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Final Technical Report

Award number:	DE-SC0022179
Project title:	Multidimensional Coherent Spectroscopy of van der Waals materials and heterostructures
Principal Investigator:	Steven T. Cundiff University of Michigan
Reporting period:	08/01/2021 – 12/31/2024
Sponsor:	U.S. Department of Energy, Office of Science

1. Project Overview and Motivation

This project advanced multidimensional coherent spectroscopy (MDCS) and related spectroscopic-imaging methods as quantitative probes of many-body optical excitations in two-dimensional (2D) van der Waals (vdW) semiconductors and their heterostructures. Monolayer transition-metal dichalcogenides (TMDs) such as $MoSe_2$ and WSe_2 provide a uniquely strong platform for excitonic physics due to reduced dielectric screening, which enhances Coulomb interactions and makes higher-order correlated states (e.g., biexcitons and exciton–trion correlations) more prominent than in conventional bulk semiconductors. At the same time, the same sensitivity that enables strong interactions also increases susceptibility to spatial inhomogeneity—e.g., strain gradients, wrinkles, nanoscale disorder potentials, and charge puddling—which can broaden resonances, obscure interaction signatures, and complicate device-to-device reproducibility.

The work reported here addressed this dual opportunity and challenge by: (i) developing and deploying coherent multidimensional methods (including double-quantum MDCS) capable of isolating interaction signals with reduced background, (ii) integrating electrostatic control to tune carrier populations and interaction strengths in situ, and (iii) introducing complementary spatially resolved photoluminescence (PL) techniques—hyperspectral PL imaging and polarization-/field-dependent PL lineshape analysis—to directly quantify disorder, strain, and localization that govern the coherent response.

2. Objectives

The research carried out under DE-SC0022179 pursued four tightly linked objectives:

1. *Measure and interpret exciton–exciton and exciton–charge interactions* in monolayer TMDs using MDCS, emphasizing *double-quantum (2Q) techniques* that selectively reveal many-body correlations through interaction-only signals.

2. *Develop experimental capability for multidimensional coherent imaging spectroscopy*, enabling spatially resolved mapping of coherent nonlinear signals without the constraints of conventional noncollinear geometries that often require sample motion.
3. *Achieve electrostatic control of the excitonic species* (exciton, trion, and higher-order states) in hBN-encapsulated TMD heterostructures through gating, and quantify how carrier injection modifies coherent many-body signatures.
4. *Quantify and visualize spatial disorder/strain and their spectroscopic consequences* using hyperspectral PL imaging and diagnostic PL lineshape asymmetries associated with localization, thereby connecting spatial heterogeneity to coherent spectroscopic observables.

3. Experimental and Analytical Approach

3.1 Multidimensional Coherent Spectroscopy and Imaging

A central technical thrust was the implementation and use of MDCS modalities tailored to excitons in 2D materials. The work employed ultrafast pulses and phase-/frequency-tagging strategies to isolate specific nonlinear signal pathways, enabling background-suppressed detection of coherent responses that encode interaction energies and dephasing. A key advance emphasized in the attached output materials is a *fully collinear-beam approach* for nonlinear imaging/spectroscopy (see Fig. 1), in which frequency-tagged pulses and lock-in detection enable flexible selection among spectroscopic modalities (e.g., linear reflectivity, four-wave mixing), while a galvanometer-based scan system steers the beam to generate images without physically translating the sample.

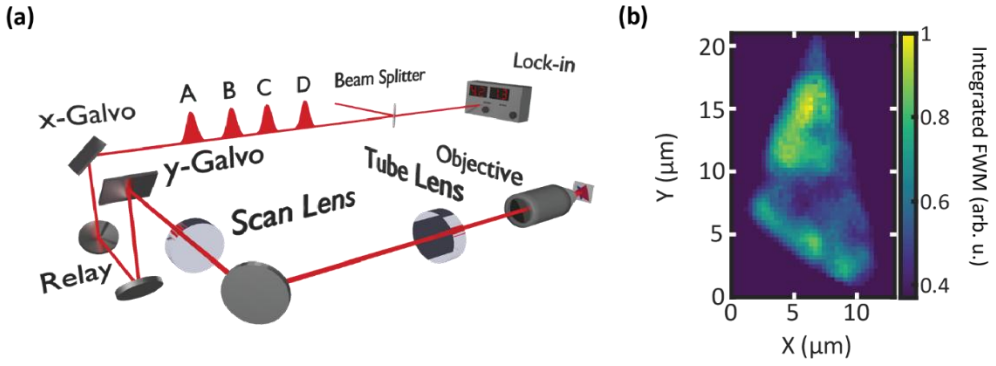

Fig. 1: (a) Schematic of the custom-built laser-scanning microscopy setup. (b) Integrated FWM of the hBN-encapsulated MoSe2 monolayer.

