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Published in:
Nature Communications

DOI (link to publication from Publisher):
10.1038/s41467-018-03864-y

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Publication date:
2018

Document Version
Publisher's PDF, also known as Version of record

Link to publication from Aalborg University

Citation for published version (APA):
Massicotte, M., Vialla, F., Schmidt, P., Lundeberg, M. B., Latini, S., Haastrup, S., ... Koppens, F. H. L. (2018). Dissociation of two-dimensional excitons in monolayer WSe2. DOI: 10.1038/s41467-018-03864-y
Dissociation of two-dimensional excitons in monolayer WSe$_2$

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Two-dimensional (2D) semiconducting materials are promising building blocks for optoelectronic applications, many of which require efficient dissociation of excitons into free electrons and holes. However, the strongly bound excitons arising from the enhanced Coulomb interaction in these monolayers suppresses the creation of free carriers. Here, we identify the main exciton dissociation mechanism through time and spectrally resolved photocurrent measurements in a monolayer WSe$_2$ p-n junction. We find that under static in-plane electric field, excitons dissociate at a rate corresponding to the one predicted for tunnel ionization of 2D Wannier-Mott excitons. This study is essential for understanding the photoresponse of 2D semiconductors and offers design rules for the realization of efficient photodetectors, valley dependent optoelectronics, and novel quantum coherent phases.
As Johan Stark first observed in hydrogen atoms, applying an electric field on Coulomb-bound particles shifts their energy levels and eventually leads to their dissociation (Fig. 1a). In condensed matter physics, Wannier–Mott excitons display features analogous to those of hydrogen, but with the crucial difference that they recombine if they are not dissociated. Thermal energy is usually sufficient to ionize excitons in 3D semiconductors owing to their small binding energy \( E_B \) (typically a few meV). In contrast, quantum confinement effects and reduced Coulomb screening in low-dimensional materials give rise to large exciton binding energy \( E_B > 100 \) meV, which prevents thermal or spontaneous dissociation even at elevated temperatures and exciton densities.

In particular, monolayer transition metal dichalcogenides (TMDs) have aroused tremendous interest due to their unique optical properties governed by prominent excitonic features and spin- and valley dependent effects. These 2D semiconductors provide an exciting testbed for probing the physics arising from many-body Coulomb interactions. Recently, all-optical experiments have revealed a wealth of physical phenomena such as exciton, triexciton, and biexciton formation, bandgap renormalization, exciton–exciton annihilation, and optical Stark effect. Exciton dissociation, on the other hand, can in principle be assessed through photocurrent measurements since photo-ions are outlined and shaded for clarity. PC is measured at the junction as a function of voltage. PC measured at the junction as a function of voltage.

**Results**

**Device structure and characterization.** Figure 1b, c presents a schematic and optical micrograph of our lateral p–n junction.

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**Figure 1** Photocurrent generation by exciton dissociation in a monolayer WSe\(_2\) p–n junction. a, Illustration of a Wannier–Mott exciton in the absence (red) and presence (blue) of a static electric field. The electric wave functions are represented by the shaded curves while the exciton potentials are shown by the thick solid lines. b, Schematic of a monolayer WSe\(_2\) device controlled by two local metal gates with voltages \( V_{G1} \) and \( V_{G2} \). Two graphite flakes (colored in black) are placed on both sides of the WSe\(_2\) layer (orange) and encapsulated between two hBN flakes (pale blue and green). c, Optical image of a p–n junction device overlaid with a spatial PC map. The graphite and WSe\(_2\) flakes are outlined and shaded for clarity. PC is measured at \( V_{asym} = V_{G1} - V_{G2} = -10 \) V and \( V_B = 0 \) V, with a laser power \( P = 1 \) \( \mu \)W and a photon energy \( h\nu = 1.65 \) eV. The scale bar is 4 \( \mu \)m. d, Side view of the electric field distribution \( F \) across a device made of hBN (20 nm thick), monolayer WSe\(_2\) (dotted blue line), and hBN (30 nm thick) atop metallic split gates separated by 200 nm (yellow rectangles). The field is calculated for \( V_{asym} = -10 \) V and \( V_F = 0 \). The color bar above indicates the magnitude of the PC as well as the internal quantum efficiency, IQE = \( \frac{PC}{A} \), where \( A = 5\% \) is the absorption coefficient.
device made by assembling exfoliated flakes on metallic split gates ($V_{G1}$ and $V_{G2}$) separated by 200 nm (see “Methods”). Few-layer graphite flakes placed on both ends of a monolayer WSe$_2$ flake serve as ambipolar electrical contacts$^{33}$ that we use to apply a bias voltage $V_B$ and collect the photogenerated charges. The lateral graphite-WSe$_2$-graphite assembly is fully encapsulated in hexagonal boron nitride, typically 20 nm thick, which provides a clean and flat substrate. Three devices were measured (see Supplementary Note 1 and Supplementary Figs. 1–3), but otherwise specified, all measurements presented in the main text are obtained at room temperature from the device shown in Fig. 1c.

