Tunable Localized Charge Transfer Excitons in a Mixed Dimensional van der Waals Heterostructure

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Abstract

Observation of interlayer, charge-transfer (CT) excitons in van der Waals heterostructures (vdWHs) based on 2D-2D systems has been well investigated. While conceptually interesting, these charge transfer excitons are highly delocalized and spatially localizing them requires twisting layers at very specific angles. This issue of localizing the CT excitons can be overcome via making mixed dimensional vdWHs (MDHs) where one of the components is a spatially quantum confined medium. Here, we demonstrate the formation of CT excitons in a 2D/quasi-2D system comprising MoSe$_2$ and WSe$_2$ monolayers and CdSe/CdS based core/shell nanoplates (NPLs). Spectral signatures of CT excitons in our MDHs were resolved locally at the 2D/single-NPL heterointerface using tip-enhanced photoluminescence (TEPL) at room temperature. By varying both the 2D material, the shell thickness of the NPLs, and applying out-of-plane electric field, the exciton resonance energy was tuned by up to 120 meV. Our finding is a significant step towards the realization of highly tunable MDHs with novel excitonic properties.

Introduction

Interlayer excitons (ILXs) are composed of Coulomb bound electron and hole (e-h) pairs confined in two different spatially separated quantum wells that are coupled together electronically. Owing to large spatial separation of e-h pairs, ILXs possess much longer lifetimes (1 – 3 order of magnitude higher) than the direct excitons of individual QWs\textsuperscript{1,2}. This allows ILXs to be subsequently explored for strongly correlated condensed matter phenomena such as Bose-Einstein condensates as well as in excitonic, and photonic devices\textsuperscript{3,4}. Experimental observation of ILXs was first reported in coupled GaAs/AlGaAs QWs and later in various III-V and II-VI QW heterostructures\textsuperscript{5}. However, the very small exciton binding energy (few meV) of conventional 3D semiconductor QW heterostructures limited the progress of this field to cryogenic measurements\textsuperscript{6}.

The recent emergence of both structural as well as electronic variety in 2D materials has opened new opportunities to study ILXs. Van der Waals heterostructures (vdWHs) composed of several combinations of distinct 2D materials, especially transition metal dichalcogenides (TMDCs), allow the formation of ILXs with remarkably high binding energies (100 – 350 meV)\textsuperscript{7}. Hence, it is possible to observe ILXs in such vdWHs at room temperature (RT), which has made it an intense research topic in recent years\textsuperscript{8,9}. ILXs formed in 2D/2D systems are generally delocalized in the 2D plane and require a specific twisting angle between the participating monolayers to create localized excitons in the 2D landscape\textsuperscript{10,11}. As a result, forming localized ILXs in a twisted heterobilayer (HB) can function as quantum dot-like (QD) confined potentials which unlock exciting opportunities towards high-performance semiconducting lasers, single photon emitters, entangled photon sources, and tunable exotic quantum phases of matter\textsuperscript{4,12,13}. Despite the recent great efforts of spatially confining ILX in HBs with precisely controlled angles, imperfection in crystals, challenges with sophisticated sample preparation, and the repulsive interaction between the confined excitons keep the localization process far from ideal both in terms of energy (spectral lines) and spatial extent\textsuperscript{14,15}. 
In this context, mixed dimensional heterostructures (MDH) composed of 2D materials on one side and 0D or spatially confined materials on the other side can be an attractive option for the creation of localized ILXs. Due to the van der Waals nature of the interface formed between 2D and 0D or spatially confined materials, MDHs favor similar charge transport phenomena analogous to all-2D vdWHs, when formed with type-II band alignment\textsuperscript{16–19}. Therefore, it is predicted that MDHs can also emit ILX-like excitons, which are known as hybrid or charge transfer (CT) excitons\textsuperscript{20,21}. Additionally, reduced dimensionality of one of the materials can introduce arbitrary spatial and energy confinement as well as additional degrees of freedom at the interfaces to tune electronic properties of MDHs\textsuperscript{20}. Hence, in contrast to delocalized ILXs in all-2D vdWHs, CT excitons formed in MDH heterointerfaces should be localized along the reduced dimensional materials in the out-of-plane direction. This leads to the possibility of investigating and manipulating localized CT excitons in the 2D landscape of the respective MDH. Moreover, owing to the differences in the density of states and dielectric screening environments on either side of the heterostructure, the mechanism of the CT exciton formation and the consequent parameters that can control it may be fundamentally different compared to all-2D systems\textsuperscript{22}. Importantly, the constraints on localization of ILX-like excitons in terms of energy and spatially are eliminated in the case of MDHs. Therefore, MDHs present a new platform to investigate charge-transfer physics and subsequent exciton formation in MDHs, and will have a broader technological impact on many device applications\textsuperscript{23,24}.