This architecture is crucial for vdW systems because it enables the correlation of nonlinear signals with sample microstructure and local disorder (such as wrinkles, bubbles, and

interfaces), and can be integrated with cryogenic and magneto-optical environments where mechanical scanning can be challenging.

3.2 Double-Quantum MDCS for Many-Body Correlations

To directly access interaction signatures among optical excitations, the project applied *double-quantum multidimensional coherent spectroscopy (DQ-MDCS)* and related 2Q coherent spectroscopy (2QCS). In these methods, as shown in Fig. 2, the signal is generated through pathways that evolve at the two-exciton (double-quantum) energy during one time interval and is then detected as a function of emission energy, producing spectra that cleanly separate signatures of different correlated states (e.g., exciton–exciton, exciton–trion, trion–trion). This interaction sensitivity is central to disentangling many-body physics from simple inhomogeneous broadening.

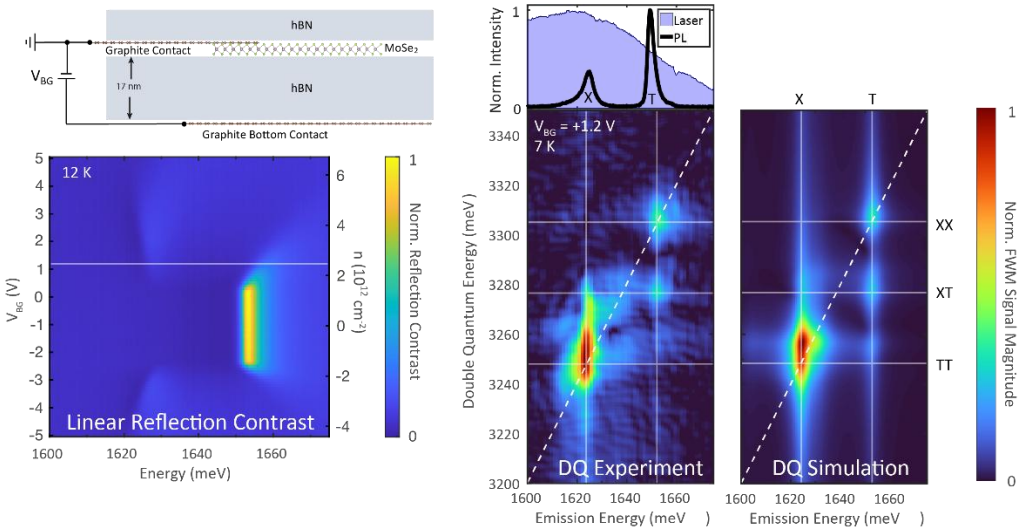

Fig. 2: Left: the structure of the sample is shown at the top, with its back-gate voltage (VBG) dependent reflection contrast spectrum shown below. On the right the DQ-MDCS results, both experiment and simulation, are shown for a VBG that results in both excitons and trions being present.

3.3 Electrostatic Gating and Sample Platforms

The project utilized high-quality, hBN-encapsulated monolayer TMDs integrated into gated heterostructures (graphite backgates and contacts) to control the free-carrier density, shown in Fig. 3. This platform enables systematic exploration of how injected electrons modify exciton populations (neutral excitons vs. trions/polarons) and how Coulomb screening reshapes the interaction-driven coherent signals. Importantly, gating also provides a controlled pathway to distinguish intrinsic exciton–exciton correlations from effects dominated by doping-induced screening and disorder.

