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# Efficient energy transfer and photoluminescence enhancement in 2D MoS<sub>2</sub>/bulk InSe van der Waals heterostructures

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Heterostructures between 2D and 3D electron systems remain critically important in developing novel and efficient optoelectronic and electronic devices. In this study, a vertical heterojunction between monolayer MoS<sub>2</sub> and bulk InSe was developed. This heterojunction exhibits a type-I band alignment that facilitates rapid energy transfer from the wide bandgap MoS<sub>2</sub> to the narrow bandgap InSe resulting in quenching of the MoS<sub>2</sub> photoluminescence (PL) emission and enhancement of the A exciton emission in InSe. Temperature-dependent PL measurements of MoS<sub>2</sub> on SiO<sub>2</sub>, MoS<sub>2</sub> on InSe, and bare InSe revealed the critical role of defect trapping and electron-phonon coupling in the optical response of MoS<sub>2</sub> on InSe. These results demonstrate that heterostructures combining monolayer MoS<sub>2</sub> on bulk InSe, showing marked improvement relative to bare InSe, would be advantageous when incorporated into optoelectronic devices such as photodetectors, light emitters, and color converters and highlights the benefit of creating van der Waals (vdW) heterostructures with tailored properties.

2D Heterostructures have become foundational in many electronic and optoelectronic devices including tunneling transistors, photodetectors, and solar cells<sup>1–8</sup>. Of the plethora of emerging heterostructures, combinations of 2D semiconducting materials have been heavily investigated due to relative atomic coordination and electronic energy scales between layers leading to unique Moiré patterns/potentials<sup>9–11</sup>, interlayer exciton formation<sup>12</sup>, and ultrafast charge transfer<sup>13</sup>. Heterostructures between 2D and 3D materials have also become incredibly important as materials such as transition metal dichalcogenides (TMDs) are integrated into more complex device architectures, necessitating control of interfacial properties between the 2D material and substrate, dielectric materials, contacts, and other semiconductors<sup>14</sup>. Electronic devices such as Schottky rectifiers between graphene and the wide bandgap semiconductor gallium nitride have shown excellent rectifying behavior, low leakage current and large barrier heights relative to devices with more conventional 3D semiconductors<sup>15</sup>. Highlighting the utility of combining the exquisite properties of 2D semiconductors with conventional bulk 3D materials, 2D/3D optoelectronic

structures such as black phosphorous/silicon and graphene/silicon photodetectors have also demonstrated utility in creating high-speed and high-responsivity devices operating in the UV and IR regimes, respectively<sup>16,17</sup>. Understanding the fundamental interactions and energy transfer processes at the interfaces of these heterostructures is challenging as conventional 3D materials possess dangling bonds at the surface which lead to strong hybridization and atomically sharp scattering centers when coupled to 2D materials. Interfacing 2D and 3D electron systems through vdW bonding alone, that is atomically thin 2D materials with bulk-like 2D materials, provides a valuable opportunity to understand the emergent effects in 2D/3D heterostructures (from the interface between 2D layered materials and 3D materials with dangling bonds) without destroying the quantum delocalization and coherence of the 2D electron system.

Of the many semiconductors currently being explored for next-generation electronics and optoelectronics, semiconducting layered InSe has demonstrated an exceptional combination of properties including electron mobility exceeding 1000 cm<sup>2</sup>/Vs and a direct band gap from nm-

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scale to bulk thicknesses<sup>18</sup>. Recently, significant advancements have been made in InSe research with demonstration of wafer-scale growth<sup>19</sup>, tunneling transistors<sup>20</sup>, ballistic transistors<sup>21</sup>, and broadband photodetectors<sup>22,23</sup>, making it an attractive material for high performance and low-power electronic and optoelectronic devices with the potential to be tuned to specific applications. For example, the band gap can be tuned by layer number to access a photoresponse from infrared through the visible range<sup>18,24</sup>, enabling band-engineered light emitting and photodetector devices. Additionally, the valence band edge transitions from a wide parabolic dispersion to a “Mexican hat” dispersion as the material is reduced from bulk to monolayer, providing a platform to tune and probe flat band physics<sup>25,26</sup>. Further, a strong luminescent response and strong exciton-exciton and exciton-phonon interactions make InSe a prospective material for near-infrared lasing<sup>27,28</sup>. Already, bulk InSe has demonstrated high-performing device implementation in photodetectors<sup>29–31</sup>, field-effect transistors<sup>32,33</sup>, gas sensors<sup>34</sup>, neuromorphic memory<sup>35</sup>, and more<sup>36</sup>.

