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Near Infrared Photo-detection with Monolayer Heterostructures

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Annual Progress Report

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A. Abstract :

This project focused on Near-infrared (NIR) photo-detection of two-dimensional (2D) transition metal dichalcogenides (TMD) and their heterostructures.

In the first year, we establish a unique measurement platform which integrated variable temperature probe stations with confocal optical systems and tunable wavelength (from visible to IR range) laser for diverse studies of optoelectronic performances of the monolayer semiconductors and their heterostructures. In addition, we developed specific transfer techniques, device fabrication techniques, and conducted experiments on optoelectronics photo-detection of monolayer TMD and their heterostructures.

In the second year, we focus on the realization of emission of the NIR transition with vertically-stacked or laterally-stitched TMDs for type II band alignments. An ideal hetero-interface of vertical TMD heterojunctions for the interlayer transition has been demonstrated with our CVD-grown samples in our home-built Raman/PL system. The interlayer excitons could be found under low temperature in vacuum condition. Also, atomically-shape interface of lateral monolayer heterojunctions has been realized by sequential CVD growth of various monolayer TMD, which is potential for NIR photo-detection and further works on fundamental issues and applications.

In the third year, WS₂/MoS₂ heterostructure device using vertically-stacked is realized for type II band alignment and NIR photo-detection. It has been expected that the tunable interlayer transition (range from 800 ~ 1200nm) can be tuned with suitable band alignment of two different monolayer semiconductors, which would enable various wavelength of NIR photo-detection. Overall, the demonstration of TMD heterojunctions with type-II band alignment will enable better understanding of fundamental mechanisms behind vdW heterostructures and further design of next-generation sensing related optoelectronics.

B. Motivation and Goals

Advanced optoelectronic devices for Near-infrared (NIR) photo-detection is emergent for the applications in military purposes, monitoring, traffic system and Internet of Things (IoT). In the past, the development of NIR photo-detection is mainly achieved with III-V compound semiconductors and significant MBE techniques. Requirements of a near-perfect material quality and specific bandgap limits fundamental research and applications on the NIR photo-detection. In this proposal, we would like to realize man-made materials that exhibits artificial bandgap for NIR photo-detection.

Recent research frontiers advance to explore hetero-structures of monolayer 2D lattices since the abundant physical properties and fundamental researches. The hetero-junctions have unusual band

bending as opposed to two individual materials, especially for type II staggered band alignment, which electrons are likely to excite from the valence band (VB) of one material to the conduction band (CB) of another material, as shown in fig1. By exploiting the band alignment of monolayer semiconductors, it is possible to realize artificially-tuned bandgap with design and construction of heterojunctions, which is in urgent demand for the study of NIR photo-detection. Compared to III-V compound semiconductors, monolayer signature of the 2D lattices make it ideal for the construction of heterojunctions with various junction geometry and the tunability of band alignment, high gate-controlled ability and high integration feasibility. Surfaces and edges of the monolayer semiconductors are ideal to produce heterogeneous stacking or stitching of different 2D monolayers with high-quality interfaces. Our current progress suggests that the heterojunction of 2D materials is potential for highly efficient NIR photodetectors and rich fascinating physics would be reached in very near future.

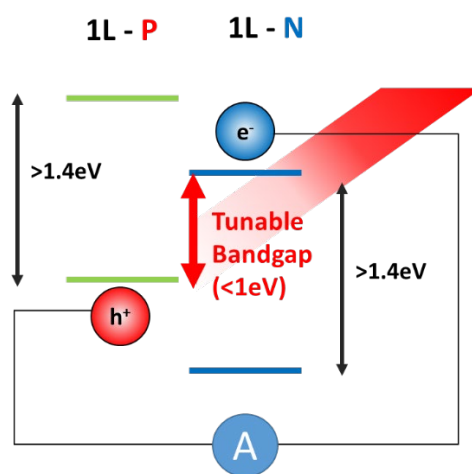


Figure 1: Schematic illustration of type II band alignment and interlayer transition.

