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Scalable Single Photon Source Using CVD-Grown Monolayer Crystals on
Nano-rod Lattices

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**SCALABLE SINGLE PHOTON SOURCE USING CVD-
GROWN 2D TMDS ON NANO-ROD LATTICES**

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September, 2021

Final Report

TABLE OF CONTENTS

1.0	Summary.....	2
2.0	Introduction.....	3
3.0	Nanoimprinted Single Photon Emitter Arrays	3
4.0	Moire Quantum Dot Arrays in van der Waals heterostructures	8
4.1.	Interlayer exciton lasing in a WSe₂/MoSe₂ bilayer.....	8
4.2.	Moire lattice induced hybrid excitons and twist angle dependence.....	9
4.3.	Moire polaritons with quantum confinement induced nonlinearity	11
5.0	APPENDIX A – Publications.....	12

1.0 Summary

Single photon emitters (SPEs) are an essential building block for quantum information systems and related technologies. Despite tremendous progress on SPEs in a variety of materials and structures, most of them are limited in scalability and working temperature. A technologically viable SPE remains a grand challenge. The newly emerged monolayer transitional metal dichalcogenides (TMDs) feature single photon emission up to the room temperature and unprecedented flexibility of integration. Seizing this opportunity, we aim to develop on-chip, high temperature SPSs through a collaborative effort that leverages the Lee's world-renowned expertise on chemical vapor deposition (CVD) growth of van der Waals materials and Deng's expertise on quantum optics and site controlled SPSs.

Main achievements of project includes:

1. Achieved promoter-assisted CVD of high-quality TMDs
2. Identified the critical role of interface cleanness in determining structural and emission properties of TMD heterostructures
3. Developed methods of ultraclean transfer of large-area TMDs that enabled direct STM imaging of moiré patterns¹.
4. Developed plasmonic structures to induce quantum dot (QD) arrays in TMDs and enhance single photon emission.
5. Developed nanoimprint method for creating SPE in a way that is flexible, high-yield, rewritable and affordable.
6. Demonstrated nonlinear phonon scattering in monolayer MoS₂².
7. Demonstrated the first interlayer exciton laser in WSe₂/MoSe₂ hetero-bilayers³, potentially originating from moiré QD arrays.
8. Demonstrated a tunable QD-array polariton system, featuring simultaneous collective light-matter coupling and a strong nonlinearity due to quantum-confinement^{4,5}.

The growth and transfer techniques developed will provide critical technologies for future work on large-area TMD monolayers and heterostructures with ultraclean interfaces, including scalable strain- and moiré-induced QD arrays. The demonstration of interlayer exciton lasers and QD-array polaritons lay the ground for SPS based on tunable, densely packed QD-arrays; they may also enable the intensively sought after quantum polaritonics, and may lead to quantum-dot array lasers with higher efficiency and power output than existing ones that are all based on random QD ensembles.

These works would not have been possible without the frequent exchanges of samples, know-hows, and understandings, and have been coordinated by a Postdoc co-supervised and co-supported by Deng and Lee, who spend a few months in each lab every year. Work leading to achievements #1-#4 and #6 was primarily carried out in Prof. Lee's lab in Taiwan with optical characterizations partly performed by Prof. Deng's lab in the US. Work leading to achievements #5, #7 and #8 was primarily carried on in Prof. Deng's lab in the US with nano-template fabrication performed in Prof. Lee's lab in Taiwan.

In the following, we will discuss work on achievements #5, #7 and #8 that are primarily carried out in Prof. Deng's lab in the US with support by the Air Force.

2.0 Introduction

Solid-state non-classical light emitters are at the heart of many quantum information technologies such as cryptography, communication, and metrology. Tremendous progress has been made on a variety of single-photon emitters (SPEs) in the past few decades. However, limitations in the positioning, scalability, integration, and operating wavelength and temperature have hampered their applications. Recently, two-dimensional (2D) semiconductors, such as transition metal dichalcogenides (TMDs), GaSe, and hBN, have been discovered as a new type of single-photon source that may overcome these limitations. They can operate at higher temperatures due to strong exciton binding. The exciton wavelength ranges from visible to near infrared in different TMDs. Most importantly, as van der Waals materials, they allow controlled fabrication and integration with diverse material platforms.

When monolayer TMDs are placed over nanostructures, strain introduced by the nanostructures has led to single photon emission from defect-bound excitons at these positions. This provides a route to position-controlled SPEs via strain engineering and have motivated this project.