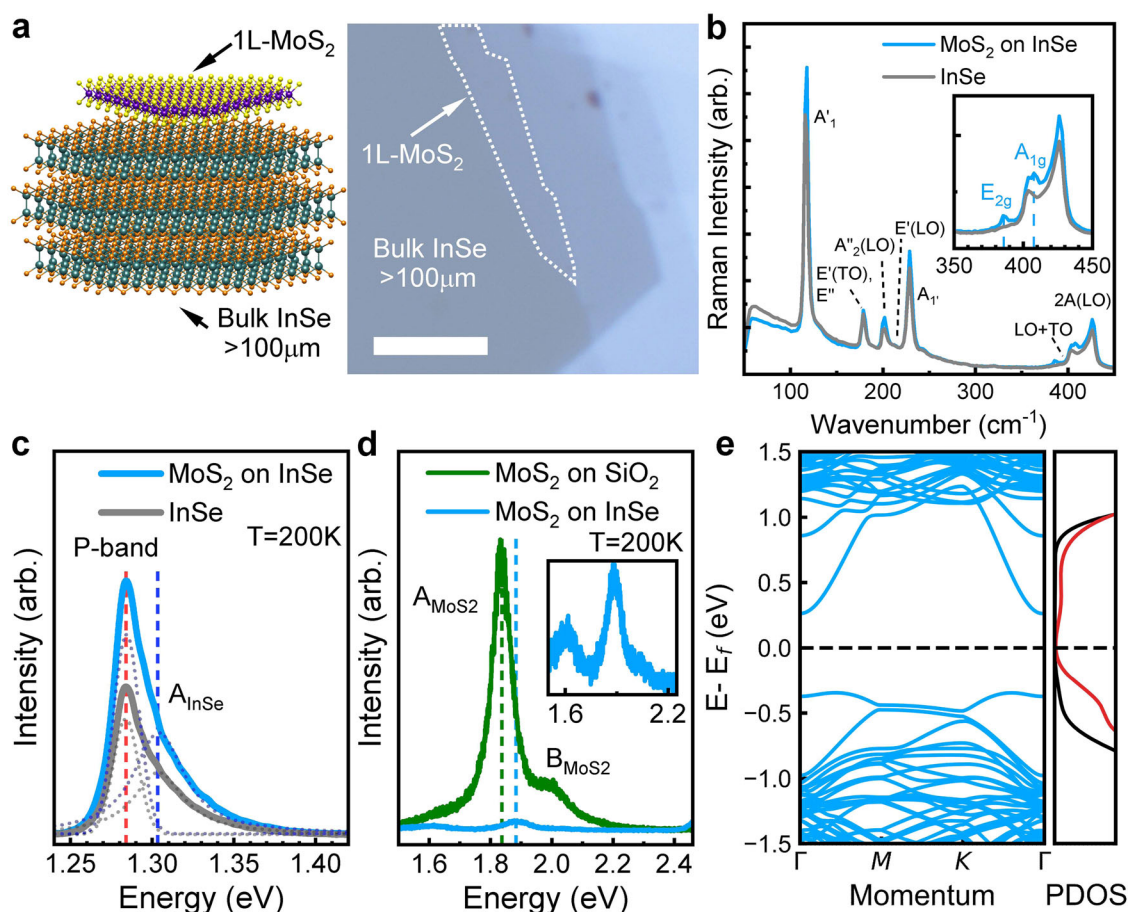
Despite the growing interest in InSe, heterostructures combining InSe with 2D semiconductors have been relatively sparse. From early examples, it is clear that semiconducting heterostructures, including InSe, exhibit enhanced performance as photoelectrochemical devices (BP/InSe<sup>37</sup> and InSe/Ge-doped InSe<sup>38</sup>), photodetectors (MoS<sub>2</sub>/InSe<sup>39</sup>, InSe/GaSe<sup>40</sup>, InSe/WSe<sub>2</sub><sup>41,42</sup>), and electronic devices (InSe/GeSe<sup>43</sup>). As the research community continues to explore heterostructures beyond those of only monolayer TMDs, understanding the roles of differences in lattice structure, band

structure, and interface defects becomes critically important towards the goal of developing heterostructure-based optoelectronics. In this work, we investigate the effect of interlayer electronic interactions on the photoluminescence response in a 2D MoS<sub>2</sub>/bulk InSe heterostructure. The results herein demonstrate ultrafast energy transfer within this Type I heterostructure leading to a suppression of PL emission from MoS<sub>2</sub> excitons and a temperature-dependent enhancement of InSe PL. In this heterostructure, monolayer MoS<sub>2</sub> is found to act as an efficient, light-absorbing passivation layer which enhances the optical output of InSe, enabling improved optoelectronic performance.

## Results

### MoS<sub>2</sub> on InSe heterostructure

The MoS<sub>2</sub>/InSe heterostructures were fabricated by exfoliation of a monolayer MoS<sub>2</sub> flake onto a PDMS stamp and transfer onto a freshly cleaved bulk piece of  $\gamma$ -InSe (schematically depicted in Fig. 1a) inside an argon-filled glove box (<1ppm O<sub>2</sub> and H<sub>2</sub>O). Thick bulk crystals of InSe were chosen (>100  $\mu$ m) as not only does InSe exhibit thickness-dependent optical properties due to quantum confinement, but also potential polariton effects for thicknesses up to 6  $\mu$ m<sup>18,44,45</sup>. The room temperature Raman spectrum (collected with 514.5 nm excitation) from bare InSe (Fig. 1b, gray) shows sharp peaks corresponding to known vibrational modes of InSe and additional harmonics indicative of a high-quality crystal. With MoS<sub>2</sub> on top (Fig. 1b, blue), additional peaks appear at 385.6 cm<sup>-1</sup> and 407.7 cm<sup>-1</sup>



**Fig. 1 | Monolayer MoS<sub>2</sub>/bulk InSe heterostructure.** **a** Ball and stick model of a MoS<sub>2</sub>/InSe heterostructure with cartoon signifying the in-plane and out-of-plane excitons of MoS<sub>2</sub> and InSe, respectively, (left) and optical image of one-few layer MoS<sub>2</sub> on bulk InSe (right). Scale bar is 10  $\mu$ m. **b** Room temperature Raman spectra of bare InSe (gray) and MoS<sub>2</sub> on InSe (blue). Peaks corresponding to the Raman modes in InSe are labelled in black. Inset: Zoomed-in spectrum showing the MoS<sub>2</sub> Raman modes (labelled in blue) among the second-order InSe Raman modes. **c** PL spectra of

