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# Synthetic 2D Materials for Quantum Light Sources and Memory

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**14. ABSTRACT**
The combined team of three institutions (University of Pennsylvania, AFRL, and Ulsan National Institute of Science and Technology (UNIST), South Korea) as part of the US/Korea Quantum initiative led by PI Deep Jariwala of Penn in collaboration with Nicholas Glavin (RX) and Joshua Hendrickson (RY) of AFRL demonstrated a bottom-up, scalable, and lithography-free approach for creating large areas of localized quantum emitters with high density (?150 emitters/um2) in a two-dimensional (2D) semiconductor tungsten diselenide (WSe2) monolayer. The team induced strain inside the WSe2 monolayer with high spatial density by conformally placing the WSe2 monolayer over a uniform array of Platinum nanoparticles of approx. 10 nm in size. Cryogenic, time-resolved, and gate-tunable luminescence measurements combined with near-field luminescence spectroscopy suggested the formation of localized states in strained regions that emit single photons with a high spatial density. The approach of using a metal nanoparticle array to generate a high density of strained quantum emitters is the first report of scalable (> centimeter square areas), tunable, and versatile quantum light sources. This work was published in ACS Nano, 2022, 16, 6, 9651–9659 and was widely highlighted by scientific news outlets. During the course of this program, the PIs won numerous prestigious awards.

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# Final Report

## Synthetic 2D Materials for Quantum Light Sources and Memory

**Summary:** This two-year collaborative program with Ulsan National Institute of Science and Technology (UNIST) was very successful in that all the major goals proposed in the initial proposal were successfully accomplished and demonstrated in practice. Despite the negative impacts of the pandemic related illnesses among students, postdocs and the supply chain delays our team was able to produce 14 high quality, peer-reviewed journal publications as a result of this grant including published papers in Nature Nanotechnology, Advanced Materials, ACS Nano, Nano Letters etc. In addition, several other key results are presently under review at major journals. Finally, the program also contributed immensely to talent development and training of graduate students as both PhD students supported on the program received multiple first authored publications that directly contribute to their PhD thesis. Further, the postdoc trained on this grant was able to secure a permanent academic/scientist position in Korea which will further strengthen the research ties between our groups and Korean universities/research institutions. In addition, the PI was also awarded with several society level awards as a result of the research emanating from this program. In summary, this was a highly successful, productive and rewarding program for all parties involved.

**Research objectives:**

To overcome the grand challenges in quantum light sources and memory, we propose the following 2 objectives:

I. Synthesize a novel in-plane epitaxial atomically-thin quantum dot platform with tunable control over optical transitions and amenable to hybrid integration.

II. 2D chalcogenides as van der Waals hosts to substitutionally doped REEs atoms.

**Major Accomplishments:**

**We were successful is accomplish a majority of the proposed goals and objectives. The resulting and related works led to a total of 12 published papers all in top tier journals and 2 papers under peer-review.**

1. **Review on Nanomaterials for Quantum Information Science and Engineering:** Quantum information science and engineering (QISE)—which entails the use of quantum mechanical states for information processing, communications, and sensing—and the area of nanoscience and nanotechnology have dominated condensed matter physics and materials science research in the 21st century. Solid-state devices for QISE have, to this point, predominantly been designed with bulk materials as their constituents. Our review considers how nanomaterials (i.e., materials with intrinsic quantum confinement) may offer inherent advantages over conventional materials for QISE. **This work was published in *Advanced Materials*** 10.1002/adma.202109621
2. **High-Density, Localized Quantum Emitters in Strained 2D Semiconductors:** In this work, we demonstrate a bottom-up, scalable, and lithography-free approach for creating large areas of localized emitters with high density (~150 emitters/um$^2$) in a $WSe_2$ monolayer. We induce strain inside the $WSe_2$ monolayer with high spatial density by conformally placing the $WSe_2$ monolayer over a uniform array of Pt nanoparticles with a size of 10 nm. Cryogenic, time-resolved, and gate-tunable luminescence measurements combined with near-field luminescence spectroscopy suggest the formation of localized states in strained regions that emit single photons with a high spatial density. Our approach of using a

metal nanoparticle array to generate a high density of strained quantum emitters will be applied to scalable, tunable, and versatile quantum light sources. **This work was published in *ACS Nano*, 2022, 16, 6, 9651–9659**

