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Vibrational Imaging and Quantification of **Two-Dimensional Hexagonal Boron Nitride** with Stimulated Raman Scattering

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Supporting Information

ABSTRACT: Hexagonal boron nitride (h-BN) is an important member of two-dimensional (2D) materials with a large direct bandgap, and has attracted growing interest in ultraviolet optoelectronics and nanoelectronics. Compared with graphene and graphite, h-BN has weak Raman effect because of the far off-resonance excitation; hence, it is difficult to exploit Raman spectroscopy to characterize important properties of 2D h-BN, such as thickness, doping, and strain effects. Here, we applied stimulated Raman scattering (SRS) to enhance the sensitivity of the E2g Raman mode of h-BN. We showed that SRS microscopy achieves rapid high resolution imaging of h-BN with a pixel dwell time 4 orders of magnitude smaller than conventional spontaneous Raman microscopy. Moreover, the near-perfect linear dependence of signal intensity on h-BN



thickness and isotropic polarization dependence allow convenient determination of the flake thickness with SRS imaging. Our results indicated that SRS microscopy provides a promising tool for high-speed quantification of h-BN and holds the potential for vibrational imaging of 2D materials.

KEYWORDS: stimulated Raman scattering, Raman mapping, two-dimensional materials, hexagonal boron nitride, vibrational imaging

s a graphene analogue, hexagonal boron nitride (h-BN) has attracted much interest in the fields of nanoelectronics and optoelectronics, demonstrating properties such as low dielectric constant, high temperature stability, high corrosion resistance, and large thermal conductivity.¹⁻⁶ h-BN has been widely used in nanoelectronics as an attractive substrate material for other two-dimensional (2D) material devices. It has been shown to support electron mobility in heterostructures,² and effectively protect sensitive materials such as black phosphorus in ambient conditions.⁷ Besides, h-BN itself offers interesting photonics and plasmonics properties. As a large direct bandgap material, it provides potential applications of ultraviolet (UV) light-emitting devices.^{8–10} Meanwhile, h-BN is a natural hyperbolic material and supports phonon polaritons in the mid-infrared region.¹¹⁻¹³ Given these fascinating properties and applications of h-BN, it is important to develop new tools to assist its characterization and quantification.

Various optical properties of h-BN have been explored. In nonlinear optics, second harmonic generation (SHG) has been extensively studied for h-BN. SHG requires the breaking of inversion symmetry; thus, it reflects the layer number, orientation, and stacking order of few-layer h-BN.^{14,15} For instance, only odd layer numbered h-BN exhibit a significant SHG signal, although it is difficult to quantify the absolute thickness directly from SHG measurements. In linear optics, both infrared (IR) absorption and Raman scattering spectroscopy of h-BN have shown a dominant phonon mode around 1367 cm⁻¹. The polar B-N bonds result in a strong IR response of the E_{1u} mode, whereas the Raman active mode is assigned to the E_{2g} vibration.^{16-21} It is known that Raman spectroscopy plays a critical role in characterizing 2D materials,

Received: August 10, 2019 Accepted: November 14, 2019 Published: November 14, 2019 revealing the important properties such as layer number,^{22–24} strain,³ stacking order,^{23,25,26} and interface effects.^{27–29} Although the Raman intensity of h-BN shows a linear dependence on the layer number for few-layer specimens,²¹ it becomes difficult to scale up as the sample thickness increases. In addition, the E_{2g} Raman intensity of h-BN was found to be ~50 times weaker than that of graphene under the same conditions,²¹ mainly because the excitation energy is usually far away from electronic resonance (~6 eV). Therefore, conventional spontaneous Raman scattering has limited application in the research of h-BN, neither in spectroscopy nor in imaging.

Coherent Raman scattering (CRS) processes, including stimulated Raman scattering (SRS) and coherent anti-Stokes Raman scattering (CARS), are the nonlinear versions of Raman scattering. $^{30-32}$ The coherent amplification of signal intensity and high chemical specificity has enabled CRS microscopy for rapid chemical imaging in various research fields including biological, biomedical, environmental, and materials sciences.³¹⁻³⁶ It is commonly accepted that SRS is usually better suited for quantitative measurements than CARS because of the absence of nonresonant background, undistorted spectra, and linear dependence of signal intensity with chemical concentration. Despite these advantages, no CRS study on any 2D material has been demonstrated up to the present date. Although graphene exhibits an enormous spontaneous Raman scattering cross section, no obvious CARS or SRS signature has been successfully detected, primarily due to the strong transient absorption (TA) from electronic resonance that overwhelms the CRS processes. In contrast, h-BN with a large bandgap may offer a good playground for CRS spectroscopy and microscopy.