InSe with and without MoS<sub>2</sub> (blue and gray, respectively), decomposed into two peaks (dotted lines) corresponding to the P-band and A<sub>InSe</sub> exciton. **d** PL emission of MoS<sub>2</sub> on SiO<sub>2</sub> and on InSe (green and blue, respectively), inset shows a rescaled MoS<sub>2</sub>/InSe PL spectrum. **e** Band structure for the heterostructure composed of a MoS<sub>2</sub> monolayer and InSe (structure described in Supplementary Fig. 2) and projected density of states (PDOS) that differentiate contributions from MoS<sub>2</sub> (black line) and InSe (red line).

corresponding to the  $E_{2g}$  and  $A_{1g}$  Raman modes of monolayer  $\text{MoS}_2$ , respectively (see Fig. 1b, inset). PL measurements (Fig. 1c, d) performed at 200 K (all PL measurements made between 4 K and 300 K are given in Supplementary Section 7) depict two major regions corresponding to excitonic emission from InSe around 1.28 eV and excitonic emission from  $\text{MoS}_2$  around 1.85 eV. The  $\text{MoS}_2$  PL emission energy confirms that the  $\text{MoS}_2$  used is monolayer, however, the spectral distance between  $E_{2g}$  and  $A_{1g}$  Raman modes for  $\text{MoS}_2$  on InSe ( $22.1 \text{ cm}^{-1}$ ) is found to be larger than the typical value for  $\text{MoS}_2$  on  $\text{SiO}_2$  ( $19.5\text{--}20.5 \text{ cm}^{-1}$ ). This separation has been shown to be influenced by interactions with the substrate including electronic doping and strain<sup>46</sup>. The Raman peak positions in the  $\text{MoS}_2$  on InSe are consistent with a small amount of strain ( $<0.1\%$ ) and significant p-type contact doping ( $\sim 7 \times 10^{12} \text{ cm}^{-2}$ )<sup>46</sup>. In the energy range pertaining to the InSe emission, two peaks corresponding to the excitonic transition and a P-band were observed in both the bulk InSe and  $\text{MoS}_2/\text{InSe}$  heterostructure around 1.304 eV and 1.284 eV, respectively<sup>47</sup>. The excitonic transition in InSe has been named the “A” exciton of InSe in analogy with the “A” excitons observed in 2D TMDs ( $A_{\text{InSe}}$ ), which originates from emission between the valence and conduction bands at the  $\Gamma$  point. The P-band emission from InSe has been attributed to exciton–exciton scattering, as observed in other semiconductor systems<sup>48</sup>, and is also evidenced by super-linear power dependence of PL intensity (further information shown in Supplementary Fig. 4). The lower intensity  $A_{\text{InSe}}$  arises from a transition between s-like conduction band to  $p_z$ -like valence band state which is selectively excited by light polarized with  $\vec{E} \parallel \hat{c}$ , where  $\hat{c}$  is the direction perpendicular to the InSe layers, leading to a smaller measured response in normal-incidence, confocal measurements<sup>49</sup>.

The PL from 2D  $\text{MoS}_2$  is also observed at a much lower intensity than the InSe (shown in Fig. 1d). The PL response of exfoliated  $\text{MoS}_2$  on  $\text{SiO}_2$  is well documented and exhibits two excitonic features labeled  $A_{\text{MoS}_2}$  and  $B_{\text{MoS}_2}$  originating from the optical transitions at the K-point in the valence band, split by spin-orbit coupling, to the K-point in the conduction band<sup>50</sup> with a contribution from defect-related emission at lower energy<sup>51,52</sup>. In this case, the integrated emission intensity of the  $A_{\text{MoS}_2}$  excitons from the  $\text{MoS}_2/\text{InSe}$  heterostructure is quenched by 92% relative to monolayer  $\text{MoS}_2$  on  $\text{SiO}_2$ . PL quenching is commonly observed in both Type I and Type II band alignments and has been attributed to ultrafast energy or charge transfer between the heterostructure constituents<sup>12,53,54</sup>. As contact with InSe introduces a non-radiative charge/energy transfer channel in the  $\text{MoS}_2/\text{InSe}$  heterostructure, the degree of quenching indicates that energy transfer must occur more than an order of magnitude faster than the lifetime of the  $A_{\text{MoS}_2}$  exciton state (expected to be approximately 100 fs)<sup>55,56</sup>. The quenching mechanism is not apparent, however, due to the orthogonality of the dipole moments of  $\text{MoS}_2$  and InSe excitons (see Fig. 1a)<sup>49</sup>, direct, Förster-type resonant energy transfer is expected to be highly suppressed in this heterostructure. Other forms of energy or charge transfer likely dictate the optoelectronic properties of the  $\text{MoS}_2/\text{InSe}$  heterostructure<sup>57</sup>.

While the PL from  $\text{MoS}_2$  becomes quenched, PL emission from InSe becomes enhanced by 80% in the  $\text{MoS}_2/\text{InSe}$  heterostructure at 200 K (Fig. 1c). The simultaneous quenching of PL from  $\text{MoS}_2$  (the wider bandgap material in this structure) and enhancement of PL from InSe (the smaller bandgap material) is a characteristic signature of a Type I heterostructure. While a Type I band alignment in a monolayer  $\text{MoS}_2/\text{InSe}$  heterostructure has been experimentally established, PL enhancement was not observed for InSe thicker than 50 nm purportedly due to variations in the band structure with thickness<sup>39</sup>. The heterostructure reported here utilizes InSe that is much thicker ( $>100 \mu\text{m}$ ) yet still exhibits PL enhancement and the quenching/enhancement may be attributed to the rapid fabrication of a pristine heterostructure in an inert environment.