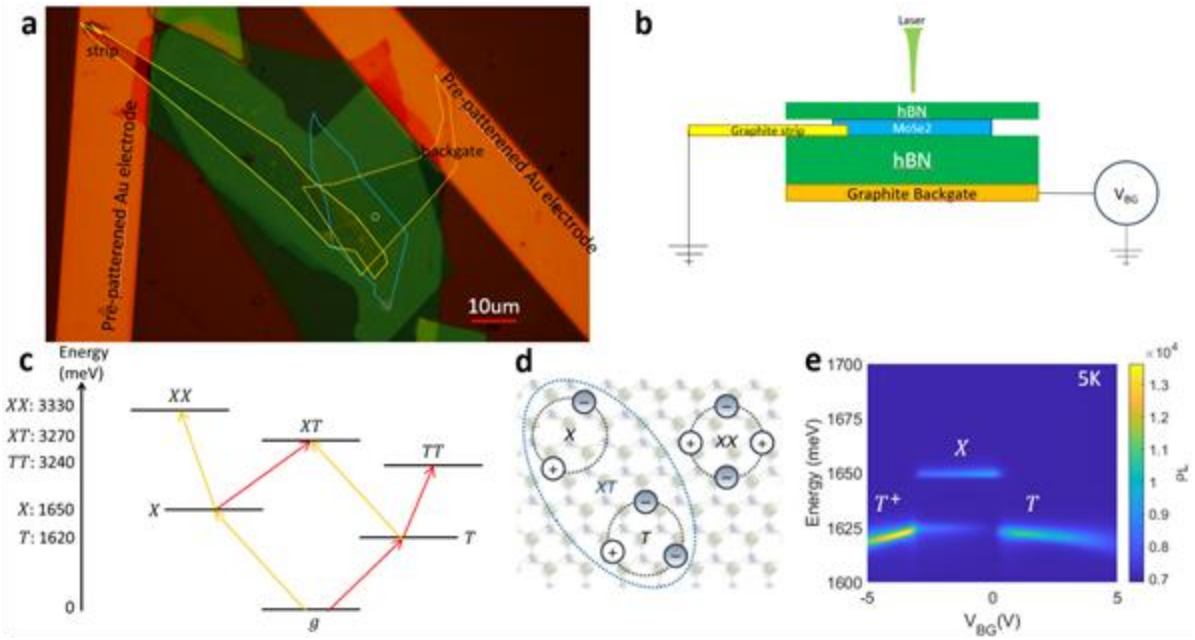

Fig. 3: (a) 100x image of the gated sample. The 15 m wide Au electrodes can be seen surrounding it; these are connected to the TMD by graphite flakes. The green circle is the laser location for all (linear and nonlinear) optical measurements. (b) Sideview cartoon of the device, the colors are matched with the outlines of the flakes in a. (c and d) Energy level scheme and spatial representation of the bound many-body states in MoSe2. [1] (e) Linear Photoluminescence data showing the exciton (X), positive trion (T+) and negative trion (T). This study focuses on the electron (n-doped) side, 0-1.6V.

3.4 Complementary Spatial/Spectral Diagnostics: Hyperspectral PL Imaging

Because spatial inhomogeneity can dominate observed linewidths and even change the apparent excitonic species present, the project developed and applied *hyperspectral photoluminescence (HSPL) imaging* (see Fig. 4). HSPL collects a full PL spectrum at each spatial pixel during a raster scan, enabling quantitative mapping of exciton/trion resonance energies, linewidths (FWHM), and derived parameters such as trion binding energy. These maps reveal strain gradients and localized disorder (wrinkles, ripples, interface bubbles) that can be weak or invisible in conventional optical images or intensity-only PL maps, but which strongly impact coherent nonlinear response.

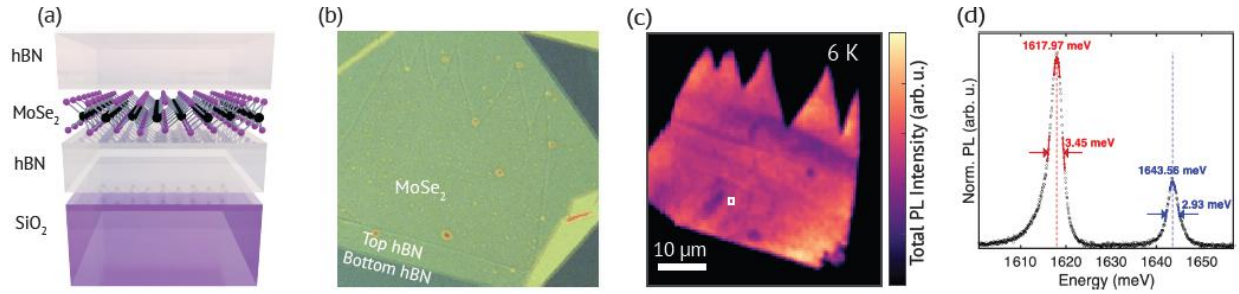

Fig. 4: (a) Diagram of heterostructure. (b) Microscope image of heterostructure. (c) Raster-scanned spatial map of the total MoSe2 PL. The scale bar also works for panel b. (d) The PL spectrum at the location marked by the white box in c. Both the trion (red) and exciton (blue) were fit with first and second-order polynomials to find their FWHMs and center energies.