Our attention was focused on three main objectives:

- 1. Realization of vertical stacking and lateral stitching of different monolayer semiconductors**
- 2. Optical interlayer transition of the vertically- stacked monolayers confirms a high-quality hetero-interface of the samples.**
- 3. Development of unique techniques on devices fabrication and measurements for NIR photo-detection and related fundamental study.**

C. Research Progress :

In the second year, we demonstrate vertical stacking and lateral stitching of monolayer semiconductors with ideal hetero-interface. The specific transfer techniques and synthesis of individual monolayer semiconductors are well developed in the first year. In the second year, we successfully realized the heterostructure of the vertical stacking and lateral stitching of more than two different monolayer semiconductors. Briefly, we have constructed vertical and lateral junctions to

create interlayer coupling. Now, we mainly focused on device fabrication, measurements, and analysis. More details will be introduced in the following section.

(1) Ideal hetero-interface and interlayer transition of vertically-stacked CVD-grown WS₂/MoS₂

In this work, high quality vdW TMD hetero-junctions has been successfully demonstrated by vertically-stacking CVD-grown WS₂ and MoS₂ monolayers in sandwich of two exfoliated hexagonal boron nitride (h-BN) flakes. Figures 2(a) show a schematic of the vertically-stacked h-BN/WS₂/MoS₂/h-BN. The CVD-grown TMD monolayers are transferred by PDMS-assisted method. Figure 2(b) shows the optical microscope (OM) image of the vertical junction of the vertically-stacked h-BN/WS₂/MoS₂/h-BN. It is worth noting that the PL mapping image over the vertically-stacked heterojunctions shows a strongly PL quenching because interlayer charge transfer appears efficiently across the hetero-interface between the two monolayer TMDs, as seen in the fig 2(c). This strongly quenching behavior was further confirmed with optical measurements as show in fig 2(d).

Interlayer excitons was checked both in room temperature and low temperature as shown in fig 2(e) and 2(f), interlayer excitons of the vdW heterojunctions were observed at 77k and disappeared at room temperature, which confirmed an ideal interface of the vertically-stacked samples. An additional PL peaks at energies significantly lower than those of individual TMDc flake has been found in the range 800 ~ 900 nm. Currently, we are working on the device fabrication of the sample of vertically-stacked monolayers to study the NIR photo-detection and fundamental physics with the interlayer transitions. Hopefully, the unique devices would pave the way for NIR photo-detection.

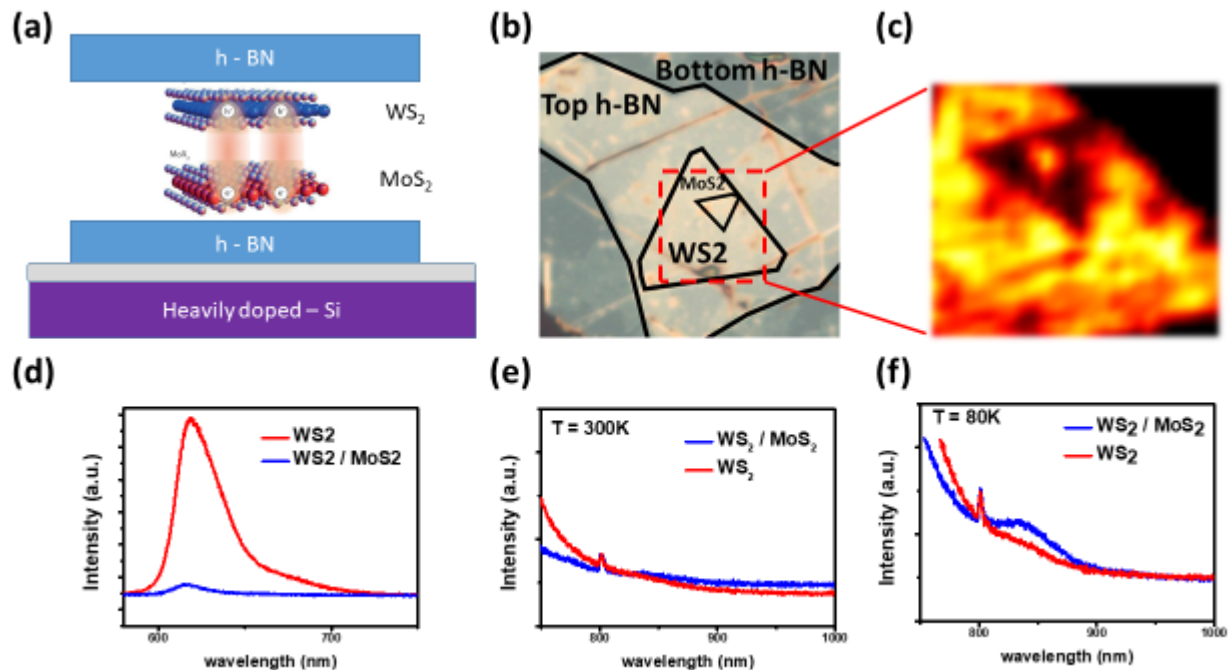


Figure 2: (a) Schematic of vertically-stacked h-BN/WS₂/MoS₂/h-BN . (b) Optical microscope (OM)

