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Nano-spectroscopy of excitons in atomically thin transition metal dichalcogenides

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Abstract

Excitons play a dominant role in the optoelectronic properties of atomically thin van der Waals (vdW) semiconductors. These excitons are amenable to on-demand engineering with diverse controls, including dielectric screening, interlayer hybridization, and moiré potentials. However, external stimuli frequently yield heterogeneous excitonic responses at the nano- and meso-scales, making their spatial characterization with conventional diffraction-limited optics a formidable task. Here, we use a scattering-type scanning near-field optical microscope (s-SNOM) to acquire exciton spectra in atomically thin transition metal dichalcogenide microcrystals with previously unattainable 20 nm resolution. Our nano-optical data revealed material- and stacking-dependent exciton spectra of MoSe₂, WSe₂, and their heterostructures. Furthermore, we extracted the complex dielectric function of these prototypical vdW semiconductors. s-SNOM hyperspectral images uncovered how the dielectric screening modifies excitons at length scales as short as few nanometers. This work paves the way towards understanding and manipulation of excitons in atomically thin layers at the nanoscale.

Introduction

Excitons, bound electron-hole pairs, govern the optical properties of two-dimensional transition metal dichalcogenides (TMDs) over near-infrared (IR) and visible frequencies due to their large binding energy and prominent oscillator strength¹. Notably, all excitonic parameters in TMDs, including their resonance energies as well as both radiative and non-radiative lifetimes, can be manipulated on demand. Relevant control mechanisms include electric and magnetic fields, hetero-structuring, moiré superlattice potentials²⁻⁵, local strain⁶, ultra-fast optical excitation^{7,8}, dielectric screening⁹, among others. The vast majority of experimental studies of excitonic phenomena in TMDs have been carried out by far-field optical methods with wavelength-limited spatial resolution. Nanoscale probes of the engineered excitonic electrodynamics are required to explore heterogeneous features. Nano-probe experiments reported here have the potential to map out the spatial evolution of exciton resonance energies in structures with (spatially) controlled dielectric screening and interlayer hybridization. In addition, nano-spectroscopy can document the potential role of extrinsic factors, such as defects and impurities, especially wrinkles and contaminations common in atomically layered heterostructures. Finally, applications of TMDs in nanophotonics and optoelectronics will benefit from characterization of excitons in nano-devices with sub-diffractive feature sizes that we demonstrated in our study.

A variety of scanning probe optical methods are in general suitable for the nanoscale characterization of the excitonic properties. Specifically, tip-enhanced photoluminescence (TEPL) studies have uncovered aspects of nanoscale excited state recombination in TMDs¹⁰⁻¹⁹. Complementary to the TEPL, absorption spectra encode not

only the exciton resonance energy but also the oscillator strength and damping rate, offering additional detailed inquiry into the excitonic response. In principle, local absorption spectra acquired by scattering-type scanning near-field optical microscopy (s-SNOM) allow one to obtain the complex dielectric function²⁰, $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ and make it possible to probe the engineered excitons at the nanoscale. This latter capability has been extensively used to study plasmons and phonons in other classes of van der Waals (vdW) materials²¹⁻²³. However, formidable technical challenges so far precluded quantitative nano-spectroscopy of excitonic absorption by means of s-SNOM.

Here, we coupled an ultra-stable and tunable continuous-wave Ti-sapphire laser (M squared) to a commercial s-SNOM (Neaspec GmbH) and investigated the nanoscale excitonic spectra in monolayer TMD semiconductors and heterostructures. The materials of interest are monolayers of WSe₂ and MoSe₂, MoSe₂/WSe₂ heterobilayers, as well as WSe₂ trilayers. The exciton resonance energy, radiative lifetime and the damping rate in vdW monolayers were extracted from the s-SNOM spectra with hitherto unattainable spatial resolution of 20 nm. After documenting the ability of s-SNOM to probe excitons in atomically thin semiconductors with the nanoscale spatial resolution, we investigated heterostructures with lateral dimensions smaller than the diffraction limit of near-IR light. We show that intralayer excitons in MoSe₂/WSe₂ heterostructures red-shift relative to their counterparts in isolated monolayers due to the enhanced dielectric screening. The screening length is found to be shorter than the spatial resolution (20 nm) of our experiments and is attributed to the small radius of tightly bound excitons. The s-SNOM spectra were also applied to probe excitons altered by interlayer hybridization in a multi-layer WSe₂ crystal.