Tuning of bias and gate voltages allows us to finely control the in-plane electric field $F$. Finite-element and analytical calculations of the electric field distribution in our device (see Supplementary Note 2 and Supplementary Figs. 4–7) provide us with a precise estimate of $F$ and the electrostatic doping inside the WSe$_2$ (Fig. 1d). Applying gate voltages of opposite polarity ($V_{\text{asym}} = V_{G1} = -V_{G2} = -10$ V) leads to the formation of a sharp $p$–$n$ junction (Fig. 1e) with an in-plane electric field reaching 21 V/$\mu$m$^{-1}$ (Fig. 1d). The photoresponse that we observed at the junction (Fig. 1c) follows a photodiode-like behavior: PC is only generated in the $p$–$n$ or $n$–$p$ configuration (see Supplementary Fig. 1c) and can be increased by applying a reverse bias voltage (Fig. 1f).

**Spectral response.** We probe the absorption spectrum in the photoactive region by measuring the PC as a function of photon energy $h\nu$ at a constant laser power $P$ and in-plane electric field $F$. Figure 2a shows the responsivity (PC/$P$) spectra of a device similar to the one presented in Fig. 1c, measured at various $V_B$ and at low temperature ($T = 30$ K) in order to reduce thermal broadening. We observe a pronounced peak at a photon energy $h\nu = 1.73$ eV, corresponding to the A exciton, and a step-like increase around 1.87 eV. For increasing electric field, this step-like feature broadens and an additional shoulder appears at 1.83 eV.

To identify the various spectral features, we compare the experimental spectra with first-principles calculations for a monolayer WSe$_2$ embedded in hBN (see Supplementary Note 3 and Supplementary Fig. 8). By including the electronic screening from the hBN layers in the many-body $\text{G}_0\text{W}_0$ and Bethe–Salpeter Equation (BSE) frameworks$^{34}$ we obtain a bandgap of 1.85 eV and a lowest bound exciton at 1.67 eV in good agreement with the experimental spectra. To account for the effect of a constant in-plane electric field we use a model based on the 2D Wannier functions$^{35}$ for the electron–hole interaction. Figure 2b shows calculated absorption spectra for different in-plane fields $F$. Excellent agreement between experiment and calculations is found assuming a bandgap of 1.9 eV, which yields a binding energy of $E_B = 170$ meV for the A excitons consistent with the first-principles calculations. The unBroadened spectrum calculated at zero field (Fig. 2b, solid black line) confirms the presence of multiple overlapping excited excitonic peaks below the
of the WSe₂. Figure 3a, b shows the strong sublinear power dependence of the photocurrent (and the corresponding responsivity) under resonant pulsed optical excitation (hν = 1.65 eV, see “Methods”). Many physical processes may be responsible for or contribute to the observed sublinearity, including phase space filling and dynamic screening effects (e.g., bandgap renormalization). These many-body effects become intrinsically extinct when the exciton gas approaches the Mott transition. However, recent time-resolved spectroscopy and photoluminescence experiments indicate that in this exciton density regime (10¹¹ ≤ N ≲ 10¹³ cm⁻²), exciton–exciton annihilation (EEA, or exciton Auger recombination) is the dominant decay process for excitons in TMDs. To account for EEA in the rate equation governing the photocurrent we add a loss term that scales quadratically with the exciton density (γN², where γ is the EEA rate). Assuming that each pulse generates an initial exciton population N₀, this model yields PC ∝ ln(1 + γtN₀), which reproduces well the observed sublinear photocurrent (black lines in Figure 3a, b, see Supplementary Note 5). Moreover, the fits capture adequately the variation of the sublinear photocurrent with bias (Figure 3a, b) and gate (Supplementary Figure 10a) voltages, from which we extract the values of 1/γt (Figure 3c). Hence, these nonlinear measurements already offer an indirect way to probe the photocurrent time.

