SEMICONDUCTOR PHYSICS

Probing the dark side of the exciton

Photoemitted electrons reveal large-momentum (“dark”) excitons in monolayer WSe_2

By **Meng Xing Na**[1,2] and **Ziliang Ye**[1,2]

Two-dimensional (2D) semiconductors, such as transition-metal dichalcogenides, may enable new optoelectronic technologies (*1*). The optical excitation in these atomically thin materials creates tightly bound excitons composed of an excited electron and a valence-state hole (*2*), as well as a plethora of exciton complexes due to the reduced screening in Coulomb attraction (*3*–*5*). So far, excitons with large momenta have not been directly probed because photons only carry very small momenta and cannot directly interact with large-momentum excitons, but these dark excitons are predicted to exist in certain 2D semiconductors (*6*, *7*). On page 1199 of this issue, Madéo *et al.* (*8*) used time- and angle-resolved photoemission spectroscopy (TR-ARPES) to directly probe dark excitons in monolayer tungsten diselenide (WSe_2). By tracking the dynamics of electrons that constitute both bright and dark excitons, the authors reveal how both are formed and show that the latter outnumber the former at steady state.

There are two families of excitons in 2D semiconductors, with electrons at different valley-like local minima of the conduction band. Each valley is named after its location in the Brillouin zone (momentum-space). Bright excitons consist of electrons and holes both located in K valleys that form through the direct transition of the electron to an excited state with the same momentum (see the first figure). As the momentum of the exciton is defined by the momentum difference between its constituting electron and hole, these so-called K-K excitons have zero momentum and can directly interact with light. Dark Q-K excitons are composed of an electron excited indirectly into a Q valley with a different momentum than that of the hole left in a K valley. Valleys with opposite momenta are equally populated in this study.

> “These results…constitute a direct probe of dark-exciton formation and its binding energy and dynamics…”

Madéo *et al.* performed their TR-ARPES experiment by combining a photoemission electron microscope (PEEM) with an extreme ultraviolet (XUV) light source (see the second figure). They first shine an ultrafast visible-light pulse at the WSe_2 monolayer. By tuning the wavelength of this pulse, they can excite either excitons or free carriers. After a variable delay time, an ultrafast XUV pulse is shone onto the sample. The high photon energy of the XUV light then ejects electrons from the monolayer.

With no surface state present, the authors directly accessed the electrons’ energy and momentum inside the material by analyzing the kinetic energy and emission angle of the ejected electron (measured here by an angle-resolved time-of-flight analyzer). Both the visible and XUV light are ultrafast pulses. The first visible pulse excites the system, and the second XUV pulse acts effectively as a camera shutter. By fine-tuning the delay between the excitation and the shutter, the authors obtain a “movie” of electrons in momentum space in which free carriers, bright excitons, and dark excitons all have distinct signatures.

The authors find that both bright and dark excitons exist in the monolayer WSe_2. Notably, the bright K-K excitons preferentially convert into dark Q-K excitons through phonon scattering and lead to a density of dark excitons double that of the

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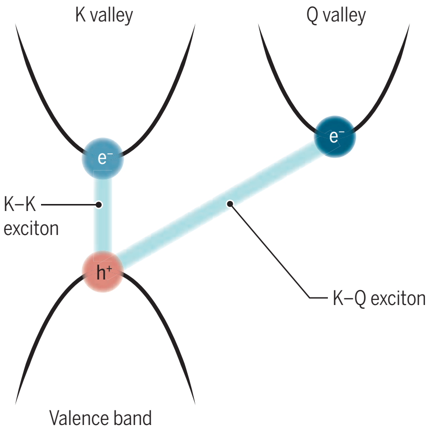
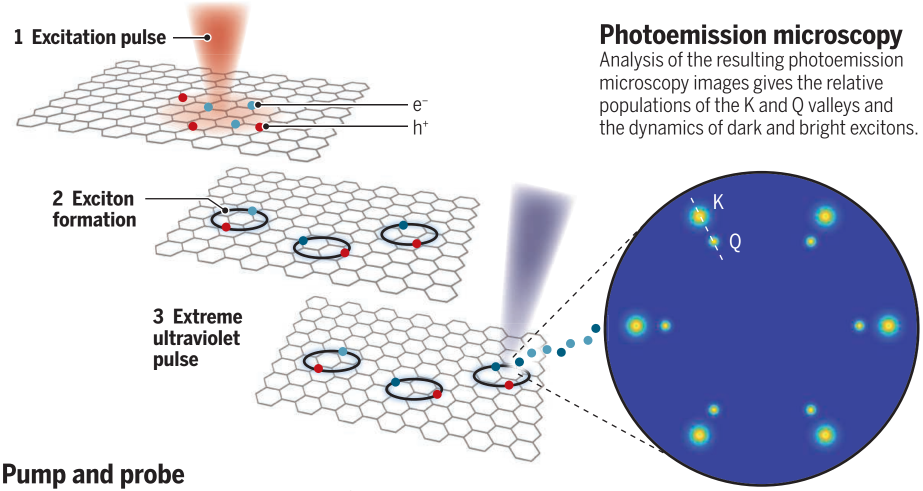
Bright and dark excitons

Bright excitons have electrons in the K valley conduction bands and have zero momentum. Dark excitons have electrons in the Q valley conduction bands and carry momentum.



