Probing excitonic dark states in single-layer tungsten disulphide

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Transition metal dichalcogenide (TMDC) monolayers have recently emerged as an important class of two-dimensional semiconductors with potential for electronic and optoelectronic devices1-2. Unlike semimetallic graphene, layered TMDCs have a sizeable bandgap3. More interestingly, when thinned down to a monolayer, TMDCs transform from indirect-bandgap to direct-bandgap semiconductors4-5, exhibiting a number of intriguing optical phenomena such as valley-selective circular dichroism6-8, doping-dependent charged excitons9-10 and strong photocurrent responses11. However, the fundamental mechanism underlying such a strong light–matter interaction is still under intensive investigation. First-principles calculations have predicted a quasi-particle bandgap much larger than the measured optical gap, and an optical response dominated by excitonic effects12-14. In particular, a recent study based on a GW plus Bethe–Salpeter equation (GW-BSE) approach, which employed many-body Green’s-function methodology to address electron–electron and electron–hole interactions, theoretically predicted a diversity of strongly bound excitons14. Here we report experimental evidence of a series of excitonic dark states in single-layer WS2 using two-photon excitation spectroscopy. In combination with GW-BSE theory, we prove that the excitons are of Wannier type, meaning that each exciton wavefunction extends over multiple unit cells, with extraordinarily large binding energy (~0.7 electronvolts), leading to a quasiparticle bandgap of 2.7 electronvolts. These strongly bound exciton states are observed to be stable even at room temperature. We reveal an exciton series that deviates substantially from hydrogen models, with a novel energy dependence on the orbital angular momentum. These excitonic energy levels are experimentally found to be robust against environmental perturbations. The discovery of excitonic dark states and exceptionally large binding energy not only sheds light on the importance of many-electron effects in this two-dimensional gapped system, but also holds potential for the device application of TMDC monolayers and their heterostructures in computing, communication and bio-sensing.

An exciton is a bound state formed by an excited electron and hole owing to the Coulomb attraction between these two quasiparticles12. Such bound states often play an important role in the optical properties of low-dimensional materials14, owing to their strong spatial confinement and reduced screening effect compared to bulk solids. In a two-dimensional (2D) gapped system with dipole-allowed interband transitions, the optical absorption spectrum in the non-interacting limit exhibits a step function. Strong electron–hole interaction redshifts a large amount of the spectral weight, resulting in a qualitatively different spectrum with a series of new excitonic levels below the quasiparticle bandgap. In quasi-2D quantum wells, the electron–hole interaction is weak. Therefore, by measuring the energy difference between the first excitonic peak and band-edge absorption step, the exciton binding energy can be unambiguously determined; it usually has an energy of tens of meV and is vulnerable to environment screening and temperature broadening. However, recent experiments on a single-layer TMDC like MoS2 found no absorption step14. Instead, two absorption peaks from spin–orbit splitting were detected5-6 around the Kohn–Sham bandgap energy, as given by density functional theory (DFT) within the local density approximation. The peaks were initially interpreted as direct band edge transitions. In sharp contrast, more accurate first-principles calculations on MoS2 monolayer using the GW method18 predicted a quasiparticle bandgap that was larger than the initial experimental reported value by nearly one electronvolt10-14. Relevant calculations based on first-principles GW–BSE theory14 showed this energy gap discrepancy to originate in strong excitonic effects. It is therefore critical to uncover the underlying physics of the strong light–matter interaction in such a 2D system.

