Efﬁcient generation of neutral and charged biexcitons in encapsulated WSe$_2$ monolayers

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Higher-order correlated excitonic states arise from the mutual interactions of excitons, which generally requires a signiﬁcant exciton density and therefore high excitation levels. Here, we report the emergence of two biexcitons species, one neutral and one charged, in monolayer tungsten diselenide under moderate continuous-wave excitation. The efﬁcient formation of biexcitons is facilitated by the long lifetime of the dark exciton state associated with a spin-forbidden transition, as well as improved sample quality from encapsulation between hexagonal boron nitride layers. From studies of the polarization and magnetic ﬁeld dependence of the neutral biexciton, we conclude that this species is composed of a bright and a dark excitons residing in opposite valleys in momentum space. Our observations demonstrate that the distinctive features associated with biexciton states can be accessed at low light intensities and excitation densities.
The strong Coulomb interaction in two-dimensional transition metal dichalcogenide (TMDCs) crystals, arising from reduced dielectric screening in the atomically thin limit, significantly modifies the optical properties of these materials and gives rise to pronounced excitonic effects. The Coulomb attraction between electrons and holes in these systems leads to the formation of tightly bound excitons, which causes a reduction in the optical band gap by a large fraction of an electron volt and yields very short intrinsic radiative lifetimes. Both trion (charged exciton) and biexciton (exciton molecule) states have been observed in TMDCs. Here we report on the characterization of a second biexciton species in monolayer WSe$_2$, in addition to the previously observed species, which we identify as the neutral and negatively charged biexciton (four-particle and five-particle) states, respectively. In our high-quality samples produced using encapsulation in hexagonal boron nitride (hBN), local inhomogeneities and nonradiative decay channels in the monolayer semiconductor are strongly reduced. As a consequence, the emission of the neutral and charged biexciton is observed at an excitation density three orders of magnitude lower than in previous reports. By comparing the emission of the different exciton species under strong magnetic fields and as a function of doping level, we deduce that the neutral biexciton is formed predominantly from the combination of a dark (spin-forbidden) and bright (spin-allowed) exciton residing in opposite valleys in momentum space. Our observations provide a unique understanding of many-body excited states in 2D semiconductors and open a path for utilizing the features of biexciton states for quantum and optoelectronic applications at low light intensities.

The lowest lying interband transition in monolayer tungsten compounds of the TMDC family has been identified as spin-forbidden. The exciton associated with the lower conduction band therefore, to first order, does not emits light; it is referred to as a dark exciton. The existence of dark excitons strongly influences the optical properties of the material, including the photoluminescence (PL) quantum efficiency at low temperatures, the ultranarrow linewidth of the PL emission along the in-plane direction, the efficient coupling to surface plasmon polaritons, and the large tip-induced enhancement of the PL. Because the dark exciton has a lifetime that is orders of magnitude longer than the bright exciton at low temperature, the steady-state density of dark excitons can be much higher than that of bright excitons for continuous-wave excitation. Correspondingly, the diffusion length of the dark exciton is also enhanced. When a dark exciton approaches another exciton, the two excitons can interact to form a biexciton. Therefore, the formation of biexcitons via the long-lived dark exciton states is much more likely than through two short-lived bright excitons. Here we report the observation of a neutral and charged biexciton composed of both bright and dark excitons.

**Results**

**Observation of biexcitons in the charge-neutral regime.** We observe the evidence of a biexciton in our high-quality encapsulated WSe$_2$ samples (see Methods). In these samples, the defect density of the TMDC is reduced by about two orders of magnitude ($5 \times 10^{10}$ cm$^{-2}$) by exfoliating flux-grown crystals. The observed bright exciton linewidth (FWHM 4.5 meV at 20 K) is approaching the radiative limit. In the low-temperature PL spectrum, the spin-allowed bright exciton emission appears at 1.723 eV (Fig. 1c). Emission from the spin-forbidden dark exciton with a linewidth of only 0.8 meV and an out-of-plane dipole radiation pattern (Supplementary Fig. 1) is observed at 1.681 eV, in agreement with previous reports. As the excitation power is increased, a new peak emerges at 1.703 eV, lying 20 meV below the bright exciton peak. Compared to the emission of the bright and dark exciton species, which rise nearly linearly with laser intensity, the new peak increases approximately quadratically. A power-law fit of the emission yields an exponent of 1.96 ± 0.03 (Fig. 1d). The quadratic intensity dependence suggests that the peak arises from a few-body state formed from two excitons, each exhibiting a concentration growing linearly with intensity (Supplementary Note 2). The new biexciton peak, we should note, is observed for rather weak continuous wave (cw) excitation, with an irradiance of $1.4 \times 10^{6}$ W/cm$^2$, more than three orders of magnitude lower than in typical experiments employing pulsed laser excitation. The asymmetric peak X$^0_1$, lying 32 meV below X$^0_0$, and the series of peaks around 1.665 eV have been attributed to indirect (momentum-dark) excitons. The lower-lying emission peaks also originate from the WSe$_2$ sample, but have an unknown origin and are beyond the scope of this work.

