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Dielectric impact on exciton binding energy and quasiparticle bandgap in monolayer WS_2 and WSe_2

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Abstract

Excitons, bound electron-hole pairs in a 2D plane, dominate the optical properties of monolayer transition metal dichalcogenides (TMDs). A large exciton binding energy on the order of 0.5 eV was theoretically predicted and experimentally determined recently. These ultrastable excitons thus open an avenue to explore the exciton physics such as Bose-Einstein condensation and superfluidity at room temperature (Kasprzak et al 2006 Nature 443 409; Plumhof et al 2014 Nat. Mater. 13 247; Fogler et al 2014 Nat. Commun. 5 4555; Jiang and John 2014 Sci. Rep. 4 7432). Recent experiments further demonstrated the concept of Coulomb engineering via dielectric environments based on either solutions or few-layer graphene. However, the conducting nature of these dielectrics can lead to quenching of optical transitions. Thus, in order to utilize 'dielectric tuning' of the exciton binding energy and quasiparticle band gaps, one must use insulating dielectrics. Here, we investigate the impact of insulating dielectric environments on the exciton binding energy of monolayer WS₂ and WSe₂ by exciton Rydberg spectroscopy, in which the dielectric environment is systematically varied from $\kappa = 1.49$ to 3.82. We found that, with increasing κ value, the exciton binding energy and quasiparticle bandgap exhibit significant reductions. Quantitatively, our result follows the prediction of nonlocally-screened Keldysh potential very well. The fitted 2D polarizability, χ_{2D} , agrees rather well with previous density function theory calculations. Their close agreement validates the nonlocally screened Keldysh model which can be used to quantitatively predict the exciton binding energy for monolayer TMDs (and possibly other 2D materials) in different dielectric environments. Such a predictive model will play an important role for the design of van der Waals heterostructures and TMD-based optoelectronic devices.

To determine the exciton binding energy, conventional experimental methods include (1) comparing the quasiparticle bandgap and optical bandgap by scanning tunneling spectroscopy (STS) and photoluminescence (PL) [1–7]; (2) measuring the optical absorption of exciton Rydberg states [8–19]. For STS measurements, highly oriented pyrolytic graphite (HOPG) or graphene are routinely used as a conducting substrate [1–5] which also causes significant PL quenching. Nevertheless, such a

combination has led to the determination of exciton binding energy for TMDs on graphite and graphene [1, 2]. Measuring the optical absorption of exciton Rydberg states is an alternate way to determine the exciton binding energy on a dielectric substrate. A common approach is using two-photon absorption to probe the *p*-like Rydberg states [8, 9, 11, 13, 14]. However, the high-intensity laser pulses may cause dynamic impacts on the electronic band structure [20], making it difficult to access the unperturbed band structure. Another approach is to measure the optical absorption of s-like Rydberg states with low optical power, avoiding the perturbations on the electronic band structure [9, 10]. In WS₂ and WSe₂, due to the large energy separation between the A and B excitons, a series of Rydberg states can be observed which in turns enables one to determine the exciton binding energy as well as the quasiparticle band gap [9, 10, 21]. However, as the exciton binding energy also depends on the dielectric environment [17, 22-29], the quantitative value determined in one system cannot generally be applied to other systems. A recent example of this is the demonstration of Coulomb engineering using graphene layers [28]. For most optoelectronic applications using TMDs, they need to be placed on insulating substrates. Thus, an accurate and systematic determination of exciton binding energy and quasiparticle bandgap as a function of dielectric environment would be very important. More significantly, such studies will enable us to assess theoretical models that can be used to predict these quantities in different dielectric environments. Here, we systematically investigate the impact of dielectric environment on the exciton binding energy and quasiparticle bandgap of monolayer WS₂ and WSe₂ by exciton Rydberg spectroscopy. The exciton binding energy is determined by measuring the s-like exciton Rydberg states using differential reflectance (DR) spectra at low white-light intensity [9, 10].