To better understand the interactions between  $\text{MoS}_2$  and InSe, a density functional theory (DFT) calculations were performed utilizing a structural model that was constructed describing the 2D/bulk 2D heterostructure composed of a monolayer of  $\text{MoS}_2$  and a bilayer of InSe with the layer furthest from the  $\text{MoS}_2$  layer fixed to its bulk geometry spacings

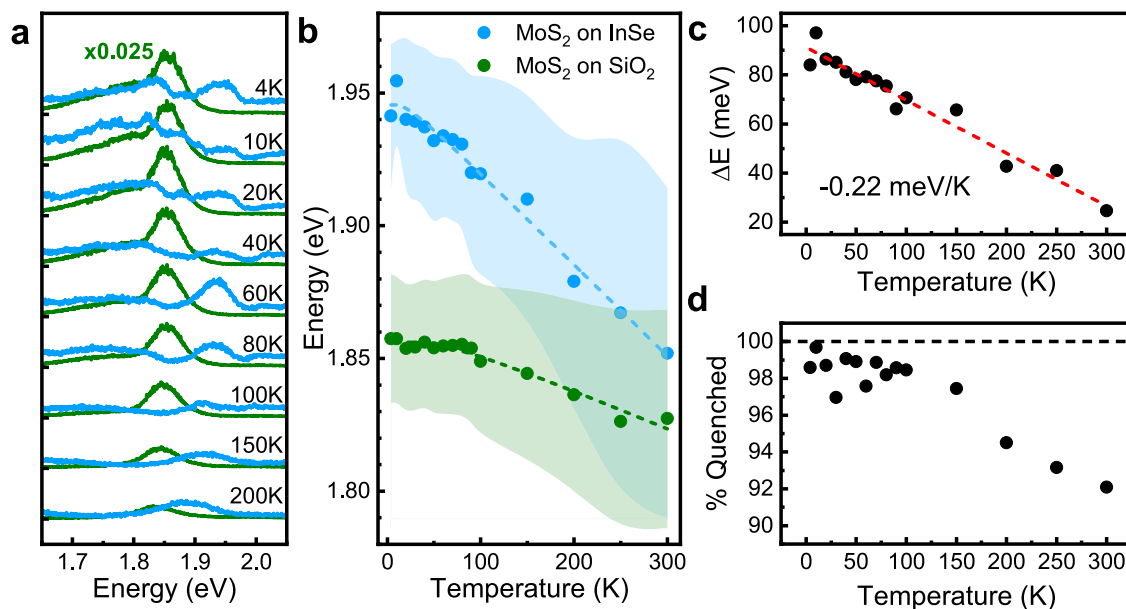
(additional information shown in Supplementary Fig. 2). As InSe exhibits a layer number-dependent band structure<sup>18,24</sup>, care must be taken to retain bulk-like InSe properties while also allowing the two atomic lattices ( $\text{MoS}_2$  and InSe) to relax at their interface. The resulting band structure and projected density of states (PDOS) for the  $\text{MoS}_2$ -bilayer InSe heterostructure (see Fig. 1e) reveals that the conduction and valence states nearest the band gap are primarily composed of InSe orbitals (further details shown in Supplementary Fig. 5). Calculations also indicate weak interlayer coupling due to the interlayer distance of  $>3 \text{ \AA}$  between  $\text{MoS}_2$  and the bilayer of InSe, and little hybridization in the electronic orbitals at the valence (conduction) band maximum (minimum) (further information shown in Supplementary Fig. 5). A type I alignment is predicted between bulk InSe and monolayer  $\text{MoS}_2$  using accurate HSE calculations of the atomic band structure, with a transition between Types I and II as InSe thickness is reduced (additional information shown in Supplementary Fig. 6). Note that TMD/TMD heterostructures form mostly Type I heterostructures<sup>58</sup>.

### Temperature-dependent photoluminescence

Photoluminescence characteristics of the heterostructure were further evaluated by temperature-dependent PL measurements performed from 300 K and 4 K. Figure 2a depicts the temperature-dependent PL emission between 1.5 and 1.9 eV with a general broad emission response between 1.5 eV and 1.8 eV due to defects within the  $\text{MoS}_2$ , the  $A_{\text{MoS}_2}$  emission around 1.9 eV, and a broad feature between 1.9 eV and 2.2 eV which comes from the InSe (additional information in Supplementary Section 8). In general, the A-exciton in  $\text{MoS}_2$  is highly quenched and blue-shifted in energy at lower temperatures in both the  $\text{MoS}_2$  on  $\text{SiO}_2$  and  $\text{MoS}_2/\text{InSe}$  heterostructure, though at a very different rate. Changes in exciton peak energy can arise from differences in the electrostatic environment (electrostatic doping and screening), the lattice structure (built-in strain and thermal expansion), and electron-phonon coupling in  $\text{MoS}_2$  on different substrates. The effects of charge transfer and screening of the exciton binding energy are too small to be responsible for the large difference in  $A_{\text{MoS}_2}$  exciton peak energy in the  $\text{MoS}_2/\text{InSe}$  heterostructure and  $\text{MoS}_2$  on  $\text{SiO}_2$  (greater than 88 meV at 4 K) (additional information found in Supplementary Section 9). Thus, contact doping and screening cannot account for the large, measured difference between  $\text{MoS}_2$  PL peak energy on  $\text{SiO}_2$  and InSe. Similarly, the effect of the different thermal expansion coefficients of  $\text{SiO}_2$  and InSe can only account for 1.25% of the measured slope of  $\Delta E = E_{\text{InSe}}(A_{\text{MoS}_2}) - E_{\text{SiO}_2}(A_{\text{MoS}_2})$  versus T shown in Fig. 2c (additional information found in Supplementary Section 10).