3.5 Disorder-Driven Localization Diagnostics from PL Lineshape Asymmetry

Finally, the project leveraged temperature- and magnetic-field-dependent PL spectroscopy to identify signatures of disorder-driven exciton localization in nominally high-quality monolayer TMDs. Rather than relying only on linewidth broadening, the analysis used lineshape asymmetry and its evolution with temperature as a diagnostic of partial localization and disorder-induced modifications to wavevector conservation, connecting the observed PL to theoretical forms previously used in quantum wells.

4. Double-Quantum Coherent Spectroscopy as a Background-Suppressed Probe of Interactions

A central outcome of this award is the deployment of *double-quantum (2Q) multidimensional coherent spectroscopy* in high-quality, hBN-encapsulated TMD heterostructures to isolate and quantify interaction-driven optical responses. In 2Q experiments, the detected third-order signal is generated through pathways that evolve at a double-quantum (two-excitation) energy, making the measurement intrinsically sensitive to many-body correlations (e.g., exciton–exciton and exciton–trion interactions) and substantially reducing ambiguity from linear background and simple inhomogeneous broadening.

In the $MoSe_2$ devices studied here, the coherent nonlinear response is detected via heterodyne interference with a local oscillator and analyzed by Fourier transforming time-domain interferograms into spectra that correlate absorption and emission energies. This produces two-dimensional maps in which doubly excited states and interaction-induced features are cleanly identified and tracked under external control parameters (notably electrostatic gating).

5. Device Platform: hBN-Encapsulated, Electrostatistically Gated $MoSe_2$

The work leveraged vdW heterostructure devices in which monolayer $MoSe_2$ is encapsulated in hBN and coupled to a graphite backgate. This geometry supports stable optical quality while enabling continuous tuning of the free-carrier population by adjusting the backgate voltage. Linear characterization (optical images, device schematics, and PL versus gate voltage) established the gate-controlled evolution of the excitonic resonances and identified operating regimes relevant to neutral excitons and charged complexes.

6. Observation of an Interacting Doubly-Excited Exciton State (XX)

Using 2Q coherent spectroscopy on gated $MoSe_2$, the project observed a clear signature of a doubly-excited exciton state (XX) in the double-quantum spectra. Importantly, the visibility of this feature in 2Q measurements directly indicates the presence of exciton–exciton interactions: in the limit of *noninteracting* excitations, the relevant coherences can cancel such that the doubly excited state does not appear in the measured signal (see Fig. 5). The experimentally observed XX response, therefore, serves as a stringent diagnostic of interaction beyond what can be inferred from linear spectra alone.

