diffusivity in freestanding and SiO<sub>2</sub>-supported WS<sub>2</sub> and consistently obtained a value close to  $0.3 \text{ cm}^2/\text{s}$  in the low-density limit.<sup>29</sup> Notably, this value was independent of the presence or absence of the SiO<sub>2</sub>/Si substrate, in agreement with our finding that the exciton diffusivity does not depend strongly on the choice of supporting substrate. Nonetheless, the diffusivity we observe in our TFSI-treated samples is at least an order of magnitude smaller than that reported in as-exfoliated flakes.

Comparison of TFSI-treated TMDs to TMDs gated in a capacitor structure strongly suggests that the dominant action of the TFSI treatment is to neutralize majority carriers, thereby preventing fast nonradiative trion recombination.<sup>18</sup> As-exfoliated monolayer MoS<sub>2</sub> is *n*-type because of donor-like chalcogenide site vacancies, whereas TFSI-treated MoS<sub>2</sub> is nearly intrinsic.<sup>17</sup> Upon removal of excess charge carriers—either by chemical treatment<sup>17</sup> or by electrical neutralization<sup>18,22</sup>—luminescence QY approaching 100% can be obtained. Native structural defects are still believed to be present in neutralized TMDs, but these sites do not appear to act as nonradiative recombination centers.

One possible explanation for the smaller-than-expected diffusivity values we measure is the persistent subtle influence of defect sites. Although defects do not limit the luminescence QY, their presence may still impact dynamics of exciton transport, annihilation, and the observed lifetime. Temperature- and density-dependent analysis of the photoluminescence spectrum suggests that, at room temperature, excitons spend a large portion of their lifetime immobilized at defect sites.<sup>48</sup> This could explain the surprisingly small value of the exciton diffusivity that we measure under similar excitation conditions: i.e., the experimentally measured exciton diffusivity is a time-weighted average of the free and immobile states. The effective diffusivity measured in our experiments is small

despite the possibility that excitons diffuse very quickly while at the band edge.

**Exciton Annihilation Rate.** The central paradox of our data set is the simultaneous observation of very small exciton diffusivity ( $D = 0.06 \text{ cm}^2/\text{s}$  on quartz) and very large exciton–exciton annihilation rate constant ( $k_{\text{XX}} = 0.8 \text{ cm}^2/\text{s}$  on quartz). In quartz-supported  $\text{MoS}_2$ , the photoluminescence QY dropped to 90% at a generation rate of only 0.5 excitons  $\mu\text{m}^{-2}$  per exciton lifetime ( $\tau_{\text{x}} = 18 \text{ ns}$ ; see Figure 1d). However, the exciton diffusion length is only  $L_{\text{D}} = 350 \text{ nm}$ .

Exciton–exciton annihilation is usually understood to be a diffusion-mediated process. In the traditional analysis based on Smoluchowski's equation for coagulation of diffusing spheres, excitons are approximated as freely diffusing neutral particles with an effective radius of interaction,  $R$ . When two excitons come within a distance  $2R$  of each other, one of the excitons is annihilated. The Smoluchowski equation predicts a quantitative relationship between the diffusivity,  $D$ , the interaction radius,  $R$ , and the annihilation rate constant,  $k_{\text{XX}}$ . In two dimensions, this equation takes the form

$$k_{\text{XX}} = \frac{8\pi D}{\ln\left(\frac{1}{n_0 4R^2}\right)} \quad (5)$$

where  $n_0$  is the exciton density at which the annihilation rate becomes equal to the spontaneous decay rate,  $k_{\text{XX}}n_0^2 = k_{\text{x}}n_0$ . According to eq 5, the annihilation rate constant  $k_{\text{XX}}$  is proportional to the diffusivity. This is intuitively sensible, since a higher exciton diffusivity leads to more frequent exciton–exciton encounters, resulting in a faster overall annihilation rate.