Experimental methods and samples preparation

The s-SNOM is based on a tapping mode atomic force microscope (AFM). A Pt-Ir coated AFM tip is illuminated by a focused near-IR beam from a tunable continuous-wave laser, as shown in Fig. 1a. An intense optical field forms in the vicinity of the tip apex and interacts with the TMD crystals underneath it. The light backscattered from the tip is registered by a silicon detector and then demodulated at the high harmonics of the tip-tapping frequency via the pseudo-heterodyne interferometric scheme. This demodulation method allows one to isolate the genuine near-field signals from the undesired far-field background²⁴. By scanning the tip on the sample, complex near-field signal is recorded with a resolution of ~ 20 nm (Fig. 1b and supplementary Fig. S1) and denoted as $se^{i\varphi}$, where s and φ are amplitude and phase, respectively. Atomically thin TMD monolayers and their heterostructures were prepared by mechanical exfoliation and stamped on a h-BN substrate. The spectral range used to investigate the samples is 1.50 - 1.75 eV, which covers the 1s exciton resonance energies of WSe₂ and MoSe₂ monolayers (see inset in Fig.1b). In this energy range, the near-field signal from h-BN is frequency-independent²⁵ and can be utilized as reference for spectroscopic data for TMD materials. The normalized near-field amplitude and phase at the n -th harmonic and energies ω are denoted by $s_n(\omega)/s_n(h\text{-BN})$ and $\varphi_n(\omega) - \varphi_n(h\text{-BN})$, respectively. A combination of our ultra-stable laser and scanner system allowed us to demodulate the scattering signal at the fifth harmonic of the tapping amplitude; high harmonic data is imperative for obtaining genuine near-field contrast devoid of far-field artifacts.

To display the excitonic responses in the near field, in Figs. 1c-e we show representative s-SNOM images for a sample with monolayers of MoSe₂ and WSe₂, MoSe₂/WSe₂ heterobilayer and unobscured h-BN all in the same field of view (FOV) of

our apparatus. An AFM topographic image is shown in Fig. 1c, where a substantial height variation from left to right is prompted by a terrace in the underlying h-BN substrate. Nevertheless, regions of monolayer, bilayer and multilayer TMDs can be readily identified by their topographic height. Our layer thickness assignment is further confirmed by the second harmonic generation (SHG) data (see supplementary Figs. S2 and S3). The co-located images of topography (Fig. 1c), near-field scattering amplitude (Fig. 1d), and phase (Fig. 1e) are all acquired simultaneously. The amplitude image (Fig. 1d) reveals nearly uniform signals collected within terraces demarcated by boundaries between the terraces. We acquired images in Figs. 1d,e by setting the excitation photon energy at 1.68 eV. At this energy, a strong phase contrast between the WSe₂ monolayer and h-BN substrate is observed (Fig. 1e). On the contrary, no discriminable phase contrast is found for the MoSe₂ monolayer. The observation is readily understood as the near-field phase is related to the absorption²⁶. The different excitonic absorption characteristics of the TMDs can give rise to phase contrast. According to our hyperspectral data in Fig. 2, the photon energy of 1.68 eV is close to the exciton resonance in WSe₂ monolayer and does not overlap with the excitonic band of MoSe₂ centered at 1.58 eV. Our data reveals that the prominent nano-optical contrast in Fig. 1 is rooted in the local excitonic response of TMD monolayers.

Near-field nano-spectroscopy of excitons in WSe₂ monolayer

For quantitative analysis of the WSe₂ monolayer excitonic response, we carried out raster-scanned nano-imaging while varying the photon energy with a step size of ~10 meV. We have simultaneously collected topographic and near-field maps at each energy over the same FOV marked by the dashed rectangle in Fig. 1d. The topography image and height profile are shown in Fig. S3. The unobscured h-BN in the upper left corner of Fig. 2 is used

as a reference for normalization purposes. Representative maps of the normalized fifth-harmonic amplitude $s_5(\omega)$ and phase $\varphi_5(\omega)$ are shown in Figs. 2a and b, respectively. In these images, both the amplitude and phase signals in WSe₂ monolayers vary systematically as a function of excitation energy. In particular, the phase images display a prominent contrast centered around 1.66 eV. Notably, we witness a highly uniform response within regions occupied by each of the TMD materials in Fig. 2. To quantify the excitonic response, we start our analysis by averaging the near-field signals over the entire region occupied by WSe₂ monolayer at each probing frequency. The net result is that each data point in spectra plotted in Figs. 2c,d is representative of the entire region imaged at the corresponding energy in Figs. 2a,b. The spectra derived from images show prominent resonance characteristics: the amplitude signal reveals a dispersive behavior around 1.66 eV, whereas the phase signal exhibits a peak centered at the same energy.