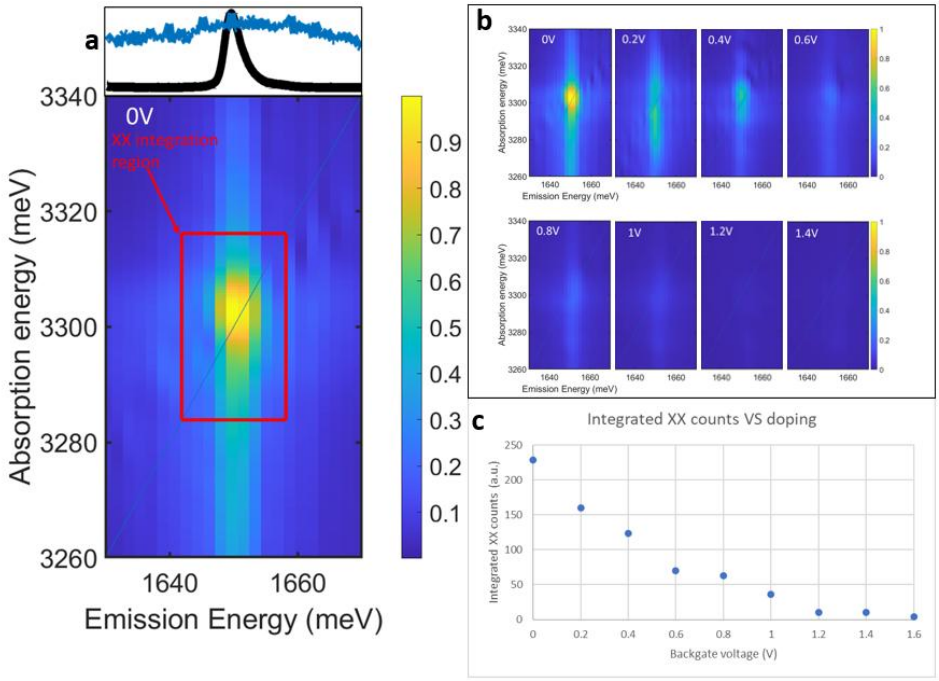

Fig. 5: (a) Double-Quantum spectral magnitude at 0V backgate bias. The red box shows the XX integration region used in c. The 0V $MoSe_2$ linear PL spectrum and laser spectrum for all nonlinear experiments are overlaid on top. (b) Normalized Double-Quantum spectral magnitude at increasing electron concentrations. (c) Red box integrated XX counts vs electron concentration.

7. Electrostatic Control: Carrier Injection Screens Many-Body Correlations

A major result of the award is the demonstration that electrostatically injected electrons can continuously suppress interaction signatures in the 2Q spectra. As the backgate voltage is increased to inject additional electrons into the $MoSe_2$ layer (via the device contacts), the XX contribution in the 2Q response decreases markedly. This behavior is consistent with electronic screening reducing the effective long-range Coulomb interaction responsible for many-body correlations. In other words, the device functions as a tunable platform in which interaction physics can be dialed from strongly correlated toward more weakly interacting behavior.

This gate-controlled suppression was quantified by integrating the 2Q spectral weight over the XX region and plotting the resulting counts as a function of gate voltage, yielding a clear monotonic reduction with increasing electron concentration. The result provides direct experimental evidence that carrier screening can "turn down" many-body coherent signatures in a controlled and reversible manner.

8. Extending to Multiple Species: Exciton/Trion Correlations in DQ-MDCS

Beyond the specific XX response in nominally excitonic regimes, the project also produced DQ-MDCS results in electrostatically tuned conditions where both neutral excitons and trions contribute to the optical response. In these regimes, DQ-MDCS resolves multiple interaction channels within the same measurement, including exciton–exciton and exciton–trion correlations, and enables a direct comparison between experiment and simulation. The combined experimental/simulation framework demonstrates how MDCS can separate and identify the nonlinear pathways associated with distinct quasiparticles, even when linear spectra overlap due to broadening.

9. Significance and Impact of the Coherent-Spectroscopy Results

Collectively, these outcomes establish that:

- **Double-quantum coherent spectroscopy offers a selective, high-contrast probe of many-body interactions** in monolayer vdW semiconductors, revealing doubly excited and correlated states that can be obscured in linear measurements.
- **Electrostatic gating enables experimental control over interaction strength**, with injected carriers screening Coulomb correlations and measurably suppressing XX signatures in the coherent response.
- **DQ-MDCS in gated devices forms a quantitative bridge between device physics and many-body spectroscopy**, enabling systematic tests of how carrier density, screening, and quasiparticle composition (exciton vs trion) reshape coherent nonlinear spectra.

These results directly advance the project's core objective: using MDCS to move beyond phenomenological linewidth/broadening descriptions and toward interaction-resolved, externally controllable spectroscopy of excitations in van der Waals (vdW) materials and heterostructures.

10. Rationale: Spatial Heterogeneity as a Limiting Factor for Coherent Spectroscopy in vdW Materials

A recurring practical barrier to quantitative spectroscopy in monolayer TMDs is that nominally "high-quality" samples often exhibit spatially varying optical transition energies and linewidths due to strain gradients, wrinkles/ripples, nanoscale disorder potentials, and charge inhomogeneity. These effects can (i) broaden resonances in a spatially nonuniform way, (ii) shift exciton and trion energies across the field of view, and (iii) introduce local regions that are unsuitable for coherent nonlinear experiments even when conventional optical inspection appears favorable. Because MDCS and double-quantum signals are intrinsically sensitive to dephasing and spectral diffusion, an ability to **map** where the material is spectroscopically pristine—and where it is locally perturbed—is essential for reproducible measurements and correct physical interpretation.

To address this, the project developed and applied *hyperspectral photoluminescence (HSPL) imaging*: a raster-scan micro-PL approach that records a full PL spectrum at each spatial pixel, followed by per-pixel extraction of resonance parameters (center energies and linewidths) for excitonic features. The key advance for this award is not merely producing intensity maps, but generating quantitative spatial maps of exciton/trion energies, linewidths (FWHM), and derived binding energies that serve as direct fingerprints of strain and disorder.

