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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 WS$_2$ and WSe$_2$ by exciton Rydberg spectroscopy, in which the dielectric environment is systematically varied from $\kappa = 1.49$ to 3.82. We found that, with increasing $\kappa$ 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, $\chi^{2D}$, 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.
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 (ΔR/R) of a monolayer WS₂ flake, where the spectral features can be further enhanced by taking the second derivative of −ΔR/R, as shown in figure 1(d). Two pronounced transitions corresponding to the A exciton (Xₐ) and B exciton (Xₐ) are identified in the spectra. The energy separation between the A and B excitons originates from the spin-orbital 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: 

\[ H = -\hbar^2 \nabla^2 / 2 \mu + V_{eh}(r), \]

where \( \mu \) 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:

\[ V_{eh}(r) = -\frac{\varepsilon^2}{8\varepsilon_0 \kappa r_0} \left[ H_0 \left( \frac{r}{r_0} \right) - Y_0 \left( \frac{r}{r_0} \right) \right], \]

where \( H_0 \) and \( Y_0 \) are a Struve function and a Bessel function of the second kind, respectively. The \( r_0 \) is the screening length and \( \kappa \) is the average dielectric constant of the environment with \( \kappa = (\varepsilon_{\text{top}} + \varepsilon_{\text{bottom}}) / 2 \), where \( \varepsilon_{\text{top}} (\varepsilon_{\text{bottom}}) \) 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
a larger exciton radius \[10\]. The measured Rydberg states were best fit when taking \(n_0 = 2.25 \text{ nm}\) and \(\mu = 0.16 \mu_0\) \[10, 34\], 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 WS\(_2\)/sapphire sample.

We have controlled the average dielectric constant \(\kappa\) 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 WSe\(_2\). Clearly, the 1s state exhibits no systematic shift with varying \(\kappa\). On the contrary, all excited states from 2s to 4s are significantly redshifted with the increasing \(\kappa\) value, indicating a reduced exciton binding energy with the increasing \(\kappa\) 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 WSe\(_2\) shown in figure 3(b). Figures 3(c) and (d) summarize the energy evolution

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**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 WS\(_2\) 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 WS\(_2\) 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 \(\mathbf{K}\) points (inset).

**Figure 2.** Determination of exciton binding energy by Rydberg states. (a) The zoomed-in second derivative spectrum of the WS\(_2\) monolayer on a sapphire substrate, showing exciton Rydberg states from 2s to 4s in the 2.15–2.35 eV range. The transition energies of Rydberg states are determined by model fitting (red curve). (b) Comparison of measured exciton Rydberg states (red dots) and calculated ones by the Keldysh potential (gray squares). The exciton binding energy \(E_b\) and quasiparticle bandgap \(E_g\) are simultaneously determined by this procedure.
of Rydberg states for monolayer WS\(_2\) and WSe\(_2\), respectively.

By fitting to the measured Rydberg state energies shown in figures 3(c) and (d), the exciton binding energy \(E_b\) and quasiparticle bandgap energy \(E_g\) can be determined, which are summarized in figures 4(a) and (b) for monolayer WS\(_2\) and figures 4(c) and (d) for monolayer WSe\(_2\). Both the exciton binding energy and quasiparticle bandgap are reduced with the increasing \(\kappa\), showing a similar trend for both materials. The evolutions of \(E_b\) 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 \(\kappa\) increases from 1.49 to 3.82, \(E_b\) is reduced significantly by \(\sim 50\%\), while the \(E_g\) is decreased by \(\sim 200\) 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.

\[ r_0 (\kappa) = \frac{2\pi \chi_{2D} \kappa^{-1}}{ \kappa} \] (gray lines), where \(\chi_{2D}\) is the 2D polarizability of the TMD. We determined the 2D polarizability to be \(\chi_{2D} = \) 0.78 nm\(^2\) and \(\chi_{2D} = \) 0.69 nm\(^2\) for monolayer WS\(_2\) and WSe\(_2\), 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 \(\mu\) affect our analysis. According to DFT calculations, \(\mu\) is in the range of \(0.15 – 0.22 m_0\) (0.17 – 0.26 \(m_0\)) for monolayer WS\(_2\) (WSe\(_2\)) [23, 34, 45–47]. Experimentally, \(\mu = 0.2 m_0\) has been reported for monolayer WSe\(_2\) [21]. If we increase the effective reduced mass to \(\mu = 0.2 m_0\) for both WS\(_2\) and WSe\(_2\) in our calculations (gray dashed lines in figures 4(a) and (c)), the resulting exciton binding energy only increases by \(\sim 10\) meV, corre-

Figure 3. Dielectric impact on exciton Rydberg states for monolayer WS\(_2\) and WSe\(_2\). Second derivative spectra of monolayer WS\(_2\) (a) and WSe\(_2\) (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 2s (solid squares), 3s (hollow circles) and 4s (solid triangles) states. The peak energies of the Rydberg states are summarized for monolayer WS\(_2\) (c) and WSe\(_2\) (d), where the corresponding average dielectric constants \(\kappa\) are labeled.
sponding to an error within ~5% induced by the uncertainty in $\mu$. 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 WS$_2$ and WSe$_2$ 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 $\kappa$. The evolution of the binding energy with $\kappa$ is well described by the Keldysh model with the 2D non-local Coulomb potential. The 2D polarizability $\chi^{2D}$ 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 exciton-polariton coupling.

**Methods**

**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 dry-transfer technique [50] to stack those 2D layers on various substrates.

**Growth of monolayer WS$_2$**

Single-crystal monolayer WS$_2$ flakes were grown on sapphire substrates via chemical vapor deposition (CVD) in a horizontal hot-wall chamber [51, 52]. The high-purity WO$_3$ and S powders were used as the source precursors. The sapphire substrate and WO$_3$ powder were placed at the central heating zone while the S powder was heated by a heating belt at the upstream end. For monolayer WS$_2$, 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/H$_2$ 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× 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.
For PL and Raman measurements, a 532 nm solid-state 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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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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