Real- and momentum-indirect neutral and charged excitons in a multi-valley semiconductor

Zhiheng Huang¹,², #, Yuhui Li¹,², #, Tao Bo³, #, Yanchong Zhao¹,², Fanfan Wu¹,², Lu Li¹,², Yalong Yuan¹,², Yiru Ji¹,², Le Liu¹,², Jinpeng Tian¹,², Yanbang Chu¹,², Xiaozhou Zan¹,², Yalin Peng¹,², Xiuzhen Li¹,², Yangkun Zhang¹, Kenji Watanabe⁴, Takashi Taniguchi⁵, Zhipei Sun⁶,⁷, Wei Yang¹,²,⁸, Dongxia Shi¹,²,⁸, Shixuan Du¹,²,⁸,*, Luojun Du¹,²,⁸,* & Guangyu Zhang¹,²,⁸,⁹, *

¹Beijing National Laboratory for Condensed Matter Physics, Key Laboratory for Nanoscale Physics and Devices, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China; ²School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100190, China; ³Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, Ningbo 315201, China; ⁴Research Center for Functional Materials, National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan; ⁵International Center for Materials Nanoarchitectonics, National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan; ⁶Department of Electronics and Nanoengineering, Aalto University, Tietotie 3, Espoo FI-02150, Finland; ⁷Quantum Technology Finland (QTF) Centre of Excellence, Department of Applied Physics, Aalto University, Aalto FI-00076, Finland; ⁸Beijing Key Laboratory for Nanomaterials and Nanodevices, Beijing 100190, China; ⁹Songshan Lake Materials Laboratory, Dongguan 523808, China

#Contributed equally to this work.
*Corresponding authors (emails: sxdu@iphy.ac.cn (Shixuan Du); luojun.du@iphy.ac.cn (Luojun Du); gyzhang@iphy.ac.cn (Guangyu Zhang))

Received 30 September 2022; Revised 2 January 2023; Accepted 16 January 2023; Published online 9 June 2023

Abstract: Excitons dominate the photonic and optoelectronic properties of a material. Although significant advancements exist in understanding various types of excitons, progress on excitons that are indirect in both real- and momentum-spaces is still limited. Here, we demonstrate the real- and momentum-indirect neutral and charged excitons (including their phonon replicas) in a multi-valley semiconductor of bilayer MoS₂, by performing electric-field/doping-density dependent photoluminescence. Together with first-principles calculations, we uncover that the observed real- and momentum-indirect exciton involves electron/hole from K/Γ valley, solving the longstanding controversy of its momentum origin. Remarkably, the binding energy of real- and momentum-indirect charged exciton is extremely large (i.e., ~59 meV), more than twice that of real- and momentum-direct charged exciton (i.e., ~24 meV). The giant binding energy, along with the electrical tunability and long lifetime, endows real- and momentum-indirect excitons an emerging platform to study many-body physics and to illuminate developments in photonics and optoelectronics.

Keywords: excitons, real- and momentum-indirect exciton, giant binding energy, electrical tunability, multi-valley semiconductor

INTRODUCTION

Excitons and their complexes (e.g., phonon replicas, biexcitons, and Fermi polarons) are elementary excitations that predominate the optical properties of a material and hence underlie the development of various...
emerging technological advances in photonics and optoelectronics [1]. According to the relative positions of the constituent electrons and holes in real- and momentum-spaces, excitons can be categorized into four types: real- and momentum-direct (type-I), real-direct but momentum-indirect (type-II), momentum-direct but real-indirect (type-III), and real- and momentum-indirect (type-IV), as shown in Figure 1. Type-I excitons can strongly couple to photons and show large luminescence quantum efficiency, setting a foundation for a wide variety of optoelectronic applications, such as light-emitting diodes, lasers, solar cells, and optoelectronic devices [2–5]. However, the rather short lifetime of real- and momentum-direct excitons strongly impedes their applications in scientific research and technological innovation where long-lived excitons are required, for example, exciton superfluid phase, exciton crystals, and exciton transistors [6,7].