We probed the excitonic effects in monolayer WS2, also an important TMDC material, using two-photon excitation spectroscopy20. At the simplest level, if an electron–hole pair interacts through a Coulomb attractive central potential, it will form a series of excitonic Rydberg-like states with definite parity, similar to the hydrogen model. For WS2, the breaking of rotational and inversion symmetry owing to the crystal structure and the spatial dependence of screening will modify the energy and symmetry of the states from those of the 2D Rydberg series. However, for exciton states with an electron–hole wavefunction that is large compared to the unit cell size (as shown below for WS2), specific parity may still be assigned to each excitonic state. Incident photons can excite the electronic system from the ground state to one of these excitonic states (Fig. 1a). In addition to energy conservation, the selection rule of such a transition depends on the symmetry of the final state: for systems with dipole-allowed interband transitions (which is the case for WS2), one-photon transitions can only reach excitonic states with even parity, while two-photon transitions reach states with odd parity. The two-photon resonances are also known as excitonic dark states as they do not appear in the linear optical spectrum. These dark states are good gauges for excitonic effects, since there is little impurity and bandgap absorption background in the two-photon spectrum. Owing to the direct bandgap in this WS2 monolayer, we monitor the two-photon absorption induced luminescence (which we abbreviate to two-photon luminescence, TPL) with a high signal-to-noise ratio. The luminescence results from the radiative recombination of the excitonic ground state, following the rapid non-radiative relaxation from the two-photon excited excitonic dark states to the exciton ground state (Fig. 1a). By scanning the excitation laser energy, we obtain a complete two-photon spectrum, assuming the relaxation and emission efficiency are independent of the excitation energy.

Our samples are WS2 monolayers directly exfoliated on fused quartz substrates. A typical light emission spectrum is shown in Fig. 1b, excited by an ultrafast laser (pulses of 190 fs duration) at a wavelength of 990 nm (1.25 eV) at a sample temperature of 10 K. The two peaks observed at 2.0 eV and 2.04 eV correspond to the exciton and negatively charged trion emissions from the direct bandgap at K and K’ valleys in the Brillouin zone, consistent with the absorption peaks in the reflectance spectrum (Supplementary Information section S1). The emitted photon energies of both peaks are much higher than those of the excitation photon, and
valence band maximum. and VBM represent respectively the conduction band minimum and the excitonic envelope wavefunction character. CBM of a plateau background. For comparison, the one-photon absorption spectrum is measured in single-layer WS₂ at 10 K. In the two-photon absorption spectrum, the peaks at 2.04 eV and 2 eV are the A exciton (1s state) and its trion peak, respectively. The lower-energy peak is stronger than the higher-energy one due to the exciton–trion equilibrium reached during the emission stage at low temperature. The excitation pulse is at 1.25 eV with a pulse width of about 190 ± 20 fs, which results in the 2.5 eV peak as the SHG signal. Inset, the power dependence of the SHG and TPL signals. At a low excitation level, both of them exhibit quadratic power dependence, confirming the two-photon absorption nature of the luminescence, until the TPL signal saturates at a high excitation level. The TPL signal represents the amplitude of the trion peak.

Figure 1 | Probing the dark exciton states in single-layer WS₂ by two-photon luminescence. a. Schematic of the two-photon luminescence (TPL) process in single-layer WS₂. Under two-photon excitation, electrons transition to one of the excitonic dark states with odd parity (double green arrow). Following the excitation, the exciton experiences a fast relaxation to the excitonic ground state (grey arrow) and emits a photon (red arrow). The two-photon selection rule exclusively eliminates the one-photon transition background and reveals the excitonic excited states. States are labelled s (red) or p (green) according to the excitonic envelope wavefunction character. CBM and VBM represent respectively the conduction band minimum and the valence band maximum. b. Main panel: measured WS₂ emission spectrum excited by an ultrafast pulsed laser at 10 K. The peaks at 2.04 eV and 2 eV are the A exciton (1s state) and its trion peak, respectively. The lower-energy peak is stronger than the higher-energy one due to the exciton–trion equilibrium reached during the emission stage at low temperature. The excitation pulse is at 1.25 eV with a pulse width of about 190 ± 20 fs, which results in the 2.5 eV peak as the SHG signal. Inset, the power dependence of the SHG and TPL signals. At a low excitation level, both of them exhibit quadratic power dependence, confirming the two-photon absorption nature of the luminescence, until the TPL signal saturates at a high excitation level. The TPL signal represents the amplitude of the trion peak.