Movies of dark-exciton formation

Dark excitons cannot be probed directly with photons. Madéo *et al.* used photoemission microscopy to reveal them in monolayer tungsten diselenide (WSe_2).



Photoemission microscopy
Analysis of the resulting photoemission microscopy images gives the relative populations of the K and Q valleys and the dynamics of dark and bright excitons.

Pump and probe
A visible pump pulse generates excitons in WSe_2, and an extreme ultraviolet probe pulse ejects electrons.

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bright excitons. The dark excitons also have a longer lifetime, so they become a reservoir for the bright excitons at steady state. Tuning the excitation light off the exciton resonance excites free electrons and holes, and after about 500 fs, a quasi-equilibrium exciton ensemble forms.

By comparing the photoemission signal from excitons with the free-electron energy at the band edge, Madéo *et al.* deduce the exciton binding energy for both bright and dark excitons. These results, which constitute a direct probe of dark-exciton formation and its binding energy and dynamics, were made possible by a convergence of improvements in the spatial resolution of the ARPES instrument as well as the high photon energy of the ultrafast high-harmonic XUV source that could probe the entire Brillouin zone of WSe_2 (*9*).

Although dark excitons do not interact directly with light, the electrons that constitute such dark excitons are accessible by photoemission (*10*, *11*). Besides the Q-K exciton, other dark excitons in 2D semiconductors that are accessible by the technique of Madéo *et al.* include intervalley excitons, spin-triplet excitons, Rydberg states with finite angular momentum, and higher-order exciton complexes (*12*–*14*). Another equally rewarding direction would be to study the wave function of a single exciton that was obscured in the current study by phonon scattering and other scattering channels (*10*, *11*). The rapid progress in van der Waals heterostructures also calls for more direct techniques to resolve their emerging electronic structures (*15*). It is expected that there will be many exciting opportunities to apply these powerful electronic probes in studying the excited states of quantum materials. ■

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PLANT SCIENCE

Constraints on selfish behavior in plants

Plants overproduce roots to secure resources nearby but avoid costly trips to neighbors' patches

By **Marina Semchenko**[1,2]

We are used to human behavior, and the actions of other animals, being described as selfish, aggressive, or cooperative. Such words come up less often when contemplating plants. Yet plants too have evolved a fascinating array of behavioral strategies in their struggle for resources, although these are hard to demonstrate and quantify. Whether and when it pays for plants to selfishly overproduce roots and preempt resource capture by competitors, or cooperate by restraining root growth, has been the subject of extended debate (*1*, *2*). On page 1197 of this issue, Cabal *et al.* (*3*) tackle this question with a new theoretical model and an empirical test that highlight spatial costs of nutrient foraging as key to resolving apparent discrepancies between previous studies.

Besides establishing which behaviors occur in the plant kingdom, determining the extent of root overproduction in the scramble for limited soil nutrients is vital for understanding global carbon cycling and finding solutions to major challenges that face humanity. Plants capture atmospheric carbon during photosynthesis, and a large fraction is channeled into root production, representing a vast capacity for carbon storage and a potential focus for approaches to mitigate climate change (*4*). Global models of primary productivity and carbon storage—and ecosystem responses to climate change—could be substantially modified by accounting for overinvestment into capture of shared resources (*5*). Moreover, understanding the factors that enhance or suppress competitive root proliferation could open new avenues in crop breeding and agricultural practice (*6*).

Rather than focusing on the total mass of roots produced by competing plants, Cabal *et al.* bring a spatial dimension to root foraging by modeling the increasing cost of nutrient transport from locations further away from the plant stem. This cost constrains the extent of root foraging, leading to partial segregation of root systems between neighboring plants. However, the situation is different in areas close to the plant stem: Low nutrient-transportation costs make excessive root production cheap and give a competitive advantage against neighbors' roots that have traveled from afar; the model predicts that plant roots should avoid costly trips to neighboring territories but invest in securing resources closer to home. Empirical observations appear to support the predictions of the model. Cabal *et al.* corroborated the model using pepper plants, and an independent study that mapped the spatial distribution of roots in several grassland species showed that some plants shrank their foraging ranges when experiencing stronger competition but aggregated roots in the remaining core areas (*7*). Therefore, it seems that a successful strategy involves excessive root production in areas with low costs, but reduced overlap with neighboring root systems (see the figure). The latter has previously been interpreted as cooperative behavior or territorial defense (*8*) but seems to emerge as part of a selfish strategy restrained by nutrient transportation costs.

By manipulating relevant model parameters, Cabal *et al.* provide further insights: Excessive root production should be strongest in dense vegetation, where short distances between competing plants preclude exclusive access to resources, and in productive ecosystems or species with low root-construction costs. This suggests that agricultural practices that involve high fertilization rates and high planting densities are particularly conducive to competitive root proliferation at the expense of economically essential yield. Hence, optimal fertilizer use efficiency and improved yield might be achieved by adjusting crop spacing and fertilization practices in light of root spatial behavior and by breeding varieties that are less responsive to neighbor presence and show more restrained growth of competitive organs (*9*). Such advances have already been achieved, sometimes unintentionally, aboveground by breeding crop

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