Notably, in some intentionally designed systems, such as van der Waals heterostructures with a staggered band alignment [8–10] and quantum wells under an external electric field [11], the wave functions of the constituent electrons and holes are spatially separated, resulting in the formation of real-space indirect excitons (also referred to as interlayer excitons or spatially indirect excitons). Thanks to the spatial separation of the electrons and holes, real-space indirect excitons exhibit a much longer lifetime than the real- and momentum-direct ones [9,12–14]. In the light of the long-lived real-space indirect excitons, a wide variety of captivating physical phenomena has been demonstrated, including but not limited to exciton Bose-Einstein condensation [15–18], correlated excitonic insulator states [19–21], and dissipationless valley exciton devices [14,22]. In addition, real-space indirect excitons harbor in-built electric dipoles and are widely tunable in applied electric fields [2,9,10,23–25], representing an advantageous scenario for technological applications. Although substantial developments and progress on understanding the real-space indirect excitons have been witnessed, the studies of real-space indirect excitons have mainly focused on the momentum-bright species (i.e., type-III excitons) with electrons and holes localized in the same valley of the Brillouin zone (BZ) [9,12,14,23,26–28]. However, the real- and momentum-indirect excitons (type-IV), which are expected to possess an even longer lifetime than the momentum-direct but real-indirect ones due to the dark nature in both real- and momentum-spaces, are still largely unexplored experimentally.

A suitable candidate for investigating real- and momentum-indirect excitons should meet two basic conditions simultaneously. First, it should possess multi-valleys in conduction and valence bands, endowing the possibility of momentum-indirect excitons. Second, for Bloch states at distinct valleys, the orbital compositions should be different. Consequently, the wave functions of different valleys reside at different positions in real-space, which enables the momentum-indirect excitons to be indirect in real-space as well.

![Figure 1](https://engine.scichina.com/doi/10.1360/nso/20220060)

**Figure 1** Real- and momentum-indirect and direct excitons. Based on the configurations of the constituent electrons and holes in real- and momentum-spaces, excitons can be divided into four types: real- and momentum-direct (type-I), real-direct but momentum-indirect (type-II), momentum-direct but real-indirect (type-III), and real- and momentum-indirect (type-IV).
particular, two-dimensional (2D) multi-valley semiconducting transition metal dichalcogenides (conduction band: Q and K valleys; valence band: K and Γ valleys) with different orbital compositions at distinct valleys provide a promising platform for real- and momentum-indirect excitons [24,25,29,30]. Despite the fact that the momentum-indirect excitons in these materials have been well uncovered [31,32], their indirect nature in real-space remains equivocal. In this work, we fabricate hexagonal boron nitride (h-BN) encapsulated dual-gate devices of a multi-valley semiconductor of bilayer MoS$_2$. Through electric-field tunable photoluminescence (PL) spectra, we identify the out-of-plane static electric dipole and quantum-confined Stark effect of momentum-indirect exciton in bilayer MoS$_2$, providing the smoking gun evidence of their real-space indirect characteristic and hence the existence of real- and momentum-indirect exciton. In conjunction with density functional theory (DFT) calculations, we further uncover that the observed real- and momentum-indirect exciton in bilayer MoS$_2$ involves electron and hole respectively from K and Γ valleys, addressing the longstanding controversy of its momentum origin. As bilayer MoS$_2$ is doped with electrons, new sets of PL peaks corresponding to real- and momentum-indirect charged excitons (namely trions) emerge below the energy of the real- and momentum-indirect neutral excitons. Remarkably, the binding energy of real- and momentum-indirect trion is giant in bilayer MoS$_2$, twice that of the real- and momentum-direct trions in transition metal dichalcogenide systems.