Figure 2 | Extraordinarily strong excitonic effect in monolayer WS₂. Two-photon absorption (blue) and one-photon absorption (green) spectra are measured in single-layer WS₂ at 10 K. In the two-photon absorption spectrum, 2p and 3p resonances are observed at 2.28 eV and 2.48 eV, respectively, on top of a plateau background. For comparison, the one-photon absorption spectrum, measured as the relative reflectance signal (δR/R), exhibits no corresponding features except a B exciton (1s) related absorption resonance at 2.45 eV. Additionally, the A exciton (1s₀) and trion (1s₋) absorption peaks are detected consistently with the TPL emission peaks (Fig. 1b), with a 20 meV Stoke shift, and are marked at 2.04 and 2 eV, respectively, by black dashed lines. The energy difference between the A exciton 1s state emission peak and the 3p state absorption peak is 0.44 eV, which yields the lower bound for the exciton binding energy in monolayer WS₂. This binding energy is extraordinarily large for a Wannier exciton, and implies a dominating excitonic mechanism for the intense light–matter interaction in 2D TMDCs. The total excitation scan is achieved by tuning an output beam of an optical parametric oscillator over a 600 meV span, with a scanning resolution of about 15 meV (Supplementary Information section S3). Similar results are repeated in more than 5 flakes.

Therefore they can only originate from TPL. The peak at 2.5 eV is the second harmonic generation (SHG) emission. The two-photon origin of these emissions is further confirmed in Fig. 1b inset. Both the TPL and SHG signals show a quadratic power dependence, suggesting that the emission is indeed induced by two-photon absorption. The TPL saturates at higher power as a consequence of heating or exciton–exciton annihilation effects. The trion peak amplitude is selected as our TPL signal.

We collect the TPL signal, while scanning the excitation laser energy from 2.05 to 2.6 eV, to acquire the full two-photon spectrum. We observed two important resonances of similar linewidths in the two-photon spectrum, occurring at 2.28 and 2.48 eV, corresponding to two excitonic dark excited states (Fig. 2). The absorption spectrum of a WS₂ monolayer is plotted for comparison, where the A exciton (the 1s state) and its trion result in two absorption peaks at 2.04 eV and 2 eV, respectively. Near these one-photon resonances, TPL is negligible, consistent with the 1s nature of these states. On the other hand, no significant one-photon absorption is observed near the excitonic dark states, except for the B exciton (the other 1s state) at 2.45 eV which results from the spin–orbit splitting in the valence band. Such a complementary feature reflects the symmetry of the observed excitonic states. Hence, we label the TPL peaks as the 2p and 3p state of the A exciton series. Accordingly, the 1s–2p and 1s–3p separations are 0.24 eV and 0.44 eV, respectively. The extraordinarily large 1s–np separations suggest that the exciton binding energy, defined as the separation between the 1s exciton ground state and the conduction band edge, is larger than 0.44 eV, which also indicates a significant self-energy contribution to the quasi-particle bandgap. Our discovery demonstrates that the previously claimed band-to-band transition mechanism in the optical response of monolayer WS₂ is inaccurate, as we show here that the optical response is dominated by excitonic states within the bandgap, in agreement with the GW-BSE calculation of MoS₂ (ref. 14). The real quasiparticle bandgap is much larger than previously reported. This finding is expected be general for other TMDC monolayers of similar structure.

We used the ab initio GW method to calculate the quasiparticle band structure and the ab initio GW–BSE approach to calculate the excitonic states and optical spectrum of a WS₂ monolayer (Fig. 3a), employing the BerkeleyGW package. The principal and orbital quantum numbers of
The calculated positions of the 1s2, 2p3 and 3p4 states of the A exciton are at 2.05 eV, 2.28 eV and 2.49 eV, respectively, and are in excellent agreement with the experimental measurements. Although the orbital notation of a 2D hydrogen atom is adopted to label the exciton states, the excitonic series significantly deviates from a hydrogenic series, as discussed in the main text. The degeneracy labels in the superscript include both the degeneracy of valleys and orbital angular momentum.