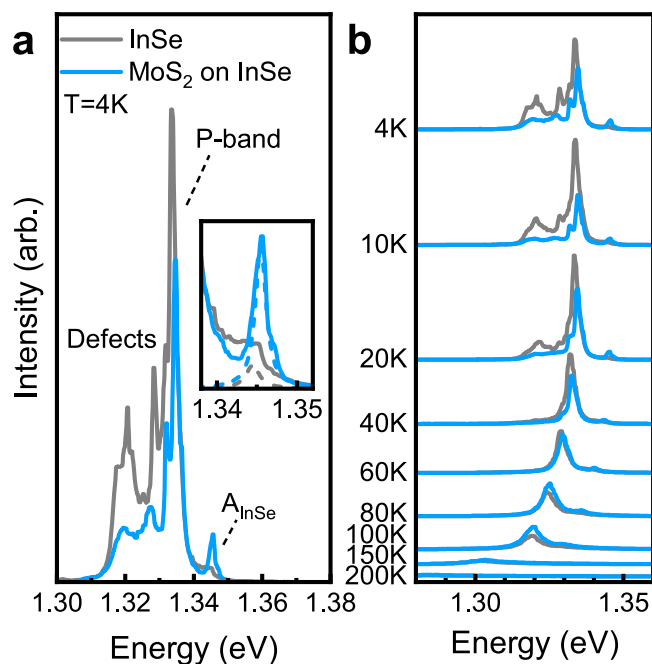
The effect of electron-phonon coupling on semiconductor band gap size has been semi-empirically modelled by O'Donnell and Chen which gives a metric for electron-phonon coupling strength and an effective phonon energy scale<sup>59</sup>. Fitting the temperature dependence of  $A_{\text{MoS}_2}$  to this model (Fig. 2b, dotted lines) gives a larger electron-phonon coupling and smaller phonon energy scale for  $\text{MoS}_2$  on InSe than on  $\text{SiO}_2$  (additional information in Supplementary Section 11). These differences may arise because InSe provides an atomically smooth and electronically homogeneous substrate for  $\text{MoS}_2$ , enhancing coherence and reducing scattering of phonons, or they can reflect the strong coupling of the  $\text{MoS}_2$  electrons to low energy phonons at the surface of InSe that modifies the  $\text{MoS}_2$  band gap.

In addition to the changes in band gap, temperature-dependent PL measurements also reveal a strong quenching of the  $A_{\text{MoS}_2}$  exciton intensity relative to the  $\text{MoS}_2$  on  $\text{SiO}_2$  (Fig. 2d), from 92% at 300 K to 99% at 4 K, indicative of efficient charge and energy transfer due to an interface with minimal defects. The PL spectrum in the region of InSe emission (1.30–1.37 eV), shown in Fig. 3a, reveals several features associated with photoemission from InSe including the A exciton (1.346 eV), P-band (1.334 eV), and defect-related emission (1.315–1.33 eV), respectively<sup>18,47,60,61</sup>. The heterostructure emission peak location shows little difference between the InSe PL peak energies with and without 2D  $\text{MoS}_2$  on top. As this is a 2D/bulk material vdW junction, the electrostatic effects of the  $\text{MoS}_2$  layer on InSe are rapidly screened away from the vdW interface leading to only a small difference in  $A_{\text{InSe}}$  emission energy ( $<1 \text{ meV}$ ) with  $\text{MoS}_2$  on top.



**Fig. 2 | Temperature-dependent MoS<sub>2</sub> PL emission.** **a** Temperature-dependent PL spectra of MoS<sub>2</sub>/InSe (blue) and MoS<sub>2</sub> on SiO<sub>2</sub> (scaled by a factor of 0.025) (green). **b** Temperature dependence of  $A_{\text{MoS}_2}$  peak energy (points) and FWHM (shaded area) for MoS<sub>2</sub>/InSe (blue) and MoS<sub>2</sub>/SiO<sub>2</sub> (green). Dotted lines are fits to the

O'Donnell-Chen model. **c** Peak energy difference between MoS<sub>2</sub>/InSe and MoS<sub>2</sub>/SiO<sub>2</sub> plotted as a function of temperature and with a linear fit (red, dashed line) yielding a slope of  $-0.22 \text{ meV/K}$ . **d** Quenching of  $A_{\text{MoS}_2}$  PL intensity measured from MoS<sub>2</sub> on InSe compared with MoS<sub>2</sub> on SiO<sub>2</sub>.



**Fig. 3 | Temperature-dependent InSe PL emission.** **a** Low temperature PL spectra of bare InSe (gray) and MoS<sub>2</sub>/InSe (blue) taken at 4 K. Inset zooms in to the  $A_{\text{InSe}}$  emission peak. **b** Temperature-dependent PL spectra of bare InSe (gray) and MoS<sub>2</sub>/InSe (blue).

### Defect trapping regime

Temperature-dependent PL shows defect peaks begin to emerge in the spectrum below the P-band energy at temperatures below 80 K (Fig. 3b and Fig. 4a). Below this temperature,  $A_{\text{InSe}}$  excitons become captured by defects, reducing the bare PL intensity and increasing emission at lower energies<sup>62</sup>. Surprisingly, the bare  $A_{\text{InSe}}$  exciton intensity increases with increasing temperature between 30 K and 80 K, that is, it exhibits negative thermal quenching (NTQ) (see Fig. 4b, inset). NTQ can be observed when defect-bound excitons or charges are thermally excited out of shallow defect-bound

states<sup>63,64</sup>. Previous experimental studies of bulk InSe PL at low temperatures have analyzed these defect-bound states and have attributed them to several sources (oxygen defects, Se vacancies, stacking faults, surface-bound excitons, etc.) although these works do not report observations of NTQ<sup>65–68</sup>. Additionally, it has been argued that these defect states in bulk InSe form as a result of strong correlations and flat bands in InSe<sup>25,66,69</sup>.