In this work, we report on the observation of CT excitons in MDHs composed of 2D transition metal dichalcogenides (TMDCs) and colloidal semiconducting CdSe/Cd\textsubscript{x}Zn\textsubscript{1−x}S core/shell nanoplates (NPLs). Even though these nanoplates are colloidal semiconducting nanocrystals, their density of states more resemble a step-like quasicontinuum similar to a 2D electronic system\textsuperscript{25}. Therefore, these nanoplates are known as quasi-2D (Q2D) systems. We adopt tip-enhanced photoluminescence (TEPL) nano-spectroscopy to resolve the spectral signature of CT excitons from a single NPL/2D heterointerface. Taking advantage of large tunability of the band structure as a function of shell thickness of CdSe/Cd\textsubscript{x}Zn\textsubscript{1−x}S based core/shell NPLs and combining them with monolayer MoSe\textsubscript{2} and WSe\textsubscript{2} we are able to tune the CT exciton up to 120 meV. Our work presents primary experimental evidence of the presence of CT excitons with large tunability in a MDH system.

**Results And Discussions**

Fig. 1a presents a schematic of the TEPL configuration used to characterize MDHs in this study. The MDHs containing monolayer MoSe\textsubscript{2} (or monolayer WSe\textsubscript{2}) and CdSe/Cd\textsubscript{x}Zn\textsubscript{1−x}S core/shell NPLs have three different excitons: two in-plane excitons from the TMDCs and NPL respectively and one out-of-plane CT exciton across the MDH interface as schematically presented. A gold tip was used to excite the plasmonic field underneath using 633 nm excitation. Fig. 1b shows an optical image of one of the representative MDH samples studied in this work. Details of the MDH device fabrication, NPLs synthesis and characterization can be found in the method section and the supplementary information section I. Far-field PL intensity maps created for NPLs and MoSe\textsubscript{2} and their overlay image for the area of interest (AOI) region marked in the optical image (Fig. 1b) are shown in Fig. 1c-e respectively. The representative
far-field-PL spectra for both MDH and monolayer MoSe$_2$ are displayed in Fig. 1f. The orange shades are the spectral region for which the NPL and MoSe$_2$ PL maps were created in Fig. 1c, d. As can be seen in Fig. 1e, the MDHs form at multiple locations between NPLs and MoSe$_2$. Wherever they form an electronic contact, MDHs emit CT excitons as revealed by TEPL. However, it is challenging to resolve CT excitons in the far-field-PL configuration due to the close proximity of this peak to the A exciton of MoSe$_2$ and the large probing cross-section of the far-field PL geometry (~ 0.2 µm$^2$) compared to a very small CT exciton emitting area (limited by the spatial extent of NPLs: 6 x 10$^{-4}$ µm$^2$). These factors ultimately, lead to very weak CT exciton signals in the far-field PL spectroscopy geometry, (see supplementary information section II for more details).

