

Light-Matter Coupling in Scalable Van der Waals Superlattices

Pawan Kumar

University of Pennsylvania

Jason Lunch

University of Pennsylvania

Baokun Song

University of Pennsylvania

Haonan Ling

University of California at Los Angeles

Francisco Barrera

University of Pennsylvania

Huiqin Zhang

University of Pennsylvania

Surendra Anantharaman

University of Pennsylvania <https://orcid.org/0000-0002-1882-5540>

Jagrit Digani

University of California at Los Angeles

Haoyue Zhu

Pennsylvania State University

Tanushree Choudhury

Pennsylvania State University

Clifford McAleese

Aixtron Ltd.

Xiaochen Wang

Aixtron Ltd.

Ben Conran

Aixtron Ltd.

Oliver Whear

Aixtron Ltd.

Michael Motala

Air Force Research Laboratory

Michael Snure

Air Force Research Laboratory, Sensors Directorate, Wright-Patterson AFB, OH 45433

Christopher Muratore

University of Dayton

Joan Redwing

Pennsylvania State University <https://orcid.org/0000-0002-7906-452X>

Nicholas Glavin

Air Force Research Laboratory

Eric Stach

University of Pennsylvania <https://orcid.org/0000-0002-3366-2153>

Artur Davoyan

University of California Los Angeles

Deep Jariwala (✉ dmj@seas.upenn.edu)

University of Pennsylvania <https://orcid.org/0000-0002-3570-8768>

Article

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Abstract

Two-dimensional (2D) crystals have renewed opportunities in design and assembly of artificial lattices without the constraints of epitaxy. However, the lack of thickness control in exfoliated van der Waals (vdW) layers prevents realization of repeat units with high fidelity. Recent availability of uniform, wafer-scale samples permits engineering of both electronic and optical dispersions in stacks of disparate 2D layers with multiple repeating units. We present optical dispersion engineering in a superlattice structure comprised of alternating layers of 2D excitonic chalcogenides and dielectric insulators. By carefully designing the unit cell parameters, we demonstrate $> 90\%$ narrowband absorption in < 4 nm active layer excitonic absorber medium at room temperature, concurrently with enhanced photoluminescence in cm^2 samples. These superlattices show evidence of strong light-matter coupling and exciton-polariton formation with geometry-tunable coupling constants. Our results demonstrate proof of concept structures with engineered optical properties and pave the way for a broad class of scalable, designer optical metamaterials from atomically-thin layers.

Introduction

Semiconducting Multi-quantum Wells (MQWs) and superlattices form the basis of all modern high performance opto-electronic and photonic components, ranging from modulators to lasers and photodetectors¹⁻⁴. However, most known and scalable MQWs and superlattice structures are epitaxially grown III-V, II-VI or oxide perovskites. While significant progress has been made over the last three decades in the commercialization of II-VI and III-V MQWs and superlattices, the inherent difficulties of their integration onto arbitrary substrates have limited their adoption and applicability^{5,6}. The advent of van der Waals (vdW) semiconductors, the ability to grow them uniformly over wafer scales, and to transfer them with high fidelity onto arbitrary substrates opens new avenues towards rational design of both electronic and photonic dispersions in artificially stacked superlattices and MQW structures⁷.

Two-dimensional (2D) vdW materials are a broad and growing family of materials with a diverse range of electronic properties, encompassing metals, semiconductors, ferromagnets, superconductors and insulators⁸⁻¹¹. This diversity allows for vdW materials to be combined with one another, or with other thin materials, into heterostructures with new or enhanced properties and improved performance in a variety of applications^{7,12}. Most of the previous research has focused on heterostructures that are made using mechanically exfoliated layers that are a few μm^2 in lateral size¹³ with uneven thickness. This presents significant challenges in making MQW or superlattice structures with sufficient reproducibility across the number of periods necessary to enable the desired photonic or electronic dispersions. Further, with every increasing layer, stacking mechanically exfoliated flakes reduces the size of the region that has the desired overall stacking sequence, a problem that is exacerbated with each additional layer that is added. This fact prohibits the scalability of this approach. For photonic and optoelectronic applications, there is another major challenge with regards to atomically-thin active layers: the nature of light-matter

interaction. Monolayer thickness of 2D materials results in a reduced cross section of light-material interaction implying weak couplings, despite naturally resonant optical responses¹⁴.

Semiconducting transition-metal dichalcogenides (TMDCs) that consist of Mo, W, Re etc. are a sub-class of vdW materials that have large, complex refractive indices due to the strong in-plane bonding of the transition metals to the chalcogenides, leading to strong light-matter interactions^{15,16}. The low dielectric screening and highly-confined exciton wavefunctions present in TMDCs result in excitonic binding energies of ~ 500 meV, creating strong excitonic resonances at room temperature¹⁷. As the thickness of TMDCs decreases from the bulk to the monolayer limit, they transition from indirect to direct bandgap semiconductors. This reduces the non-radiative energy loss of exciton relaxation and leads to an enhancement in photoluminescent (PL) emission^{18,19}. However, reducing the thickness to monolayer dimensions adversely impacts the net interaction with light. Therefore, to engineer strong interaction with light and still maintain the key advantages to monolayer scaling it is necessary to make either a metamaterial or superlattice structure with monolayer repeat units in one dimension^{20,21}.

