Brightening and controlling dark excitons in monolayer TMDCs

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An exciton is a bound state formed by an excited electron and hole *via* the Coulomb attraction. Such bound states often play an important role in the optical properties of low dimensional materials such as quantum dots, nanowires and two-dimensional (2D) materials, owing to their strong spatial confinement and reduced screening effect compared to bulk sample. The 2D nature of transition metal dichalcogenides (TMDCs) brings a tightly bound exciton with large exciton binding energy. 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 [1]. Usually we can observe A, B and C excitons in those TMDCs materials. A and B features involve the band edge states at *K* points, while the C exciton is related to the parallel bands near *Γ* point at higher energies. According to the selection rule of dipole transition, these exciton states either are optical transition allowed bright excitons or optical transition forbidden dark excitons depending on the relative spin orientation of electrons in conduction and valence band [2–4]. In short, bright excitons correspond to the transition from electron-hole pairs with the same spin orientation, while the dark exciton corresponds to the transition from electron-hole pairs with the opposite spin orientation. Generally, the dark excitons have a much longer lifetime, which makes it to have potential applications in quantum information processing [5]. Meanwhile, strong spin-orbit coupling in monolayer TMDCs leads to a larger spin splitting of the valence band and a much smaller splitting of the lowest conduction band at *K* point [6]. In WX_2 ($X=S, Se$), since electrons in the lowest conduction band are expected to have the opposite spin to holes in the highest valence band, it forms dark A exciton (X_D) that is out-plane (*Z* direction) polarized and optically forbidden

for the in-plane (*X*-*Y* plane) polarized excitation [2,3]. In MoX_2 ($X=S, Se$), the spin orientations of this two states are parallel each other and form bright A exciton (X_0 , *X*-*Y* plane polarization), but the dark state lies at the higher energy level of split conduction band, as shown in Fig. 1a.

The *Z* polarized dark excitons are difficult to be directly observed with normal incident excitation. However, we should note that dark A exciton X_D slightly mixes different orbital and spin wave functions due to the spin orbit coupling. As a result, the oscillator strength of the corresponding transition is quite small but not completely forbidden transition [3]. Therefore, there are still some possibilities to directly observe the dark A exciton X_D under certain experimental configuration. Actually, several groups have independently observed the X_D with different experimental methods. Both of Heinz's group and Molas's group applied a large in-plane magnetic field (> 14 T) to induce the mixing oscillator strength of bright and dark state pairs and lead to X_D in WX_2 with a weak in-plane polarization and become bright [7,8]. Similar technique has already been successfully applied to observe the dark exciton in quantum dots [9]. Meanwhile, Kim and co-workers probed dark excitons in atomically thin semiconductors *via* near-field coupling to surface plasmon polaritons (SPP) by placing a monolayer WSe_2 on the atomically smooth single-crystal silver film [10]. Urbaszek *et al.* [11,12] observed X_D emission in WX_2 by using the polarization-selective detection from the sample edge. However, owing to the small splitting of conduction band and the thermal excitation effects, all of these experiments are limited within low temperature (< 30 K).

Recently, Raschke and his colleagues [13] from University of Colorado, Boulder in USA reported the observation of dark exciton in monolayer WSe_2 at room temperature by combining the near-field optics and

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Figure 1 (a) The splitting of conduction band at around K point and the transition of bright (X_0) and dark (X_D) exciton in WX_2 and MoX_2 , respectively. (b) Schematic of tip-enhanced photoluminescence (TEPL) spectroscopy, selective excitation and probing of the transition dipole moments of dark (out-of-plane) and bright (in-plane) excitons by polarization control. (c) Excitation polarization dependent TEPL spectra of monolayer WSe_2 on an Au substrate at ~ 1 nm tip-sample distance with tip selective X_D emission (orange). (d) Time-series TEPL response (X_D , X_0 and gap plasmon PL) in continuous On state of X_D emission at 1 nm tip-sample distance and discrete On/Off switching of X_D emission with discrete tip-sample distance variation between 1 nm and 5 nm, respectively. (e) Time-series of peak intensity of TEPL response with correlation between corresponding X_D emission and gap plasmon, derived from d. Reprinted with permission from Ref. [13], Copyright 2017, Nature Publishing Group.

changing the polarization of excitation light relative to the sample surfaces. Fig. 1b shows their schematic of tip-enhanced photoluminescence (TEPL) spectroscopy, where the polarization of excitation light is changed by $\lambda/2$ plate. The samples are mounted to a piezoelectric transducer (PZT) and the sample surface is tilted by $\sim 60^\circ$ with respect to the incident k -vector for effective excitation. The distance between tip and sample was controlled electrically with ~ 0.2 nm precision. When the distance is fixed at around 1 nm, the dark exciton can couple to laser with Z polarization component at room temperature, as shown in Fig. 1c. In this case, the transition dipole moment and the spontaneous emission rate of dark exciton are greatly enhanced by this nano-gap due to the plasmonic Purcell effect. In particular, the nanocavity below 1.5 nm gap gives rise to a large Purcell factor ($>2,000$) compared to dielectric substrates and lead to a huge enhancement of the dark excitons emission. Remarkably, by switching the tip distance between 1 nm and 5 nm, they have achieved the switching between On and Off state of X_D , as shown in Fig. 1d, e. Furthermore, the intensity of X_D emission can be programmably controlled by changing this gap distance. This work provides a new way to

actively control the emission of dark excitons by changing the polarization of laser and the distance of between plasmonic tip and sample surfaces, which may broaden potential applications of dark excitons in information processing. As pointed by the authors, similar method of brightening and controlling the dark excitons could be applied to other semiconductors, such as carbon nanostructures, quantum dots, other van der Waals materials beyond TMDCs.

In addition to the direct measurement of dark exciton, Zhang and colleges [14] also indirectly measured the X_D and related energy splitting between dark and bright A exciton in few-layer WS_2 by using resonant Raman scattering technique, where the selection rule of dipole transition is satisfied by coupling odd-parity infrared active phonons and even parity dark excitons. From above reports, it must also be noted that the X_D in MoX_2 is still hard to be observed in experiment, because the dark states in MoX_2 lies at the higher energy compared to bright states, which leads to a lower population and thus lower transition probability [2,3,12]. In order to brighten and control these X_D in MoX_2 , a feasible way is to combine exciton-phonons coupling with special experimental

configuration such as tip-enhanced exciton-SPP coupling strain field. In future, an important direction is to develop more easy and reliable techniques to brighten and control the dark exciton in 2D and 2D van der Waals heterostructures.

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