Using the experimentally measured values of  $D = 0.06 \text{ cm}^2/\text{s}$  and  $k_{\text{XX}} = 0.8 \text{ cm}^2/\text{s}$  on quartz, eq 5 implies that excitons interact across distances as large as  $2R = 500 \text{ nm}$ . Such a long-range interaction is inconsistent with current understanding of the exciton size and the strength and distance dependence of dipole and Coulomb potentials in TMDs. A more reasonable estimate for  $R$  is the Bohr radius of the 1s exciton in  $\text{MoS}_2$ , which has been calculated to be only 5–10 Å.<sup>3,49</sup> Though the possibility of excitons interacting across hundreds of nanometers is intriguing, it is not likely the correct conclusion to draw from the experimental results.

One possible explanation for the discrepancy between eq 5 and the measured values of  $D$  and  $k_{\text{XX}}$  is substrate-induced disorder. Roughness of the underlying substrate can induce local strain in a supported TMD, leading to a spatially inhomogeneous bandgap. Strain-induced excitonic energy gradients will drive excitons toward low-energy “pools” where they are more likely to meet and annihilate. This behavior is analogous to exciton transport and annihilation in QD solids, which is strongly influenced by site energy disorder.<sup>47,50,51</sup> Encapsulation of TMDs in hBN has been shown to suppress exciton–exciton annihilation,<sup>23,31,33,36</sup> partly by protecting the 2D material from substrate-induced disorder.<sup>34</sup>

Another possible explanation for the failure of eq 5 to predict our experimental results is the presence of long-lived free carriers that persist from the previous excitation event. Though the exciton binding energy in  $\text{MoS}_2$  and  $\text{WS}_2$  is many times larger than  $k_{\text{B}}T$  at room temperature,<sup>2</sup> entropic forces still drive efficient exciton ionization into free carriers<sup>36,52</sup>—especially at the low excitation densities used here. Free or trapped charges could persist longer than the repetition rate of

our pulsed laser ( $1/40 \text{ MHz} = 25 \text{ ns}$ ), leading to a high free carrier density that interacts with the photogenerated exciton population via fast trion recombination.

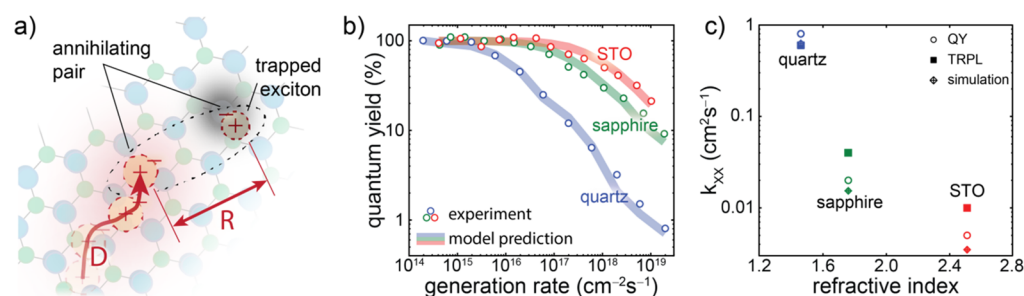
**Substrate Dependence.** As shown in Figure 1c, the room-temperature photoluminescence spectrum of  $\text{MoS}_2$  was unchanged when the sample was transferred from quartz ( $n = 1.45$ ,  $\epsilon_{\text{r}} = 3.8$ ) to sapphire ( $n = 1.76$ ,  $\epsilon_{\text{r}} = 8$ ) to STO ( $n = 2.50$ ,  $\epsilon_{\text{r}} = 320$ ). This observation is consistent with theoretical predictions that opposing changes in the quasiparticle gap and exciton binding energy result in an optical gap that is relatively insensitive to the supporting substrate,<sup>34,53,54</sup> and is consistent with experimental observations by other groups.<sup>55,56</sup> Moreover, we also found that the first-order decay constant,  $k_{\text{x}}$ , was unchanged for  $\text{MoS}_2$  on all three substrates (see low-density regime of Figure 1e) despite large changes in the absolute absorption (Figure S1). Local field effects should cause the radiative rate to vary with substrate refractive index;<sup>57</sup> the observed insensitivity of  $k_{\text{x}}$  to the supporting substrate despite large changes in the absolute absorption is yet another indication that the measured recombination rate is not primarily determined by the true intrinsic radiative rate.<sup>48</sup>