The situation can be changed by introducing TEPL, which excites/emits signal locally under the tip apex with high spatial resolution. Fig. 1g,h show atomic force microscope (AFM) and corresponding TEPL intensity images of NPLs on MoSe$_2$ respectively. Our sub-20 nm spatial resolution was enough to resolve CT exciton from a single NPL/2D MDH interface (see supplementary information Fig. SI-2ii). Despite the excellent sensitivity of TEPL (both enhancement and spatial resolution), the large extent of the 2D plane can still introduce an additional challenge in resolving spectral features from the MDH areas since the TEPL signal needs to overcome a large far-field background (see supplementary information section III). Hence, all the TEPL measurements were treated with far-field background subtraction to resolve the CT excitons in MDHs clearly. Two representative TEPL spectra, one averaged from the NPL region (black rectangle area) and the other from MoSe$_2$ (white rectangle area) marked in Fig. 1h can be seen in Fig. 1i.

It is Important to note that MDH spectrum is averaged over 4 pixels (pixel size is 20x20 nm) corresponding to two NPLs (see table S1 in the supplementary section I) making it noisier than the MoSe$_2$ spectra (averaged over 42 pixels). We can clearly observe three PL features in the MDH spectrum in Fig. 1i. Among them, two main excitonic features, NPL PL and MoSe$_2$ A exciton peak are observed at 1.87 eV and 1.60 eV respectively. The third PL peak is observed 50 meV below the MoSe$_2$ A exciton peak in the MDH spectra. We assigned this peak as the CT exciton via e-h recombination from NPL to MoSe$_2$ and will provide further evidence to our claim in the following sections.

To understand the CT mechanism and the consequent exciton formation at the MDH interface under investigation, we analyse the band diagram using the band values available in the literature for both the semiconductors in the MDH$^{26,27}$. The band alignment presented in Fig. 2a predicts photoexcited electron transfer from MoSe$_2$ to NPLs and then e-h recombination from NPL CB to MoSe$_2$ VB, which can be observed as CT exciton in our system. We followed two approaches to confirm the origin of this emission peak. The first one is via changing the 2D material as shown in the band alignment diagram of Fig. 2b. Since the band edges of monolayer WSe$_2$ move higher in energy compared to monolayer MoSe$_2$, it should create CT excitons of smaller energy (larger energy offset) when paired with NPLs of the same bandgap. TEPL spectra acquired for NPL/WSe$_2$ system presented in Fig. 2c demonstrates this hypothesis. For comparison, TEPL spectra of bare WSe$_2$ acquired from a nearby area and the NPL/MoSe$_2$ spectrum of Fig. 2d is also plotted together. The main excitonic feature (bright exciton, A) of
WSe$_2$ is observed at 1.66 eV as a shoulder to the strong dark exciton, X$_D$ around 1.62 eV in our TEPL spectra. Even though dark excitons in WSe$_2$ are not permitted in far-field geometry, they can be observed in TEPL at RT due to the strong coupling between the out-of-plane exciton dipole moment and the plasmonic field in the nano-cavity$^{28,29}$. Nevertheless, most importantly, the CT exciton peak can be observed at 80 meV below the WSe$_2$ A exciton. Hence, from Fig. 2c, it is clear that the NPL/WSe$_2$ interface creates CT excitons with larger band offset than the NPL/MoSe$_2$ interface. Note that the slight deviation of the bandgap of NPL is due to thickness variation (a consequence of NPL synthesis process) of the NPL.

As a second approach, we also test the possibility of tuning the CT exciton energy via changing the NPL shell thickness. As predicted in the literature, quasi-type II CdSe/CdS based core/shell NPLs exhibit strong (negligible) thickness dependent conduction band (CB) (valence band (VB)) tunability due to the small (large) conduction (valence) band offsets$^{26}$. Hence, we can adjust the band alignment of the studied MDH systems via shell thickness to tune the CT exciton energy position. Fig. 2d displays NPL shell thickness dependent TEPL spectra of NPL/MoSe$_2$ MDH systems. As the shell thickness increases (from 4.5 ML to 7.5 ML), the CT exciton energy can be tuned up to 90 meV via tuning the band alignment. The process of band alignment tuning via NPL shell thicknesses is schematically presented in Fig. 2e-g. Larger shell thickness results in a smaller NPL bandgap, which moves the NPL CB minimum away (towards lower energy) from the MoSe$_2$ CB minimum. This results in a larger band offset and consequently smaller CT exciton energies for thicker NPLs. In order to decouple CT excitons from strain and other local heterogeneity induced shift we also conducted a comprehensive TEPL investigation of the systems. Detailed studies of the local heterogeneities in the PL can be found in the supplementary information section IV.