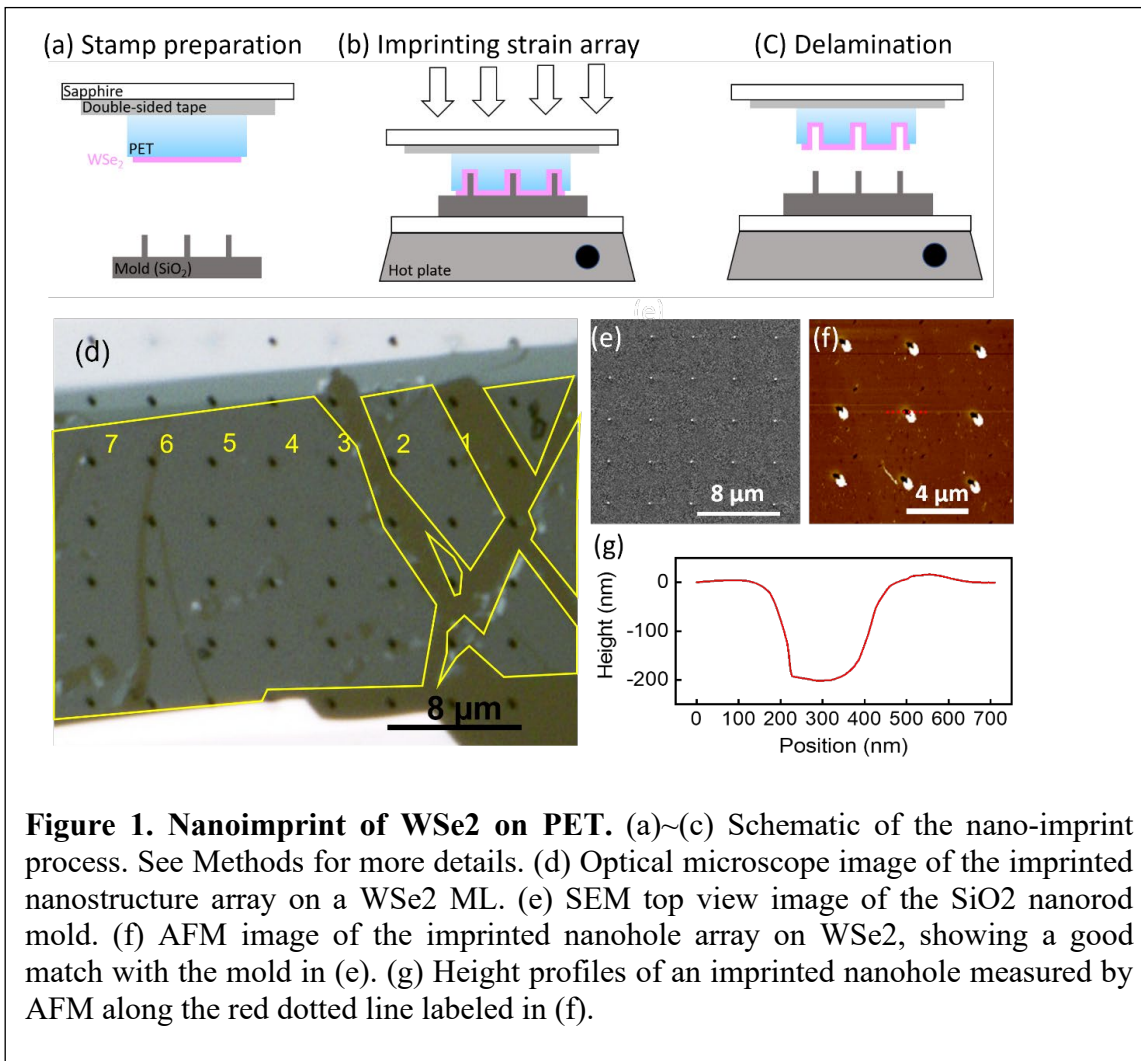
However, when straining TMD MLs with protruding nanostructures, the wrinkle in the 2D crystals formed around the nanostructures is non-conformal, it is difficult to predict or control the resulting strain potential and SPE properties. Protruding nanostructures also pose a risk to pierce the 2D crystals, limiting the creation yield of the SPEs. Furthermore, the nanostructured substrate makes it difficult to integrate the SPE with commonly used photonic structures, such as photonic crystal cavities and waveguides, which are necessary for efficient coupling with the single photons and further on-chip integration.

To take advantage of the flexibility provided by TMDs while circumventing some of the difficulties of existing approaches of creating TMD based SPEs, we have explored alternative approaches to QDs in TMDs. The first approach is based on nanoimprinting, extending the method to quantum structures and 2D materials to allow large-scale, high yield, and more controllable SPE arrays. The second approach is based on moire superlattice that provide a way to create densely packed, homogeneous QD arrays.