In this work, TMD monolayers were first prepared by mechanical exfoliation on a polydimethylsiloxane (PDMS) substrate. Next, the monolayers were transferred to other substrates and/or capped by a top dielectric layer. The transition energies of exciton Rydberg states were measured by DR spectroscopy at room temperature. By combining these results with theoretical calculations, the exciton binding energy and quasiparticle bandgap were determined. The impact of the dielectric environment was further investigated by replacing the bottom substrate and top capping layer. We observed a fixed lowest excitonic state energy and significant redshifts of excited-state energy with the increasing dielectric constant, demonstrating the simultaneous shrinkage of exciton binding energy and quasiparticle bandgap. We found the evolution of exciton binding energy was in excellent agreement with the theoretical prediction of the Keldysh potential. We also compared the difference between exfoliated and chemically-grown samples on sapphire substrate. Finally, the overall evolution of the exciton binding energy and quasiparticle bandgap were determined. The 2D polarizability was also obtained from the analyses.

Results

The strong Coulomb interaction between the electrons and holes in monolayer TMDs originates from the carrier confinement in the two-dimensional

(2D) plane, the weak dielectric screening, and the large carrier effective mass [19]. As shown in figure 1(a), the strong Coulomb potential on the order of ~1 eV confines not only the lowest excitonic state but also a few excited states. These 2D excitons with in-plane transition dipoles can be easily accessed by optical measurements [30, 31]. A typical optical image of an exfoliated WS₂ crystal on a sapphire substrate is shown in figure 1(b). The monolayer region (white dashed line) has been identified by PL and Raman spectra (see supplementary figure S1 (stacks.iop. org/TDM/6/025028/mmedia)). Figure 1(c) shows the measured DR spectra $(\Delta R/R)$ of a monolayer WS₂ flake, where the spectral features can be further enhanced by taking the second derivative of $-\Delta R/R$, as shown in figure 1(d). Two pronounced transitions corresponding to the A exciton (X_A) and B exciton (X_B) are identified in the spectra. The energy separation between the A and B excitons originates from the spinorbital splitting in both the conduction and valence bands at the K point of the Brillouin zone [32].

Figure 2(a) shows a zoomed-in second derivative spectrum in the 2.15–2.35 eV range, where some weaker absorption peaks can be observed. These peaks are identified as the Rydberg states with quantum numbers n = 2s - 4s, which are consistently observed in the spectra in different sample areas (see supplementary figure S2). According to the optical selection rule, the measured Rydberg states are dominated by s-like states [9, 10]. We determined the peak energies by using a line-shape model fitting (red curve in figure 2(a) including the multilayer interference effect in the structure. The obtained peak energies are displayed in figure 2(b), showing a large energy difference between the 1s and the 2s states, but much smaller energy differences between higher excited states, consistent with previous reports [9, 10]. The energies of Rydberg states and the exciton binding energy can be calculated by the Keldysh model [33, 34] in the framework of the 2D effective-mass Hamiltonian: $H = -\hbar^2 \nabla_r^2 / 2\mu + V_{eh}(r)$, where μ is the exciton reduced mass with $\mu = (m_e^{-1} + m_h^{-1})^{-1}$ and $V_{eh}(r)$ is the nonlocally-screened 2D Coulomb potential. The non-local Coulomb potential has been derived by Keldysh [33] in the limit of a 2D nanosheet and can be expressed as:

$$V_{
m eh}(r) = -rac{e^2}{8arepsilon_0\kappa r_0} \left[H_0\left(rac{r}{r_0}
ight) - Y_0\left(rac{r}{r_0}
ight)
ight],$$

where H_0 and Y_0 is a Struve function and a Bessel function of the second kind, respectively. The r_0 is the screening length and κ is the average dielectric constant of the environment with $\kappa = (\varepsilon_{top} + \varepsilon_{bottom})/2$, where $\varepsilon_{top} (\varepsilon_{bottom})$ is the dielectric constant of the top (bottom) dielectric layer. In the following analyses, we used the high-frequency dielectric constants in the range of 1.65-2 eV [35, 36]. Note the 'non-local' effect of the dielectric screening has been captured by this potential, showing a reduced dielectric screening for