CT excitons have an out-of-plane dipole moment similar to the case of interlayer exciton formation at a 2D/2D TMDC interface. This necessitated a study of the effect of out-of-plane $E$ field on the evolution of CT excitons in the 2D/QD MDHs. For the $E$ field dependent TEPL study, we used the same experimental configuration shown in Fig. 1a with a bias applied between the tip and the substrate during measurements. Fig. 3a,b presents a NPL TEPL map and corresponding AFM topography of the NPL/MoSe$_2$ MDH system acquired simultaneously at 0V bias. For each bias voltage a complete TEPL map was acquired for the same region of interest and an averaged TEPL spectra was created over the rectangle area marked in Fig. 3a. $E$ field dependent TEPL spectra of the MDH for the spectral region between 1.65 to 1.38 eV are shown in Fig. 3c. Evolution of NPL PL peak position as a function of bias voltage can be found in the supplementary information section V. For a NPL PL peak of 1.85 eV we observed the CT exciton at 60 meV below the MoSe$_2$ A exciton at 0V bias as schematically presented in the band diagram of Fig. 3d. As the bias increases in the negative direction, the CT exciton drifted further away in energy from the A exciton with a red shift of 120 meV observed at -2 V. The opposite trend was observed in the positive bias direction, though at a slower rate. It was not possible to decouple CT exciton from the A exciton peak above 1 V due to the close proximity and low single-to-noise ratio. Fig. 3d-f are sketched to explain the CT exciton evolution under an out-of-plane $E$ field. At 0 V, we have the standard
band alignment for which the CT exciton is observed. However, at negative bias, the CB of MoSe$_2$ (NPL) increases (decreases) in energy. As a result, the CT exciton moves away energetically from the A exciton to a lower energy. The opposite situation occurs at a positive bias for which we observe the CT exciton move closer in energy to the A exciton of MoSe$_2$. A similar behavior was recently reported for delocalized analogous CT excitons (IL excitons) in a TMDC HB system$^{2,30}$.

A further proof of forming type II band alignment (prerequisite for CT exciton formation) at NPL/TMDC (both MoSe$_2$ and WSe$_2$) heterointerfaces can be demonstrated by electrical characterization. Fig. 4a,b present AFM and corresponding contact potential difference (CPD) images of a NPL/WSe$_2$ MDH system. The height profile of the MDH (inset of Fig. 4a) indicates a cluster of NPLs with a possible pilling of two individual NPLs on top of each other since the thickness of each NPL should be around 3 nm (see sample 1 in Table S1). The CPD image in Fig. 4b exhibits a more interesting and informative electronic picture of the MDH. Even though ML-WSe$_2$ wraps the NPLs well and creates a single bulge in the topography, the CPD image shows traces of several NPL/WSe$_2$ interfaces. To extract the Fermi level information at charge neutrality conditions, we took three line profiles and plotted them in Fig. 4c. A gaussian fit to the line profile 1 provides a width of 13 nm (see supplementary information VI), which agrees well with the width of a single NPL. Interestingly, CPD line profiles 2 and 3 show several dips of the same value as line profile 1. Line profile 3 was fitted with three Gaussians: among them, the two outer ones have slightly higher width, and the middle one has the same width as line profile 1. Using the dimensions of the NPL, CPD line profiles and TEPL map (see Fig. SI-6), we sketched the MDH area with five NPLs, as shown in Fig. 4a,b. To explain the interfacial charge transfer phenomenon a schematic of the band diagram is plotted in the inset of Fig. 4c. Due to the Fermi level adjustment via interfacial charge transfer, the surface potential of WSe$_2$ decreases by 30 - 40 mV at the MDH interface, which is equivalent to a ~30 meV Fermi level rise at charge equilibrium conditions.