Here, we report the experimental realization of superlattices that are specifically designed to achieve near-unity absorption while concurrently maintaining the enhanced PL emission and optoelectronic properties of monolayer TMDCs. Our superlattices are cm^2 in scale and comprise of repeating unit cells of metal organic chemical vapor deposition (MOCVD) grown TMDCs (MoS_2 and WS_2) + insulating spacers (h-BN and Al_2O_3) stacked on an Au back reflector (Fig. 1A). We observe the emergence of strongly coupled exciton-polaritons in the superlattices when light is coupled into the superlattices at incident angles $> 45^\circ$. Further, both the exciton-polariton dispersion and coupling strength are observed to be tunable by altering geometric parameters of the superlattice and its unit cells. This assembly process is both general and simple and allows extreme flexibility regarding materials choice due to the lack of microfabrication constraints. Thus, it can be expanded to allow the integration of several different 2D chalcogenides and spacer layers, as demonstrated here. The resulting approach opens up a broad field of artificially engineered, scalable vdW superlattices for electronic, opto-electronic, and photonic applications.

Results And Discussion

We adopt a highly scalable approach to the fabrication of vdW MQWs and superlattice structures. Wafer-scale samples of WS_2 , MoS_2 and h-BN grown using the MOCVD technique were used for sample fabrication. Details of sample growth and synthesis are available in the methods section and supporting information. We have adopted and demonstrated two different structures in this work, as shown in Fig. 1a: 1) An all-vdW superlattice comprised of alternating layers of TMDC and h-BN, and 2) a mixed dimensional superlattice with alternating layers of TMDC and 3D oxides grown via atomic layer deposition (ALD). The all-vdW superlattice predominantly studied in this work is comprised of a unit cell of monolayer WS_2 as the excitonic layer with insulating h-BN (3 nm) as a spacer layer which was repeated on top of an $\text{Al}_2\text{O}_3/\text{Au}$ substrate. In the TMDC-oxide superlattice, the h-BN layers are replaced by

Al₂O₃ layers. Our proposed concept and fabrication scheme is quite general and has been extended to monolayers of WS₂, MoS₂, and few-layer MoSe₂ as the excitonic media in this study.

We prepare our superlattice structures via wet transfer of the 2D chalcogenide and h-BN layers. In addition, we use atomic layer deposition growth of aluminum oxide for the base spacer layer as well as a component of unit cells, in some cases. These large area superlattice samples require wafer-scale grown TMDCs and h-BN with uniform thicknesses. The MoS₂, WS₂ and h-BN samples were grown via MOCVD while the MoSe₂ samples were grown via selenization of Mo thin films in H₂Se gas at elevated temperatures (see methods and supporting info, Figure S1 and S2). The increased absorption of the superlattices as the number of unit cells increases can be seen by the naked eye, as shown in Fig. 1b. WS₂-based superlattices transition from a near transparent film at N = 1 to a deep green color at N = 5. The large area (cm²) realization of these superlattices (Fig. 1b) is a particularly important demonstration of this study, given that any practical application of 2D TMDCs in photonics/optoelectronics will require large area, uniform material. Experimentally measured absorptance spectra for two-different superlattices have been shown in Fig. 1c. A detailed discussion on the absorption properties is in following section.

To examine the spatial uniformity of this multilayer superlattice structure, we perform cross-sectional transmission electron microscopy of our representative sample (WS₂/h-BN: N = 5) (Fig. 1d). An annular bright field (ABF)-STEM image of the cross section of our superlattice sample (Fig. 1e) clearly shows the multilayer structure and five dark lines running horizontally in the image contrast, indicating the heavy element layer (WS₂). Corresponding energy dispersive X-ray spectroscopic (EDS) elemental maps shows the layers clearly. Layers of W, S and N signals are apparent, as are weak signals for B and Au corresponding to the substrate location (Fig. 1f). The white contrast (gap) between the TMDC layers and the bottom alumina (Fig. 1d) is a result of delamination of the superlattice during the ion milling process (Xe⁺ ions) for cross-sectional TEM sample preparation (see supporting info, Figure S3).

A two-variable optimization scheme using Transfer Matrix Method (TMM)-based modelling combined with a genetic algorithm-based optimization approach was used to determine the desired thickness of the superlattice samples. The objective of the optimization was to maximize (minimize) narrow band absorptance (reflectance) at the excitonic resonance. The unit cell spacer and bottom spacer thicknesses were optimized to maximize the excitonic absorptance (see methods and supporting info, Figure S4-S7 for details). We performed this TMM modelling and optimization for four different superlattices (WS₂/h-BN, WS₂/Al₂O₃, MoS₂/Al₂O₃ and MoSe₂/Al₂O₃) where the number of unit cells varied from N = 1 to 8. We found a distinct absorptance enhancement up to N = 4 and N = 5 for Al₂O₃ and h-BN based superlattices, respectively, as experimentally demonstrated in Fig. 2.

The modelling and optimization identifies three key features in terms of designing superlattice geometric parameters for maximizing (minimizing) absorption (reflection) at the excitonic resonance. They are: 1) the thickness of the spacer layer in the unit cells must be as low as possible (Fig. 2a and b); 2) the bottom alumina thickness should be reduced as the number of unit cells (N) increases (see supporting Figure S5-