Figure 1. Measurement of optical transitions by DR spectra. (a) Schematic showing strong Coulomb potential between an electron and hole, confining multiple quantum states of the exciton. In the measurements, we modified the dielectric environment by replacing the bottom substrate and top capping layer. (b) Optical image of exfoliated WS₂ crystal on a sapphire substrate, where the monolayer region is indicated by the white dashed line. (c) DR spectra and (d) the corresponding second derivative spectra for the monolayer WS₂ region shown in (b). Two optical transitions known as X_A and X_B excitons are observed. The energy separation between the A and B excitons originates from the spin–orbit splitting at the *K* points (inset).





a larger exciton radius [10]. The measured Rydberg states were best fit when taking $r_0 = 2.25 \text{ nm}$ and $\mu = 0.16 m_0$ [10, 34], as shown by the gray squares in figure 2(b). The corresponding exciton binding energy E_b (quasiparticle bandgap E_g) is $E_b = 282 \text{ meV}$ ($E_g = 2.3 \text{ eV}$) for the WS₂/sapphire sample.

We have controlled the average dielectric constant κ by replacing the bottom substrate and the top capping layer. Four types of samples were prepared for comparison: (A) PDMS substrate ($\kappa = 1.49$) [37], (B) sapphire substrate ($\kappa = 2.07$) [38], (C) hBN/sapphire substrate ($\kappa = 2.75$) [39] and (D) encapsulated

sample with top hBN capping layer and bottom sapphire substrate ($\kappa = 3.82$). Figure 3(a) shows the second derivative spectra for monolayer WS₂. Clearly, the 1s state exhibits no systematic shift with varying κ . On the contrary, all excited states from 2s to 4s are significantly redshifted with the increasing κ value, indicating a reduced exciton binding energy with the increasing κ value. The nearly unchanged 1s-state energy thus indicates a shrinkage in quasiparticle bandgap by a similar amount of energy. The same phenomenon is observed for monolayer WSe₂ shown in figure 3(b). Figures 3(c) and (d) summarize the energy evolution



Figure 3. Dielectric impact on exciton Rydberg states for monolayer WS₂ and WSe₂. Second derivative spectra of monolayer WS₂ (a) and WSe₂ (b) with different dielectric environments, in which the experimental data (gray dots) are fitted by the line-shape model (color curves) with vertical shifts for clarity. The peaks of Rydberg states are indicated for 2*s* (solid squares), 3*s* (hollow circles) and 4*s* (solid triangles) states. The peak energies of the Rydberg states are summarized for monolayer WS₂ (c) and WSe₂ (d), where the corresponding average dielectric constants κ are labeled.

of Rydberg states for monolayer WS₂ and WSe₂, respectively.

By fitting to the measured Rydberg state energies shown in figures 3(c) and (d), the exciton binding energy $E_{\rm b}$ and quasiparticle bandgap energy $E_{\rm g}$ can be determined, which are summarized in figures 4(a) and (b) for monolayer WS₂ and figures 4(c)and (d) for monolayer WSe2. Both the exciton binding energy and quasiparticle bandgap are reduced with the increasing κ , showing a similar trend for both materials. The evolutions of $E_{\rm b}$ for both materials show a similar trend and agree very well with the prediction of the Keldysh model (orange and blue curves in figures 4(a) and (c)). As κ increases from 1.49 to 3.82, E_b is reduced significantly by 50%, while the $E_{\rm g}$ is decreased by ~200 meV for both TMDs. In the literature, the reported exciton binding energy largely varies due to the different measurement techniques, samples, and substrates, etc (see supplementary figure S3 for comparison). Our results based on exciton Rydberg spectroscopy thus provide a unified database for future references. We have also determined the screening length r_0 as a function of κ (figures 4(e) and (f)). Since r_0 is inversely proportional to κ [23, 34], we fit the screening length by $r_0(\kappa) = 2\pi \chi_{2D} \kappa^{-1}$ (gray lines), where

 χ_{2D} is the 2D polarizability of the TMD. We determined the 2D polarizability to be $\chi_{2D} = 0.78$ nm and $\chi_{2D} = 0.69$ nm for monolayer WS₂ and WSe₂, which are close to the values calculated by density functional theory (DFT) [23, 34].