The optical gap, first-order decay constant, and exciton diffusivity were all unchanged (within experimental precision) when the sample was transferred to different substrates. In contrast, the exciton–exciton annihilation rate constant varied by 2 orders of magnitude (Figure 1f). When the substrate was changed from quartz to sapphire to STO, the annihilation rate constant monotonically decreased from  $k_{\text{XX}} = 0.8$ – $0.02$  to  $0.005 \text{ cm}^2/\text{s}$ . Equation 5 predicts a proportionality between  $k_{\text{XX}}$  and  $D$ . Some reduction in the exciton radius of interaction  $R$  is expected with increasing substrate permittivity due to environmental screening of the Coulomb and dipole–dipole interaction potentials<sup>53,54</sup> (though this effect could be offset by a larger exciton Bohr radius). However, the two-orders-of-magnitude reduction in  $k_{\text{XX}}$  that was experimentally observed under constant  $D$  is more dramatic than eq 5 can account for. We note, for completeness, that eq 5 does not take into account final state structure—i.e., higher exciton resonances that could increase the efficiency of the annihilation event itself—which could depend on the dielectric environment.

One clue as to the origin of the substrate-dependent variation in  $k_{\text{XX}}$  comes from analysis of the emission spectrum at lower temperature. The PL spectrum at 77 K for  $\text{MoS}_2$  on all three substrates exhibits a weak tail on the lower-energy side of the dominant exciton emission peak (Figure S6). The energetic extent of this tail is strongly substrate-dependent, varying monotonically with the substrate permittivity. The lower-permittivity substrate (quartz) exhibits the deepest/most prominent emission tail, whereas the higher-permittivity substrate (STO) exhibits the shallowest/least prominent emission tail (we note that the permittivity of  $\text{SrTiO}_3$  is strongly temperature-dependent<sup>43</sup>). These low energy features correspond to emission from long-lived weakly radiative states, which we previously assigned to structural defects in the native  $\text{MoS}_2$  crystal,<sup>48</sup> presumably chalcogenide site vacancies. Quantitative analysis of the emission spectrum suggests that the number of defect states per unit area does not depend on the underlying substrate but that the energetic distribution of defect-associated emission is strongly substrate-dependent (see Supporting Information).

**A Model for Defect-Mediated Annihilation.** We present a model for defect-mediated annihilation in TMDs. We performed Monte Carlo simulations of exciton transport





**Figure 4.** Monte Carlo simulation of defect-mediated annihilation. (a) Diffusing excitons meet long-lived trapped excitons or charges and annihilate according to an interaction radius,  $R$ . (b) A Monte Carlo model invoking trapped and diffusing band edge excitons quantitatively reproduces steady-state QY data. The simulated behavior is plotted here (thick transparent lines) against the experimental data (open circles) for  $\text{MoS}_2$  on quartz (blue), sapphire (green), and strontium titanate (red). (c) The annihilation rate constant inferred from the model (diamonds) is plotted along with the experimentally derived values (open circles, QY; filled squares, time-resolved photoluminescence) against the supporting substrate refractive index.

and annihilation including both mobile and defect-immobilized excitons (see [Supporting Information](#)). The results of these simulations, shown in [Figure 4](#), reproduce most of the experimental observations. Key parameters involving the interaction between trapped and freely diffusing excitons are illustrated in [Figure 4](#) and summarized in [Table S1](#). In the model, long-lived, immobile trapped excitons or charges act as nonradiative recombination centers for freely diffusing excitons, resembling a defect-mediated Auger recombination process. When diffusing excitons come within a critical radius  $R$  of a charged defect, they annihilate in a bimolecular process. Detrapping is allowed within the model, but a non-negligible portion of the trapped population does not possess sufficient thermal energy to detrapp. This subpopulation of deeply trapped excitons persists for a long time ( $\sim$ microseconds) when compared to the exciton lifetime and the laser repetition rate (tens of nanoseconds).<sup>48</sup>