S8); and 3) the peak absorbance (at exciton resonance) approaches near unity with increasing N and then dips again, suggesting that there is an optimal unit cell number (N) for perfect absorption (Fig. 2d-i). We note that this optimal N can vary with spacer index and thickness. Given that electronic interactions between two TMDC layers are non-negligible at spacer thicknesses of 1-1.5 nm^{22,23}, there is little room for further improvement in light trapping while maintaining electronic isolation. The complex refractive index values used in the TMM simulations were obtained through spectroscopic ellipsometry measurements of the samples that were used for the fabrication of the superlattices. The simulated reflectance of the stack decreases with each successive unit cell deposition at the WS_2 excitonic resonance (Fig. 2d, g), for both $WS_2/h\text{-BN}$ and WS_2/Al_2O_3 superlattice samples. This is in strong agreement with the experimentally measured spectra (Fig. 2e, h). This agreement between simulated and experimentally measured spectra suggests that the dielectric function of WS_2 is unperturbed from its as-grown state on sapphire, when integrated into this multilayer superlattice stack. It also suggests that there is no electronic interaction between neighbouring the WS_2 layers when they are separated by $h\text{-BN}$ or Al_2O_3 . Therefore, they maintain their monolayer electronic character when integrated into this superlattice stack. The insulating layers serve two primary purposes: 1) they act as spacer layers between TMDCs to reduce the electronic coupling between individual TMDCs layers, allowing them to maintain monolayer properties and 2) they act as light trapping agents, because the refractive index difference between the TMDCs and insulating layers also results in enhanced reflection. Given the low reflectance (high absorption) at the excitonic resonance, an important parameter to consider is the extent of useful absorption in the semiconductor vs parasitic absorption in the underlying Au. This absorption into individual components of the superlattice was extracted through the TMM simulations (Fig. 2f, i), where a negligible contribution from the bottom Au layer is observed around the primary exciton wavelength (613 nm for WS_2) (see supporting info, Figure S8 for additional details). It is further worth noting that there is a pronounced dip in reflectance in the bottom Au at the excitonic resonance. This is a peculiar observation and is attributed to lack of sufficient incident light intensity reaching the Au surface because of multiple reflections and trapping in the layers above. This observation can be generalized to other bottom metals such as Ag, where the parasitic absorbance is further diminished, yet the reflectance dip remains (see supporting info, Figure S9). Likewise, MoS_2/Al_2O_3 superlattices also show similar behavior (see supporting Figure S10). We have also analyzed and compared the reflectance behaviour of a multilayer, mechanically exfoliated WS_2 control sample with similar thickness to that of the WS_2 present in the superlattices (WS_2/Al_2O_3 : $N = 4$ and $WS_2/h\text{-BN}$: $N = 5$) (see supporting info, Figure S11, S12). The comparative analysis confirms that while a similar degree of absorbance can be achieved with equivalent thickness of WS_2 on an alumina spacer, there is loss of the direct band gap nature of the TMDC. Additionally, the superlattice exciton peaks remain unshifted, as opposed to the red-shift seen in few-layer WS_2 of equivalent absorber thickness. This lack of energy shift further confirms that the WS_2 is electronically isolated in the multilayer. Finally, it is worth noting that the oscillator strength of the exciton is higher in monolayers. This is because of the reduced dielectric screening and quantum confinement, which also results in larger absorption per unit thickness (see supporting info, Figure S12).

The ability of these multilayer superlattices to both trap light and retain their monolayer electronic and optical character is a defining feature of our approach. In contrast to their bulk counterparts, the presence of strong quantum confinement in monolayer WS₂ and MoS₂ leads to a direct band gap, which in turn leads to high intensity PL due to low, non-radiative energy loss during electron-hole recombination²⁴. This extraordinary feature of monolayer TMDCs makes them strong candidates for light emitting devices. The superlattice structures demonstrated herein – which combine insulating spacer layers – between monolayer TMDCs allows the monolayers to maintain their direct-gap electronic structure. We verify this using a series of vibrational and luminescence spectroscopy measurements shown in Fig. 3.

We observe that our multilayer superlattices remain highly luminescent with an increasing number of unit cells (Fig. 3a). Not only are the luminescent properties maintained, but the luminescence intensity is even enhanced with increasing N due to the increased due to enhanced light-material interactions (Fig. 3b). When normalized to total useful light absorption with increasing N, using layer resolved absorption calculations we observe that the luminescence intensity increases with N which is expected due to stronger light-material interaction (see supporting info, Figure S13 for additional details). We also observe a small red shift in PL peak positions with increasing number of unit cells (from N = 1 to 5) which can be attributed to the increasing density of defect emission or doping arising from trapped contaminants such as PMMA, organic solvents and water that are used in the wet chemical transfer process (see supporting info, Figure S2). Similar PL behavior was observed in other monolayer TMDC based superlattices, namely WS₂/Al₂O₃ and MoS₂/Al₂O₃ (see supporting info, Figure S14). To further understand any possible effects of enhanced absorption and light trapping on the luminescence characteristics, we have also performed PL characterization as a function of incident pump power. At high powers, emission from various higher order and charged excitonic species are observed. Individual excitonic components (neutral exciton, trion, dark exciton, biexciton, defect bound exciton, or localised state exciton) can be identified by analyzing the power-dependent PL emission of the WS₂/h-BN superlattice (N = 5) and decomposing the spectra into individual Lorentzian peaks (Fig. 3c, d and supporting info, Figure S15). A notable observation in our power dependent PL analysis is the sharp rise in emission contribution from biexcitons with increasing power. Biexcitons comprise of two-electrons and two-holes and are known to recombine by either decomposing into two excitons or emitting two photons in sequence or a pair entangled photons²⁵. Biexcitons tend to form at high excitation levels. In our case the high excitation not only occurs due to increased incident power but also due to enhanced light trapping (~ 2x). Such cavity-induced enhancement of biexcitons have been reported earlier in perovskite quantum dots and MoSe₂ layers^{26,27}. The N = 1 case (single monolayer) does not show a similar power dependence (see supporting info, Figure S16), further suggesting the that light trapping causes the enhanced excitation in multilayers. Along with increasing biexciton emission, luminescence contributions from defect bound and localised state excitons also appear to increase in the N = 5 superlattice. This can again be attributed to defect accumulation during the repeated transfers and thermal cycles of ALD with each increasing N of the superlattice. However, the overall relation between emission intensity vs. excitation stays linear at both room and low temperatures (80 K) within the range of excitation powers probed, thereby suggesting an absence of any non-linear phenomena in this range. While we do observe significant enhancement of

emission peak intensity and full width half maxima (FWHM) sharpening of the emission spectra (see supporting Figure S17), there are no obvious signatures of new states or presence of non-linear phenomena.