**3. Spatially controlled two-dimensional quantum heterostructures:** In this brief overview, we summarize recent advances in approaches for the growth of spatially controllable 2D quantum heterostructures. These growth methods enable the achievement of various 2D lateral/vertical heterostructures with controlled positions and dimensions while minimizing defects across the heterointerfaces. In addition, we provide an outlook on the future direction of developments and applications of 2D quantum-confined heterostructures. **This work was published in *Materials Research Letters* 2023, 11, 327-346**

**4. Ultrathin Broadband Metasurface Superabsorbers from a van der Waals Quantum Semimetal:** In this work we experimentally demonstrate a broadband metasurface superabsorber based on large area, semimetallic, van der Waals quantum semi-metal platinum diselenide ($PtSe_2$) thin films in agreement with electromagnetic simulations. The results show that $PtSe_2$ is an ultrathin and scalable semimetal that concurrently possesses high index and high extinction across the vis-NIR range. Consequently, the thin-film $PtSe_2$ on a reflector separated by a dielectric spacer can absorb >85% for the unpatterned case and ≈97% for the optimized 2D metasurface in the 400–900 nm range making it one of the strongest and thinnest broadband perfect absorbers to date. The results present a scalable approach to photodetection and solar energy harvesting, demonstrating the practical utility of high index, high extinction semimetals for nanoscale optics. **This work was published in *Advanced Optical Materials*, *DOI:* 10.1002/adom.202202011**

**5. Direct Opto-electronic Imaging of 2D Semiconductor/3D Metal Buried interfaces:** In this work, we report the direct measurement of electrical and optical responses of 2D semiconductor–metal buried interfaces using a recently developed metal-assisted transfer technique to expose the buried interface, which is then directly investigated using scanning probe techniques. We characterize the spatially varying electronic and optical properties of this buried interface with <20 nm resolution. **This work was published in *ACS Nano*, 2021, 15, 5618–5630**

**6. Self-Hybridized Polaritonic Emission from Layered Perovskites:** In this work, we report strong light–matter coupling in Ruddlesden–Popper phase 2D HOIP crystals without the necessity of an external cavity. We report the concurrent occurrence of multiple orders of hybrid light–matter states via both reflectance and luminescence spectroscopy in thick (>100 nm) crystals and near-unity absorption in thin (<20 nm) crystals. We observe resonances with quality factors of >250 in hybridized exciton-polaritons and identify a linear correlation between exciton-polariton mode splitting and extinction coefficient of the various 2D HOIPs. **This work was published in *Nano Letters* 2021, 21, 6245-6252**

**7. Light-Matter Coupling in Van der Waals Superlattices:** In this work, 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. **This work was published in *Nature Nanotechnology* 2022, 17, 182–189**

**8. Tunable Localized Charge Transfer Excitons in a Mixed Dimensional van der Waals Heterostructure: In this work,** we demonstrate the formation of CT excitons in a 2D/quasi-2D system comprising MoSe2 and WSe2 monolayers and CdSe/CdS based core/shell nanoplates (NPLs). Spectral signatures of CT excitons in our MDHs were resolved locally at the 2D/single-NPL heterointerface using tip-enhanced photoluminescence (TEPL) at room temperature. By varying both the 2D material, the shell thickness of the NPLs, and applying out-of-plane electric field, the exciton resonance energy was tuned by up to 120 meV. Our finding is a significant step towards the realization of highly tunable MDH-based next generation photonic devices. **This work is currently under peer review.** arXiv:2210.12608 **2022**

**9. Lateral confinement in two-dimensional quantum heterostructures:** In this work, we demonstrate the observation of lateral exciton confinement in large-area 2D quantum heterostructures composed of MoSe2 quantum dots inside a matrix of WSe2 monolayer. We created the lateral heterostructures with an ultraclean interface using sequential epitaxial growth, and the size of triangular MoSe2 quantum dots (10~50 nm) could be controlled with a short reaction time. Optical spectroscopies revealed the size-dependent exciton confinement in the MoSe2 monolayer quantum dots, which also showed quantum emission on 10 nm-sized quantum dots in the cryogenic condition. Our study will be applied to developing in-plane quantum-confined devices in 2D materials for potential applications in quantum information. **This work is currently under preparation.**

## Dissemination of results:

18 invited conference presentations and 7 invited department seminars

14 peer reviewed journal publications. See below.