11. HSPL on hBN-Encapsulated $MoSe_2$: Mapping Strain Gradients and Hidden Micro-Disorder

In a residue-free, hBN-encapsulated $MoSe_2$ monolayer heterostructure (Sample-1), HSPL imaging revealed that the spatial distribution of optical parameters is more structured than indicated by optical microscopy or total PL intensity alone. Even when the PL map appears broadly uniform, fitting the exciton and trion resonances at each pixel produces parameter maps that separate smooth, device-scale gradients (consistent with strain accumulation upon cooling) from localized disruptions (wrinkles/ripples) that primarily manifest as linewidth enhancement and subtle binding-energy perturbations.

The representative dataset in Fig. 6 shows (i) the heterostructure layout and optical micrograph, (ii) a spatial map of total PL intensity, and (iii) a representative local spectrum demonstrating the extraction of exciton and trion resonance positions and linewidths. These data establish the basis for generating large-area, quantitative spatial maps.

Applying HSPL across the mapped area, the exciton center energy exhibits a smooth spatial trend, while the exciton linewidth (FWHM) reveals a more granular landscape: localized regions of broadening correlate with micro-wrinkles and ripples that may be difficult to identify in standard optical images. Importantly, the maps enable a distinction between "globally strained but spectroscopically coherent" regions (characterized by smooth energy shifts with limited broadening) and regions where local disorder increases dephasing/broadening, which are less favorable for coherent nonlinear spectroscopy. In parallel, mapping the trion binding energy (via the exciton–trion energy difference) provides an internal metric that is comparatively uniform in high-quality areas but becomes sensitive to certain localized perturbations, helping to separate strain-dominated energy shifts from effects more consistent with local disorder or doping variation.

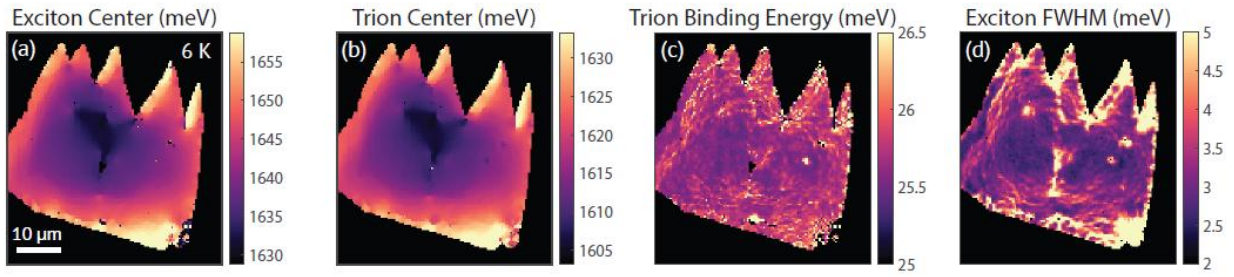

Fig 6: Spatial mapping of exciton and trion spectral parameters. (a) Exciton center energy. (b) Trion center energy. (c) Trion binding energy. (d) Exciton linewidth (FWHM), with local features showing wrinkles and ripples due to strain.

These HSPL results directly supported the broader goals of the award by providing (a) a screening tool to identify spatial regions best suited for MDCS/DQ-MDCS and (b) a quantitative disorder/strain context for interpreting measured coherent linewidths and interaction signatures.

12. HSPL in More Complex Device Architectures: Gated WSe_2 and Spatially Resolved Many-Body Spectral Features

The project further demonstrated HSPL imaging on more complex heterostructures incorporating electrostatic gating and contacts, including an hBN-encapsulated WSe_2 monolayer device (Sample-2) with few-layer graphene electrodes and a graphene backgate, as shown in Fig. 7. In these structures, HSPL enables spatial visualization not only of exciton and trion energies/linewidths, but also of higher-order emission features (e.g., biexciton-related signatures) and their robustness across the device. The ability to map these features spatially is particularly important for vdW devices, where fabrication steps can introduce nonuniformities and where gate control can interact with pre-existing disorder landscapes.

HSPL maps at a representative gate condition provide a compact view of how total PL intensity, exciton linewidth, biexciton linewidth, and biexciton binding energy vary across the device footprint—highlighting that multi-parameter hyperspectral mapping can be used to locate regions where many-body signatures are spectrally resolvable and sufficiently uniform for follow-on coherent measurements.