In addition to PL, Raman spectra provide a strong signature of interlayer interaction and hybridization. Specifically, the out-of-plane vibration mode (A_{1g} : 418 cm^{-1}) stiffens with increasing number of layers and therefore the separation between $2LA(M)$ and A_{1g} modes reduces with increasing layer thickness²⁸. We observe no noticeable peak shifts in the Raman spectra of WS_2 in our superlattices with increasing N . Once again this suggests no interaction between layers and no detectable strain within the layers. The only noticeable difference with increasing N is the rising peak intensity and narrowing FWHM of the peaks (Fig. 3e). This is likely due to increased Raman scattering signal due to strong interaction of the medium with pump laser, again caused by the light trapping geometry in addition to the increased total volume of WS_2 . In addition, we also observe a defect-bound Raman mode ($LA(M)$: 176 cm^{-1}) appearing for the $N = 5$ structure of the $WS_2/h\text{-BN}$ superlattice (Fig. 3e). This is likely due to increased defect accumulation as number of layer transfers and thermal cycles of ALD increases. Despite this, the characteristic Raman modes, such as $2LA(M)$ and A_{1g} , maintain constant positions and separations as a function of N , as plotted in Fig. 3f.

Thus far, our discussion concerning the light trapping and optical properties of these multilayer superlattices has been focused on normal incidence illumination. We now explore angle dependent coupling of light into this multilayer superlattice structure. Standard TMM simulations show that the excitons in the superlattice hybridize with cavity modes to form exciton-polaritons, with their splitting energy depending on the incident angle and number of unit cells (Fig. 4a). With a fixed number of unit cells and angle of incidence, a characteristic anti-crossing behavior, signifying exciton coupling with polaritons, can also be seen when the cavity resonance is tuned by varying bottom alumina layer thickness. We use a coupled oscillator model to fit to the simulation data and calculate the Rabi splitting of the system. Our analytical model is in good agreement with the simulated UEP and LEP energies (see supporting info and detailed discussion, Figure S20-24). The Rabi splitting can be increased to 170 meV for a stack of $N = 8$ at $> 80^\circ$ incident angles. The Rabi splitting can also be achieved at lower incident angles as the number of unit cells is increased, due to a sharpening in the cavity mode peak, which indicates a lower mode volume, V_m (based on the pathlength of the light inside the superlattice for N layers). The lower mode volume for increased unit cells also results in higher Rabi splitting since the Rabi splitting is inversely proportional to the $\sqrt{V_m}$. The increased Rabi splitting with increased incident angles is due to sharpening in the cavity mode peak, which can be observed in the increased Q-factor (see supporting Info, Figure S23).

This Rabi-splitting is also observed in our superlattice samples and matches well with the simulations (Fig. 4c-f). Furthermore, this splitting appears only under TE polarized light (Fig. 4e-f) and not under TM polarized illumination (Fig. 4c-d). This is because monolayer TMDs can only support TE waveguide modes, unlike their bulk counterparts which can support both TE and TM waveguide modes¹⁸. As the

reflection spectra are acquired away from normal incidence the exciton mode stays unperturbed up until an incident angle of 50° in the simulation. Thereafter, the cavity-induced splitting of the exciton mode emerges with increased incident angles. The emergence of the cavity mode at slightly higher incident angles in experiments when compared to the simulated values can be attributed to presence of polymer and other contamination between the layers, which reduces the quality of the cavity. The Q-factor was obtained by fitting the absorptance peaks to a Lorentzian line shape and was found to follow similar trends to incident angle and number of unit cells as the Rabi splitting (Figure S19). TMM simulations show that the Q-factor of 100 nm thick $N = 5$ $\text{WS}_2/\text{Al}_2\text{O}_3$ superlattices can reach 300 at a moderate incident angle of 70° at room temperature (see supporting Figure S23). The observation of high Q factors in un-patterned multilayer films over square centimetre length scales is potentially valuable for colorimetric sensing applications. In this regime, the exciton-polariton splits into an upper exciton-polariton (UEP) and lower exciton-polariton (LEP) branch for WS_2 . Both branches were observed simultaneously at room temperature. A third branch was observed in MoS_2 since the energy of the A and B excitons are closer than for WS_2 , and both excitons interacted with the microcavity (see supporting info, Figure S26). The Q-factor of the cavity mode was found to be ~ 300 at an incident angle of 70° in a subwavelength thick device (100 nm). Since exciton-polaritons maintain light-like and matter-light characteristics, they can be used for non-linear effects in devices such as lasing.

Conclusions

In summary, we have demonstrated a centimetre square scale, multilayer superlattice structure based on atomically-thin 2D chalcogenide monolayers acting as quantum wells. The structure of the superlattice was deterministically designed to maximize light trapping at the exciton ($\sim 90\%$) in < 4 nm thickness of active layer absorber. These superlattices not only maintain a monolayer structure but also support exciton-polaritons at room temperature, with Rabi splitting of up to 170 meV, and cavity modes with quality factors as large as 300 in deep-subwavelength thick devices. Our results show a proof of concept for optical dispersion engineering using atomically thin layers over scalable and arbitrary substrates with broad applications ranging from lasing, sensing as well as optical-modulator devices and lays the foundation towards a materials platform for substrate agnostic integrated nanophotonics.