Fig. 4d displays the I − V curves measured locally using conductive-AFM on two different spots of the sample marked by black circles in Fig. 4a. More I − V curves are presented in the supplementary information section VI. Fig. 4d clearly demonstrates a rectification behavior for the MDH. Whereas, on WSe$_2$ we observed a linear I-V response due to direct electrical tunnelling or conduction through the ultra-thin layer of monolayer WSe$_2$.

Finally, we have used time-resolved photoemission electron microscopy (tr-PEEM) to investigate the exciton dynamics of CT excitons in MDH. Fig. 4e,f show the optical and PEEM image of the AOI region (outlined by circles). Exciton decay curves shown in Fig. 4g were derived from spatially-averaged dynamics within the AOI region. The femtosecond pump- probe tr-PEEM results of the MDH were acquired at two different pump excitation lasers: one at 1.65 eV covering the MoSe$_2$ exciton region and the other at 1.51 eV which predominately excites CT exciton. To fit the dynamics of the excitons both decay curves were fitted with bi-exponential functions with the fit parameters listed in the table S2. From the fit, the MoSe$_2$ A exciton lifetime (excited by 1.65 eV) is determined to be 1.1 ps. However, CT excitons generated at 1.51 eV show a shorter lifetime of 0.6 ps, which is in stark contrast to the lifetime of analogous ILXs in
all 2D vdW heterostructures\textsuperscript{2}. Indeed, the decay signal is the combination of both radiative and non-radiative recombination of excitons. At elevated temperature (tr-PEEM measurements were performed at RT) non-radiative decay through Augur scattering or charge trapping at defects dominates, which occurs on a faster time scale than radiative recombination \textsuperscript{31,32}. Since CdSe/Cd\textsubscript{x}Zn\textsubscript{1-x}S core/shell nanocrystals are known for surface defects/trap states\textsuperscript{33}, the probability of non-radiative recombination of CT excitons is higher at the MoSe\textsubscript{2}/NPL interface than for the MoSe\textsubscript{2} A exciton in the 2D plane. A similar behavior was also observed by Bouleshba et al\textsuperscript{34} at a WS\textsubscript{2}/QD heterointerface. Hence, we observe a shorter CT exciton life time relative to the MoSe\textsubscript{2} A exciton in the present work.

**Conclusion**

In summary, we report the formation of CT excitons in a MDH containing 2D TMDCs and quasi-2D NPLs. We adopted TEPL to spatially resolve CT exciton formation sites at the single NPL/TMDC interface. To the best of our knowledge, this is the primary observation of such localized CT excitonic phenomena in a MDH at RT. To confirm the origin of CT excitons, we adopted a systematic approach via changing both the TMDC material and the shell thickness of NPLs. Both approaches give a wide range of tunability of the CT exciton energy, up to 100 meV. Out-of-plane $E$ field dependent TEPL also provides an excellent knob to tune the CT exciton with a tunable range of 120 meV. Our work opens a new pathway for manipulating excited states at mixed-dimensional interfaces, which offers great promise both for fundamental studies and optoelectronic applications, opening doors to electrical control of colloidal quantum materials via electronic heterointerfaces with 2D materials.

**Methods**

**Synthesis of rectangular CdSe nanoplatelets:** The cadmium myristate precursor is prepared by following the literature\textsuperscript{35}. Colloidal, rectangular CdSe nanoplatelets with a thickness of 4.5 monolayers are synthesized following the literature\textsuperscript{36} with slight modifications\textsuperscript{37,38} that are described in detail in the supplementary information section SI-I.

**Synthesis of square-like CdSe nanoplatelets:** Colloidal, square-like CdSe nanoplatelets with a thickness of 4.5 monolayers are synthesized by following prior literature\textsuperscript{39} with slight modifications that are described in detail in the supplementary information section SI-I.

**Growth of Cd\textsubscript{x}Zn\textsubscript{1-x}S shell:** Cadmium (Cd(OI))\textsubscript{2} and zinc oleate (Zn(OI))\textsubscript{2} are synthesized according to the literature\textsuperscript{39,40}. The growth of a Cd\textsubscript{x}Zn\textsubscript{1-x}S shell with increasing thickness on CdSe nanoplatelets is performed by following the literature\textsuperscript{39} with minor modifications that are described in detail in the supplementary information section SI-I.