3.0 Nanoimprinted Single Photon Emitter Arrays

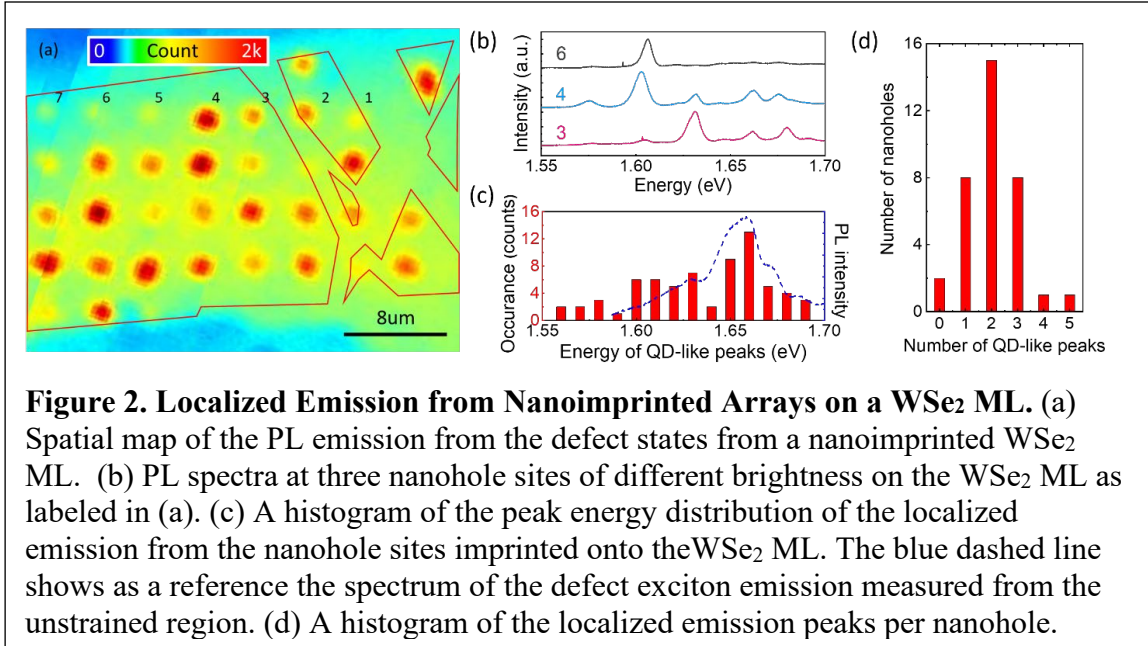
[Under Review at Nano Letters]

In this project, we developed a nanoimprint-based method for low-cost, rapid creation of large arrays of localized emitters, with high yield and controlled strain morphology. Nanoimprint has been widely used with conventional materials to create sub-micron photonic structures, for it is flexible, scalable and cost-effective. Here we demonstrate for the first time using nanoimprint to create quantum emitters, made possible with atomically thin crystals.



We use a SiO₂ nanorod array (designed and fabricated by Prof. Lee's lab) as an imprinting mold to strain a WSe₂ ML on a PET film with a nanohole morphology, so as to localize the defect-bound exciton in the nanohole region. Figure 1a~1c shows the schematic of the nanoimprint process. The principle is similar to that of the thermal imprint lithography, where a nanostructure pattern is created in an etch mask by pressing a mold onto the mask at elevated temperatures. Here a ML crystal is placed on a polyester (PET) stamp and pressed onto the mold. When the mold temperature is raised to above the glass transition temperature of the polymer, the PET and ML crystal together conform to the morphology of the mold, and the nanostructure pattern of the mold is imprinted onto the ML crystals. After imprinting, the temperature is lowered to the room temperature and the strained ML crystal is delaminated from the mold while retaining the nanostructure morphology.

Success of imprinting is confirmed by imaging the imprinted pattern with an optical microscope under microscope light source (Figure 1d) and comparing the imaged



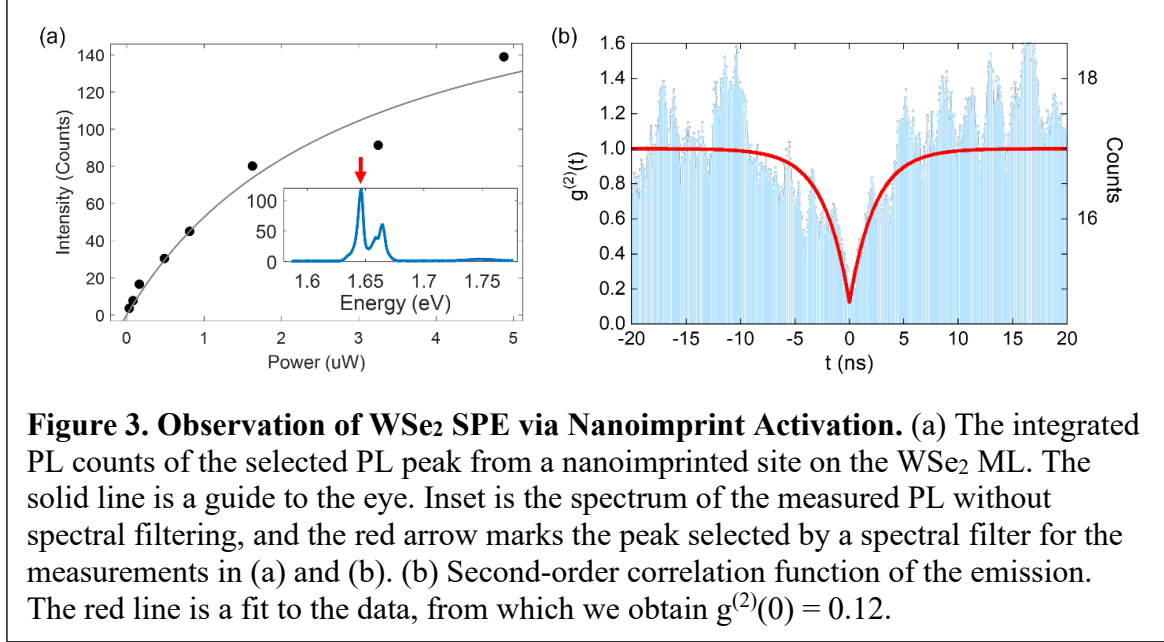
imprinted pattern with the pattern of the nanorod mold measured by scanning electronic microscope (SEM) (Figure 1e).