image of the vertically-stacked h-BN/WS₂/MoS₂/h-BN. (c) Photoluminescence (PL) mapping from the overlapped region of the WS₂ and MoS₂. (d) PL spectrum of the overlapped region shows strongly quenching. (e)(f) Photoluminescence spectrum of the overlapped region observed in room temperature and low temperature, respectively.

(2) Synthesis of In-Plane Artificial Lattices of Monolayer Multi-junctions

Vertical heterojunctions are vdW stacking of the monolayers along vertical direction, while in-plane heterojunctions are formed through lateral atomic stitching of different monolayers. The atomically sharp hetero-interface is the key feature for the fundamental study and diverse applications of these artificial materials that do not exist in nature. Figure 3(a) shows a schematic illustration of the multistep synthesis of the in-plane multi-junctions for monolayer WS₂/WSe₂/MoS₂. In the sequential CVD growth steps, low-pressure CVD (LPCVD) is adopted to reduce oxygen for possible compositional fluctuations and eventually realizes the edge epitaxy of sequential TMDs monolayers (WSe₂ and MoS₂) in independent growth systems. The interface quality of the in-plane TMDs multi-junctions was significantly improved by controlling the growth condition of the LPCVD. Figure 3(b) shows the optical microscope (OM) image of the in-plane multi-junctions of monolayer WS₂/WSe₂/MoS₂ synthesized using the multistep CVD synthesis. Figure 3(c)(d) shows Raman and photoluminescence (PL) spectra, respectively, collected from WS₂, WSe₂, and MoS₂ regions in the multi-junctions as marked using blue, green, and orange dots in Figure 3(b), which verify the high-quality monolayer and lateral hetero-epitaxy without compositional alloying. Figure 3(e–j) shows the Raman and PL mapping images constructed by integrating correlated Raman peak intensity (340–360 cm⁻¹ for WS₂; 240–260 cm⁻¹ for WSe₂; and 380–410 cm⁻¹ for MoS₂) and the PL intensity (620–630 nm for WS₂; 730–790 nm for WSe₂; and 650–680 nm for MoS₂) in the confocal optical measurements. The clear boundaries indicate that the multi-junctions of the WS₂/WSe₂/MoS₂ artificial lattices are synthesized without any alloying phases. Uniformly distributed signals in the Raman and PL mapping confirm the excellent crystallinity and uniformity of the artificial lattices.

The in-plane multi-junctions of the TMDs artificial lattices preserve triangular domain shape of the original WS₂ after two sequential growth steps, showing an ideal in-plane hetero-epitaxial growth and edge epitaxy of the monolayer TMDs. To further investigate the artificial lattices, atomic structures and composition of the hetero-interfaces, high-angle annular dark-field (HAADF) images of the Cs-corrected scanning transmission electron microscopy (STEM) are collected at the in-plane junctions of WS₂/WSe₂ and WSe₂/MoS₂, as shown in Figure 3(k) and (l). Atomically sharp interface along the zigzag crystalline direction indicates that perfect quality of the heterointerface forms in the sequential in-plane growth via edge epitaxy of the monolayer TMDs. This work is published in *Advanced Materials* in 2018. In the coming year, we will fabricate devices of the vertical stacking and lateral stitching of more than two different monolayers with type II band alignments for realization of NIR photodetection and related studies of fundamental issues.