**Spin and valley configuration of the biexciton.** In the following, we focus on identifying the composition of the newly observed biexciton state. Regarding the spin degree of freedom, biexcitons can be classified as composed of dark–dark, dark–bright, and bright–bright exciton components. Here we assume the electron and hole of the constituent excitons remain in the same band when forming a biexciton. The emission energy of the biexciton precludes it from being composed of two dark excitons, as this would require a negative binding energy. The bright–bright configuration is unlikely to occur given our experimental conditions: At the greatest applied laser intensity, we estimate an upper limit of 52 $\mu$m$^{-2}$ of bright excitons in the steady state, for a 2-ps lifetime of the bright exciton and assuming a 100% conversion efficiency from absorbed photons to bright excitons. This density is smaller than the dark exciton density at our lowest excitation level, as the dark exciton has a lifetime more than 50 times longer than the bright species, as reported by Robert et al. and confirmed in our sample. The low density of bright excitons renders the bright–bright biexciton much less likely to form. (A simple kinetic model is presented in Supplementary Note 3 to describe the biexciton formation process.) We therefore conclude that the observed biexciton is a combination of one bright and one dark exciton (Fig. 1b). This assignment is further supported by the magnetic field and doping dependences of the biexciton emission, as discussed below.

To investigate the biexciton valley configuration further, we apply a strong out-of-plane magnetic field, which acts to break the valley degeneracy. As a magnetic field along the normal direction of the sample shifts the conduction and valence bands in the different valleys in opposite directions, the exciton peaks are split into pairs, associated with their valley index. Since the dark exciton has a total spin angular momentum of 1, its Zeeman splitting is larger than that of the bright exciton with its vanishing total spin. As the emission of the biexciton results from its bright component, leaving behind a dark exciton in the final state, the biexciton emission energy is given by the bright exciton emission energy reduced by the biexciton binding energy $\Delta_{XX}$ (see Methods). Neglecting any difference in magnetic field dependence of the (small) biexciton binding energy $\Delta_{XX}$, we predict within our picture that the XX peak should exhibit the same $g$-factor as the bright exciton. This agrees with our experimental observations: X$^0_0$ and XX have $g$-factors of 4.4 ± 0.5 and 4.6 ± 0.5, respectively, while X$^D_0$ has a $g$-factor of 9.6 ± 0.5 (Fig. 2a).

The distribution of the exciton population between the different branches of the Zeeman-split pairs will, in thermal equilibrium, follow a Boltzmann distribution. This suggests that
have exponents of 1.22 and 1.03, respectively.

excitation intensities. All spectra are normalized to the X0 peak. A new peak (green shading) emerges at high excitation levels and is attributed to biexciton emission.

LEB, an intervalley conformation (Fig. 2c), the dark component in the HEB (LEB) of the biexciton is associated with the LEB (HEB) of the dark exciton residing in opposite valleys. In the intervalley conformation, the density of biexcitons needs to involve two holes sharing the same valence band, which costs extra energy.

More importantly, the emission intensity from the biexciton pair is also observed to be inverted, with an inversion even naturally to an inverted distribution for the biexciton emission.

More quantitatively, the LEB/HEB ratio of the biexciton pair is strictly limited to the intrinsic regime. Under stronger excitation conditions, the emission of another exciton state emerges, and its emission is also restricted to the intrinsic regime.

Distinguishing neutral and negatively charged biecxtons. Finally, we are able to elucidate the relationship between the newly observed and the previously reported biexciton by tuning the static carrier density in the material (Fig. 3a). In the low excitation regime, the emission spectra agree well with those reported in the literature: the bright and dark excitons are observed in the intrinsic regime while different types of trions emerge in the n-doped and p-doped regimes. Unlike the bright exciton state, which extends to strong doping levels with an asymmetric gate dependence, the dark exciton is strictly limited to the intrinsic regime. Under stronger excitation conditions (~4 x 10^5 W cm^-2), the biexciton peak at 1.703 eV appears, and its emission is also restricted to the intrinsic regime. The doping dependence therefore confirms that this newly observed XX peak results from a neutral biexciton formed by a bright and a dark exciton, as it appears only in the doping regime where both types of excitons coexist (Fig. 3b).

Under strong excitation conditions, the emission of another biexciton is observed in our spectra, which exhibits a superlinear power dependence with an emission strength scaling with the pump laser intensity as I^1.56 (Supplementary Fig. 2). This peak lies 52 meV below the bright exciton and has been reported in the literature. However, this biexciton only appears at the crossover from the intrinsic to the n-doped regime (Fig. 3b), suggesting that it is a negatively charged biexciton XX^-, formed from a trion and a neutral exciton, as opposed to its earlier assignment as a neutral biexciton. In contrast to the negatively charged trions, no fine
Fig. 2 Zeeman splitting and non-equilibrium distribution of biexciton emission. a A strong out-of-plane magnetic field splits most emission peaks into pairs. The splitting of XX is similar to that of the X⁰ feature (g-factor 4.4 ± 0.5), whereas the splitting of the X⁰ feature is larger because of its non-zero spin. b The ratios of amplitudes of the fitted low-energy branch (LEB) and high-energy branch (HEB) of the emission spectra. Unlike the X⁰ pair, the XX emission pair exhibits inverted populations between the HEB and LEB. The LEB/HEB ratio of the XX pair is similar to that of X⁰/X⁰. The error bars for X⁰, X⁰, and XX are conservative estimates. c A diagram of the biexciton intervalley configuration as probed through the PL measurements in a magnetic field. The B-field splits the bright (light blue) and dark (dark blue) exciton into pairs according to their valley index (K, K'). Analysis of the PL intensities shows that the biexciton is composed of excitons from different valleys.

