Resonant laser spectroscopy of localized excitons in monolayer WSe$_2$

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Coherent quantum control and resonance fluorescence of few-level quantum systems is integral for quantum technologies. Here we perform resonance and near-resonance excitation of three-dimensionally confined excitons in monolayer WSe$_2$ to reveal near-ideal single-photon fluorescence with count rates up to 3 MHz. Using high-resolution photoluminescence excitation spectroscopy of the localized excitons, we uncover a weakly fluorescent exciton state $\sim 5$ meV blue shifted from the ground-state exciton, providing important information to unravel the precise nature of quantum states. Successful demonstration of resonance fluorescence paves the way to probe the localized exciton coherence in two-dimensional semiconductors.

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1. INTRODUCTION

Near-resonance optical excitation of quantized matter underpins the field of quantum photonics. It enables the initialization, coherent manipulation, and readout of the quantum states [1–6] and, via resonance fluorescence [7,8], the generation of indistinguishable single photons [9–12], a crucial resource for future quantum technologies [13]. In the solid state, such quantum optical demonstrations have been made with quantum dots [1–4,7,12], single molecules [8,9], and crystal defects [5,6,11]. For fundamental investigations, resonant or near-resonant optical excitation is invaluable to probe the coherence and dephasing mechanisms in few-level quantum systems.

Rapid progress has recently been made in understanding the two-dimensional exciton (2D-X), spin, and valley-pseudospin properties in monolayer transition metal dichalcogenide (TMD) semiconductors [14–16]. The first Brillouin zone of a monolayer TMD, such as MoS$_2$, WSe$_2$, WS$_2$, or MoSe$_2$, has a hexagonal shape that accommodates three pairs of degenerate but inequivalent edges, often denoted by $K$ and -$K$, which exhibit a direct bandgap with unique selection rules: for W-based TMDs, left-(right-) handed circular polarized photons couple to interband transitions in the $K$ (-$K$) valley only [15–18]. Further, strong spin-orbit coupling links the spin and the valley pseudospin, giving rise to spin-dependent optical selection rules. Also unique to these semiconductors with intrinsic two-dimensional confinement are very strong Coulomb interactions, large effective masses, and reduced dielectric screening, which lead to large exciton binding energies ($\approx 0.5$ eV) and small Bohr radii ($<1$ nm) [19,20].

Recently, localized excitons that exhibit substantially reduced linewidths compared to 2D-X have been discovered in two-dimensional materials [21–28]. However, besides their basic magneto-optical properties, these quantum emitters have yet to be explored in detail. Fundamental open questions revolve around the precise nature of three-dimensional confinement and its effect on emitter properties, e.g., spin-orbit coupling and valley hybridization [29], which impact the potential for a coherent spin-valley qubit that can be coherently controlled with near-resonance optical excitation [30].

Here we focus on single quantum emitters in WS$_2$, in which a range of observed magneto-optical properties are broadly categorized as follows: (i) emitters with a fine-structure splitting (FSS) of 0.6–0.8 meV caused by exchange interactions that exhibit a large (7–10) exciton g-factor [21–24,26]. The FSS doublet typically exhibits equal intensity and orthogonal linear polarization, but not exclusively [26]. (ii) Emitters with a smaller FSS doublet ($\approx 0.3$ meV) with approximately parallel linear polarization and a very small g-factor. (iii) Spectral lines without measurable FSS that do not exhibit any or extremely small Zeeman splitting even for $B_{ext} = 9$ T [22]. These emitters are typically linearly polarized, and the degree of linear polarization is unchanged with a magnetic field. In this paper, we investigate emitters in categories (ii) and (iii).
2. ISOLATED QUANTUM EMITTER WITH HIGH-PURITY SINGLE-PHOTON EMISSION

First, we show in Fig. 1 that monolayer WSe$_2$ is a suitable host for a pure single-photon emitter. Under nonresonant excitation, a highly spectrally and spatially isolated emitter delivers single-photon emission with a single-photon purity $g^{(2)}(0) \approx 2\%$ and a single-photon count-rate $> 3$ MHz at saturation. A low-resolution microphotoluminescence ($\mu$-PL) spectrum of emitter A, described by emitter category (iii) above, is shown in Fig. 1(a). In contrast to all previous observations, where sharp emission lines have been accompanied by extraneous emissions from other localized emitters or 2D-X [21–28], here we demonstrate an emission spectrum dominated by a single quantum emitter. The 2D-X emission is highly suppressed as the optically excited electron-hole pairs are efficiently captured by a single confined exciton. The left inset of Fig. 1(a) shows the high-resolution $\mu$-PL spectrum, revealing the zero-phonon line (ZPL) and a low-energy phonon sideband (PSB). The intensity ratio of ZPL:PSB is $\approx 60:40$. Figure 1(b) presents the second-order correlation function $g^{(2)}(\tau)$ under nonresonant CW excitation. Using Bayesian statistics (see Section IV of Supplement 1 for details) to fit (solid lines) the measured data (closed circles), we obtain a deconvolved $g^{(2)}(0) = 0.022 \pm 0.004$ (see also the right inset of Fig. 1(b) for the probability density plot). This high single-photon purity is essential for future quantum photonic applications.