## Impacts

In the primary research conducted under this program, we have demonstrated an approach to fabricating strain-induced localized quantum emitters with high spatial density in a WSe2 monolayer on a uniform Pt NP array. This strained WSe2 structure shows LX at room temperature that is significantly red-shifted from both neutral excitons and trions. The sample topography and Pt NP density create compressive strain in spaces between the Pt NPs where the LX emission originates via the tuning of dark excitons by compressive strain. Our approach is free of top-down lithography and is highly scalable to large-area TMDCs, as well as demonstrated to be applicable for other 2D semiconductors. Finally, our structure allows observation of quantum emission at low temperature, which is further tunable passively via Pt NP size and density as well as actively via a gate voltage. Our results, therefore, advance the state of the art in producing a high density of strain-induced, localized quantum emitters in TMDC monolayers in a scalable, controllable, and lithography-free approach, which is critical for future progress in the science and technology of quantum light sources. Similarly our in preparation work on lateral confinement in 2D quantum heterostructures establishes a key principle that composition modulation can be used to attain quantum confined single photon sources with bottom up control.

In addition, our work on quantum semi-metal PtSe2 pioneers the use of ultrathin $PtSe_2$-based metasurfaces for broadband visible and near infrared light absorption. Our approach presented can be generalized to other existing and to-be-discovered van der Waals semimetallic and semiconducting materials exhibiting high broadband extinction due to interband transitions, presenting an exciting opportunity to design future metasurfaces for photodetection, photochemistry, and solar energy harvesting. We expect that our metasurfaces will be particularly promising as a photocathode for solar photoelectrocatalysis given the strong solar absorbance in a catalytically active material, electric field enhancement, and hot electron generation.

**Training opportunities:**

One REU student and one undergraduate student were trained as part of the research project who received co-authorship on multiple publications. PhD students and postdocs presented in both online (due to pandemic) and in-person conferences (MRS and AVS) and career development workshops (AVS).

Postdoctoral Scholar Dr. Gwangwoo Kim has tentatively secured a permanent research position in South Korea to continue his research and academic career.

## Changes

**Impact/Delays due to COVID19:** After the COVID19 related shutdown, the labs were reopened on June 25th 2020 however in a very limited capacity with every student coming in on alternative days. Further, no training on task involving more than one person was allowed. These rules were in place until early August 2020 close to the time the work on the grant initiated. Later on, most restrictions remained until March 2021 however students and postdocs were allowed to access labs without much issue. Since April 2021 the restrictions were mostly removed but starting July 2021 with the rise of Delta variant some restrictions have been put back on however the pace of research remains largely unaffected. More than the COVID related lockdowns, the subsequent supply chain crisis hindered our progress due delayed orders and servicing on malfunctioning equipment in the later part of 2021 and early 2022.

## Technical Updates

### Future work:

A key outcome from the above project is that we were able to establish scalable quantum light sources via strain engineering. However, substitutional doping and composition engineering combined with strain is more promising for not only higher purity light sources but also for quantum memory applications. This has not been achieved yet and therefore important for future work/follow up program. Substitutional doping of both 2D and 3D semiconductors and insulators have now been widely achieved. An rare-earth element (REE) atom dopant can not only serve as a dopant or defect site for single photon quantum emission but rather also has outstanding optically addressable electron and nuclear spins. This has been successfully achieved in fiber lasers by doping of oxide glasses and more recently, also in chalcogenide glasses as 3D hosts. A 3D host is far from ideal to address the problem of weak-oscillator strengths and enhancement of light-matter coupling. Therefore, we propose doping of an atomically-thin semiconductor or insulator layer with substitutional REE atoms and ions. By doping REEs in atomically-thin layers, we will not only understand the limits of control and isolation over individual quantum memory elements but will also be able to explore their interaction with under strong-light matter coupling environments due to the 2D nature of the host. The 2D nature of the host will allow modification of the crystal field via both strain and external electric fields which will further allow manipulation of the 4f intra-shell transitions. Finally, we propose to achieve spatial control and explore the limits of doping on the lower end using bottom up and top down techniques. We note that REE doping in 2D materials has been scarcely studied. Hence, we believe this is an opportune time and right collaboration. Specifically, we will focus our REE doping efforts on $MoS_2$ and $WS_2$ as hosts with $Er^{3+}$ as the REE dopant. Er is the selected REE since it is well known dopant emitter in III-V, goes in substitutionally in the $MX_2$ lattice and has a wide variety of metal organic precursor compounds available.

