Opportunities and challenges of interlayer exciton control and manipulation

Advances in van der Waals heterostructures allow the control of interlayer excitons by electrical and other means, promising exciting opportunities for high-temperature exciton condensation and valley–spin optoelectronics.

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Interlayer excitons (or spatially indirect excitons) are electrons and holes that are bound by Coulomb interactions but spatially separated in two different quantum wells (Fig. 1a). The first studies of interlayer excitons were reported in the context of optical modulators based on the quantum-confined Stark effect in coupled GaAs/AlGaAs quantum wells[1]. With a much longer lifetime than spatially direct excitons, owing to the separation of the electrons and holes, indirect excitons have been subsequently explored to create exciton condensates at low temperatures[2,3]. The recent emergence of two-dimensional (2D) materials, such as graphene and transition metal dichalcogenides (TMDs), and of their van der Waals heterostructures (in which different 2D materials are layered together), has opened new opportunities to study interlayer excitons.

Why are 2D van der Waals heterostructures, particularly bilayers of TMD semiconductors (MX_2, where M = Mo, W; X = S, Se, Te), a fruitful material platform in which to study interlayer exciton phenomena? Monolayer TMDs are direct-bandgap semiconductors with two degenerate copies of energy gaps located at the K and K′ points (or valleys) of the Brillouin zone[4,5]. Extremely strong excitonic effects and contrasting properties for different valleys are the two hallmarks of this class of materials[6,7]. In principle, these properties can be translated into interlayer excitons, and one can envisage rich exciton physics and unique optoelectronic applications that make use of the valley and spin degrees of freedom of TMDs. In addition, the availability of a large family of 2D van der Waals materials that can form vertical heterostructures in any combination presents a unique opportunity in engineering coupled quantum wells and designing the properties of interlayer excitons. Finally, the atomic thickness of TMD bilayers, in combination with the flexibility of building field-effect devices with van der Waals heterostructures[8], is particularly well suited for application of large electric fields (up to about 1 V nm^{-1}) and for electrical control of interlayer excitons.

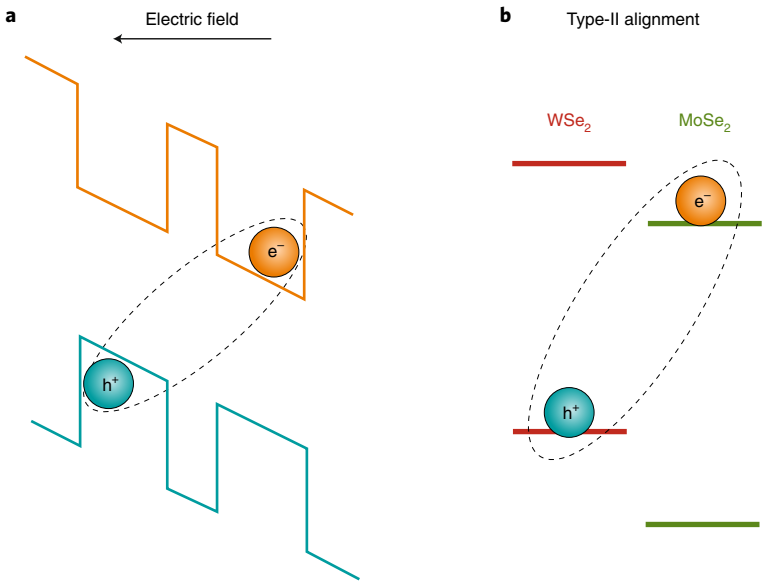

Fig. 1 | Interlayer excitons. a, Electrons and holes are separated into two coupled quantum wells by an external electric field but are bound by Coulomb interaction to form interlayer excitons. **b**, Hetero-bilayers such as MoS_2/WSe_2 and $MoSe_2/WSe_2$ form type-II band alignment. Electrons and holes are separated by a built-in interlayer field.

Interlayer excitons have been experimentally observed in several TMD bilayers[9–13]. Among the first observations are the combinations of MoS_2/WSe_2 and of $MoSe_2/WSe_2$. These form 'type-II' hetero-bilayers[9,10] — that is, the conduction-band and valence-band edges are located in different layers (Fig. 1b). Control of these interlayer excitons by either external fields or structural tuning remains largely unexplored.