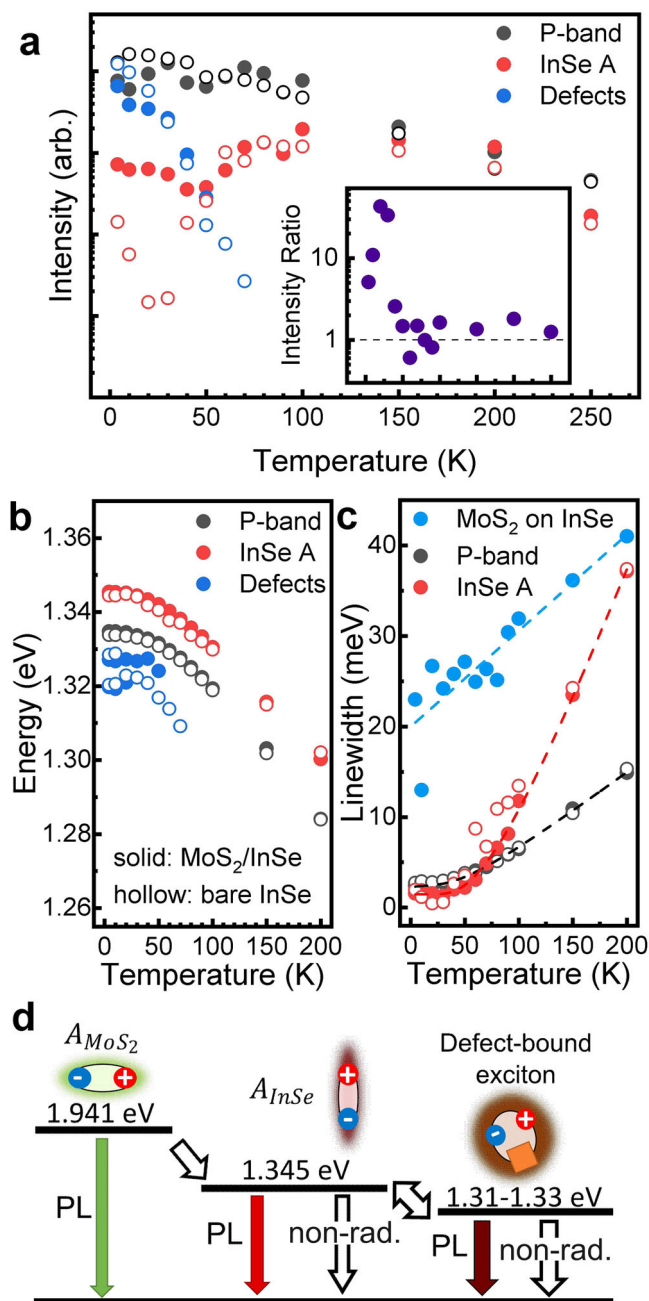
Although NTQ of PL in InSe has not been observed before, Nicholas et al. also noted a defect-related transition in temperature-dependent cyclotron resonance measurements around 25 K<sup>70</sup>. Below 25 K an extended 2D defect state was observed, attributed to acceptor states at stacking faults, which transitions to a three dimensional state above this temperature. Additionally, a defect of selenium substituted with oxygen was chosen for investigation by DFT calculations due to its low formation energy. It is found that oxygen substitution does not induce significant band structure changes or mid-gap states (additional information found in Supplementary Fig. 10). This observation is corroborated experimentally by ARPES measurements before and after oxygen exposure<sup>71</sup>. Even though oxygen substituted selenium defects are found to not impact the electronic band structure, it is possible that isoelectronic defects induce large exciton-defect binding energies leading to exciton trapping as seen in similar semiconductor systems<sup>72</sup>. At this time the particular defect state(s) responsible for the observed behavior is not apparent from the experiments made in this work and further experimental and theoretical exploration is required.

Surprisingly, as the free exciton population varies rapidly below 80 K, there is no corresponding change in P-band intensity. As the P-band is typically attributed to exciton-exciton scattering, it is expected that the P-band emission intensity to be proportional to the free exciton concentration squared, as evidenced by power-dependence of peak intensity (see Supplementary Information)<sup>47,48</sup>. The insensitivity of the P-band intensity to the  $A_{\text{InSe}}$  exciton density change with temperature and the decrease of P-band intensity with MoS<sub>2</sub> on top suggests that the P-band in InSe is not solely due to exciton-exciton scattering within the InSe bulk.

### Temperature-dependent PL enhancement

In the MoS<sub>2</sub>/InSe heterostructure, the  $A_{\text{InSe}}$  exciton peak intensity is larger by 25–81% between 100 K and 250 K suggesting that the MoS<sub>2</sub> enhances  $A_{\text{InSe}}$





**Fig. 4 | Comparison of temperature-dependent PL emission in the heterostructure.** **a** Integrated intensity for the P-band,  $A_{\text{InSe}}$ , and all defect emission as a function of temperature with and without MoS<sub>2</sub> (solid and hollow, respectively). Inset: Intensity ratio as a function of temperature of the  $A_{\text{InSe}}$  intensity for MoS<sub>2</sub>/InSe compared to bare InSe. **b** Peak positions and **c** FWHM as a function of temperature for InSe emission with and without MoS<sub>2</sub> (solid and hollow, respectively). **d** Energy level diagram of the excitonic states and transitions in the MoS<sub>2</sub>/InSe heterostructure. Colored arrows depict radiative decay pathways and hollow arrows depict non-radiative transition pathways.