### Publications in print from the full two-year program in reverse chronological order (14):

1. Alfieri, A. D.; Motala, M. J.; Snure, M.; Lynch, J.; Kumar, P.; Zhang, H.; Post, S.; Muratore, C.; Hendrickson, J. R.; Glavin, N. R., **Jariwala, D.**[#] Ultrathin Broadband Metasurface Superabsorbers from a van der Waals Semimetal. *Advanced Optical Materials DOI:* 10.1002/adom.202202011
2. Kim, G.; Song, S.; **Jariwala, D.,**[#] Spatially Controlled Growth of 2D Quantum Heterostructures for Optoelectronics. *Materials Research Letters* **2023,** 11, 327-346.
3. Beagle, L. K.; Moore, D. C.; Kim, G.; Tran, L. D.; Miesle, P.; Nguyen, C.; Fang, Q.; Kim, K-H.; Prusnik, T. A.; Michael Newburger, M.; Rao, R.; Lou, J.; **Jariwala, D.**; Baldwin, L. A.; Glavin, N. R., Microwave Facilitated Covalent Organic Framework/Transition Metal Dichalcogenide Heterostructures *ACS Applied Materials and Interfaces* **2022***,* 14, 46876–46883
4. Lynch, J.; Guarneri, L.; **Jariwala, D.**[#]; van de Groep, J.,[#] Exciton resonances for atomically-thin optics. *Journal of Applied Physics* **2022**, 132, 091102 (**Feature Article, Invited review**)
5. Singh, A.; Lynch, J.; Anantharaman, S. B.; Hou, J.; Singh, S.; Kim, G.; Mohite, A. D.; Singh, R.; **Jariwala, D.,**[#] Cavity-Enhanced Raman Scattering from 2D Hybrid Perovskites. *Journal of Physical Chemistry C* **2022,** 126, 11158–11164.
6. Kim, G.; Kim, H. M.;[‖] Kumar, P.; Rahaman, M.; Stevens, C. E.; Jeon, J.; Jo, K.; Kim, K.-H.; Trainor, N.; Zhu, H.; Sohn, B.-H.; Stach, E. A.; Hendrickson, J. R.; Glavin, N.; Suh, J.; Redwing, J. M.; **Jariwala, D.,**[#] High Density, Localized Quantum Emitters in Strained 2D Semiconductors. *ACS Nano* **2022,** 16, 6, 9651–9659. **(Highlighted by AzoNano.com)**
7. Kim, K-H.; Andreev, M.; Choi, S.; Shim, J.; Ahn, K-H; Nassiri Narif, K.; Kumar, A.; Lynch, J.; **Jariwala, D.**; Saraswat, K.; Park, J-H,[#] High-Efficiency $WSe_2$ Photovoltaic Devices with Carrier Selective Contacts. *ACS Nano*. **2022,** 16, 6, 8827–8836.
8. Motala, M.; Beagle, L. K.; Lynch, J.; Moore, D. C.; Stevenson, P. R.; Benton, A.; Tran, L. D.; Baldwin, L. A.; Austin, D.; Muratore, C.; **Jariwala, D.**;[#] Glavin, N. R.[#] Selective vapor sensors with thin-film MoS2-coated optical fibers. *Journal of Vacuum Science & Technology A* **2022,** 40, 032202. **(Editor's Pick, Highlighted in AIP *Scilight,* Winner of Young Author Award in the journal)**
9. Alfieri, A. D.; Anantharaman, S. B.; Zhang, H.; **Jariwala, D.,**[#] Nanomaterials for Quantum Information Science and Engineering. *Advanced Materials* **DOI:** 10.1002/adma.202109621
10. Kumar, P.; Lynch, J.; Song, B.; Ling, H.; Barrera, F.;[‖] Zhang, H.; Anantharaman, S. B.; Digani, J.; Zhu, H.; Choudhury, T. H.; McAleese, C.; Wang, X.; Conran, B. R.; Whear, O.; Motala, M.; Snure, M.; Muratore, C.; Redwing, J. M.; Glavin, N.; Stach, E. A.; Davoyan, A. R.; **Jariwala, D.**[#] Light-Matter Coupling in Scalable Van der Waals Superlattices. *Nature Nanotechnology* **2022**, 17, 182–189. **(Highlighted in SciTech Daily, Phys.Org and many news outlets.)**
11. Vincent, T.; Liang, J.; Singh, S.; Castanon, E. G.; Zhang, X.; McCreary, A.; **Jariwala, D.;**[#] Kazakova, O.;[#] Balushi, Z. Y. A.,[#] Opportunities in Electrically Tunable 2D Materials Beyond Graphene: Recent Progress and Future Outlook. *Applied Physics Reviews,* **2021,** 8, 041320. **(Feature Article)**
12. Anantharaman, S. B.; Stevens, C. E.; Lynch, J.; Song, B.; Hou, J.; Zhang, H.; Jo, K.; Kumar, P.; Blancon, J.-C.; Mohite, A. D.; Hendrickson, J. R.; **Jariwala, D.**[#] Self-Hybridized Polaritonic Emission from Layered Perovskites. *Nano Letters* **2021**, 21, 6245-6252
13. Jo, K.; Kumar, P.; Orr, J.;[‖] Anantharaman, S. B.; Miao, J.; Motala, M.; Bandyopadhyay, A.; Kisslinger, K.; Muratore, C.; Shenoy, V. B.; Stach, E. A.; Glavin, N. R.; **Jariwala, D.**[#] Direct Opto-Electronic Imaging of 2D Semiconductor- 3D Metal Buried Interfaces. *ACS Nano*, **2021,** 15, 5618–5630.
14. Zhang, Q.; Zhen, Z.; Liu, C.; **Jariwala, D.**;[#] Cui, X., Gate-tunable polariton superlens in 2D/3D heterostructures. *Optics Express* **2019**, 27, 18628-18641