We have also checked the CVD samples grown on sapphire substrates (see supplementary figure S4). As shown by gray triangles in figures 4(a)and (b), the exciton binding energy is very close to the exfoliated samples albeit the CVD sample shows a somewhat smaller bandgap (~25 meV). CVD samples are known to have higher defect densities and exhibit residual strains [40–44]. Our results indicate that while the bandgap could be affected by strains and/or defects, the exciton binding remains largely unaffected. We have also examined how the value of the exciton reduced mass μ affect our analysis. According to DFT calculations, μ is in the range of $0.15 - 0.22 m_0 (0.17 - 0.26 m_0)$ for monolayer WS₂ (WSe₂) [23, 34, 45–47]. Experimentally, $\mu = 0.2 m_0$ has been reported for monolayer WSe₂ [21]. If we increase the effective reduced mass to $\mu = 0.2 m_0$ for both WS₂ and WSe₂ in our calculations (gray dashed lines in figures 4(a) and (c)), the resulting exciton binding energy only increases by ~10 meV, corre-



Figure 4. Summary of exciton binding energy, quasiparticle bandgap and screening length. (a) and (b) Evolution of the exciton binding energy (a) and quasiparticle bandgap (b) for monolayer WS₂. (c) and (d) Evolution of the exciton binding energy (c) and quasiparticle bandgap (d) for monolayer WSe₂. The dots (triangles) are data from exfoliated (CVD) samples. The simulation curves are based on Keldysh potential. The dielectric impact on the screening length for monolayer WS₂ and WSe₂ is shown in (e) and (f), respectively. The 2D polarizability χ_{2D} are obtained by fitting (gray curves) as explained in the main text.

sponding to an error within ~5% induced by the uncertainty in μ . According to a recent report [48], we noted that the dipole-forbidden p states could be brightened by the disorders in the sample, leading to finite contributions in the linear spectroscopy. However, after estimating the error introduced due to the presence of p states (see supplementary note 1 and supplementary figures S5 and S6), we conclude the measured excitonic states are still dominated by the s states and the effects of p states on the quantitative determination of the exciton binding energy are minimal.

In conclusion, the impact of dielectric environment on the exciton binding energy in monolayer WS₂ and WSe₂ was investigated by exciton Rydberg spectroscopy. We found that both the exciton binding energy and quasiparticle bandgap are reduced with the increasing environmental dielectric constant κ . The evolution of the binding energy with κ is well described by the Keldysh model with the 2D nonlocal Coulomb potential. The 2D polarizability χ_{2D} determined from the fitting of the screening length r_0 agrees with the DFT calculations reported previously [23, 34]. Compared with exfoliated samples, CVD-grown samples show the same exciton binding energy, even though the PL is slightly red-shifted, presumably due to a higher concentration of defects or different strain conditions. Apart from providing a good foundation for future theoretical studies, the exciton binding energy determined in this work is valuable for the studies on exciton physics in monolayer TMDs, van der Waals heterostructures, and TMDs embedded in dielectric cavities for excitonpolariton coupling.

Methods

$\label{eq:stars} Exfoliating and stacking of monolayer WS_2 and \\ WSe_2$

High-quality WS_2 and WSe_2 single crystals (purchased from 2D Semiconductors) were used in this experiment. The TMD monolayers and thick hBN layers were mechanically exfoliated on the PDMS substrate. The thickness of the hBN film was kept larger than 30 nm in order to avoid the incomplete screening effect [49]. We used the modified drytransfer technique [50] to stack those 2D layers on various substrates.

$Growth\,of\,monolayer\,WS_2$

Single-crystal monolayer WS₂ flakes were grown on sapphire substrates via chemical vapor deposition (CVD) in a horizontal hot-wall chamber [51, 52]. The high-purity WO₃ and S powders were used as the source precursors. The sapphire substrate and WO₃ powder were placed at the central heating zone while the S powder was heated by a heating belt at the upstream end. For monolayer WS₂, the growth temperature was 920 °C and the temperature of S powder was set to 150 °C during the growth. All growths were performed in Ar/H₂ gas flow at low pressure condition (5 Torr).

