2D MATERIALS

Brightening the dark excitons

Two independent methods using near-field coupling to surface plasmon polaritons and magnetic brightening allow the observation of dark excitons in WSe_2.

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Optical properties of semiconductors are dominated by excitons, which are electron–hole pairs bound by Coulomb interactions. Excitons can be bright or dark depending on the spin orientation of the individual carriers. In a bright exciton the electron and the hole have antiparallel spins and can recombine easily through the emission of a photon. In a dark exciton the spins are parallel and the recombination cannot occur via direct emission of a photon as this would not allow for spin momentum conservation. Thus, dark excitons have much longer radiative lifetimes than bright excitons. This large difference in recombination time can potentially be harnessed to create 'fast' or 'slow' light. Besides, the highly stable, non-radiative nature of dark excitons makes them attractive for optically controlled information processing.

To take advantage of the features of dark excitons, it is essential to create conditions in which these excitonic species can exist. It turns out that the formation of dark excitons occurs in WS_2 or WSe_2, where rotational and inversion symmetry-breaking together with strong spin–orbit coupling leads to spin-split energy states. In these materials dark excitons are lower in energy than the bright excitons in the conduction band[1]. However, in order to access the stored spin information, the dark exciton needs to have the ability to respond to light. Making use of the optical selection rules in 2D transition metal dichalcogenides (TMDs)[2], it is possible to selectively control spin and valley excitation to initialize this state (Fig. 1). This has piqued the interest of researchers and efforts are ongoing to find ways to optically detect and manipulate dark excitons.

Writing in *Nature Nanotechnology*, two teams, Xiao-Xiao Zhang and co-workers[3], and You Zhou and co-workers[4], independently describe two approaches to induce light emission from dark excitons in monolayer WSe_2, thus opening new possibilities to store and manipulate valley and spin information.

Applying a magnetic field to a semiconductor can mix electronic wave functions and shift the spectral weight between bright and dark excitons depending on the magnetic field direction[5]. An in-plane magnetic field does not couple to the in-plane motion of charge carriers in 2D materials and hence, does not perturb the electronic structure. Instead, it alters the spin alignment of carriers, which relaxes the spin-selection rule and makes dark excitons optically detectable by photoluminescence (PL) spectroscopy. Zhang *et al.*[3] demonstrated that by applying an in-plane magnetic field greater than 10 T, a magnetic brightening of the dark exciton can be achieved in WSe_2. Using circularly polarized light to excite the dark state, the researchers show that the dark exciton is defined by its spin state as well as the chiral information characteristic of the valley it resides in. By measuring the polarization of the light emitted from the dark exciton, the team discovered that the dark exciton, in addition to having an opposite chirality to that of the bright exciton, also has a much longer valley recombination lifetime. Although the exact mechanism is not clear, Zhang *et al.* suggest that it could be due to the transfer of electrons from one photo-excited valley to another. This result in particular could have implications for valley-selective spin injection. Besides, because dark excitons in WSe_2 emit light of certain chirality, this process is also attractive for developing photon emitters for chiral optics[6]. It is worth investigating if, instead of applying a high magnetic field, a similar effect can be achieved by coupling the 2D TMD to a ferromagnetic layer.

Although magnetic brightening is fundamentally important for the understanding of, for example, the structure of the spin-split conduction bands in 2D TMDs, it is not easy to make use of this effect in conventional device fabrication schemes. Luckily, an alternative way of probing the dark exciton is available, which simply involves placing WSe_2 monolayers on patterned silver surfaces — the approach pioneered by Zhou and colleagues[4]. Silver surfaces have a high density of free electrons, which can be collectively excited to form plasmons. When light interacts with these species, a combined electromagnetic radiation called the surface plasmon polariton (SPP) is generated. Coupling with SPPs can be used to selectively enhance optical transitions with dipole moments normal to the 2D plane. Dark excitons in WSe_2 have a nonzero dipole moment along the z direction, allowing them to couple to the SPP modes, which are also z-polarized. This 'switches on' the PL response from the dark excitons, yielding a PL intensity equivalent to that achieved by a 30 T in-plane magnetic field.

The advantage of the SPP approach is its ease of integration with atomically thin 2D materials. Silver mirrors can be patterned in the form of subwavelength structures called metasurfaces to create optical interference effects, which enables spatial variation of the optical response from WSe_2 coupled to the silver mirror. It is worth noting that since such excitonic effects enhance optical nonlinear properties by orders of magnitude, regions with locally varying nonlinear effects can be fabricated by using metasurfaces to

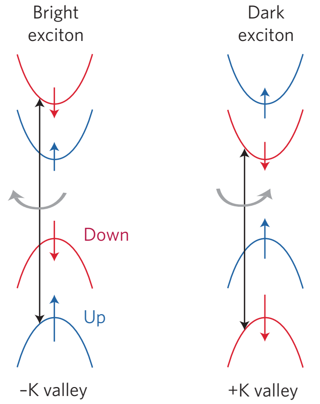

Figure 1 | Schematic illustration of bright and dark excitonic states. Bright excitons (left) are optically allowed and dark excitons (right) are optically forbidden. Bright and dark excitons can have different chirality due to valley separation. The black arrows indicate photons with different chirality. Blue and red lines indicate levels containing 'up' and 'down' spins, respectively.

control the brightening of dark exciton states on a 2D monolayer (for example, WSe_2). Going forward, optical schemes based on quantum coherence[7] and multiphoton excitation[8,9] can be used to manipulate the dark excitons on such metasurfaces to generate light with different frequencies, enabling quantum information processing and storage.

In future nanophotonic devices, 2D materials can be integrated into a photonics platform to make optical circuitry in which dark excitons can be used for encoding and transporting information on a chip. ❐

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