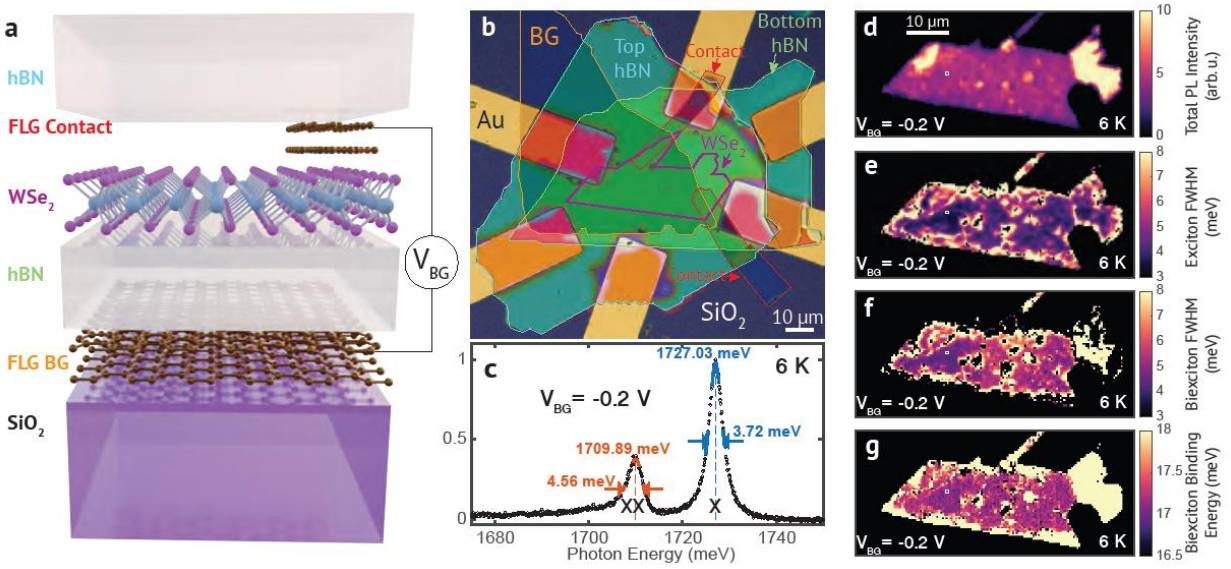

Fig. 7: a, Diagram of electrostatically gated WSe2 heterostructure Sample-2. b, Microscope image of the heterostructure. c, Intrinsic PL spectrum from the location marked by the white boxes in the following panels. d, Total PL intensity of the intrinsically doped WSe2 monolayer, which contains both biexciton and exciton integrated resonances. e, Exciton FWHM. f, Biexciton FWHM. g, Biexciton binding energy.

13. Role Within the Award: Connecting Imaging-Derived Disorder Metrics to Coherent Spectroscopy

Throughout the reporting period, HSPL imaging served as a complementary capability that enhanced MDCS outcomes in three key ways. First, it provided a region-selection workflow to maximize the likelihood of observing narrow resonances and stable coherent signals. Second, it offered a spatial taxonomy of heterogeneity (smooth strain gradients versus localized micro-disorder) that clarifies when broadening is primarily inhomogeneous (resulting from spatial averaging) versus when it reflects locally enhanced dephasing. Third, it created a practical basis for correlating coherent nonlinear observables (e.g., interaction-induced features in DQ spectra) with the local optical quality and microstructure of the 2D material—an essential step toward reproducible spectroscopy in vdW heterostructures.

14. Motivation: Localization as a Hidden Variable in Optical Coherence of vdW Excitons

For coherent spectroscopies in monolayer TMDs, it is not sufficient to characterize "optical quality" only by a narrow low-temperature linewidth. Even in hBN-encapsulated samples with low inhomogeneous broadening, thermally activated disorder can qualitatively change the nature of the emitting state by driving partial localization of the exciton center-of-mass wavefunction. Such localization is expected to alter dephasing, spectral diffusion, and interaction pathways that underlie MDCS and double-quantum responses.

To directly diagnose localization in a manner that is experimentally accessible and complementary to MDCS, the project analyzed photoluminescence (PL) lineshape asymmetry as a function of temperature and out-of-plane magnetic field in monolayer $MoSe_2$. The central observation is that a transition from a symmetric (Lorentzian-like) lineshape to an asymmetric lineshape with a low-energy shoulder occurs as temperature increases, and that this asymmetry can be suppressed (symmetry restored) by applying an out-of-plane magnetic field at fixed temperature—behavior consistent with disorder-induced localization akin to models previously applied in disordered quantum wells.