Quantum-confined Stark effect

In the presence of an external electric field, the electron states of a quantum well shift to lower energies, and the hole states to higher energies. This electric-field dependence of the energy of spatially confined excitons is called the quantum-confined Stark effect[14]. In the initial study of $MoSe_2/WSe_2$ bilayers, Rivera et al.[10] have already shown that the intensity and energy of the broad emission associated with interlayer excitons can be varied by a gate. But with a single gate, they were not able to separate the effects of an electric field and electrostatic doping. With the advent of high-quality dual-gate devices that control the charge carrier density and the out-of-plane electric field independently, Wang et al.[12] have achieved effective tuning of the interlayer exciton energy in WSe_2 homo-bilayers by the quantum-confined Stark effect. Figure 2b and c shows the electric-field dependence of the photoluminescence spectra of a WSe_2 homo-bilayer. The external electric field creates an interlayer electrostatic potential difference in WSe_2 homo-bilayers, manifested in the energy shift of the interlayer exciton (Fig. 2a). Near zero doping (Fig. 2b), the interlayer exciton

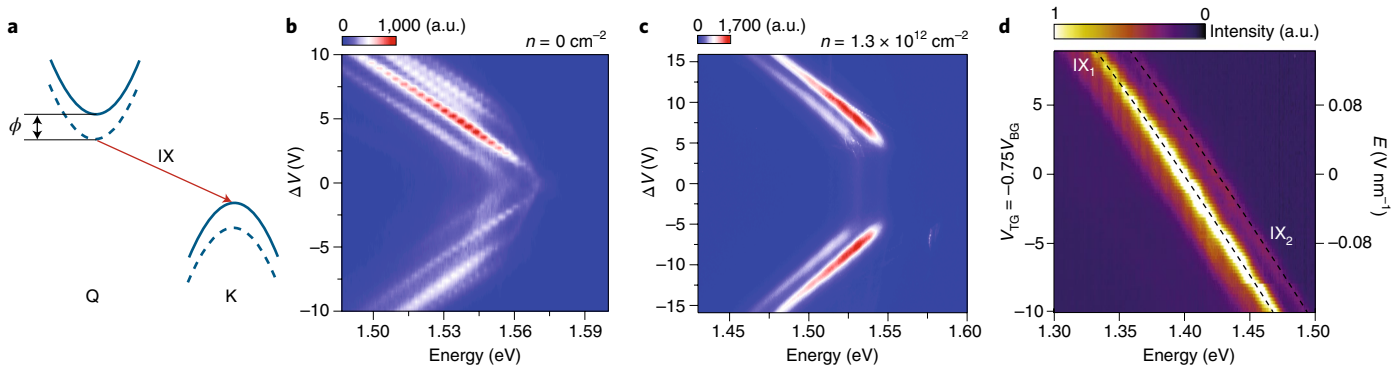

Fig. 2 | Quantum-confined Stark effect in TMD bilayers. a, Electronic band structure of homo-bilayer WSe_2 with conduction-band and valence-band edges at the Q and K/K′ point, respectively. The solid and dashed lines denote the bands of the two layers, respectively. An out-of-plane electric field creates an interlayer electrostatic potential difference ϕ. The red line denotes the interlayer exciton transition IX. **b**–**d**, Contour plots of photoluminescence spectra as a function of gate voltage (left vertical axis) for neutral bilayer WSe_2 (**b**), doped bilayer WSe_2 with a doping density 1.3×10^{12} cm^{-2} (**c**) and hetero-bilayer $MoSe_2$/WSe_2 (**d**). The combination of a top gate voltage (V_{TG}) and back gate voltage (V_{BG}) is used to vary the out-of-plane electric field while keeping the doping density constant. In **b** and **c**, ΔV is the voltage difference between two symmetric gates. In **d**, the corresponding electric field is shown on the right vertical axis. The energy of the interlayer excitons (bright photoluminescence features) depends linearly on gate voltage. Adapted with permission from ref. [12], American Chemical Society (**a**–**c**); ref. [13], courtesy of Andras Kis (**d**).

energy redshifts linearly with external field by about 100 meV. The shift depends only on field magnitude. With finite doping (1.3×10^{12} cm^{-2}; Fig. 2c), electric fields above a certain critical value are required to produce the linear Stark effect. This is because the free carriers screen the external field, and the energy bands start to shift with field only after the free carriers are fully transferred to one of the layers.