In order to directly extract τ, we resonantly excite A excitons in the p–n junction with a pair of 200 fs-long laser pulses separated by a variable time delay Δt, for various values of Vₛₐₓₚ. Due to the sublinear power dependence, the photocurrent displays a symmetric dip when the two pulses coincide in time (Δt = 0). By extending our nonlinear photocurrent model to the case of two time-delayed pulses (see Supplementary Note 5 and Supplementary Figure 10), we can show that the time dependence of this dip is dominated by an exponential time constant corresponding to the intrinsic photocurrent time τ of the device. The photocurrent rate Γ = τ⁻¹ is extracted from TRPC measurements at various values of Vₛₐₓₚ (Figure 3d, e) and Vₚ (see Supplementary Figure 10d) and presented in Figure 3c. We observe

Excitonic Stark effect. Turning our attention to the A exciton photocurrent peak, we observe a pronounced red-shift as Vₑ increases. We attribute this to the DC Stark effect. In first approximation, the Stark shift of a 1s exciton (without dipole moment) is given by ΔE = −1/2 αF², where α is the in-plane polarizability. As shown in Figure 2d, the A exciton energy shows a quadratic dependence with the maximum in-plane electric field Fₘ calculated for different values of Vₛₐₓₚ and Vₑ (Figure 2e), yielding a polarizability of α = (1 ± 0.2) × 10⁻⁶ Dm/V. This shift matches well with the predicted polarizability of α = 9.4 × 10⁻⁷ Dm/V for Eₑ = 170 meV, thus supporting our previous spectral analysis. Interestingly, we note that the measured in-plane polarizability is two order of magnitude larger than the out-of-plane value recently obtained in PL experiments. This strong anisotropy confirms the 2D nature of the A exciton and demonstrates the advantage of using in-plane electric fields for controlling the optical properties of TMDs.

Photoresponse dynamics. Along with the Stark shift, the application of a large in-plane electric field shortens the lifetime of excitons, which eventually decay into free electrons and holes (Figure 2a). We probe these decay dynamics by assessing the photoresponse time τ of the device with time-resolved photocurrent measurements (TRPC), banking on the nonlinear photoresponse of the WSe₂. Figure 3a, b shows the strong sublinear power dependence of the photocurrent (and the corresponding responsivity) under resonant pulsed optical excitation (hν = 1.65 eV, see “Methods”). Many physical processes may be responsible for or contribute to the observed sublinearity, including phase space filling and dynamic screening effects (e.g., bandgap renormalization). These many-body effects become intrinsically extinct when the exciton gas approaches the Mott transition. However, recent time-resolved spectroscopy and photoluminescence experiments indicate that in this exciton density regime (10¹¹ ≤ N ≲ 10¹³ cm⁻²), exciton–exciton annihilation (EEA, or exciton Auger recombination) is the dominant decay process for excitons in TMDs. To account for EEA in the rate equation governing the photocurrent we add a loss term that scales quadratically with the exciton density (γN², where γ is the EEA rate). Assuming that each pulse generates an initial exciton population N₀, this model yields PC ∝ ln(1 + γtN₀), which reproduces well the observed sublinear photocurrent (black lines in Figure 3a, b, see Supplementary Note 5). Moreover, the fits capture adequately the variation of the sublinear photocurrent with bias (Figure 3a, b) and gate (Supplementary Figure 10a) voltages, from which we extract the values of 1/γt (Figure 3c). Hence, these nonlinear measurements already offer an indirect way to probe the photocurrent time.

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bandgap. The calculated spectra for higher field reproduce remarkably well the field-induced increase of the sub-bandgap absorption observed experimentally. This is a manifestation of the Franz–Keldysh effect, which results from the leakage of the free electron and hole wave functions into the bandgap (inset of Figure 2b). We note that our experimental value of E₀₉ agrees well with the one estimated from the diamagnetic shift of a monolayer WSe₂ encapsulated between silica and hBN. Largely E₀₉ has been observed in SiO₂-supported WSe₂ samples, underlining the role of the dielectric environment on the excitonic properties.