The degeneracy is known as the anti-screening effect in 1D carbon nanotubes and as the dielectric confinement effect in 2D quantum wells. Since the wavefunction of excitonic states with higher principal or higher orbital quantum number features a larger nodal structure near the hole (that is, a larger average electron–hole separation), weaker screening at larger separation leads to enhanced Coulomb attraction in the excited states and therefore a lowering of their excitation energies as compared with those of the hydrogen model. Also, because of the degeneracy of the K and K' valleys in the TMDC system, each s level has two degenerate states, while each p and d level has four degenerate states if perfect rotational symmetry is assumed. All of these features are expected to be quite general for 2D TMDC excitons.

The GW quasiparticle bandgap is calculated to be ~2.7 eV, indicated by the blue arrow in Fig. 3. Comparing this with the 1s exciton energy found in either our experiments or our GW-BSE calculations, we obtain an exciton binding energy of ~0.7 eV. Such an exceptionally large binding energy is more than ten times that found for the excitons in bulk WS2 (ref. 3) and other traditional bulk semiconductors such as Si and GaAs (ref. 16), and comparable to those found for excitons in carbon nanotubes and inorganic–organic hybrid perovskites.

In spite of its Wannier character, we found that the exciton series in monolayer WS2 deviates significantly from a 2D hydrogen model. Much smaller splitting between 1s and other excited states is observed, in accordance with recent GW–BSE calculations (see detailed comparisons in Supplementary Information section S4). In addition, in a hydrogen atom, orbitals with the same principal quantum number are degenerate. However, for the WS2 excitons, our calculations show that states in the same shell but of higher orbital angular momentums are at lower energy levels, that is, E3d < E3p < E3s. These two exotic energy-level behaviours are caused by a strong spatial-dependent dielectric screening: in an atomically thin semiconductor, the screening effect at more than a certain distance is weaker when the separation between the electron and hole is bigger, which is known as the anti-screening effect in 1D carbon nanotubes and as the dielectric confinement effect in 2D quantum wells. Since the wavefunction of excitonic states with higher principal or higher orbital quantum number features a larger nodal structure near the hole (that is, a larger average electron–hole separation), weaker screening at larger separation leads to enhanced Coulomb attraction in the excited states and therefore a lowering of their excitation energies as compared with those of the hydrogen model. Also, because of the degeneracy of the K and K’ valleys in the TMDC system, each s level has two degenerate states, while each p and d level has four degenerate states if perfect rotational symmetry is assumed. All of these features are expected to be quite general for 2D TMDC excitons.
The excitonic ground state and low-energy excited states with large binding energy are robust to environmental perturbations due to the opposite effects of the dielectric screening on the exciton binding energy and the quasiparticle self-energy\textsuperscript{23,24}. We demonstrate this by measuring two-photon spectra of monolayer WS\textsubscript{2} with different dielectric capping layers, including water, immersion oil and aluminium oxide; the average dielectric constants of these capping layers at optical frequency range from 1.7 to 2.5. In all capped samples, we observed the 2p and 3p resonances even at room temperature (Fig. 4a). We find no significant shift in the excitation energy of either the s or the p states with different capping layers, except for an overall temperature-related redshift (0.04 eV) and linewidth broadening compared with measurements at 10 K (Fig. 2). The 1s–2p and 1s–3p energy differences remain roughly unchanged, ~0.2 and 0.5 eV, respectively. This robustness indicates that the measured excitation energies for the 2p and 3p states are intrinsic to the monolayer, thus agreeing well with those from an ab initio GW-BSE calculation for the vacuum condition. Together with the TPL signal, SHG is also observed as a slanted straight line in the excitation-emission spectra (Fig. 4b). At room temperature, the exciton–trion separation is no longer distinguishable, but the 2p and 3p absorption peaks remain prominent. An SHG resonance occurs as the TPL and SHG lines cross each other, and this resonance is known as the exciton enhanced SHG effect\textsuperscript{25}.

We have experimentally revealed 2D excitonic dark states in a WS\textsubscript{2} monolayer. These observations unveil an intense many-electron effect in this class of 2D gapped systems. The determined bandgap size would allow us to accurately design heterostructures consisting of a TMDC monolayer and other materials. Our discovery of extraordinarily strong excitons in a TMDC provides a basis for exploiting the unusual light–matter interactions resulting from strong many-electron effects, and should also help the development of emerging 2D electronic and optoelectronic applications.

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