emission through charge and/or energy transfer. Below approximately 80 K, the effect of the MoS<sub>2</sub>/InSe heterostructure becomes more apparent. While the PL intensity of the  $A_{\text{InSe}}$  state drops dramatically for the bare InSe surface, the  $A_{\text{InSe}}$  intensity from the MoS<sub>2</sub>/InSe region remains significantly larger (as much as 44×) and the transition temperature between regular thermal quenching and NTQ regimes increases to higher temperature. The apparent enhancement in this temperature regime is coincident with the onset of defect-induced quenching of  $A_{\text{InSe}}$  exciton emission and the emergence of

defect-related PL at low temperatures (Figs. 3b and 4a). Not only does the NTQ effect correlate with the defects in InSe, the MoS<sub>2</sub> appears to alleviate much of the defect-induced quenching of the  $A_{\text{InSe}}$  emission. Below 30 K, the defect and P-band intensities are both smaller in the heterostructure region. The origins of the P-band and defect-bound exciton states are not yet understood, and more work is needed to investigate the interactions of excitons and defects in InSe. As such, it is difficult to speculate on how the addition of the MoS<sub>2</sub> monolayer reduces the P-band intensity and defect emission below 30 K. It is probable that, as MoS<sub>2</sub> is inert in ambient conditions, it protects the bare InSe surface from chemical interactions with the environment in the time between sample fabrication and measurement. Additionally, contact doping as well as photoinduced carriers or excitons may contribute to the passivation of defect centers in InSe. The ratio of integrated intensity of the  $A_{\text{InSe}}$  peak with and without MoS<sub>2</sub> ( $I_{\text{MoS}_2}(A_{\text{InSe}})/I_{\text{bare}}(A_{\text{InSe}})$ ) is shown in the inset of Fig. 4a and summarizes the effect of the MoS<sub>2</sub> in the heterostructure. Between 100 K and room temperature, the  $A_{\text{InSe}}$  peak intensity is larger for the MoS<sub>2</sub>/InSe heterostructure with little variation with temperature, despite a large change in MoS<sub>2</sub> bandgap size. As the temperature approaches the defect binding regime, the exciton intensity ratio fluctuates while below ~60 K, it rises to a peak value of 44 revealing the strong influence of MoS<sub>2</sub> on enhancing  $A_{\text{InSe}}$  emission.

### Estimation of time scales

Fits of the Lorentzian linewidth of the  $A_{\text{InSe}}$  exciton peak and P-band to a phenomenological phonon-coupling model reveal a very small effect of acoustic phonon scattering at low temperature. Excitonic relaxation in InSe is mediated by optical and zone-edge acoustic phonons both with and without MoS<sub>2</sub>. For MoS<sub>2</sub> on InSe,  $A_{\text{MoS}_2}$  emission linewidth is observed to be linear with temperature indicating that exciton interactions with acoustic phonons primarily dictate the linewidth broadening, in agreement with the peak energy analysis above. As the temperature approaches zero, the  $A_{\text{InSe}}$  peak linewidth approaches  $\gamma_0 = 1.45$  meV corresponding to a coherence time of  $\tau_{\text{InSe}} = \frac{h}{\gamma_0} = 0.45$  ps, much smaller than the 9.5 ns value reported in the literature<sup>73</sup>. To confirm, time-resolved PL measurements at 4 K (further information in Supplementary Fig. 12) find that the  $A_{\text{InSe}}$  lifetime is far less than this value while the lifetime of defect-bound excitons is comparable to 9.5 ns. This suggests that in bare InSe,  $A_{\text{InSe}}$  excitons or charges are rapidly captured by defects (in less than 250 ps, see Supplementary Section 13) and that spectrally overlapping signals from  $A_{\text{InSe}}$  exciton and defect-related photoemission at higher temperatures could lead to an overestimation of the  $A_{\text{InSe}}$  exciton lifetime. Compared to bulk InSe, excitons in monolayer MoS<sub>2</sub> have exceptionally large binding energies and ultrafast formation timescales<sup>74</sup>. Additionally, our DFT calculations show no interlayer potential which might separate charges. Thus, most  $A_{\text{MoS}_2}$  excitons form on the order of tens of femtoseconds within the MoS<sub>2</sub> layer. Upon transit to bulk InSe (<12 ps), the exciton then thermalizes through interactions with phonons into the  $A_{\text{InSe}}$  state before either radiative recombination, phonon-assisted non-radiative recombination, or defect trapping (<1 ps)<sup>75</sup>. Thus, without defect trapping, we estimate that the entire process of energy funneling from MoS<sub>2</sub> to InSe and the subsequent emission of light at the  $A_{\text{InSe}}$  energy is ultrafast (<250 ps).

### Discussion

Future optoelectronic devices harnessing the impressive versatility of 2D/2D and 2D/3D van der Waals heterostructures require an improved understanding of how defects, band structures, and excitons influence charge/energy transfer and resultant optical properties. In this work, a heterostructure of monolayer MoS<sub>2</sub> and bulk InSe was fabricated and shown to be a Type I heterostructure with a large enhancement of InSe excitonic emission compared to monolayer MoS<sub>2</sub>/thinner InSe heterostructures. Temperature-dependent PL revealed that bulk InSe exciton emission intensity was highly sensitive to native defects which may accumulate due to exposure to the atmosphere. In the monolayer 2D MoS<sub>2</sub>/bulk InSe heterostructure, degradation of the InSe surface was minimal as MoS<sub>2</sub> passivated the surface and prevented oxidation. This enhancement also resulted

in a quenching of the MoS<sub>2</sub> PL by more than 98% at 4 K. Interestingly, the A exciton in InSe was enhanced substantially at temperatures below 60 K, coinciding with the onset of defect-induced quenching of the A<sub>InSe</sub> exciton emission at low temperatures. Finally, we demonstrate ultrafast transport between the two layers, where the entire energy funneling occurs at sub 250 ps. This study suggests the use of 2D MoS<sub>2</sub> as both a passivation layer and as a strong light-to-charge converter when combined into a Type I heterostructure with InSe, enabling utility for optoelectronic applications such as photodetectors, light emitters, and color converters.