3. RESONANCE FLUORESCENCE FROM A SINGLE QUANTUM EMITTER

We now present resonance fluorescence (RF) from a single quantum emitter in monolayer WSe$_2$. Emitter B, belonging to emitter category (ii) above, was chosen due to its favorable wavelength ($\lambda \approx 784.69$ nm) for our tunable laser diode and good spatial and spectral isolation [see right inset of Fig. 1(a)]. Nonresonant $\mu$-PL was first used to identify the ZPL wavelength, and then the excitation laser was tuned into the resonance. The background laser scattering was highly, but not completely, suppressed using orthogonal linear polarizers in the excitation and collection arms of the microscope (see Section 7). We split the RF signal into two parts: 70% was measured by an avalanche photodiode (APD) [see Fig. 2(a)] and 30% by a spectrometer [see Fig. 2(b)]. By fitting each spectrum in Fig. 2(b), the emitter peak energy detuning ($\delta = E_{\text{emitter}} - E_p$, where $E_p$ is the peak emission energy), is determined [see Fig. 2(c)]. Two example spectra with fits are shown in Fig. 2(e). The single photon count-rate dynamics are directly correlated with $\delta$. We ascribe the slow spectral fluctuations to charge noise in the emitter environment, similar to that observed in semiconductor quantum dots [31,32]. A maximum count rate (mean background level) of $\approx 1.7 \times 10^{-4}$ MHz is observed when the emitter is in resonance (out of resonance) with the excitation laser. A second-order coherence measurement during a time interval when the emitter was in resonance with the excitation laser yielded $g^{(2)}(0) = 0.341 \pm 0.007$, conclusively demonstrating that the RF signal is indeed composed of quantum light [see Fig. 2(d)]. A signal-to-background of $\approx 4.3$ is obtained by fitting the measured antibunching data, in agreement with the maximum signal and background count rates shown in Fig. 2(a).

4. HIGH-RESOLUTION LASER SPECTROSCOPY AND OBSERVATION OF A WEAKLY FLUORESCENT BLUE-SHIFTED EXCITON (BS-X)

The polarization properties of emitter B under nonresonant excitation are shown in Fig. 3(a). The brightest peak $p_1$ is accompanied by peak $p_2$ ($p_0$) on its low- (high-) energy side, energetically separated by $\approx 330$ (600) $\mu$eV. The polarization-resolved $\mu$-PL map [see Fig. 3(a): bottom] shows that peaks $p_1$ and $p_2$ are linearly polarized along almost the same direction, and peak $p_0$ is polarized at slightly different angle (see Section I of Supplement 1 for the quantitative analysis). Notably, under resonant excitation conditions [see Figs. 2(b) and 2(e) and Figs. S2 and S3 of Supplement 1], emission from $p_2$ is highly suppressed compared to the nonresonant excitation. This result provides a hint that a specific valley index can be optically addressed, encouraging further investigations.

The photoluminescence excitation (PLE) spectrum of emitter B over an extended range of detuning is shown in Fig. 3(b). The closed (open) circles are obtained using the conventional (high-resolution) PLE method. For the conventional method, the resonant laser was scanned manually with a step size of $\approx 100$ $\mu$eV, and the integrated intensity of peak $p_1$ was recorded. This method...
Fig. 2. Simultaneous time traces of the fluorescence from emitter B under resonant CW excitation at $\lambda = 784.69460$ nm with a power of 1 $\mu$W as recorded on (a) an APD and (b) a high-resolution spectrometer with 70 ms and 5 s integration, respectively. The background level of 0.4 MHz shown by a horizontal dashed line in (a) and the line at $\sim 1580.03$ meV in (b) is due to the scattered excitation laser. (c) The time trace of emitter detuning $\delta = E_{\text{laser}} - E_{\text{p1}}$ of the dominant emission line $p_1$ of emitter B. The gray area is the fitting errors of $\delta$. (d) $g^{(2)}(r)$ for a time interval when $\delta \neq 0$. The solid thick line is a 95% confidence band for fitting of the measured data. The dashed line shows the experimental limitation for $g^{(2)}(0)$ due to the scattered laser background. (e) The fluorescence spectra of emitter B at two different time instances marked by black (blue) dashed lines in (a)–(c) corresponding to time $t = 12.8$ (16.2) min for $\delta = 10$ (190) $\mu$eV. The black (blue) closed circles are measured data and solid lines are fits.

does not allow us to measure the resonances with an accuracy better than $\sim 100$ $\mu$eV due to the spectral fluctuations that could occur over the acquisition time of a single $\mu$-PL spectrum. We take advantage of these spectral fluctuations over time to perform high-resolution PLE spectroscopy. This is done by keeping the laser at a fixed wavelength and allowing the spectral fluctuations to detune the emitter randomly, which can then be determined with a fitting limited accuracy of $\pm 5$ $\mu$eV. This allows us to measure several $\delta$ values and corresponding intensities at a single excitation wavelength. The resonances of peaks $p_1$, $p_0$, and a high-energy PSB are clearly resolved. More importantly, an additional resonance peak, blue shifted by $\sim 4.75$ meV from $p_1$, is also observed. The $\mu$-PL spectrum of emitter B under nonresonant excitation shows negligible emission at this energy (see Fig. S2 of Supplement 1).