Experimental Details

Materials and Method: Uniform and wafer scale TMDCs (monolayer WS_2 and MoS_2) were grown on c-plane sapphire substrates by MOCVD. Details of the monolayer WS_2 and MoS_2 used for $\text{WS}_2/\text{Al}_2\text{O}_3$ and $\text{MoS}_2/\text{Al}_2\text{O}_3$ superlattice samples have been published earlier^{29,30}. The monolayer WS_2 and h-BN (3 nm thick) samples for $\text{WS}_2/\text{h-BN}$ superlattice were grown by Aixtron Ltd. (UK) using a Close Coupled Showerhead® metal organic vapour deposition reactor using tungsten hexacarbonyl and ditertiarybutylsulfide, and borazine respectively. Atomic layer deposition (ALD) of Al_2O_3 layer was performed with Cambridge Nanotech (USA) where metal organic precursor of TMA was used with water vapor in each cycle. PVD of Au/Ti (100/10 nm) films were done with the e-beam evaporation technique

utilizing an instrument manufactured by K. J. Lasker, USA. Mechanically exfoliated samples were prepared using the scotch tape method and placed onto reflective substrates with the help of PDMS stamp using a dry transfer technique. Bulk WS_2 crystal purchased from hq-Graphene (Netherlands) was used for the exfoliation of few layered sample. Wafer-scale few-layer $MoSe_2$ thin films were synthesized by first sputtering of Molybdenum (Mo) via an asymmetric bi-polar pulsed direct current magnetron sputtering system at 65 KHz (0.4 sec reverse time) from a Mo target. A sputtering time of 4 seconds resulted in a uniform atomically smooth Mo film with thicknesses of 0.6 nm. Following the Mo deposition, the thin metal films were then transferred into a hot wall CVD reactor evacuated and purged with a flow of H_2 . The films were heated to 650° C under a flow of N_2/H_2 (95%:5%). After reaching 650° C, films were selenized under a flow of H_2Se for 30 min then cooled to 400° C before turning off the flow of H_2Se and cooled to room temperature under N_2/H_2 .

Characterization: The surface roughness of the Au/Al_2O_3 layer on the Si/SiO_2 substrates were analyzed with atomic force microscopy (AFM; AIST, USA). As received MOCVD grown monolayer TMDCs as well as 3 nm thick h-BN samples were analyzed with Raman, photoluminescence (PL) and Reflectance spectroscopy, performed at integrated system available in Horiba Scientific Confocal Microscope (LabRAM HR Evolution). This instrument is equipped with an Olympus objective lens (up to 100x) and three different grating (100, 600 and 1800) based spectrometers, which are coupled to a Si focal plane array (FPA) detector. A continuous-wave excitation source with excitation wavelength at 405 nm and 633 nm was used to perform PL and Raman spectroscopy studies, respectively. 10% laser power of 405 nm wavelength corresponds to 22 micro Watt while utilizing 100x objective lens for power dependent study. Visible white light incident through the fibre probe was utilized for reflectance spectral analysis, using the Horiba Scientific confocal microscope. Temperature-dependent spectroscopic analysis was performed on the same Horiba instrument utilizing Linkam heating/cooling stage where temperature was precisely calibrated by the equilibration time. Spectral spectroscopic ellipsometry analysis of all the samples was performed using a J. A. Woollam Ellipsometer (Model: M-2000 – detector spectral range of 371–1687 nm) to obtain optical constants. Similarly, multi-incidence, angle-dependent reflectance spectral behaviour was also analyzed with Spectroscopic Ellipsometry (SE). ABF-STEM, TEM and EDS measurements were performed at 200 keV using Transmission Electron Microscopes (F200-JEOL). Images were captured by a Gatan annular detector using Gatan's GMS Software. Cross-sectional samples were prepared with Xe^+ plasma based focused ion beam / scanning electron microscope (S8000X-TESCAN).

Theoretical Modelling:

A 2x2 transfer matrix method³¹ was used to simulate the reflectance of the superlattice structure/heterostructures. We adopted the open-source TMM code³² and further developed it in MATLAB™. The TMM was used to simulate the Rabi splitting, and a coupled oscillator model fit was performed to calculate the Rabi energy. The coupled oscillator models the system using a 2x2 Hamiltonian where the diagonal terms are the undisturbed microcavity and exciton energies while the off-

diagonal terms are the Rabi energy and characterize the strength of the interaction between the excitonic and optical states. A three-body coupled oscillator model was used for MoS₂ and MoSe₂ (see supporting Info, Figure S22 and S27).

Declarations

Author contributions:

D.J. and A.R.D. conceived the idea/concept. D.J. directed the collaboration and execution. F.B. and J.L. optimized the superlattice design computationally. P.K. reduced the design to experiments including performing all superlattice fabrication, mechanical exfoliated sample preparation, Cross-sectional TEM sample preparation, optical spectroscopy (including low temperature) and electron microscopy characterization. J.L. with help of H.L. and J.D. performed simulations and fitting the experimental data to computational models. B.S. assisted with measurement, optimization, and fitting of optical constants. H. Zhang and S.B.A. assisted in sample preparation and characterization respectively. M.K. assisted with theoretical modelling and interpretation. H. Zhu, T.H.C. and J.R. synthesized MoS₂ and WS₂ samples used in Al₂O₃ spaced superlattices. C.McA., X.W., B.R.C and O.W. led the synthesis of WS₂ and h-BN used in the h-BN spaced superlattice samples. M.J.M., M.S., C.M. and N.J.G. synthesized and characterized the MoSe₂ samples. E.A.S. supervised the electron microscopy experiments. P.K., J.L. and D.J. wrote the manuscript and all authors contributed to the writing and editing of the manuscript.