Fig. 3 Determination of the photoresponse time τ by nonlinear and time-resolved photocurrent measurements. a PC vs. laser power P for various Vₑ at Vₛₐₓₚ = 10 V and hν = 1.65 eV. b Responsivity (PC/P) in the same conditions as a. The solid black lines in a and b are fits to the data of PC ∝ ln(1 + γtN₀). c Photoresponse rate Γ = 1/(τₑ) (filled circles, left axis) obtained from the TRPC measurements (shown in d, e and Supplementary Figure 10d) and Δt = 1/(open circles, right axis) obtained from the power dependence measurements (shown in a, b and Supplementary Figure 10a) as a function of Vₛₐₓₚ at Vₑ = 0 V (orange, lower axis) and Vₑ at Vₛₐₓₚ = 10 V (blue, top axis). Good agreement between TRPC and nonlinear PC measurements is found for an EEA rate of γ = 0.05 cm² s⁻¹. The error bars correspond to the standard deviations obtained from the fits. d PC as a function of time delay Δt between two pulses (illustrated above the plot) at various value of Vₛₐₓₚ with time-averaged P = 100 µW and Vₑ = 0 V. e Same data as in d but plotted with the normalized AP'C = PC(Δt=∞)/PC(Δt=0). The solid black lines in d and e are fits to the data using the model described in the Supplementary Note 5.
that $\Gamma$ increases markedly with gate and bias voltages, and remarkably follows the same trend as the values of $1/\tau r$ obtained from the power dependence measurements. Comparing these two results, we obtain an EEA rate of $\gamma \approx 0.05 \text{ cm}^2/\text{s}$, which is similar to those found in WSe$_2$, MoS$_2$, WS$_2$, and TMDs.

**Discussion**

To directly address the exciton dissociation caused by the in-plane electric field $F_M$, we examine the dependence of the photoresponse rate $\Gamma$ on $F_M$ at the p-n junction (Fig. 4a). Clearly, two regimes can be distinguished. The rapid increase of $\Gamma$ with $F_M$ is attributed to dissociation by tunnel ionization. We verify this by comparing the measured $\Gamma$ to the calculated tunnel ionization rate $\Gamma_{\text{tunnel}}$, obtained by introducing the complex scaling formalism in the 2D Wannier–Mott exciton model (see Supplementary Note 4 and Supplementary Table 1). According to this model, $\Gamma_{\text{tunnel}}$ can be evaluated in first approximation by the product of the “attenuated frequency” $\gamma_{\text{attenuated}}$, which scales with $E_B/h$, and the exponential tunneling term $\exp(-E_B/e_0dF_M)$, where $e_0$ is the elementary charge, $d$ is the exciton diameter, and $h$ is the Planck constant. We find that the dependence of $\Gamma$ at low field ($F_M < 15 \text{ V} \mu\text{m}^{-1}$) coincides well with the calculated dissociation rate of excitons with $E_B = 170 \text{ meV}$, in agreement with our photocurrent spectroscopy analysis. More importantly, this shows that in the low-field regime the exciton dissociation process is the rate-limiting step governing the generation of photocurrent. We note that in multilayer TMDs, where $E_B = 50 \text{ meV}$, the ionization rate is two orders of magnitude larger than in the monolayer case, and hence this process was not found to limit the photocurrent rate of multilayer devices.

At high electric field ($F_M > 20 \text{ V} \mu\text{m}^{-1}$), the photocurrent deviates from the dissociation rate-limited model and enters a new regime characterized by a more moderate increase of $\eta$ with $F_M$. The observed linear scaling of $\Gamma(F_M)$ suggests that, in this regime, the photocurrent rate is limited by the drift-diffusive transport of free carriers out of the p–n junction. By considering a carrier drift velocity $v_{\text{drift}} = \mu F$, we estimate that carriers generated in the center of the junction of length $L = 200 \text{ nm}$ escape the junction at a rate $\Gamma_{\text{drift}} = 2\mu F/L$. Comparing this simple expression (dotted line in Fig. 4a) to the measured $\Gamma$ at high field, we find $\mu = 4 \pm 1 \text{ cm}^2/\text{V} \cdot \text{s}$, which is very similar to the room temperature field-effect mobility that we measure in our sample ($\mu_{\text{FE}} \sim 3 \text{ cm}^2/\text{V} \cdot \text{s}$, see Supplementary Note 1).