**Publications under review/revisions/preparation (2):**

15. Rahaman, M.; Marino, E.; Alan, J.; Song, S.; Jiang, Z.; O'Callahan, B.; Rosen, D.J.; Jo, K.; Kim, G.; El-Khoury, P.Z.; Murray, C.B.; **Jariwala, D.,**[#] Observation of Localized Charge Transfer Excitons in a Mixed Dimensional van der Waals Heterostructure. (submitted) *arXiv:2210.12608* **2022**

16. Kim, G.; Jariwala, D.,et al. **Lateral confinement in two-dimensional quantum heterostructures** (under preparation)

**Other Information:**

**# of PhD students supported by the grant:** 0.5 (50% support for Adam Alfieri)

**# of Postdoctoral Scholars supported by the grant:** 0.5 (50% support for Gwangwoo Kim)

**PI Awards during the two-year grant period (2020-2022)**

- Office of Naval Research, Young Investigator Program (ONR-YIP) Award **2023**
- IEEE Nanotechnology Council Young Investigator Award **2023**
  (one or two awarded every year)
- Bell Labs Prize **2022**
  (one awarded every year, 100 K USD cash award)
- Distinguished Alumnus Award, Young Achievers Category, IIT-BHU **2022**
  (one awarded each year in each category. < 10 total/year)
- International Union for Vacuum Science, Technique and Applications (IUVSTA) EBARA Award **2022**
- S. Reid Warren Jr. Award, Penn Engineering **2022**
  (Student body administered award for outstanding service in stimulating and guiding the intellectual and professional development of undergraduate students. Awarded to one faculty member/year across the school)
- Alfred P. Sloan Fellowship **2022**
- International Union of Pure and Applied Physics (IUPAP) Early Career Prize in Semiconductor Physics **2022**
  (two awarded every two years)
- IEEE Photonics Society Young Investigator Award **2022**
  (one awarded every year)
- Paul H. Holloway Young Investigator Award, American Vacuum Society (AVS) **2021**
  (one awarded every year)
- Intel Rising Star Award **2021**
- Young Electrical Engineer Award, IEEE Philadelphia/Delaware Valley Section **2021**
- Frontiers of Materials Award, The Metals Minerals and Materials Society (TMS) **2021**
- iCANX Young Scientist Award **2021**
- Young Alumni Achiever Award, Association of IIT-BHU Alumni **2021**
- IEEE Senior Member **2021**