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Figures

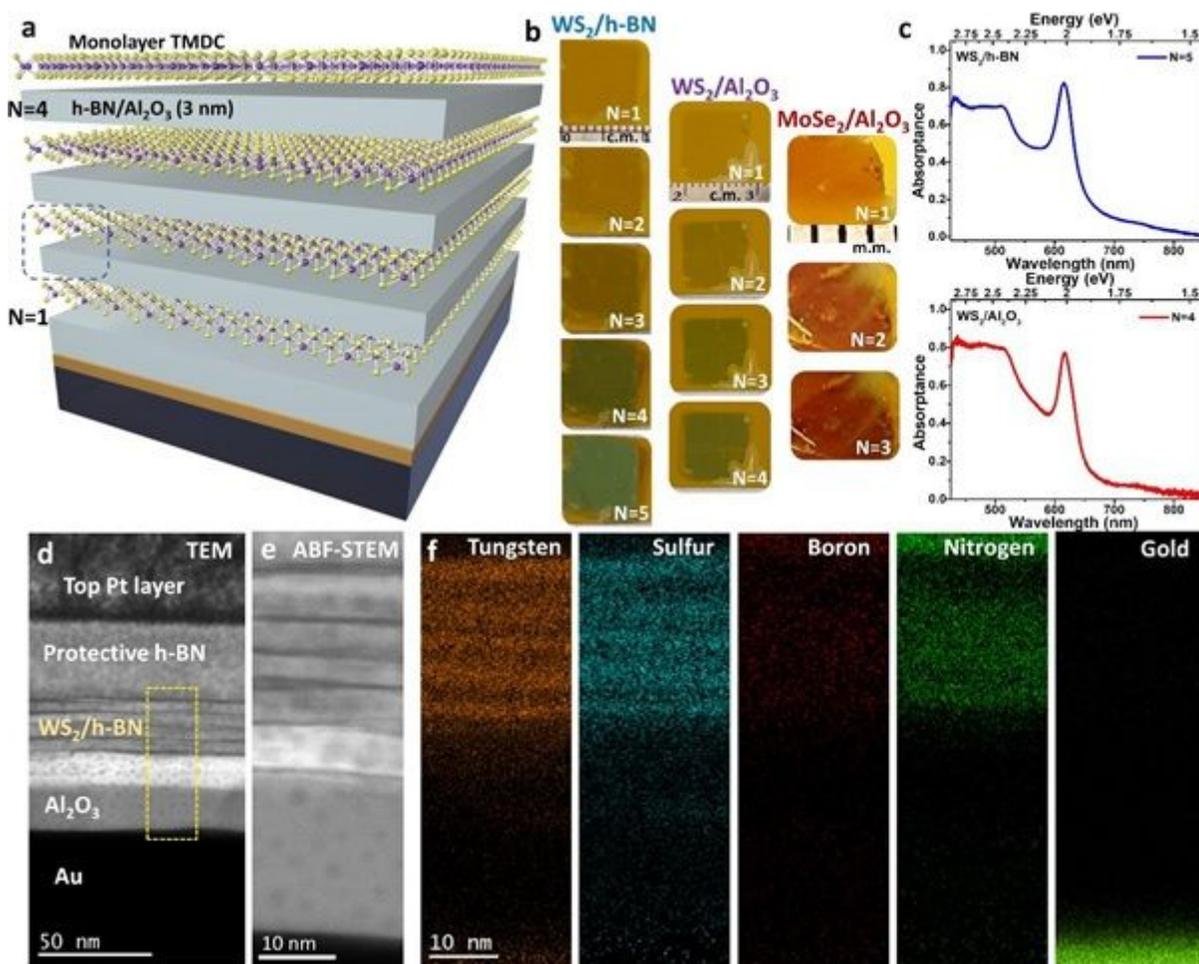


Figure 1

Structure and Composition of Multilayer Excitonic Quantum Well Superlattices (a) Schematic structure of the multilayer superlattice structure, N=1 and N=4 respectively indicates unit cell number. (b) Optical camera images of ~ 1x1 cm² samples of the superlattice with progressively increasing number of unit

cells, for monolayer WS₂/3 nm h-BN, monolayer WS₂/3 nm Al₂O₃ and few layer MoSe₂/3 nm Al₂O₃. The sample color contrast evidently improves with increasing N. (c) Experimentally measured absorptance spectra for WS₂/h-BN (N=5) (top) as well as WS₂/Al₂O₃ (N=4) (bottom) superlattice samples where > 80% absorption at the WS₂ excitonic peak is observed. (d) Cross-sectional transmission electron micrographs (bright field), (e) Annular bright field and (f) Energy dispersive x-ray spectroscopy (EDS) maps of the WS₂/h-BN: N=5 sample. The electron micrographs and elemental maps show the layered structure clearly.