RESULTS AND DISCUSSION

High-quality, h-BN-encapsulated dual-gate bilayer MoS$_2$ devices (as schematically shown in Figure 2A) are fabricated by a van der Waals mediated dry-transfer method (please see Section I in Supplementary Information (SI) for more details) with few-layer graphene (FLG) as top and bottom gate electrodes. The dual-gate configuration enables us to independently tune the carrier density $n_0$ and out-of-plane electric field $F_z$.

$$n_0 = (C_{bg}V_{bg} + C_{tg}V_{tg}) / e$$
$$F_z = (C_{bg}V_{bg} - C_{tg}V_{tg}) / 2\epsilon_0\epsilon_B$$

Here $e$ is the elementary charge, $\epsilon_0$ denotes the vacuum permittivity, $\epsilon_B$ is the out-of-plane dielectric constant of bilayer MoS$_2$, $C_{bg}(V_{bg})$ and $C_{tg}(V_{tg})$ are the geometrical capacitances per area (applied voltages) for the bottom and top gates, respectively (details in Section IV in SI).

Figure 2B depicts the PL spectrum of device D1 at $F_z = -0.074$ V/nm. Unless otherwise specified, the data presented in the main text are taken from the high-quality device D1 in a high vacuum at 10 K with a continuous wave optical excitation at ~2.33 eV (532 nm). In addition to the well-known momentum-direct excitons, including both the real-direct transition at around 1.92 eV (labeled as $X_A$) and real-indirect emissions at around 1.95/2.02 eV (dubbed as $IX_1/IX_2$), three momentum-indirect excitons in the energy range of 1.50–1.58 eV (marked as RMX$_1$, RMX$_2$ and RMX$_3$, in the sequence of decreasing emission energy) can be unequivocally observed. Note that the existence of two momentum-direct but real-indirect exciton species of IX$_1$ and IX$_2$ can be ascribed to the fact that the external electric field breaks the layer degeneracy of band structure [23]. Figure 2C presents the color contour of PL spectra against the applied out-of-plane electric field $F_z$. To better distinguish the fine features, we extract the first-order derivative of intensity $I$ over photon energy $E$ ($\partial I / \partial E$) as the function of $F_z$, as depicted in Figure 2D. Obviously, momentum-direct but real-indirect excitons IX$_1$ and IX$_2$ vary linearly with the external electric field $F_z$, yet have reversed slops,
evidencing their opposite out-of-plane static electric dipole moments. Via linear fitting (green dashed lines in Figure 2D and section IX in SI), we extracted the out-of-plane electric dipole moments of \( \text{IX}_1 \) and \( \text{IX}_2 \): 
\[
\mu_z(\text{IX}_1) = (0.526 \pm 0.009) \text{e}\cdot\text{nm} \quad \text{and} \quad \mu_z(\text{IX}_2) = -(0.530 \pm 0.004) \text{e}\cdot\text{nm},
\]
in good agreement with the previous results [23] and our theoretical calculations (±0.578 e·nm, as discussed in Section VII in SI). It is noteworthy that when an enough high electric field \( F_z \) is applied, the shifts of \( \text{IX}_1/\text{IX}_2 \) deviate from a simple linear Stark shift (Figure S5). This can be understood as the strong coupling between \( \text{IX}_1/\text{IX}_2 \) and real- and momentum-direct B excitons, as demonstrated by recent experimental measurements [33] and theoretical calculations [34].