A complete photocurrent model is achieved by introducing competing loss mechanisms caused by the radiative and non-radiative recombination of excitons (see Supplementary Note 6). Good agreement with the experimental data is obtained by considering the finite lifetime of excitons ($\tau_{r} = 1/\Gamma_{r,N} \sim 1 \text{ ns}$, see Supplementary Note 1) and free carriers ($\tau_{r} = 1/\Gamma_{r,N} \sim 30 \text{ ps}$) at zero electric field. This comprehensive picture of the dynamical processes (Fig. 4b) offers valuable insights into the internal quantum efficiency (IQE) of the photocurrent generation mechanism in this device. Indeed, the efficiency $\eta$ of each
photocurrent step depends on the competition between the PC-generating (τ_{drift}, τ_{diff}) and the loss (τ_{R,N}/,) pathways, such that \( \eta_{\text{loss}} = \frac{\tau_{R,N}}{\tau_{R,N} + \tau_{\text{diff}}/\text{drift}} \). In the inset of Fig. 4a, we compare the IQE measured at low power as a function of \( V_B \) with the total extraction efficiency \( \eta_{\text{extract}} = \eta_{\text{drift}}/\text{derived from the kinetic model shown in Fig. 4b}. We find that \( \eta_{\text{extract}} \) captures very well the bias dependence of the IQE, indicating that we correctly identified the relevant PC-generating processes. The field-independent discrepancy of 30% is attributed to the collection efficiency \( \eta_{\text{collect}} \), which we define as the ratio between the number of excitons reaching the p–n junction and the number of absorbed photons. This value coincides with our analysis of the measured photocurrent profile and with the prediction of our exciton diffusion model (see Supplementary Note 7 and Supplementary Methods).

In summary, our study offers a global understanding of the fundamental mechanisms governing the exciton dynamics and associated photocurrent in monolayer TMDs under in-plane electric field. We demonstrate that despite their large binding energy, photogenerated excitons can rapidly dissociate into free carriers via tunnel ionization, thereby outcompeting recombination processes. Importantly, this knowledge allows us to identify the main material properties that limit photocurrent generation in TMDs such as carrier mobility, exciton binding energy, and lifetime. This provides guidelines in terms of device design, material quality improvement, and Coulomb engineering of the van der Waals heterostructure to further improve the performances of TMD-based optoelectronics devices and develop their applications in vanlelectronics. We finally note that the observed Stark and Franz–Keldysh effects open up exciting opportunities for modulating light with 2D materials.47

Methods

Device fabrication. Exfoliated layers are assembled in a van der Waals heterostructure using the same technique as described in ref. 48. The monolayer of WSe2 is identified by photoluminescence measurement (see Supplementary Note 1). The heterostructure is deposited onto metallic split gates (15 nm palladium) defined by electron-beam lithography on a degenerately doped silicon substrate covered with a 285-nm-thick SiO2 layer. The two graphite flakes are electrically connected by one-dimensional contacts made of Ti/Au (2/100 nm).

Photocurrent measurements. Photocurrent measurements are performed using a photocurrent scanning microscope setup, where a laser beam is focused by a lens into the sample. The monolayer of WSe2 is excited using a pulsed supercontinuum laser (NKT Photonics SuperK Extreme), with a pulse duration of 50 fs and a repetition rate of 40 MHz and tunable wavelength (from 500 to 1500 nm). The data that support the findings of this study are available from the corresponding author on request.

Received: 6 October 2017 Accepted: 19 March 2018
Published online: 24 April 2018

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Acknowledgements

T.G.P. and K.S.T. acknowledge support for CNG by the Danish National Research Foundation, project DNRF103. T.P.G. also acknowledges support for the VKR center of excellence QUASCOPE by the Villum Foundation. M.M. thanks the Natural Sciences and Engineering Research Council of Canada (PGSD3-426325-2012). P.S. acknowledges financial support by a scholarship from the Government of Catalonia trough the SGR grant (2014-SGR-1535), and from the Spanish Ministry of Economy and Competitiveness, through the “Severo Ochoa” Programme for Centres of Excellence in R&D (SEV-2015-0522), support by Fundacio Cellex Barcelona, CERCA Programme/Generalitat de Catalunya and the Mineco grants Ramón y Cajal (RYC-2012-12281) and Plan Nacional (FIS2013-47161-P and FIS2014-59639-JIN). Furthermore, the research leading to these results has received funding from the European Union Seventh Framework Programme under grant agreement no. 696656 Graphene Flagship and the ERC starting grant (307806, CarbonLight).

Author contributions

M.M. conceived and designed the experiments under the supervision of F.H.L.K., M.M., D.D., and F.V. fabricated the samples. M.M. and F.V. carried out the experiments. M.M. performed the data analysis and discussed the results with F.H.L.K., F.V., and P.S. T.G.P. developed the Wannier–Mott exciton model. T.P.G, M.B.L., M.D., and V.I.F. performed the electrostatic calculations, and S.H., S.L., and K.S.T. performed the ab-initio calculations. K.W. and T.T. provided hBN crystals. M.M., F.V., P.S., and F.H.L.K. co-wrote the manuscript, with the participation of T.G.P. and K.S.T.

Additional information

Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-018-03864-y

Competing interests: The authors declare no competing interests.

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