We modeled experimental near-field spectra of WSe₂ in Fig. 2 with the Lorentzian form of the dielectric function²⁷⁻²⁹:

$$\varepsilon(\omega) = \varepsilon_{bg} - \frac{c}{\omega_0 d} \frac{\gamma_{r,0}}{\omega - \omega_0 + i\left(\frac{\gamma_{nr}}{2} + \gamma_d\right)}, \quad (1)$$

where ε_{bg} is the background dielectric constant, c is the speed of light in vacuum, ω_0 is the exciton resonance energy, d is the monolayer thickness, $\gamma_{r,0}$, γ_{nr} , γ_d are radiative, non-radiative, and dephasing decay rates, respectively. The oscillator strength of the Lorentzian in Eq.1 is related to the radiative rate $\gamma_{r,0}$. We choose the point dipole model³⁰ to interpret the data as it is well documented to capture the response of atomically thin samples laid on thick substrates^{30,31}. As shown in Figs. 2c,d, the point dipole model with

Eq.1 as the input dielectric function provides an adequate fit to the data (see SOM for details on fitting).

Now we analyze the parameters inferred from the fitting procedure (Table 1). The obtained dielectric function is plotted in Fig. 2e. The radiative rate for monolayer WSe₂ is 1.4 meV, which corresponds to the radiative lifetime $\tau_0 = \frac{\hbar}{2\gamma_{r,0}}$ of ~ 233 fs. This latter finding is consistent with the first principles theoretical values³² and experimental results derived from the ultrafast exciton 1s-2p transition, which reveal 150 fs radiative lifetime in WSe₂ monolayers³³. The shorter radiative lifetime compared to that of conventional semiconductors stems from the exceptionally large exciton oscillator strength in two-dimensional TMDs, evidenced by the high optical absorption in monolayer^{34,35}. We obtained the damping rate $\frac{\gamma_{nr}}{2} + \gamma_d = 15$ meV. We remark that this substantial damping at room temperature inhibits the real dielectric function from crossing zero, and thus the exciton polariton regime cannot be reached. Recently, reflection measurements at cryogenic temperature demonstrated the negative real dielectric function in the vicinity of the excitonic line³⁶. Therefore, by reducing the damping rate, for example, through experiments conducted at cryogenic temperature^{29,36}, it may become possible to access the exciton polaritons in monolayer TMDs. So far, all experiments on exciton polaritons in TMDs conducted at ambient required integration of the active semiconductor in various forms of photonic cavities³⁷⁻³⁹. A notable exception is an observation of the excited state Rydberg exciton polaritons demonstrated in pump-probe experiments for multilayer WSe₂ at room temperature⁸.

Next, we comment on the contributions of bright and dark excitons to the s-SNOM spectra. These two types of excitonic species result from the spin splitting of the conduction band edge and they obey different optical selection rules^{40,41}. In TMD literature, excitons that can be excited by light with polarization in the sample plane, as in normal incidence experiments, are referred to as bright excitons. Excitons that can be activated only when light polarization is perpendicular to the sample plane, are referred to as dark excitons. Dark excitons can be visualized using TEPL for TMD samples on metallic substrates because the electric field strength perpendicular to the sample surface is drastically enhanced^{12,19}. In contrast, the s-SNOM signal for atomically thin TMDs is governed by the in-plane dielectric function³⁰, which arises from bright excitons (see SOM). To experimentally confirm the dominant role of bright excitons in our data, we compared the bright exciton resonance energy obtained from far-field PL spectra on the same sample⁴² with the resonance energy in our s-SNOM spectra. The bright exciton resonance energy from PL (see supplementary Fig. S4) is about 1.66 eV, in close agreement with s-SNOM data. We therefore conclude that bright excitons dominate the s-SNOM response of monolayer and few-layer TMD crystals.