## Methods

### InSe crystal growth

Nominally undoped  $\gamma$ -phase InSe single crystals were grown by the vertical Bridgman method using a non-stoichiometric polycrystalline In<sub>1.04</sub>Se<sub>0.96</sub> charge. The InSe charge was vacuum-sealed in a graphitized quartz ampoule. The melt was equilibrated at 720 °C for several hours, and then the ampoule was translated across a temperature gradient at a rate of 0.5 mm/h. The  $\gamma$ -phase of InSe used in this study has been unambiguously confirmed by X-ray diffraction and transmission electron microscopy (TEM) measurements and the stoichiometric composition of InSe crystals was confirmed by TEM/EDX and SEM/EDX measurements as reported in our previous paper<sup>24</sup>.

### Heterostructure fabrication

MoS<sub>2</sub> flakes are exfoliated from bulk (2D Semiconductors) onto a freshly prepared PDMS stamp (Sylgard 184, Dow Corning). Monolayers are first identified with optical contrast and later verified with PL and Raman measurements. Bulk pieces of  $\gamma$ -phase InSe (>100  $\mu$ m thick), affixed to a substrate, are freshly cleaved with tape and the chosen MoS<sub>2</sub> monolayer is quickly placed onto the InSe surface inside an Ar-filled glovebox (see Supplementary Fig. 1 for images). The vdW interactions between MoS<sub>2</sub> are stronger than the PDMS-MoS<sub>2</sub> bond and the MoS<sub>2</sub> layer remains with the InSe crystal when PDMS is removed, resulting in a dry transfer. Optical images of several samples are shown in Supplementary Fig. 1. Only regions with optically smooth interfaces, fabricated in an Ar atmosphere, are reported here. MoS<sub>2</sub> on SiO<sub>2</sub> is fabricated by exfoliating a monolayer from bulk directly onto the 300 nm SiO<sub>2</sub> on Si substrate using tape.

### Raman and room temperature PL

Room temperature Raman and PL spectra were collected using a Renishaw inVia Raman spectrometer. The 514.5 nm excitation was focused on the heterostructures through a 100 $\times$  objective lens, and Raman and PL spectra were collected by setting the laser power to a few hundred microwatts (to prevent burning by the laser) and using a collection time of 10 s for a minimum of 3 acquisitions.

### Temperature-dependent PL

The sample was loaded into a Montana Instruments S200 Cryostation and cooled down to 4 K. Varying the temperature was performed via an agile temperature sample mount (ATSM, Montana Instruments) which contains a resistive heater and temperature sensor allowing for precise target temperatures to be achieved. The heterostructure was excited using a tunable 120 fs, 80 MHz Ti:Sapphire laser centered at 580 nm through a 0.75 NA in-situ objective. The resulting emission was collected and dispersed in a grating spectrometer (Princeton Instruments, SP-2750) and analyzed using a PyLoN BRX silicon CCD camera. For the time-resolved PL measurements, the emission was passed through a tunable short- and long-pass filter to select the wavelength range of interest prior to the spectrometer. The corresponding signal was sent to a single photon avalanche diode (MPD) for photon counting. The timing information was then obtained via a Pico-Quant HydraHarp 400 event timer resulting in the time-resolved PL measurement. Additionally, TRPL measurements were performed using a Universal Streak Camera (Hamamatsu, C10910-04) providing an improved instrument response function allowing for the reduction of the upper bound for resolution-limited lifetime.

### DFT calculation

DFT calculations were performed using the Vienna ab initio simulation package<sup>76–78</sup>. Core electrons are described using the projector-augmented wave method<sup>79,80</sup>. The Perdew-Burke-Ernzerhof exchange-correlation functional within the generalized gradient approximation (GGA)<sup>81</sup> was employed, including a correction for van der Waals (vdW) interactions by the D3 parametrization (vdW-D3)<sup>82</sup>. The relaxation of each structure involves optimizing the lattice parameters and the internal positions of the atoms using conjugate-gradient algorithms<sup>83</sup>. To mimic the InSe bulk, the atomic positions of one of the InSe layers were fixed at the bulk geometry during the relaxation (additional information shown in Supplementary Fig. 1). The system's total energy and lattice parameters were determined once the unit cell was fully relaxed. Total energy convergence during all self-consistent calculations was achieved when the difference in the total energy between steps was less than 0.01 meV. Memory constraints limited the energy cutoff and Monkhorst-Pack<sup>84</sup> mesh of k-points to an energy cutoff of 300 eV and a k-point density of 14 points per Å for our heterostructure calculations. An energy cutoff of 400 eV was used for all monolayer calculations. Spin-orbit coupling was not used. For accurate band structure calculations, we utilized the Heyd-Scuderia-Ernzerhof exchange-correlation functional<sup>85</sup>, using the relaxed PBE+vdW-D3 structure as a starting point.

### Data availability

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

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## Author contributions

M.A.A. performed sample fabrication, optical measurements, interpreted data and drafted manuscript. C.E.S. performed optical measurements and data analysis. N.A.P. performed DFT calculations and analysis. R.P. aided in the DFT analysis and interpretation. S.K. grew InSe crystals. A.V.D. grew and characterized InSe crystals. J.R.H. aided in the optical measurement analysis. R.R. aided in the PL measurements and analysis. D.J. interpreted the optical data. M.S. interpreted and analyzed data as well as finalized drafting manuscript. N.R.G. provided data analysis, project guidance, and paper review and editing. All authors have contributed to writing the paper.

## Competing interests

The authors declare no competing interests.

## Additional information

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