Very similar results have been reported in $MoSe_2$/WSe_2 hetero-bilayers by Ciarrocchi et al.[13] (Fig. 2d). The main difference lies in the shape of the field dependence of the interlayer exciton energy. Because of the presence of a large built-in electric field in hetero-bilayers, the energy of the interlayer exciton redshifts when the applied field is aligned with the built-in field, and blueshifts when the applied field opposes the built-in field, producing a total Stark shift of about 200 meV in Fig. 2d. Such a widely tunable exciton resonance is promising for applications in electrically tunable light emitters and modulators.

The quantum-confined Stark effect not only effectively controls the interlayer exciton energy, but also alters the overlap of the electron and hole wavefunctions in the out-of-plane direction, affecting the interlayer exciton lifetime. Wang et al.[12] have demonstrated tuning of the interlayer exciton lifetime, over an order of magnitude, by an external electric field in WSe_2 homo-bilayers, and an interlayer exciton lifetime of over 20 ns. The lengthened exciton lifetime is an important step towards exciton condensation in this material system.

Interlayer exciton valley polarization and lifetime

In addition to the interlayer exciton energy and lifetime, electrical gating can also tune the valley-dependent physics in TMD bilayers. As in TMD monolayers[7], interlayer exciton valley polarization can be generated by circularly polarized optical pumping in TMD bilayers[11,13]. Similarly, it can be probed by the degree of conservation of the pump polarization in the interlayer exciton emission. Rivera et al. have shown in the study of $MoSe_2$/WSe_2 hetero-bilayers that both the interlayer exciton valley polarization and the polarization lifetime can be tuned by electrostatic gating[11]. A valley lifetime as long as 40 ns has been demonstrated. With improvements in sample quality, later works were able to resolve two or more features in the interlayer exciton photoluminescence spectra (WSe_2 homo-bilayers[12], Fig. 2b and c; $MoSe_2$/WSe_2 hetero-bilayers[13], Fig. 2d). Interestingly, Ciarrocchi et al. have observed that the two main interlayer emissions in $MoSe_2$/WSe_2 hetero-bilayers have opposite helicities under circularly polarized optical pumping, one conserving and the other reversing the pump polarization[13] (Fig. 3c). The two features also exhibit a Zeeman shift of opposite sign under a perpendicular magnetic field. Furthermore, because the emission intensity of the two transitions has different doping dependences, Ciarrocchi et al. were able to control the emission polarization by electrostatic gating (Fig. 3a–d). The physics of the multiple interlayer exciton transitions and the gating dependence of the valley polarization and lifetime remain poorly understood. These findings, however, show the potential of interlayer excitons in TMD bilayers for applications in valley–spin optoelectronics.

The way forward

The demonstration of long interlayer exciton lifetimes[11,12] opens an exciting opportunity to cool excitons for exciton condensation in TMD bilayers. The extremely strong exciton binding in this system implies a very small exciton Bohr radius (about 1 nm) and the possibility of achieving a high exciton density, and in turn a high-temperature exciton condensate (theory has predicted a condensation temperature of about 100 K for an exciton density of about 10^{12} cm^{-2})[15]. However, the recent study by Wang et al. has shown that nonlinear relaxation processes, such as the Auger process, limit the steady-state exciton density to around 10^{11} cm^{-2} in TMD bilayers[12]. Ingenious approaches are needed that can suppress the Auger recombination process but maintain the strong interlayer excitonic interaction at the same time. This, for instance, can be explored by inserting atomically thin barriers between two TMD monolayers[9,15]. The question of high-temperature exciton condensation in TMD bilayers remains open. With better experimental control of the physical properties of the interlayer excitons in TMD systems, interlayer excitons promise a bright future for scientific discovery.

In addition to electrical control, manipulating interlayer excitons by structural tuning could become another powerful tool. When two monolayer