Optical measurements

PL, Raman and DR spectroscopies were performed at room temperature using a back-scattering optical microscope. The light sources were focused on the sample by a $80 \times$ objective lens with N.A. = 0.95, and the signal was sent to a 0.5 m monochromator, then detected by a nitrogen-cooled CCD camera.

- [1] Zhang C, Johnson A, Hsu C-L, Li L-J and Shih C-K 2014 Nano Lett. 14 2443
- [2] Ugeda M M et al 2014 Nat. Mater. 13 1091
- [3] Liu H J, Jiao L, Xie L, Yang F, Chen J L, Ho W K, Gao C L, Jia J F, Cui X D and Xie M H 2015 2D Mater. 2 034004
- [4] Chiu M-H, Zhang C, Shiu H-W, Chuu C-P, Chen C-H, Chang C-Y S, Chen C-H, Chou M-Y, Shih C-K and Li L-J 2015 *Nat. Commun.* 67666
- [5] Zhang C, Chen Y, Johnson A, Li M-Y, Li L-J, Mende P C, Feenstra R M and Shih C-K 2015 *Nano Lett.* **15** 6494
- [6] Rigosi A F, Hill H M, Rim K T, Flynn G W and Heinz T F 2016 *Phys. Rev.* B 94 075440
- [7] Wang Y, Zhang S, Huang D, Cheng J, Li Y and Wu S 2017 2D Mater. 4 015021
- [8] Ye Z, Cao T, O'Brien K, Zhu H, Yin X, Wang Y, Louie S G and Zhang X 2014 *Nature* 513 214
- [9] He K, Kumar N, Zhao L, Wang Z, Mak K F, Zhao H and Shan J 2014 Phys. Rev. Lett. 113 026803
- [10] Chernikov A, Berkelbach T C, Hill H M, Rigosi A, Li Y, Aslan O B, Reichman D R, Hybertsen M S and Heinz T F 2014 *Phys. Rev. Lett.* **113** 076802
- [11] Poellmann C, Steinleitner P, Leierseder U, Nagler P, Plechinger G, Porer M, Bratschitsch R, Schüller C, Korn T and Huber R 2015 Nat. Mater. 14 889
- [12] Hill H M, Rigosi A F, Roquelet C, Chernikov A, Berkelbach T C, Reichman D R, Hybertsen M S, Brus L E and Heinz T F 2015 Nano Lett. 15 2992
- [13] Wang G, Marie X, Gerber I, Amand T, Lagarde D, Bouet L, Vidal M, Balocchi A and Urbaszek B 2015 Phys. Rev. Lett. 114 097403
- [14] Zhu B, Chen X and Cui X 2015 Sci. Rep. 5 9218
- [15] Hanbicki A T, Currie M, Kioseoglou G, Friedman A L and Jonker B T 2015 Solid State Commun. 203 16
- [16] Stier A V, McCreary K M, Jonker B T, Kono J and Crooker S A 2016 Nat. Commun. 7 10643
- [17] Stier A V, Wilson N P, Clark G, Xu X and Crooker S A 2016 Nano Lett. 16 7054
- [18] Robert C et al 2018 Phys. Rev. Mater. 2 011001
- [19] Wang G, Chernikov A, Glazov M M, Heinz T F, Marie X, Amand T and Urbaszek B 2018 Rev. Mod. Phys. 90 021001
- [20] Cunningham P D, Hanbicki A T, McCreary K M and Jonker B T 2017 ACS Nano 11 12601
- [21] Stier A V, Wilson N P, Velizhanin K A, Kono J, Xu X and Crooker S A 2018 *Phys. Rev. Lett.* **120** 057405
- [22] Andersen K, Latini S and Thygesen K S 2015 Nano Lett. 15 4616
- [23] Kylänpää I and Komsa H-P 2015 *Phys. Rev.* B 92 205418
- [24] Latini S, Olsen T and Thygesen K S 2015 Phys. Rev. B 92 245123
- [25] Ryou J, Kim Y-S, Kc S and Cho K 2016 *Sci. Rep.* **6** 29184
- [26] Steinke C, Mourad D, Rösner M, Lorke M, Gies C, Jahnke F, Czycholl G and Wehling T O 2017 Phys. Rev. B 96 045431
- [27] Lin Y, Ling X, Yu L, Huang S, Hsu A L, Lee Y-H, Kong J, Dresselhaus M S and Palacios T 2014 Nano Lett. 14 5569
- [28] Raja A et al 2017 Nat. Commun. 8 15251
- [29] Borghardt S, Tu J S, Winkler F, Schubert J, Zander W, Leosson K and Kardynał B E 2017 *Phys. Rev. Mater.* **1** 054001
- [30] Schuller J A, Karaveli S, Schiros T, He K, Yang S, Kymissis I, Shan J and Zia R 2013 *Nat. Nanotechnol.* 8 271
- [31] Wang G et al 2017 Phys. Rev. Lett. 119 047401
- [32] Zhao W, Ghorannevis Z, Chu L, Toh M, Kloc C, Tan P-H and Eda G 2013 *ACS Nano* **7** 791
- [33] Keldysh LV 1979 JETP Lett. 29 658
- [34] Berkelbach T C, Hybertsen M S and Reichman D R 2013 *Phys. Rev.* B 88 045318
- [35] Knox R S 1963 Theory of Excitons (New York: Academic)
- [36] Bechstedt F 2015 Many-Body Approach to Electronic Excitations (Berlin: Springer)
- [37] Meichner C, Schedl A E, Neuber C, Kreger K, Schmidt H-W and Kador L 2015 AIP Adv. 5 087135
- [38] DeFranzo A C and Pazol B G 1993 Appl. Opt. 32 2224
- [39] Geick R, Perry C H and Rupprecht G 1966 Phys. Rev. 146 543