The morphology of the imprinted holes are measured with AFM, as shown in Figure 1f and 1g. The nanoholes conform well to the morphology of the nanorods, with the same depth of about 200 nm and width of about 200 nm.

Localization of SPS is characterized by photoluminescence (PL) under 532 nm continuous wave (CW) laser excitation. As shown in the wide-field PL microscopy image in Figure 2a, significantly brighter PL intensity is observed from the nanohole sites of the WSe₂ ML, consistent with strain-induced exciton funneling towards the lower energy states.²⁵ The different nanoholes exhibit different brightness, which we found to be correlated with the number of localized defect excitons (Figure 2b). The energy distribution of the localized emitters at all the nanohole sites follows very well the defect-exciton emission of the unstrained WSe₂ ML (Figure 2c). These results confirm efficient localization of the defect-excitons by the nanoimprint process.

The yield of the nanoimprint process is well over 90%, as can be seen by comparing Figure 1d and Figure 2a. In comparison, transferring a ML onto nanostructures typically have a yield below 70%, as the ML is prone to piercing by small nanostructures during the transfer. In the nanoimprint approach, the ML is molded into and remains on the PET substrate, which protects the ML from piercing.

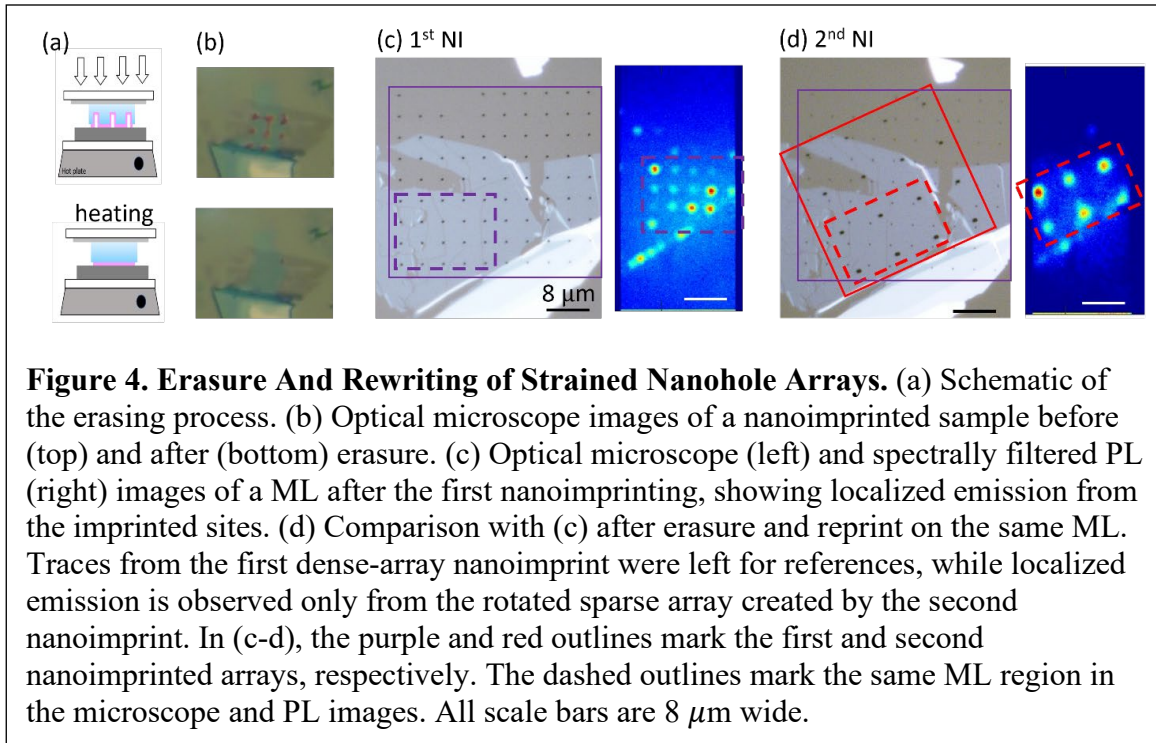
Single photon property of the localized emitter emission was verified by power dependence and second order correlation of the emission. As shown in Figure 3a, the emission intensity from one of the localized emitters shows strong saturation with increasing laser excitation power, characteristic of QD emission. We then performed a Hanbury Brown and Twiss type measurement of the photon correlation function $g^{(2)}(\tau)$ for τ the time delay. Figure 3b shows a $g^{(2)}(0) = 0.12$ and $g^{(2)}(\tau)$ decay time of 2.35 ns.



The measured photon antibunching confirms the localized emitter at the imprinted site functions as a single photon emitter.

The localized emission is observed up to 150 K, which is to our knowledge the highest operating temperature of position-controlled defect exciton emission without additional enhancement via the Purcell effect or e-Beam irradiation. The high operating temperature may be related to the surface passivation of the ML by the PET, which reduces non-radiative channels of the defect exciton. The highest temperature before the emission is quenched is an indication of the strength of the localization potential and efficiency of the single photon emitter. It is also a key factor for applications of SPEs.