Within the model framework, the predominant effect of changing substrate is to change the quasi-static charged defect density under equivalent laser irradiation conditions. TFSI treatment removes excess electron density but does not heal native structural defects. Photogenerated charges can become associated with these defect sites and persist for a long time ( $\sim$ microseconds) relative to time-resolved spectroscopy measurements. Comparison of model simulations to experimental results suggests that the density of defect sites is not changed by TFSI treatment or transfer to different substrates; rather, it is the energetic depth of the trap state distribution that is most affected by the substrate. Higher substrate permittivity is correlated with a shallower trapping depth, thus reducing the fraction of quasi-permanently trapped carriers and allowing near-unity PL QY to be observed experimentally at significantly higher excitation density.

## CONCLUSIONS

Though TMD lasers<sup>58,59</sup> and LEDs<sup>10,60,61</sup> have been demonstrated, practical use requires operation at high exciton densities. For instance, a  $\text{MoTe}_2$  laser<sup>59</sup> exhibited a threshold pump generation rate,  $R \approx 4 \times 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$ , in the regime where exciton–exciton annihilation is dominant. Achieving high brightness LEDs or sufficiently high exciton densities for lasing or polariton condensation in the presence of competitive second-order nonradiative decay channels necessitates excessive pump rates. Exciton–exciton annihilation places a fundamental limit on the operating efficiency of such devices. Understanding the mechanism behind this efficiency loss and

raising the maximum achievable operating efficiency by tuning the dielectric environment are critical advances for the future of TMD optoelectronic devices.

Strong exciton–exciton interactions and the tuning of those interactions through the surrounding dielectric are both manifestations of reduced dielectric screening in 2D materials. Coulomb interactions are poorly screened in monolayer TMDs, resulting in large exciton, trion, and biexciton binding energies. Though these many-body interactions can be exploited to observe physics characteristics of 2D materials, here they facilitate exciton–exciton and exciton–charge annihilation, limiting radiative efficiency. We take advantage of the sensitivity of exciton dynamics in TMDs to their surrounding dielectric environment to suppress exciton–exciton interactions. Tuning the strength of many-body interactions through the dielectric environment is a powerful design paradigm accessible in low-dimensional materials.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.0c04000>.

Additional experimental results (absorption spectra, PL decay traces, quantum yield values for  $\text{WS}_2$ , exciton diffusivity experimental results and continuum modeling, diffusion images, results showing the effect of vacuum and cooling on the PL spectrum) as well as additional analysis (detailed description of the Monte Carlo model and fitting of the low-temperature emission spectrum) (PDF)

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## Author Contributions

<sup>○</sup>A.J.G. and D.-H.L. contributed equally. A.J.G. performed time-resolved spectroscopy, diffusion imaging, and low-temperature spectroscopy under the supervision of W.A.T. D.-H.L. prepared samples and performed power-dependent quantum yield and TCSPC experiments under the supervision of A.J. A.J.G. developed and implemented the numerical model, with assistance from L.L.S., A.P.W., and W.A.T. G.H.A. assisted with sample preparation and M.A. contributed to data interpretation. All authors discussed the results and interpretation. W.A.T., A.J.G., and D.-H.L. wrote the manuscript with contributions from the other authors.

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

Transient photoluminescence microscopy and numerical modeling performed at MIT were supported as part of the Center for Excitonics, an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Basic Energy Sciences (BES) under Award No. DE-SC0001088. Sample preparation and transient PL characterization at U.C. Berkeley was supported by the Electronic Materials Program funded by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division of the U.S. Department of Energy, under contract no. DE-AC02-05Ch11231. A.J.G. acknowledges partial support from the US National Science Foundation Graduate Research Fellowship Program under Grant No. 1122374. W.A.T. was partially supported by the US Department of Energy, Office of Science, under Award No. DE-SC0019345.

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