Remarkably, the three momentum-indirect excitons RMX\(_{1,3,1}\) in bilayer MoS\(_2\) also vary linearly with the applied out-of-plane electric field \( F_z \) (gray dashed lines in Figure 2D), evidencing the quantum-confined Stark effect and their indirect nature in real-space. This demonstrates that RMX\(_{1,3,1}\) belong to real- and momentum-direct type-IV exciton. To further confirm their indirect nature in both real- and momentum-spaces of RMX\(_{1,3,1}\), we perform DFT calculations with the Perdew-Burke-Ernzerhof generalized gradient approximation for exchange-correlation interaction (Section VII in SI). Figure 3A shows the orbital-resolved band structure of bilayer MoS\(_2\). For the valence band, its maximum is located at the center of the first BZ (i.e.,
For the conduction band, there are two critical points (i.e., K and Q valleys) whose energies are almost degenerate. As a consequence, Q-Γ and K-Γ transitions are the two possible configurations of momentum-indirect excitons in bilayer MoS$_2$. Since it is difficult for conventional techniques to directly distinguish the two transitions, the exact origin of momentum-indirect excitons in bilayer MoS$_2$ is highly contentious. Some indicate the momentum-indirect exciton in bilayer MoS$_2$ to be K-Γ transition [31,35], while the others reveal that it should be Q-Γ transition [36–38]. To solve the longstanding controversy, we derive the real-space distribution of the spin-up wavefunctions at valence band Γ, and conduction band K/Q (Figures 3B–3D). For spin-down wavefunctions, the real-space distribution can be evidently acquired by time-reversal symmetry. Obviously, the spin-up wavefunction at valence band Γ is symmetrically distributed in both layers, and shows 100% interlayer hybridization (Figure 3B). In stark contrast, the spin-up wavefunction at conduction band K is only distributed in the lower layer and hence fully layer-polarized (Figure 3C). While the spin-up wavefunction at the conduction band Q shows strong delocalization, it still has a slight layer polarization (Figure 3D). Because of the various real-space distributions and interlayer hybridization at diverse valleys, the equivalent positions in real-space of wave functions at conduction band K/Q, and valence band Γ should be quite different. Quantitatively, the equivalent positions of wave functions in real-space, defined as $r_z = \int_{-\infty}^{+\infty} r |\varphi(r)|^2 dr$, are $r_z = -0.5t$ (0.5t), $-0.08t$ (0.08t) and 0 for spin-up (spin-down) wavefunctions at conduction band K, conduction band Q, and valence band Γ, respectively. Here, $|\varphi(r)|^2$ denotes the probability density of wavefunction $\varphi(r)$ at real-space position $r$, and $t = 0.615$ nm represents the interlayer distance [39]. The origin point is set at the midpoint of the constituent two layers. Consequently, both the two possible momentum-indirect transitions are real-space indirect and possess nonvanishing out-of-plane static electric dipole moments: $\mu_z(K-Γ) = e \cdot [r_z(Γ) - r_z(K)] = \pm0.5e \cdot t = \pm0.308e \cdot nm$ for K-Γ excitons and $\mu_z(Q-Γ) = e \cdot [r_z(Γ) - r_z(Q)] = \pm0.08e \cdot t = \pm0.049e \cdot nm$ for Q-Γ excitons, as shown in Figure 3E. On applying an external electric field $F_z$, the exciton energies would vary linearly due to the quantum-confined Stark effect:

$$E = E_0 - \mu_z F_z,$$

where $E_0$ is the exciton energy at zero electric field. Importantly, the experiment results of RMX$_{1,3}$ (hollows in Figure 3F) can be described perfectly by Eq. (1) using the out-of-plane static electric dipole moment of K-Γ transition (i.e., $\mu_z(K-Γ) = 0.308e \cdot nm$), as shown by solid lines in Figure 3F (please refer to Section VI in SI for more information). This clearly manifests that the constituent electrons/holes of real- and momentum-indirect RMX$_{1,3}$ originate from K/Γ valley in the BZ, solving the longstanding debate on momentum origin. It is noteworthy that the energy difference between RMX$_1$ and RMX$_2$ (RMX$_3$) is ~22 meV (~46 meV), which coincides with the energy of phonon mode TA(K) or ZA(K) [2TA(K) or 2ZA(K)] [40]. Thus, the RMX$_1$ transition is probably a kind of zero-phonon line which may be activated by defect [25], and RMX$_2$ and RMX$_3$ should correspond to the one-phonon and two-phonon replicas of RMX$_1$, respectively. Note that two-phonon replica RMX$_3$ is too weak to be distinguished at zero electric field, but exhibits an intensity comparable to or even stronger than that of RMX$_1$ at high electric fields (Figures 2C and 2D). This may indicate a largely enhanced electron-phonon coupling by electric fields and deserves further studies.