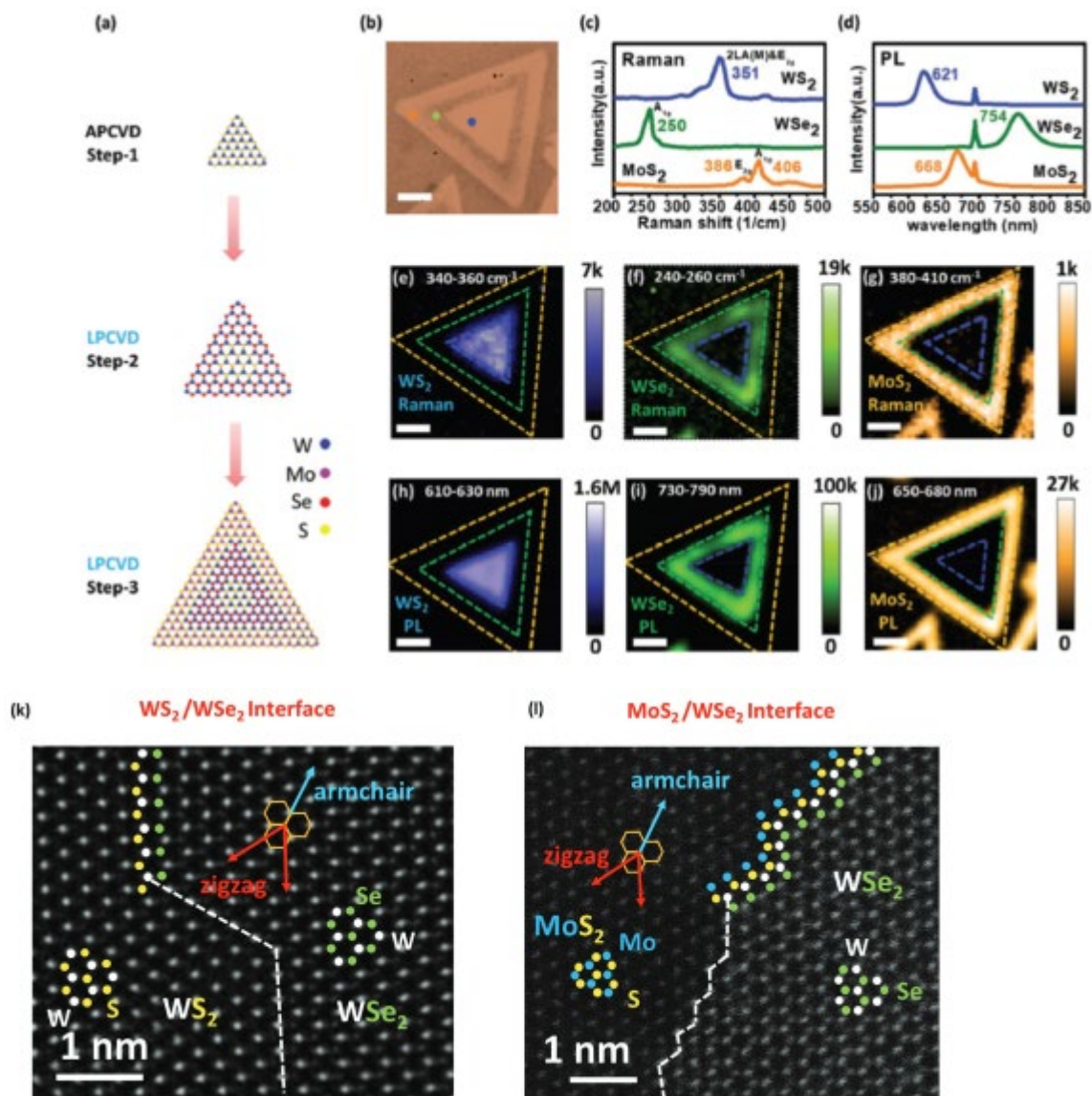


Figure 3:(a) Schematic illustrations of three-step CVD synthesis of the $\text{WS}_2/\text{WSe}_2/\text{MoS}_2$ multi-junctions. (b) OM image of the $\text{WS}_2/\text{WSe}_2/\text{MoS}_2$ multi-junctions. (c) Raman and (d) PL spectra obtained on the region of WS_2 (blue), WSe_2 (green), and MoS_2 (orange). (e–g) Raman mapping and (h–j) PL mapping images of the spectra of WS_2 , WSe_2 , and MoS_2 (Scale bar: $5\ \mu\text{m}$). (k,l) high magnification images of the atomic-resolution STEM-HAADF imaging of the hetero-interface of WS_2/WSe_2 and $\text{WSe}_2/\text{MoS}_2$.