Lastly, we implemented the unique rewritable feature of the nanoimprint approach. The imprinted nanohole morphology can be erased by proper pressure and temperature control, as depicted in Figure 4a-b top panel shows the optical microscope image of a nano-imprinted WSe₂ ML before erasure, which is placed in contact with a flat SiO₂ substrate under a gentle press. A clear nanohole array is observed. After increasing the temperature to the glass transition temperature of the PET stamp (63°C), the PET softens and the ML can be flattened under pressure, similar to a wrinkled shirt being ironed. Figure 4b bottom panel shows the optical microscope image of the WSe₂ ML after erasure of the nanoimprints. No nanoholes are observed and the WSe₂ ML becomes flat again. Erasure ability allows rewriting of different patterns on the same ML after an erasure as we illustrate in the example in Figure 4c-d. After a first nanoimprint with a dense nanorod array (Figure 4c), we apply the erasure process to partially remove the nanoimprints with only a faint trace of the sites left, and rewrite onto it a rotated sparse array. As shown in Figure 4d, the new sparse array is imprinted onto the ML, creating localized emission from the imprinted sites, while no localized emission is observed from dense array sites of the first nanoimprint. The erasure and rewrite capabilities not only allow the reuse of MLs but also, and error-correction and improved spatial positioning in



creating SPE arrays, which can be especially important such as when the SPEs need to be precisely positioned to couple with waveguides or photonic-crystal cavities. In summary, we demonstrate nanoimprinting as a flexible, fast, controlled method to create strain induced SPE arrays in 2D materials. The imprinted nanoholes conform well to the morphology of the nano-mold. Bright, discrete defect-exciton emission from the imprinted sites suggests efficient exciton funneling via nano-scale strain engineering. Single-photon emission from the imprinted site is verified by photon anti-bunching. The high yield of localized emitters and high operating temperature of the emission suggest both effectiveness of the nanoimprint method in creating localized SPE and the potential of creating SPE in TMDs under more practical conditions. Furthermore, the method allows erasing and re-writing of SPE arrays, which will facilitate applications that need high spatial precision and controllability. The imprinted nanohole morphology remains protected in polyester substrate and thus can be readily integrated with additional photonic structure, such as waveguides and nanocavities, which are often critical for applications of SPEs. The method should be applicable to nanoscale strain engineering of a wide range of 2D material systems, including hexagon boron nitride, atomically thin heterostructures, and wafer-scale grown 2D materials. It may provide a new pathway to scalable quantum photonic circuits.

The work is currently under review at *Nano Letters*.

4.0 Moire Quantum Dot Arrays in van der Waals heterostructures

Moiré lattices formed in twisted van der Waals bilayers mark a new frontier in condensed matter physics. In semiconductors, TMD heterobilayers, the moiré lattice has a period on the length scale of an exciton, thereby providing a unique opportunity to create coupled exciton lattices hitherto unavailable in any other systems. In this project, we explored the possibility of quantum dot arrays formed naturally in a moire lattice and how moire lattice influence the optical properties of the system.

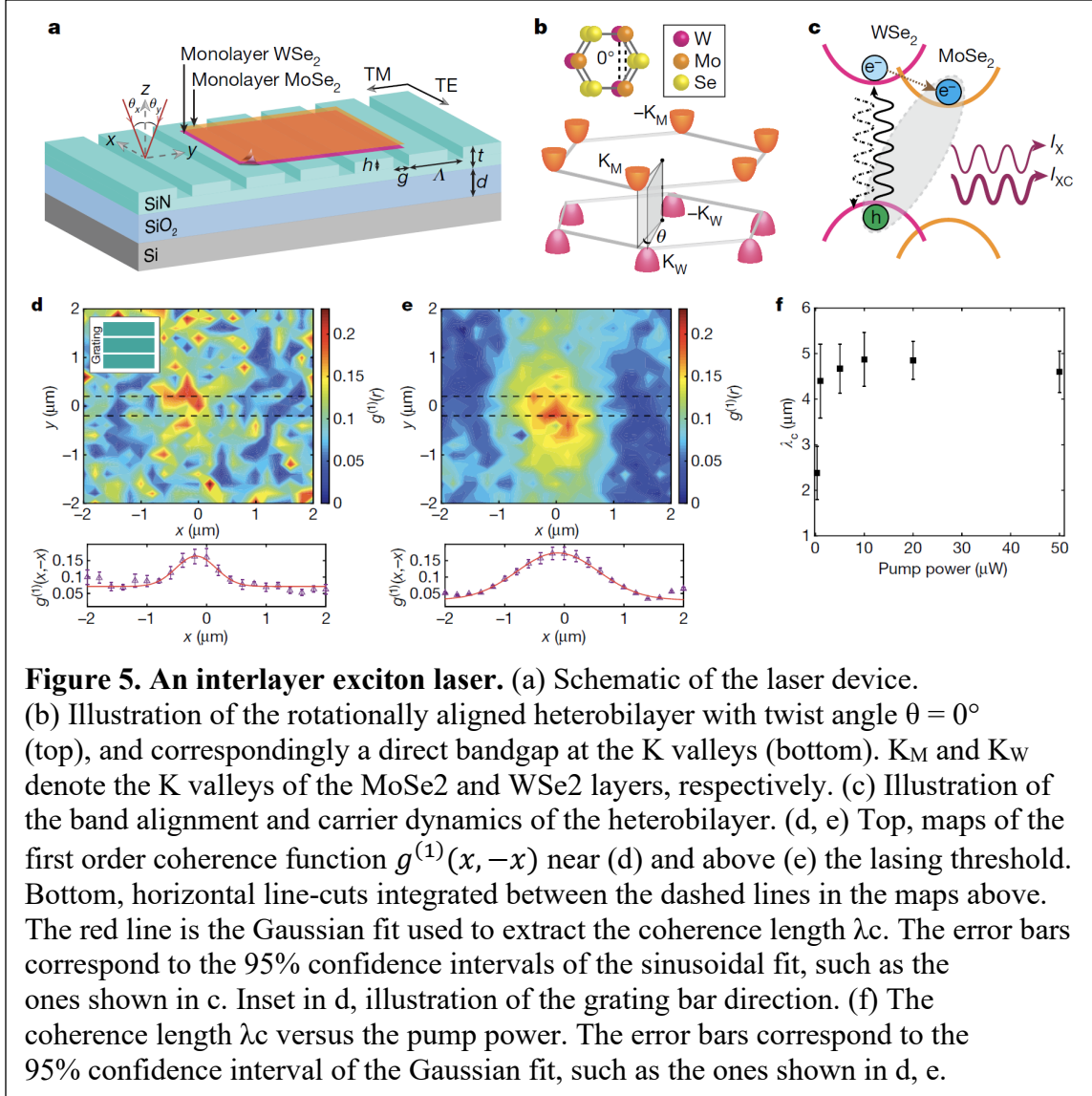
4.1. Interlayer exciton lasing in a WSe2/MoSe2 bilayer