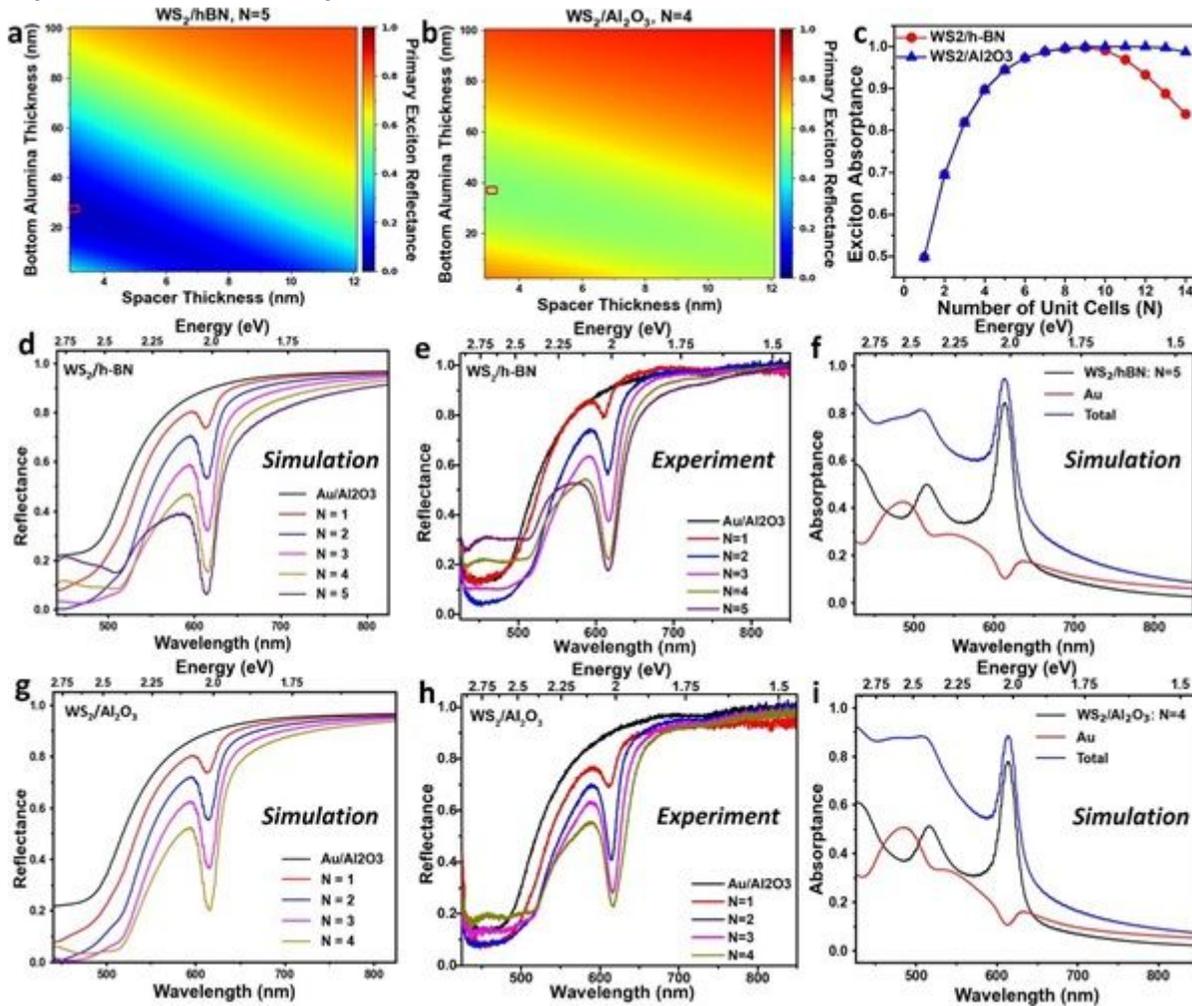


Figure 2

Thickness and Optical Property Optimization. 3D color map of the excitonic reflectance (~ 620 nm) as a function of thickness parameters for the bottom alumina layer and spacer layer, for (a) WS₂/h-BN and (b) WS₂/Al₂O₃ samples. (c) The layer dependent, optimized absorptance for WS₂/h-BN (N=5), and WS₂/Al₂O₃ (N=4) follows a trend of increasing rapidly before asymptotically approaching a limit. (d, g) Simulated and (e, h) Experimental normal incidence reflectance spectra for a function of increasing number of unit cells in the stack for WS₂/h-BN and WS₂/Al₂O₃ superlattices, respectively. The decreasing reflectance with increasing N is evident and shows excellent qualitative and quantitative agreement between simulations and experiments. (f, i) Simulated total absorbance decomposed into absorbance of individual component layers for the corresponding superlattice stacks.