(3) Observation of NIR response in vertically-stacked CVD-grown WS₂/MoS₂ junctions

Vertical stacking of two different CVD-grown monolayers (WS₂ and MoS₂) has been realized by developed transfer techniques. High quality vdW TMD hetero-junctions have been successfully demonstrated by vertically stacking CVD-grown WS₂ and MoS₂ monolayers directly on top of h-BN flake. The CVD-grown TMD monolayers were transferred by PMMA-assisted method and the thin h-BN flakes were exfoliated with PDMS dry transfer techniques. The schematic illustration of the hetero-device was displayed in Fig 4(a), the bilayer metal Ti/Au (about 3/40 nm thick) was used to contact respectively. According to previous reports, both of individual WS₂ and MoS₂ showed no response to near infrared light, but the band alignment of WS₂/MoS₂ heterostructures narrowed the interlayer transition energy gap and made infrared light detection possible.

To verify the interlayer transition or NIR response performance, we fabricated photodetectors based on this structure, and found diode-like feature with obvious rectification curve, as shown in Fig 4(b). This rectification characteristic or on/off ratio could be enhanced with increasing back-gate voltage and reach up to 150 times. Then we conducted NIR experiments to confirm the performance of hetero-device. As shown in fig 4(c)-(e), the hetero-device the NIR laser induced strong photo-response at infrared range (700~950 nm) and cut off at about 950 nm, which is consistent with previous predictions about the energy difference of interband transition. Time resolved analysis indicated that the photodetector has distinct response under 700 ~ 900 nm NIR source. It is necessary to emphasize that the detectable response to NIR region can be exclusively ascribed to the individual WS₂ and MoS₂ because both materials show no response under NIR laser. In conclusion, it was the first time that demonstrated infrared response based on CVD-grown sample, making heterostructure-based NIR devices more likely to be realized. In addition, by stacking various TMD materials together, we could easily modulate the energy gap of transition and control the response region. Such devices pave the way for photo-detection of man-made bandgap in the urgent need range with the construction artificial heterostructure.

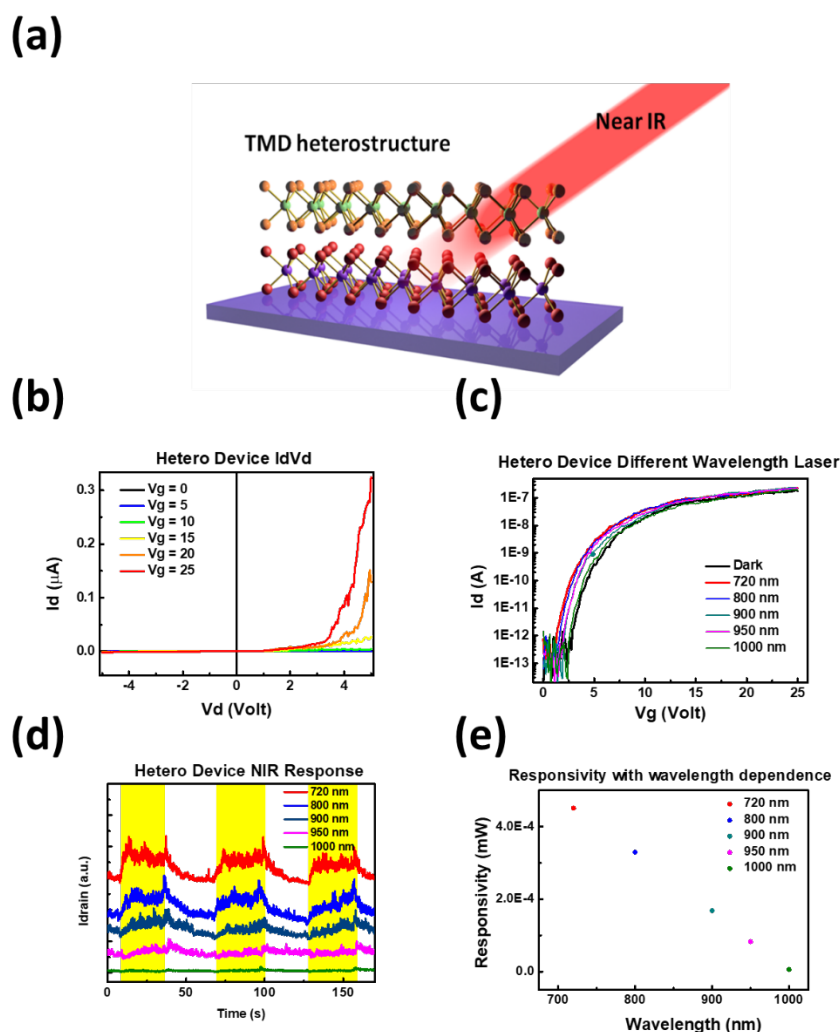


Figure 4:(a) Schematic illustration of vertical stacking of the WS₂/MoS₂ hetero-device illuminated by near-infrared laser. (b) I_d - V_d output curves for hetero-device at different back-gate voltage. (c) I_d - V_g transfer curves for hetero-device with different wavelength laser. (d) Time resolved analysis for NIR response with different wavelength laser. (e) Comparison of responsivity at different wavelength.