Table 1. The parameters of Lorentz model used to describe TMD dielectric function as obtained from fitting s-SNOM spectra with the point dipole model.

	1L WSe ₂	1L MoSe ₂	MoSe ₂ /WSe ₂ bilayer	3L WSe ₂
ϵ_{bg}	9.7 ± 0.5	15.6 ± 0.7	13.6 ± 0.7	13.8 ± 0.8
Exciton energy ω_0 (meV)	1660 ± 2	1583 ± 3	1573 ± 5 (MoSe ₂) 1648 ± 6 (WSe ₂)	1639 ± 3
Radiative rate $\gamma_{r,0}$ (meV)	1.4 ± 0.2	1.7 ± 0.3	0.9 ± 0.5 (MoSe ₂) 2.1 ± 0.6 (WSe ₂)	5.4 ± 0.7

$\frac{\gamma_{nr}}{2} + \gamma_d$ (meV)	15 ± 3	18 ± 4	13 ± 8 (MoSe ₂) 24 ± 9 (WSe ₂)	20 ± 4
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Excitonic spectra of TMD monolayers

Before exploring the nanoscale response of heterostructures and multilayers, we take a closer look at the near-field response of the constituent monolayers. The spectra of the normalized amplitude and phase for MoSe₂ are shown in the middle panels of Figs. 3a,b (See supplementary Fig. S5 for complete data sets). Each data point in these spectra is attained by averaging the near-field signal over the entire MoSe₂ regions. The near-field spectra for MoSe₂ are akin to those of WSe₂ and exhibit nearly the same resonance features, manifesting as a derivative-type lineform of the amplitude and a peak in the phase. The resonance energy observed in MoSe₂ using s-SNOM (1.583 eV) is consistent with the dominant peak in PL spectra⁴³ (see supplementary Fig. S4), supporting the notion of bright excitons. The radiative rate obtained by fitting the spectra for MoSe₂ is as high as 1.7 meV and is slightly larger than that of WSe₂ (see Table 1). In general, the prominent radiative rates stem from the two dimensional nature of excitons in TMDs, which are tightly bound to monolayers and have a small exciton radius⁴⁴. Even though the spectral lineforms of excitonic lines in MoSe₂ and WSe₂ are nearly identical, the near-field amplitude detected for MoSe₂ is considerably larger than that of WSe₂ below the exciton resonance energies (top and middle panels of Fig. 3a). We also found that the magnitude of the real part of the dielectric function ϵ_1 at energies below the exciton resonance is enhanced in MoSe₂ compared to that of WSe₂. This latter finding is consistent with the enhanced radiative rate in MoSe₂.

MoSe₂/WSe₂ heterobilayers and WSe₂ trilayers

Now we turn to the spectra acquired for the MoSe₂/WSe₂ heterostructures with the width of less than 1 μm , as shown in the s_5 amplitude map (Fig. 3c, where HB denotes the heterobilayer region). The amplitude and phase spectra are displayed in the bottom panels in Figs. 3a and b, respectively. In these spectra, two resonances emerge at the energies close to the frequency positions of the excitonic bands in MoSe₂ and WSe₂ monolayers in Fig. 2 and Fig. S5, indicating a dominant contribution of intralayer bright excitons. The role of interlayer excitons remains to be negligible in the data plotted in Fig. 3. Indeed, the resonance energies of indirect excitons^{4,45,46} ($\sim 1.3 - 1.4$ eV) fall outside the spectral range investigated in Fig. 3.

We analyzed spectra of the MoSe₂/WSe₂ heterostructure assuming that the dielectric function is given by the sum of two Lorentzians in Eq. 1. The fit with PDM shows that both the intralayer exciton resonance energies red-shift compared to their counterparts in monolayers (vertical dashed lines in Figs. 3a,b). Red-shift of the exciton resonance energies can also be clearly identified in the hyperspectral measurements of the amplitude s_5 and phase φ_5 (in Figs. 3d and e, respectively) along the line trace in Fig. 3c. The frequency red-shift of the two exciton resonances is around 10 meV compared to their monolayer counterparts (Table 1 and Figs. 3a,b).