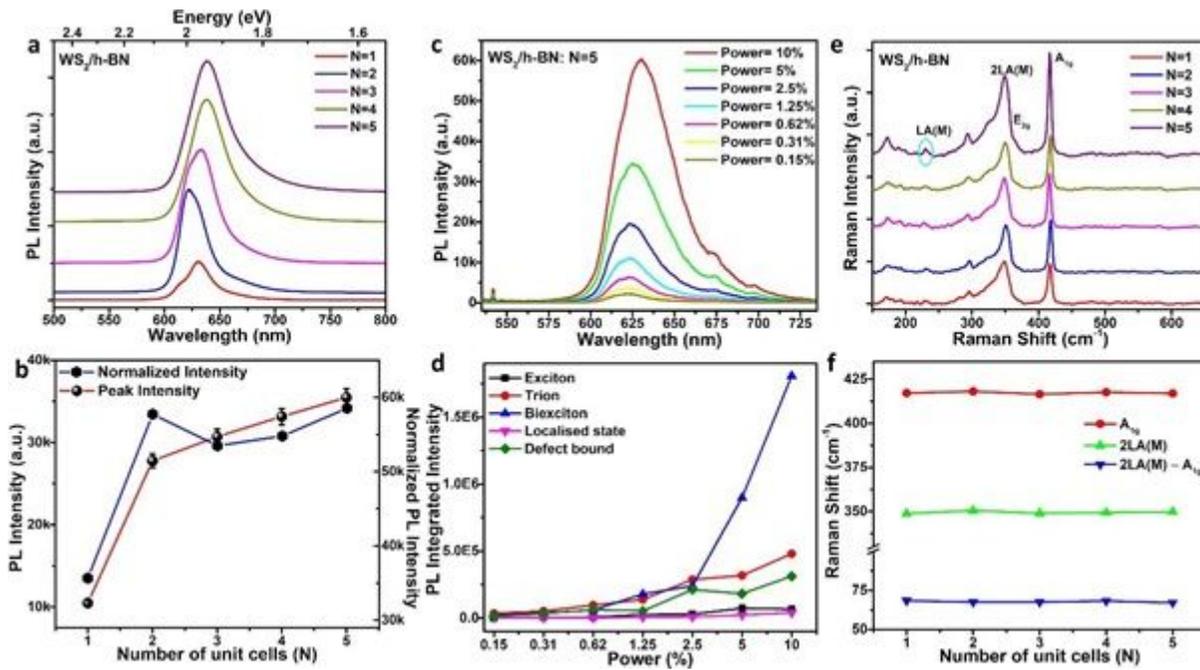


Figure 3

Maintenance of monolayer properties. (a) Room temperature photoluminescence (PL) spectra of the multilayer superlattice as a function of increasing number of unit cells for the WS₂/h-BN superlattice. (b) Corresponding PL peak intensity and absorption normalized PL vs. number of unit cells, showing increasing PL intensity with increasing number of unit cells. The net PL intensity saturates when the total absorption saturates, while the increase in normalized absorption (at pump wavelength of 405 nm) suggests enhanced light outcoupling by the multilayer superlattice structure. (c) Power-dependent PL spectra for the WS₂/h-BN: N=5 superlattice and (d) PL peak intensities emerging from various excitonic components of the power dependent spectra in (c), extracted using Lorentzian fits. The sharp increase in bi-exciton intensity is evident. (e) Raman spectra of the same multilayer superlattice with increasing number of unit cells showing the same peak positions. The peak intensity sharpens and rises with enhanced light interaction for the samples with larger N. (f) Unchanged characteristic Raman peak positions with increasing N.

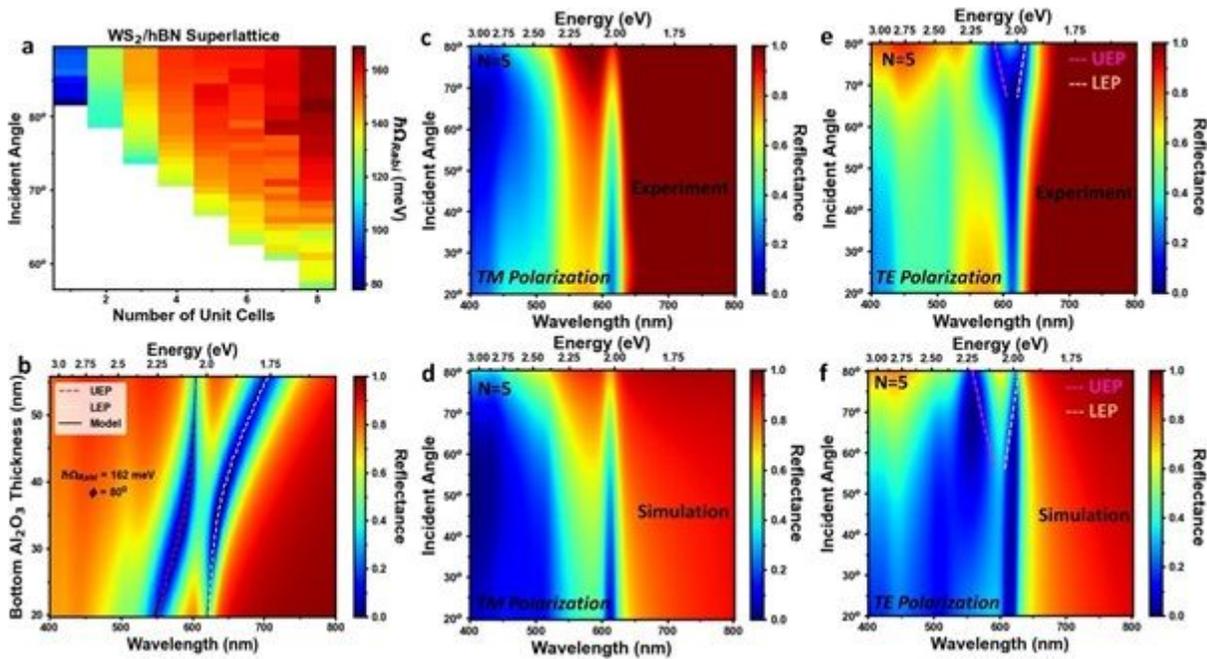


Figure 4

Observation of exciton-polaritons in un-patterned multilayer superlattices. (a) The simulated Rabi splitting dependence on the incident angle and number of unit cells (b) shows reflectance spectrum dependence on the bottom alumina layer thickness at an incident angle of 80° , which shows the characteristic anti-crossing behaviour of exciton-polaritons. (c-d) The experimental and simulated reflectance spectra, respectively, for various angles of incidence of transverse magnetic (TM) polarized light. (e-f) Experimental and simulated reflectance spectra, respectively, for various angles of incidence of transverse electric (TE) polarized light showing the exciton-polariton splitting starting at an angle of 50° . The upper (UEP) and lower (LEP) exciton-polariton peaks are indicated with dashed lines.

Supplementary Files

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