Fig. 3 Doping dependence of the PL emission of neutral and charged biexcitons. a Gate dependence map of the PL intensity above the onset for observing both biexciton species (Iₒ = 4 × 10⁴ W cm⁻²). The intrinsic regime is characterized by the strong emission from X⁰. In the n-doped and p-doped regimes, trions and other species emerge. The XX peak at 1.703 eV is only observed in the intrinsic regime, indicating a neutral biexciton composed of a neutral X⁰ and X⁰. Another peak with superlinear power dependence is observed at 1.671 eV, 52 meV below X⁰. It is assigned to a charged biexciton state, as it appears only in the low n-doped regime. b Normalized PL intensity of the exciton species relevant for the formation of biexcitons as a function of doping level. The neutral biexciton (green) emission is limited to the intrinsic regime, in which X⁰ (dark blue) is observed, showing the important role of X⁰ in the formation of XX. The XX⁻ emission (dark red) is strongest in the low n-doped regime, where X⁰ (light blue), X⁰ and the two X⁻ species coexist (light red, only lower X⁻ shown for clarity).

Discussion
The identification of neutral and charged biexcitons resolves the discrepancy of the biexciton binding energy found between previous experiments and theories: as calculated, the biexciton binding energy is indeed smaller than the trion binding energy due to the form of the screened Coulomb potential in two-dimensional TMDCs. The 20-meV binding energy also matches that of the neutral biexciton in MoSe₂ monolayers observed by Hao et al. using two-dimensional coherent spectroscopy and of WSe₂ in pump-probe spectroscopy, even though both works describe bright–bright excitons, which would suggest the biexciton binding energy is only weakly sensitive to the spin configuration of the two constituent excitons.
Methods

**Samples.** Single crystals were grown by sealing W powder, 99.999% purity, and Se shot, 99.999% purity, in an evacuated quartz ampoule with excess Se as the flux. Subsequently, the ampoule was heated to 1000 °C for 2 days and cooled to 450 °C at a rate of 0.85 °C h⁻¹. The crystals were removed, centrifuged, and annealed at 250 °C for 2 days to remove excess Se. Encapsulated monolayers of WSe₂ were then prepared from these single crystals by a dry stamping technique, with all materials exfoliated on Si/SiO₂ substrates. In order to contact the WSe₂ film, two fewer-layer graphene strips were picked up by an hBN flake, followed by the monolayer WSe₂. Finally, a bottom (Ar/O₂ cleaned) hBN crystal and a thin layer of graphite were picked up to act as the backgate for controlling doping and screening the effects of the SiO₂. Contact was made to the graphite leads and backgate by etching with CHF₃ and making edge contact using Cr/Pd/Au film deposition (2/25/50 nm).

**Measurements.** In all but the magnetic field experiments, the samples were mounted in a continuous flow optical cryostat and cooled with liquid helium to temperatures of ~15 K. PL spectra were taken with an imaging spectrometer after 640 nm cw laser excitation. We note that for laser excitation at shorter wavelengths (e.g., 532 nm), we observed photodoping of the sample starting at moderate power levels. Spectra on bare hBN were taken to verify that all features in Fig. 1b originate from the WSe₂ sample. Magnetic field measurements were conducted at the National High Magnetic Field Laboratory, at sample temperatures of 10 K and cw laser excitation at 660 nm. The PL spectra were fitted with a series of pseudoVoigt lineshapes to obtain the emission intensity (area) as a function of the relevant experimental parameters.

**Bie exciton binding energy.** The binding energy Δ of the neutral bie exciton is obtained from the relation for energy conservation in the formation and radiative decay of the bie exciton species: Eₜ – Eₓ = Δ = ℏωₓ + Eₓ. Here we consider a bie exciton formed from a pair of bright and dark excitons and assume that the final state after radiative decay is a dark exciton in its ground state. It follows that the bie exciton binding energy is directly related to experimentally observable emission energies such that Δ = Eₓ - ℏωₓ. A.

**Data availability.** The data supporting the plots within this paper and other findings of this study are available from the corresponding author upon request.

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**Author contributions**

Z.Y., L.W. and T.F.H. conceived the project. D.R., A.A. and B.K. grew the WSe₂ crystals and prepared encapsulated and backgated samples. K.W. and T.T. produced the hBN crystals. Z.Y., L.W., E.Y.M., Y.I., X.Z. and M.D. conducted the measurements. Z.Y. and...
L.W. analyzed the data. Z.Y., L.W. and T.F.H. wrote the manuscript with input from all authors.

**Additional information**

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