[Paik et. al. *Nature* 576, 80–84 (2019).]

We first studied WSe2/MoSe2 bilayers integrated in a grating resonator. we show that in rotationally aligned 2D WSe2–MoSe2 heterobilayers integrated on a silicon nitride (SiN) cavity (Fig. 5), interlayer excitons form an efficient gain medium, supporting lasing with extended spatial coherence at a low population inversion density. As illustrated in Fig. 5b, by forming a direct bandgap between the two monolayers that are less than one nanometre apart, the interlayer excitons retain a sufficiently large oscillator strength. With type-II band alignment, the heterobilayer forms a three-level system that allows efficient pumping through the intralayer exciton resonances followed by rapid electron transfer to a lower-energy empty conduction band (Fig. 5c). As a result, population inversion is readily achieved at the reduced bandgap while avoiding fast intralayer radiative loss of the carriers. Moreover, unlike some of the cavities used for monolayer exciton lasers, the cavity mode in our device fully covers the heterobilayer, allowing gain over the full area of the bilayer, and supporting extended spatial coherence (Fig. 5a). We observe lasing accompanied by an abrupt increase in the spatial coherence length as the photon occupancy exceeds unity (Fig. 5d-f). The emission intensity increases nonlinearly more than 100-fold across the threshold, and then continues to increase linearly with pump power (without saturation) up to the highest power used.

Our results establish interlayer excitons in engineered TMDC heterobilayers as an efficient lasing medium, which, compared to excitons in monolayer TMDCs, feature electrically tunable long-range dipole interaction and oscillator strength, robust valley polarization, and a type-II band alignment.