Finally, we study the doping-density dependent responses of real- and momentum-indirect excitons in bilayer MoS$_2$. Figures 4A and 4B respectively depict the contour plot and line-cuts of PL spectra as a function...
Here the out-of-plane electric field $F_z$ is fixed at zero. Remarkably, when bilayer MoS$_2$ is doped with electrons, new sets of PL peaks emerge below the energy of the neutral real- and momentum-indirect RMX$_1$ and RMX$_2$, which can be fitted to two new peaks with Lorentzian function (Figure 4B) and correspond to real- and momentum-indirect trions (labeled as RMT$_1$ and RMT$_2$, respectively). This is in close resemblance to the well-studied real- and momentum-direct exciton $X_A$, which is tuned into charged exciton ($X_A^-$) upon electrostatic doping [41]. Note that at $F_z = 0$, only RMX$_1$ and RMX$_2$ can be probed (Figures 2C and 2D). Figure 4C plots the energies of RMT$_1$/RMX$_1$ and RMX$_2$/RMX$_2$, as well as $X_A^+/X_A^-$, as a function of doping density. Notably, the binding energy of real- and momentum-indirect RMT$_1$ (RMX$_1$), i.e., the energy difference between RMX$_1$ (RMX$_2$) and RMT$_1$ (RMX$_2$), can reach up to $\sim$59 meV ($\sim$57 meV), which is more than twice that of real- and momentum-direct $X_A^-$ ($\sim$24 meV) in bilayer MoS$_2$ and also larger than the state-of-the-art results of previously reported trion in 2D semiconductors [42–45].

CONCLUSION

In short, we demonstrate the real- and momentum-indirect neutral/charged excitons (including their phonon replicas) in a multi-valley semiconductor of bilayer MoS$_2$ by the combination of electric-field/doping-density tunable PL measurements and first-principles calculations. Because of the sizable in-built electric dipoles, real- and momentum-indirect excitons present quantum-confined Stark effect and are widely tunable in
applied electric fields. Moreover, the Coulomb interaction between real- and momentum-indirect excitons and free carriers is astonishingly strong in bilayer MoS$_2$, endowing the giant binding energy of real- and momentum-indirect trion of $\sim$59 meV, more than twice that of real- and momentum-direct trion (i.e., $\sim$24 meV). Our work not only fulfills the knowledge on real- and momentum-indirect neutral and charged excitons, but also sheds light on the understanding and engineering of many-body physics and optoelectronics based on multi-valley semiconductors.

**Data availability**

All data needed to evaluate the conclusions are presented in the paper and/or the Supplementary Information. Additional data related to this paper may be requested from the authors.

**Funding**

This work was supported by the National Natural Science Foundation of China (NSFC) (12274447, 61888102, 11834017, 61734001, and 12074412), the National Key Research and Development Program (2021YFA1202900 and 2021YFA1400502), the Strategic Priority Research Program of Chinese Academy of Sciences (XDB30000000), and the Key-Area Research and Development Program of Guangdong Province (2020B0101340001).
Author contributions
G.Z. and L.D. supervised this work; L.D. and Z.H. conceived the project and designed the experiments; Z.H. fabricated the devices with the assistance from J.T., Y.C., X.Z., Y.P., X.L. and Y.Z., and carried out the optical measurements with the help of F.W.; Z.H. conducted AFM measurements with the help of L.L., Y.Y. and Y.J.; Z.H. and L.D. analyzed the data; Y.Z., L.L., W.Y., D.S. and Z.S. helped with data analysis; Z.H., Y.L., L.D. and G.Z. co-wrote the manuscript. All authors discussed the results and commented on the paper.

Conflict of interest
The authors declare no conflict of interest.

Supplementary information
The Supporting Information is available free of charge at https://doi.org/10.1360/nso/20220060. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

References