To unravel the origin of the red-shifts, the twist angle of the two layers comprising our heterostructure was characterized by polarization-resolved SHG experiments. The SHG data show that the twist angle between layers is either 15 degrees or alternatively 45 degrees (see supplementary Fig. S2). Either of the two layer arrangements implies the misalignment between the Brillouin zones of monolayers^{46,47} and therefore produce only

negligible hybridization between the two atomic planes. However, excitons in the heterostructure experience stronger dielectric screening compared to the isolated monolayers, because the dielectric function of TMDs is larger than that of h-BN (~ 4). Therefore, we conclude that, in heterostructures with a large twist angle, the redshift of intralayer exciton resonance energies mainly arises from dielectric self-screening^{9,47}.

Although the effect of dielectric screening on excitons has been widely investigated, the screening length is difficult to infer from previous reports based on diffraction-limited far-field data^{9,48}. Here the screening length refers to the spatial span over which the exciton energies are altered by abrupt changes in the dielectric environment. s-SNOM experiments visualize the spatial evolution of the exciton lines across interfaces and thus can potentially quantify the screening length. Representative s-SNOM images in Figs. 4a,b show that the amplitude and phase contrasts abruptly change across the boundary between the monolayers and heterostructure. From the high-resolution images and the line profiles (Fig. 4c), one can see that the exciton resonance energy is altered over the length scale of about 20 nm, which is the spatial resolution of the s-SNOM. We conclude that our nano-IR scans yield only the upper bound estimate of this length scale limited by the spatial resolution of our method. Our estimate is consistent with the theoretically predicted value of about 10 nm (Ref.[⁹]).

In addition to the dielectric screening, interlayer hybridization also plays a role in controlling the excitonic properties of vdW materials. Our nano-IR data provides an experimental access to interlayer hybridization in trilayer WSe₂ exfoliated from 2H-stacked crystal. We anticipate that in these crystals neighboring layers are twisted by an angle of 60 degrees. The amplitude and phase spectra acquired on the WSe₂ trilayer are

shown in Figs. 4d and e, respectively, with fitting results presented in Table 1. These data show that the exciton resonance energy decreases from 1.660 eV in WSe₂ monolayer (dashed vertical line in Fig. 4e) to 1.639 eV in the trilayer (solid vertical lines in Fig. 4e). Before discussing the origin of the observed redshift, we comment on the appearances of direct and indirect interband transitions in the s-SNOM spectra. The indirect transitions in few-layer TMD crystals have negligible oscillator strength, and thus make only a minute contribution to the dielectric function and/or to the s-SNOM signal. Therefore, the observed redshift of the exciton resonance energy originates from direct transitions. For trilayer WSe₂ with twist angle of 60 degrees, interlayer electronic hybridization splits both conduction and valance band edges at the corner of the Brillouin zone, thus reducing the energy gap and the corresponding exciton resonance energy^{47,49,50}. Therefore, the large shift observed here (21 meV) is likely to be caused by the interlayer hybridization. We note that the dielectric screening could also reduce the exciton resonance energy, but its effect is subtle (~ 10 meV, as demonstrated in last section), compared to the interlayer hybridization.

In summary, the bright excitonic responses of TMD monolayers were revealed by s-SNOM hyperspectral nano-imaging. New data allowed us to extract the exciton resonance energy, oscillator strength, and damping rate all with the nanometer resolution. Nano-IR spectra and images uncovered the spatial evolution of the dielectric screening and interlayer hybridization. We obtained the upper bound of the dielectric screening length of 20 nm limited by the spatial resolution of s-SNOM. Our results lay the groundwork for future spatio-temporal^{35,53} studies of excitonic states, including moiré excitons^{2,51-53}, exciton liquid⁵⁴, and exciton phase transitions⁵⁵ in a wide range of quantum materials.

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Figures and figure captions

Figure 1 Near-field nano-probing of excitons in atomically thin transition metal dichalcogenides (TMDs). **a**, Schematic illustration of near-field measurement of excitons. The metallized AFM tip is illuminated by focused incident light and the tip-scattered light is collected. Pairs of electrons and holes with strong Coulomb interactions in atomically thin TMDs form excitons with large binding energies. The nanoscale response of excitons is extracted from the back-scattered light. **b**, Scanning the tip across the TMD sample allows one to investigate the excitonic response below the diffraction limit and extract the dielectric function at the nanometer scale. The inset shows the dielectric function of monolayer WSe₂ from ref.⁵⁶ **c**, An AFM topographic image of the TMDs in this study. The height difference between the left and right regions is due to the h-BN terrace. **d**, **e**, Near-field images of normalized scattering amplitude s_5 and phase ϕ_5 on the same region of **c**.