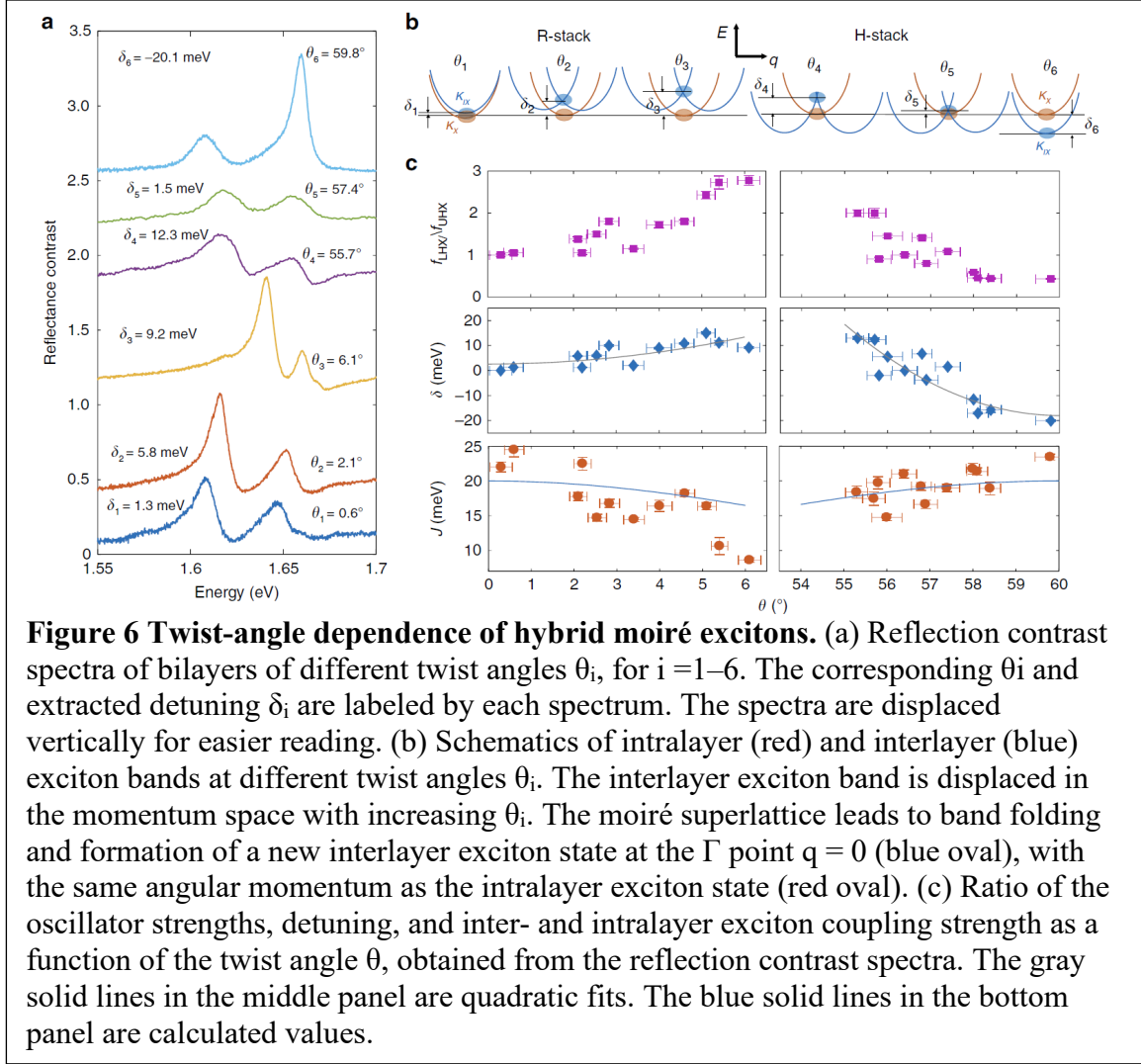
Most intriguingly, the threshold carrier density is only $n_{\text{th}} = 5.7 \times 10^{10} \text{ cm}^{-2}$. It is in good agreement with the density required for the transparency condition $n_{\text{tr}} \approx 8 \times 10^{10} \text{ cm}^{-2}$, but still far below the Mott density of $0.1/a_B^2 \sim 10^{13} \text{ cm}^{-2}$. This suggests that localization of the interlayer excitons in a moiré lattice may have led to increased phase space density and the low threshold for lasing, compared to free two-dimensional excitons. The localization may also lead to reduced non-radiative loss of the trapped interlayer excitons, enhancing the performance of heterobilayer lasers. To clarify the existence of moire lattices and to investigate the possibility of quantum dot like nature of excitons in moire lattices, we investigate a different bilayer with direct optical signatures of a moire lattice.



4.2. Moire lattice induced hybrid excitons and twist angle dependence

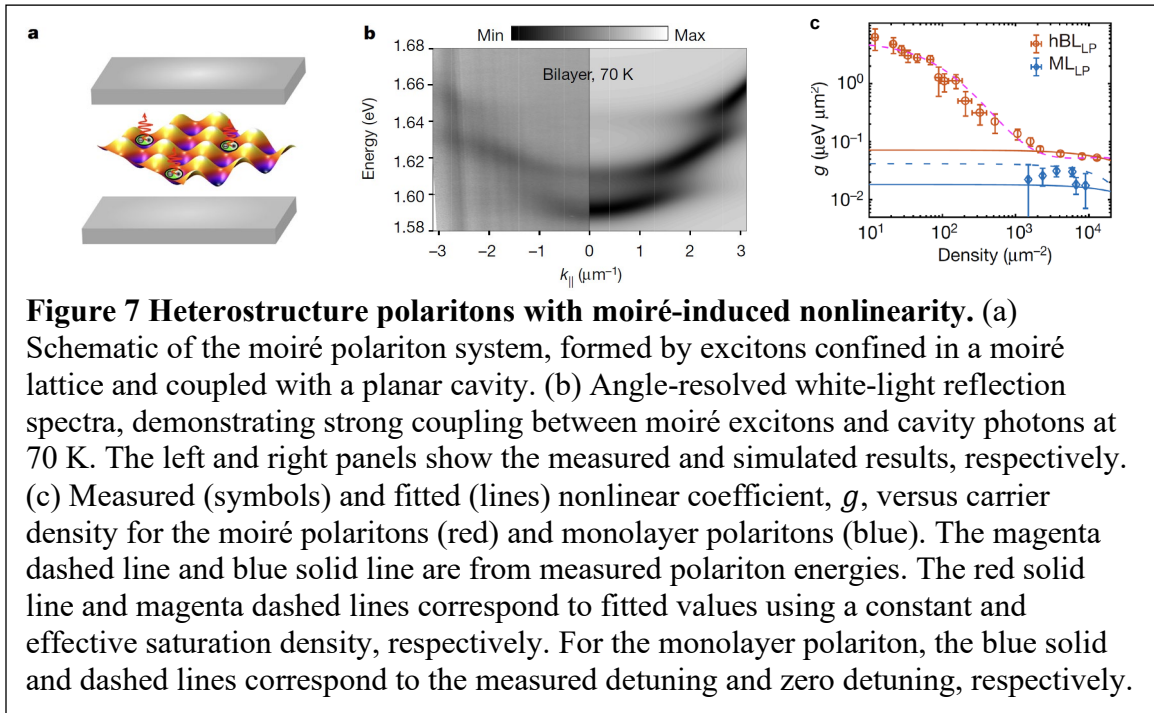
[Zhang et. al. Nature Communications 11, 5888 (2020).]