16. Interpretation: Disorder-Induced Localization and Violation of Wavevector Conservation

The observed asymmetry is interpreted within a disorder-localization framework previously used for disordered quantum wells, adapted here to a 2D vdW exciton. In brief, as the exciton center-of-mass becomes more localized by a random disorder potential, its momentum-space distribution broadens. This relaxes strict wavevector conservation in radiative recombination and produces an asymmetric emission lineshape with a characteristic low-energy shoulder. In the attached work, an asymmetric functional form (involving an error function) yields significantly improved fits at elevated temperature compared to a symmetric Lorentzian description.

The temperature dependence is attributed to thermally activated lattice fluctuations (acoustic phonons) that, on the timescale of the exciton lifetime, act as a quasi-static random potential landscape. The magnetic-field dependence is consistent with reducing localization by breaking interference conditions that promote localization in a random medium, thereby driving the lineshape back toward symmetry.

17. Relevance to Award Goals: Linking Disorder Physics to Coherent Spectroscopy Outcomes

These localization diagnostics strengthen the overall project in two ways. First, they provide a mechanistic explanation for why spectroscopic responses can change qualitatively with

temperature even in samples that appear homogeneous at low temperature. Second, they provide practical guidance for coherent nonlinear experiments: localization can be induced by thermally activated disorder, and external fields can modify it—both of which can significantly affect coherent dephasing and the visibility of interaction signatures in MDCS/DQ-MDCS.

18. Integrated Outcomes Across Coherent Spectroscopy, Electrostatic Control, and Disorder/Strain Metrology

Over the reporting period, DE-SC0022179 advanced both the capabilities and the physics reach of multidimensional coherent spectroscopy (MDCS) in van der Waals (vdW) materials and heterostructures. The project's core technical and scientific outcomes form a connected workflow:

First, we established and applied multidimensional coherent imaging spectroscopy concepts that are well-suited to 2D materials, where spatial heterogeneity can significantly impact measured spectra. The collinear, frequency-tagged, scanned-beam approach enables nonlinear signal collection without the constraints of conventional noncollinear geometries, creating a direct pathway to correlate nonlinear response with microstructure in the same optical platform.

Second, we employed double-quantum coherent spectroscopies (2QCS/DQ-MDCS) to selectively reveal many-body correlations among optical excitations in monolayer TMDs. In electrostatically gated $MoSe_2$, measurements directly observed interaction-enabled doubly excited features and showed that increasing the free-electron density suppresses these signatures. This provides clear experimental evidence that carrier injection screens long-range Coulomb interactions, offering a practical handle to tune correlated optical physics in situ.

Third, to make coherent spectroscopy in vdW heterostructures both reproducible and physically interpretable, we developed and deployed hyperspectral photoluminescence (HSPL) imaging to quantify spatial variations in exciton/trion resonance energies and linewidths. These maps separate smooth, device-scale strain trends from localized micro-disorder (wrinkles/ripples/bubbles) that can drive spatially localized broadening. The resulting parameter maps serve as an efficient diagnostic for "spectroscopy readiness" and provide quantitative context for interpreting coherent dephasing and nonlinear interaction signals.

Finally, we connected disorder physics to optical lineshapes through temperature-dependent PL that reveals signatures of disorder-driven exciton localization via asymmetric lineshapes and their field-induced recovery of symmetry. This provides an experimentally accessible indicator of when exciton center-of-mass motion is being modified by disorder, which is directly relevant to coherence lifetimes and interaction pathways in MDCS.

Together, these results demonstrate a unified, experimentally grounded picture: many-body coherent signals in TMDs are both strongly enabled by Coulomb interactions and strongly conditioned by local environment, including carrier screening and disorder/strain landscapes. The project outputs, therefore, deliver not only specific observations (e.g., gate-controlled suppression of XX signatures), but also a practical methodological toolkit for future DOE-relevant investigations of correlated excitations in quantum materials.

19. Key Deliverables

This award produced (i) experimental implementations and demonstrations of MDCS approaches adapted to vdW materials, including coherent imaging-compatible geometries; (ii) double-quantum coherent spectra in electrostatically gated monolayer TMD devices that isolate interaction signatures and quantify their suppression by carrier screening; and (iii) complementary spatial and disorder diagnostics (HSPL mapping and PL lineshape localization analysis) that directly address the dominant experimental challenge in vdW spectroscopy: spatial heterogeneity and disorder.