**MDH device preparation:** Both ultra-smooth Au and 5 nm Al\textsubscript{2}O\textsubscript{3} coated Au substrates were used for the sample preparation. Al\textsubscript{2}O\textsubscript{3} films were deposited on Au using ALD (Cambridge Nanotech) via chemical
reaction of metal organic precursor, Trimethylaluminium with water vapors in each cycle at 150 °C, which typically yielded a deposition rate of 0.9 Å/cycle. To prepare the ultra-smooth Au surface, ~100 nm of Au was first deposited on Si with native oxide (without any adhesion layer) using the thermal evaporation technique. After that, the buried ultra-smooth Au face was stripped-off using an epoxy resin supported Si substrate, which were then used as the active substrates for the MDH devices.

To prepare the devices, a very dilute solution of NPL (0.001 mg/mL) was first spin coated at a speed of 3000 rpm for 60 s on the Au (or Al₂O₃/Au) substrate. After that, monolayer TMDCs were transferred on top of NPLs/Au via deterministic dry transfer method. All the sample were then annealed in an Ar/H₂ atmosphere for 2 h at 120 °C.

**Micro-PL characterization**: A Horiba LabRam HR evolution equipped with 633 nm excitation laser and an electron multiplying charge coupled detector was used for micro-PL measurements. PL measurements were carried out using 100 l/mm grating and 100 µW power (measured at the sample surface) focused on the sample surface via a 100 x, 0.9 NA objective. PL maps were acquired using 500 x 500 nm step size, which is well above the diffraction limit at this wavelength. Signal acquisition time was set at 0.2 s during the mapping.

**TEPL characterization**: TEPL measurements were carried out using a Horiba NanoRaman platform consisting of the same Horiba LabRam HR evolution coupled with an AIST-NT AFM. Commercially available Au TERS tips were used for the measurements under p-polarized 633 nm excitation in side illumination/collection geometry at an angle of 65° from the normal to the sample surface. The laser power was kept at 20 µW focused onto the tip apex using a 100x 0.7 NA objective and the acquisition time was set at 0.2 s. Both the near-field PL spectra and far-field background were collected for each pixel one after another during TEPL map acquisition via a hybrid tip operating mode. Far-field background was measured during the tip normal oscillation period in non-contact mode and the near-field signal was collected by bringing the tip in contact to the sample. Both measuring steps were repeated one after another at each pixel to collect complete near-field plus far-field and far-field only PL maps of the sample. A step size of 20 x 20 nm was used for the all the TEPL mapping except for the E-field dependent study, for which a 40 x 40 nm step size was used. For the E-field dependent study, a bias was applied to the tip and kept constant during map acquisition.

**I – V characterization**: I – V characterization of the MDH were performed using conductive AFM and commercially available Cr/Au probes.

**Time-resolved PEEM**: The PEEM experiments were performed using a commercial titanium-sapphire oscillator (Griffin-10, KM Labs) producing sub-20 fs pulses centered at 780 nm at a 90 MHz repetition rate. A slit within the laser cavity is used for fundamental wavelength (740-840 nm range) and bandwidth tuning. Approximately 30% of the pulse is split to produce the second harmonic probe pulse in a 200 µm thick BBO crystal. The resulting blue light is recompressed in a CaF₂ prism pair to yield second harmonic pulses of less than 50 fs. A variable delay line controls the relative timing between the red (~800 nm)
Pump and blue (~400 nm) probe pulses. $P$-polarized laser pulses are recombined on a dichroic beam splitter and directed collinearly onto the PEEM sample at a 75° angle of incidence with respect to the surface normal. The spot sizes of the separate beams are adjusted such that typically the red pulse spot size is roughly 50% smaller than the blue pulse spot size at the sample position. A typical spot size for the red laser is 40 x 120 microns at the sample. PEEM images are collected as a function of probe delay time, yielding time resolved movies of photoelectron emission dynamics. Cross-correlation of the red and blue pulses yields time resolution of less than 80 fs for all wavelengths pairs used in this study. Typically, 50-100 mW of ~800 nm power is used in combination with 3-6 mW of ~400 nm laser light for experiments described herein.