When two monolayer crystals of the same lattice symmetries overlay on each other, a moiré superlattice may form due to a small mismatch in their lattice constants or angular alignment. The latter — the twist angle between the two layers — provides a powerful tuning knob of the electronic properties of the heterostructure. To search for the effects of moiré lattices on excitons, split exciton states were first reported in TMD bilayers with very small twist angles, demonstrating localization of exciton states likely in moiré supercells. However, increasing the twist angle has led to the suppression of measurable features of moiré excitons.



In WS₂/MoSe₂ heterobilayers, it was suggested that the resonant interlayer hybridization amplifies the moiré superlattice effects on the electronic structure. Using WS₂/MoSe₂ heterobilayer formed with a wide range of twist angles, we demonstrate tuning of their properties by the moiré lattice or the twist angle (Fig 6). Utilizing the inter- and intralayer hybrid excitons in WS₂/MoSe₂ bilayers, we reveal the formation of moiré reciprocal lattices with Brillouin zones of different sizes at different twist angles.

We furthermore show how the moiré reciprocal lattices drastically change the properties of the moiré excitons, such as their resonance energies, oscillator strengths, and inter-/intralayer mixing. The twist-angle dependence of the moiré exciton states is well-explained by an analytical theory model based on band folding in the moiré lattice, which also consistently explain the dependence on the spin-orbit splitting of the conduction band, valley selection rules, atomic stacking orders, and the lattice symmetries. Comparing the experimental results with the model, we obtain the effective mass of the interlayer excitons and the interlayer electron-tunneling strength.



These results showcase how to unambiguously identify the existence of moiré lattice via the new exciton species introduced by the moiré lattice. They furthermore show moiré lattice as a new route to uncover and tune fundamental properties of heterobilayer systems.

4.3. Moire polaritons with quantum confinement induced nonlinearity

[Zhang et. al. Nature 591, 61–65 (2021).]

Building on our work that identifies unambiguous signatures of moiré lattices in WS₂/MoSe₂ heterobilayers, we investigate if these moiré excitons are 2D like or 0D like, as well as their collective coupling with light.

Integrating the moire lattice in a cavity (Fig 7a), we establish for the first time cooperative coupling between moiré-lattice excitons and microcavity photons up to the temperature of liquid nitrogen (Fig 7b).

The nonlinear response of the moire polaritons is in stark contrast with those of monolayer polaritons. The density dependence of the moiré polaritons reveals strong nonlinearity due to exciton blockade, suppressed exciton energy shift and suppressed excitation-induced dephasing, all of which are consistent with the quantum confined nature of the moiré excitons, showing each moire lattice site functions as a quantum dot. As a result of the quantum dot confinement, the moiré polaritons acquires a strong nonlinearity, circumventing limitations of a small Bohr radius (Fig. 7c).

Compared to other polariton systems, the moiré polariton system combines microscopic-scale tuning of matter excitations with cavity engineering and long-range light coherence, providing a platform for studying collective phenomena from tunable arrays of quantum emitters.

Unlike any existing quantum dot systems, the moire quantum dots are naturally formed between two pristine crystals and therefore are relatively uniform and densely packed, making them promising as an ideal medium for thresholdless, efficient and scalable semiconductor lasers.

5.0 Appendix A – Publications

1. Chen, P.-Y., Zhang, X.-Q., Lai, Y.-Y., Lin, E.-C., Chen, C.-A., Guan, S.-Y., Chen, J.-J., Yang, Z.-H., Tseng, Y.-W., Gwo, S., Chang, C.-S., Chen, L.-J. & Lee, Y.-H. "Tunable Moiré Superlattice of Artificially Twisted Monolayers". *Adv. Mater.* **31**, 1901077 (2019).
2. Liu, X., Yi, J., Yang, S., Lin, E.-C., Zhang, Y.-J., Zhang, P., Li, J.-F., Wang, Y., Lee, Y.-H., Tian, Z.-Q. & Zhang, X. "Nonlinear valley phonon scattering under the strong coupling regime". *Nat. Mater.* 1–6 (2021). doi:10.1038/s41563-021-00972-x
3. Paik, E. Y., Zhang, L., Burg, G. W., Gogna, R., Tutuc, E. & Deng, H. "Interlayer exciton laser of extended spatial coherence in atomically thin heterostructures". *Nature* **576**, 80–84 (2019).
4. Zhang, L., Zhang, Z., Wu, F., Wang, D., Gogna, R., Hou, S., Watanabe, K., Taniguchi, T., Kulkarni, K., Kuo, T., Forrest, S. R. & Deng, H. "Twist-angle dependence of moiré excitons in WS₂/MoSe₂ heterobilayers". *Nat. Commun.* **11**, 5888 (2020).
5. Zhang, L., Wu, F., Hou, S., Zhang, Z., Chou, Y.-H., Watanabe, K., Taniguchi, T., Forrest, S. R. & Deng, H. "Van der Waals heterostructure polaritons with moiré-induced nonlinearity". *Nature* **591**, 61–65 (2021).