D. Summary and Future Work :

In the second year, we realized heterojunctions that are constructed using CVD-grown monolayer of the vertically-stacked and laterally-stitched TMDs. The interlayer exciton is successfully observed with the vertically-stacked MoS₂/WS₂ at a low temperature of 77K, suggesting a high interface quality of the stacked monolayers. Lateral stitching of more than two different monolayer semiconductors has been realized with the development of unique multi-step synthesis methods. An atomically-sharp hetero-interface of the laterally-stitched monolayers is found, which is potential for NIR photo-detection and further works on fundamental issues and applications.

In the final year, we further fabricate and demonstrate the devices of the TMD heterostructures based on CVD-grown sample for the NIR photo-detection and the interlayer transition, which will enable further development of next-generation large area or wafer-scale infrared optoelectronics.

Reference:

1. Akinwande, Deji, Nicholas Petrone, and James Hone. "Two-dimensional flexible nanoelectronics." *Nature communications* 5 (2014): 5678.
2. Huang, Hai, et al. "Highly sensitive visible to infrared MoTe₂ photodetectors enhanced by the photogating effect." *Nanotechnology* 27.44 (2016): 445201.

E. Publications in the period :

1. Chen, Po-Yen, et al. "Tunable Moiré Superlattice of Artificially Twisted Monolayers." *Advanced Materials* 31.37 (2019): 1901077.
2. Chiu, K. C. et al., "Synthesis of In-Plane Artificial Lattices of Monolayer Multijunctions". *Advanced Materials*, 30(7), 1704796, (2018).
3. Mahmood, F., Alpichshev et al., "Observation of Exciton–Exciton Interaction Mediated Valley Depolarization in Monolayer MoSe₂", *Nano letters*, 18 (1), 223-228, (2017)
4. Yang, T. H. et al, "Electron Field Emission of Geometrically Modulated Monolayer Semiconductors", *Adv. Func. Mater.* 28 (7), 1706113(2018).
5. Wang, J. W. et al, . Controlled Low-Frequency Electrical Noise of Monolayer MoS₂ with Ohmic Contact and Tunable Carrier Concentration. *Adv. Elec. Mater.*, 4(1), 1700340 (2018).
6. E. J. Sie et al, "Large, valley-exclusive Bloch-Siegert shift in monolayer WS₂", *Science* 355 (6329), 1066-1069 (2017)
7. E. J. Sie et al, "Observation of Intervalley Biexcitonic Optical Stark Effect in Monolayer WS₂", *Nano Letters*. 16, 7421–7426 (2016)
8. K.C. Chiu et al, "Strong and broadly tunable plasmon resonances in thick films of aligned carbon nanotubes", *Nano Letters*. 17, 5641-5645(2017).
9. J. Shi et al, "Cascaded exciton energy transfer in a monolayer semiconductor lateral heterostructure assisted by surface plasmon polariton", *Nature Communications* 8 (1), 35 (2017).

F. Invited talks in the period :

1. 2019, Engineering Materials Genome of Artificial 2D Lattices, Academia Sinica, July 16
2. 2019, Synthesis and Analysis of Artificial 2D Lattice, National Chiao Tung University, Jan 23
3. 2018, Engineering Materials Genome of Artificial 2D Lattices, Stanford University, Stanford,

USA, Mar. 13

4. 2017, Heterostructure and Applications of monolayer semiconductors, ISSS8, Tsukuba-Japan, Oct. 24

G. Additional Grants received last year (2017)

Projects	Projects number	Projects name	Year	Amount of funding
Ministry of Science and Technology Projects	105-2112-M-007-032-MY3	Synthesis of novel Transition Metal Dichalcogenides and Artificial Heterostructures of Two-Dimensional Materials	2016/08/01~ 2019/07/31	100,000 USD
Ministry of Science and Technology Projects	106-2119-M-007 -023 -MY3	Platform of 2D materials-integrated cavity: Strong light-matter interaction and tunable optical properties of 2D materials.	2017/08/01 ~ 2020/07/31	130,000 USD