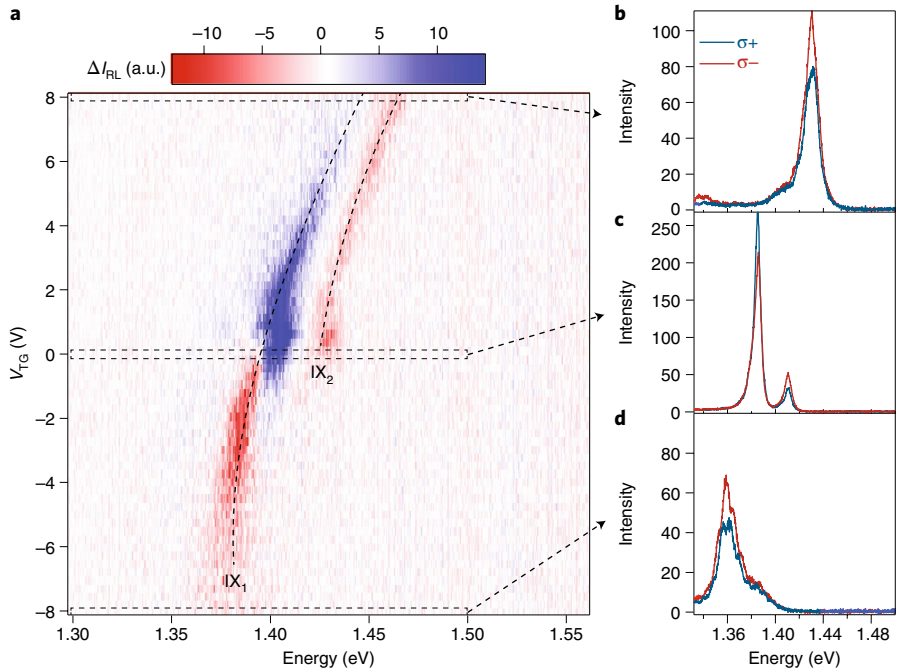

Fig. 3 | Electrostatic gating effect on interlayer excitons in $MoSe_2/WSe_2$ hetero-bilayers. a, Contour plot of the intensity difference of left-handed (σ+) and right-handed (σ−)emission (ΔI_{RL})as a function of top gate voltage V_{TG}. The device was pumped with left circularly polarized light. Two interlayer emission features (IX_1 and IX_2) of opposite helicities can be clearly resolved for positive gate voltages. **b**–**d**, Handedness-resolved photoluminescence spectra of interlayer excitons for three representative gate voltages marked by dashed lines in **a**. Adapted with permission from ref. [13], courtesy of Andras Kis.

TMDs are coupled vertically by the van der Waals interaction, the band alignment is determined by the work function of the individual layers, the interlayer interaction and the alignment of the crystal axes of the two layers[16–18]. The electronic structure of TMD bilayers is very sensitive to the relative angle of rotation between the two layers[19–21], which presents a huge opportunity for rotational control of interlayer excitons and their response to external electric and magnetic fields. The presence of small relative rotations between two TMD layers has been predicted to produce a moiré pattern in real space and a momentum shift between the electron and hole bands located in different layers[19]. Such an effect on the optical selection rules for interlayer excitons is of great current interest[20,21]. The flat exciton moiré bands are expected to enhance the effects of exciton–exciton interactions and thus the optical nonlinearity of the system. In addition, topological exciton moiré bands with enhanced optical conductivity at sample edges due to the formation of chiral excitonic edge states have been predicted[19]. Meanwhile, experimental studies on interlayer excitons in twisted TMD bilayers have just started to emerge. In a recent study of AB-stacked (that is, 60° rotation) $MoSe_2/WSe_2$ hetero-bilayers, Nagler et al.[22] have shown an exciton *g*-factor of about 15 for interlayer excitons[22], in contrast to that of about 4 for excitons in a single TMD layer. The result has been explained by the alignment of the K valley in one layer with the K′ valley in the other layer, and the combined valley contributions to the exciton magnetic moment. We expect to see many advances in the same vein in future.

Another interesting development in the study of 2D materials is the control of electronic properties and moiré mini-bands by applying pressure (for instance in graphene–boron nitride heterostructures[23]). In general, because of the weak van der Waals bonding between layers in a vertical heterostructure of 2D materials, applied pressure can strongly affect the interlayer separation and electronic coupling, shift the mini-bands and change the mini-bandgaps. We expect that pressure will also effectively tune the interlayer excitons and the exciton moiré bands in TMD bilayers. Pressure control of the moiré superlattice and the moiré potential landscape can aid trapping of excitons at the moiré potential minima, leading to the formation of an array of localized exciton emitters in TMD bilayers[20].

With rich new physics and unprecedented engineering flexibility and controllability, we believe that 2D van der Waals heterostructures in general, and TMD bilayers in particular, offer a truly unique materials system in which to pursue interlayer exciton-related research and applications. ❐

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