**Declarations**

**Author Contribution**

M.R. and D.J. conceived the idea and designed the research. M.R. implemented the project via sample fabrication, performing far/near-field-PL, CPD and, c-AFM measurements and analyzing and interpreting the data. E.M. and Z.J. synthesized the nanoplates under the supervision of C.B.M. A.G.J and B.T.O-C. conducted time-resolved exciton lifetime measurements under the supervision of P.Z.K. S.S. and K.J. contributed to the sample fabrication. G.K. contributed to far-field PL measurements. D.R. performed TEM of nanoplates. M.R. and D.J. wrote the manuscript with inputs from all coauthors.

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**Figures**

**Figure 1**

**Micro- and nano-optical characterization of CT excitons in MDHs.** (a) Schematic representation of TEPL measurements of the MDHs containing TMDC monolayers (MoSe\textsubscript{2} and WSe\textsubscript{2}) on top of CdSe/CdS\textsubscript{x}Zn\textsubscript{1-x}S core/shell NPLs on an Au (or Al\textsubscript{2}O\textsubscript{3}/Au) substrate. For the electric field dependent study an out-of-plane bias was applied through the tip and metal substrate. (b) Optical image of one representative MDH device investigated in this work. Area of interest (AOI) is outlined by a dashed rectangle. (c), (d) Far-field PL intensity map of NPL and MoSe\textsubscript{2} acquired for the AOI region. (e) PL intensity overlay image using (c) and (d) showing the MDH interface formation on a MoSe\textsubscript{2} monolayer. Scale bar is 10 µm. (f) two representative far-field PL spectra of MoSe\textsubscript{2} and MDH acquired from two nearby pixels as marked in the overlay image. NPL Spectral regions are multiplied by 5 for better visibility. Orange shades are the spectral regions for which PL maps were created for NPL and MoSe\textsubscript{2} respectively. (g), (h) AFM topography and corresponding TEPL intensity map of NPLs on monolayer MoSe\textsubscript{2} acquired.
simultaneously. (i) Two representative TEPL spectra averaged over the rectangle areas marked by 1 and 2 in the TEPL image.

Figure 2

Band alignment engineered tunability of CT excitons in MDH. (a), (b) Band alignment diagrams at 2D/Q2D interfaces studied in this work. Values are taken from the refs\textsuperscript{26,27}. (c) TEPL spectra acquired for the WSe\textsubscript{2}/NPL system. For comparison TEPL spectra of bare WSe\textsubscript{2} and MoSe\textsubscript{2}/NPL of Fig. 1i are also plotted. (d) Tuning of CT excitons via NPL shell thickness variation for NPL/MoSe\textsubscript{2} system. (e) – (g) Schematic illustration of band alignment for CT exciton tuning via NPL shell
**Figure 3**

**E-field dependent tuning of CT excitons in MDH.** (a) TEPL map of NPL and (b) corresponding AFM topography of the NPL/MoSe$_2$ system acquired simultaneously at 0V bias voltage. (c) Contour plot of $E$ field dependent TEPL spectra of the MDH system averaged over the rectangular area shown in (a). (d) – (f) Band alignment of the MDH at three different bias conditions.
Figure 4

Electrical and temporal characterization of MDH. (a), (b) AFM and corresponding CPD images of a WSe$_2$/NPL MDH system. The height profile of the MDH along the dotted red line is shown in the inset of (a). (c) Three separate CPD profiles extracted along the dashed lines in (b). The top panel is fitted with three Gaussians. Inset: schematic illustration of MDH band alignment at charge equilibrium condition. (d) Locally measured I – V curves on two different spots marked by black circles in (a) using conductive AFM. (e), (f) Optical and PEEM images of a MDH sample used for tr-PEEM measurements. (g) Time-resolved PEEM of the MDH acquired using two different excitation laser energies to determine the CT exciton dynamics. Decay curves were spatially-averaged over the dashed circle in (e).

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