The excitation energy is 1.68 eV. The dashed bright and blue lines trace the edges of the different sample regions. The dashed rectangle marks the position of Fig. 2**a**.

Figure 2 Evolution of the scattering amplitude and phase for the monolayer WSe₂ as a function of the excitation energy. **a**, Representative near-field images of the normalized scattering amplitude $s_5(\omega)/s_5(h\text{-BN})$. The excitation energies are indicated in the images, which are acquired by scanning over a rectangular area marked with the dashed line in Fig. 1d. Boundaries of the monolayer WSe₂ region are displayed with black dashed lines. The area enclosed by blue lines in bottom left image was investigated in Fig. 4a. **b**, Near-field images of the normalized phase $\varphi_5(\omega) - \varphi_5(h\text{-BN})$. The images with the same excitation energy in **a** and **b** are acquired simultaneously. **c** and **d**, Normalized near-field amplitude $s_5(\omega)/s_5(h\text{-BN})$ and phase $\varphi_5(\omega) - \varphi_5(h\text{-BN})$ spectra for WSe₂ monolayer (data points). Fits to the spectra using the point dipole model (PDM) and a single Lorentz oscillator (Eq.1)

are shown as solid curves. The arrow in **c** marks the peak energy of PL spectra (Fig. S4).
e, Dielectric function of WSe₂ monolayer extracted from the fits with PDM in **c**, **d**.

Figure 3 Nano-spectroscopy of different types of excitons. **a** and **b**, Normalized amplitude $s_5(\omega)/s_5(h\text{-BN})$ and phase $\varphi_5(\omega) - \varphi_5(h\text{-BN})$ spectra for different sample regions (data points). The near-field data is fitted by the point dipole model and Lorentz oscillators (solid curves). The vertical dashed lines are used to mark the exciton energies of WSe₂ and MoSe₂ extracted from the point dipole model. The arrows in **a** mark peak energies of the PL spectra (Fig. S4). **c**, Near-field image of the amplitude s_5 taken at an excitation energy of 1.52 eV. HB: heterobilayer. **d** and **e**, Near-field amplitude s_5 and phase φ_5 evolution along the line trace shown in **c**. The horizontal dashed lines in **d** and **e** denote the exciton energies extracted from the point dipole model.

Figure 4 Screening length of excitons in heterostructure and the effect of hybridization on exciton resonance in WSe₂ trilayer. **a** and **b**, Near-field images of the normalized amplitude $s_5(\omega)/s_5(h\text{-BN})$ and phase $\varphi_5(\omega) - \varphi_5(h\text{-BN})$. The images in the left and right panels were taken at 1.68 eV (around the monolayer WSe₂ exciton resonance energy) and 1.57 eV (around monolayer MoSe₂ exciton resonance energy), respectively. The scale bars indicate 400 nm. **c**, Line profiles of the normalized amplitude and phase across the monolayer and heterobilayer along the black lines in the right panels in **a** and **b**. **d** and **e**, Normalized scattering amplitude $s_5(\omega)/s_5(h\text{-BN})$ and phase $\varphi_5(\omega)$ spectra for WSe₂ trilayer (data points). The near-field data are fitted by the point dipole model (solid curves). The vertical blue dashed and solid lines in **e** are used to mark the exciton energies of WSe₂ monolayer and WSe₂ trilayer extracted from the point dipole model, respectively.

Contributions

S.Z. and D.N.B. designed the experiments. B.C.L., W.J.W., S.S., L.Z., Z.Y.W., E.R. and N.W. fabricated the devices. X.Y.X characterized the sample twist angle. S.Z. performed the experimental measurements with input from Y.M.S. and L.X.. S.Z. and D.N.B analyzed the experimental data. X.Z, M.K.L, F.L.R developed the theoretical model to analyze of the experimental data with input from A.J.S., A.S.M., Z.Y.S. and S.L.M.. S.Z. and D.N.B. co-wrote the manuscript with input from all co-authors. D.N.B. supervised the project. All authors contributed to the discussions.

Competing interests

The authors declare no competing interests.

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