To investigate if the blue-shifted exciton (BS-X) observed in PLE is an intrinsic property of the quantum emitters in monolayer WSe$_2$, we probe a third emitter. Emitter C, from the same monolayer flake and belonging to emitter category (iii), exhibits a BS-X detuned from the ground state exciton by $5.07 \pm 0.01$ meV. We compare the PLE spectrum [Fig. 4(a)] with a $\mu$-PL spectrum [Fig. 4(b)], which has a high-resolution, logarithmic intensity scale spectrum shown in the inset. Compared to the ground-state exciton, the $\mu$-PL emission from BS-X is suppressed by a factor of 1,250.

5. HIGH-PURITY SINGLE-PHOTON EMISSION UNDER RESONANT EXCITATION OF BS-X

Finally, we establish high-purity single-photon emission from the ground-state exciton under the resonant excitation of the BS-X state. Figure 4(c) shows a spectrum consisting of the low-energy bright exciton emission and the scattered excitation laser due to imperfect polarization cancellation. This laser peak can be filtered with high fidelity, enabling clean $g^{(2)}(r)$ measurements, as shown in Fig. 4(d). A deconvolved $g^{(2)}(0)$ value of $<0.002$ is achieved, demonstrating a single-photon source with perfect purity.
and BS-X. Tantalizingly, unlike with strict resonance fluorescence, the BS-X offers future opportunities to investigate spin-valley coupling using excitation and fluorescence detection in both co-polarized and cross-polarized configurations.

We have demonstrated that monolayer WSe$_2$ is a benevolent host for a pure single-photon emitter. These quantum emitters yield bright, stable, and highly pure quantum light. The two-dimensional nature of the platform provides unique opportunities to engineer the light-matter interaction and integrate onto quantum photonic chips. We unambiguously achieve resonance fluorescence from the quantum emitters in spite of significant spectral fluctuations and background laser scattering. Strategies such as incorporating the single-photon emitters into tunable electronic devices and surface passivation or encapsulation are likely to provide significant improvement. While the spectral fluctuations create challenges for quantum control and resonance fluorescence, we also demonstrate its utility for high-resolution PLE spectroscopy. PLE yields the direct observation of a three-dimensionally confined weakly fluorescent exciton state that is energetically blue shifted by $\sim$5 meV. Resonant excitation of this BS-X state provides an extremely robust and pure single-photon source. The high-resolution characterization of the bright-exciton fine structure and the experimental observation of the BS-X are important results to better understand the specific nature of these localized excitons. The resonance fluorescence and laser spectroscopy techniques demonstrated here raise the prospect for indistinguishable single-photon generation and investigations of the spin and valley coherence of strongly confined excitons in 2D-TMDs.

7. METHODS

Sample fabrication: Using an all-dry viscoelastic stamping procedure [36], we integrate a mechanically exfoliated WSe$_2$ flake onto a few layers of h-BN on top of a piezoelectric actuator so that in-plane dynamic strain could be induced in the flake by applying an out-of-plane electric field to the actuator. The actuator is made of a PMN-PT substrate. In the context of this paper, all experiments have been performed at the zero external electric field to the actuator, and therefore, both the top and bottom Ti/Au (5/100 nm) electrodes of the actuator have been grounded. All measurements have been performed on a single monolayer, which has been identified using optical micrographs and spatial maps of $\mu$-PL.

Experimental Setup: A confocal microscope with an objective lens with an NA of 0.82, yielding a diffraction limited focus of $\sim$460 nm at $\lambda = 750$ nm, was used for resonant laser spectroscopy. A CW tunable laser diode, covering a wavelength range of 765–805 nm, was used for resonant excitation. $\lambda = 532$ nm was used for nonresonant CW excitation. The fluorescence signal was separated from the excitation laser via orthogonally oriented linear polarizers in the excitation and collection arms of the microscope. This yields a $10^7$ suppression of laser counts on smooth substrates, but the rough gold surface used here yields $10^5$ suppression at best. The sample was placed on automated nanopositioners at $T = 4$ K in a closed-cycle cryostat. All spectra were acquired with a 0.5 m focal length spectrometer and a nitrogen-cooled charge-coupled device with a measured spectral resolution of $\sim$75 $\mu$eV at $\lambda = 784$ nm for an 1800 l/mm grating. A separate confocal microscope is used to perform the polarization-resolved $\mu$-PL measurements. A fiber-based Hanbury Brown and Twiss interferometer was used for second-order correlation measurements, and photon counting was performed using Si APDs.
REFERENCES