For PL and Raman measurements, a 532 nm solidstate laser (coherent verdi v10) was used as the excitation source. For DR measurements, the light source was a fiber-coupled tungsten-halogen lamp. The integration time per spectra is around 0.5-1 s, where the signal-to-noise ratio is further improved by averaging >200 spectra. The second derivative spectra is numerically smoothed using the Savitzky– Golay method [53], resulting in an overall energy resolution of ~10 meV.

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Author contributions

CKS and WTH conceived the idea and designed the experiment. WTH performed the spectroscopy measurements and simulations. The samples were exfoliated and stacked by WTH, JMQ, and MC, and supervised by XQL. The CVD samples were grown and characterized by CYW and LSL, and assisted by WHC and LJL. CKS and WTH wrote the paper. All authors discussed the results and commented on the manuscript.

Additional information

Supplementary information is available in the online version of the paper. Correspondence and requests for materials should be addressed to CKS (shih@physics. utexas.edu).

Competing financial interests

The authors declare no competing financial interests.

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- [40] Amani M, Chin M L, Mazzoni A L, Burke R A, Najmaei S, Ajayan P M, Lou J and Dubey M 2014 Appl. Phys. Lett. 104 203506
- [41] Liu Z et al 2014 Nat. Commun. 5 5246
- [42] Park K-D, Khatib O, Kravtsov V, Clark G, Xu X and Raschke M B 2016 *Nano Lett.* **16** 2621
- [43] Amani M et al 2016 ACS Nano **10** 6535
- [44] Hsu W-T et al 2017 Nat. Commun. 8 929
- [45] Ramasubramaniam A 2012 *Phys. Rev.* B **86** 115409
- [46] Xiao D, Liu G-B, Feng W, Xu X and Yao W 2012 Phys. Rev. Lett.
 108 196802
- [47] Shi H, Pan H, Zhang Y-W and Yakobson B I 2013 Phys. Rev. B 87 155304
- [48] Berghäuser G, Knorr A and Malic E 2017 *2D Mater.* 4 015029
- [49] Gerber I C and Marie X 2018 Phys. Rev. B 98 245126
- [50] Kim K et al 2016 Nano Lett. **16** 1989
- [51] Lee Y-H et al 2013 Nano Lett. **13** 1852
- [52] Huang J-K, Pu J, Hsu C-L, Chiu M-H, Juang Z-Y, Chang Y-H, Chang W-H, Iwasa Y, Takenobu T and Li L-J 2014 ACS Nano 8 923
- [53] Savitzky A and Golay M J E 1964 Anal. Chem. 36 1627