In this work, we conducted a multimodal nonlinear optical microscopy study of 2D h-BN, including simultaneous SHG, CARS, and SRS imaging. SRS images of exfoliated h-BN were clearly captured based on the E_{2g} band with high speed and sensitivity. Meanwhile, we verified that the SRS signal shows a linear dependence on the sample thickness, whereas the CARS signal has a quadratic dependence. Unlike SHG of h-BN with significant polarization and stacking order dependence, SRS exhibits an isotropic orientational response and is insensitive to stacking order. Our results indicate that SRS could provide a quick and reliable means for quantifying the thickness of h-BN flakes up to ~70 nm, and the combination of SHG and SRS microscopy may offer opportunities for optical characterization of 2D materials.

RESULTS AND DISCUSSION

Characterization of Multimodal Nonlinear Optical Microscopy. The diagrammatic illustration of the nonlinear optical processes of SHG, CARS, and SRS is shown in Figure 1A. The optical setup of our microscope system is shown in Figure 1B, with more detailed descriptions in the Methods section. Two linearly chirped picosecond laser beams (913 nm as pump and 1040 nm as Stokes) are overlapped in space and time, and focused on the samples through a laser scanning microscope to produce the above nonlinear optical signals. The SHG signal of the 1040 nm beam was directly collected in the epi direction with a photomultiplier tube (PMT) and a narrowband filter (FF01-520/15, Semrock, Inc.). CARS and SRS were generated by the simultaneous interactions of the pump and Stokes photons with their energy difference matching the vibrational energy of a given Raman active



Figure 1. Characterization of multimodal nonlinear optical microscope. (A) Nonlinear optical processes of SHG, CARS, and SRS. (B) Optical layout of the microscope system. DM: dichroic mirror; GM: galvo mirror; EOM: electro-optical modulator; PD: Photodiode; SF57: long SF57 glass rods to chirp the pulses. (C) Illustration of spectral focusing technique; shifting the pump frequency is equivalent to adjusting the time delay. (D) Time and frequency dependence of the SRS signal. The dashed line is a linear fit to the peak positions.

phonon mode or chemical bond/group. CARS signal was simply detected in the epi direction with a PMT and a bandpass filter (FF01-795/150, Semrock, Inc.), whereas the detection of the SRS signal requires the modulation of the Stokes beam and demodulation with a lock-in amplifier to extract the differential reduction of the pump beam intensity (stimulated Raman loss, SRL). In our setup, the spectral focusing technique was used to tune the detection Raman frequency by scanning the time delay between the chirped pump and the Stokes pulse (horizontal dashed arrow, Figure 1C), which is equivalent to the conventional method of adjusting the pump frequency (vertical arrow, Figure 1C).^{35,37–39}

Thin flakes of h-BN were mechanically exfoliated onto quartz substrates and used as is. The achieved flake thickness varied from several nanometers to tens of nanometers. The SRS spectra of the E_{2g} mode could be readily seen as we scanned the time delay (from -4 to 4 ps, with 0.067 ps step), showing a single peak with varying peak positions as we changed the pump frequency (Figures 1D and S1A), which is direct evidence of the Raman spectral feature.⁴⁰ For each SRS spectra with delay scanning, the Stokes wavelength was fixed at 1040 nm while the pump wavelength was varied from 900 to 920 nm with a 2 nm step. The 2D plot in Figure 1D is similar to the frequency-resolved optical gating (FROG) result, where the optical chirp could be measured by fitting the peak envelope of the pump frequency-dependent SRS spectra with a linear function^{41,42} (Figure S1): $\Delta \omega = \alpha \Delta \tau (\alpha = 54.1 \text{ cm}^{-1}/\text{ cm}$ ps). This agrees with the group velocity dispersion (GVD) of the system (Supporting Information), and allows us to convert

the time delay to Raman shifts (wavenumbers) in the CRS measurements throughout the work. Note that the SRS spectra shown here (Figures 1D and S1a) contain a small broad background, which is mainly originated from cross-phase modulation (XPM), reflecting the cross-correlation and temporal alignment between the two laser pulses. The XPM could be minimized by optimizing the optical setup: (1) choose a condenser with numerical aperture (NA) higher than the objective; (2) use a photodiode with area larger than the beam spot on it.

We performed various imaging modalities on the same specimens for direct comparisons. Figure 2 demonstrates all



Figure 2. Images of an h-BN thin flake with different modalities. (A) Bright field, (B) SRS, (C) CARS, and (D) SHG images of the same sample. Scale bar: 20 μ m.

different types of images of a typical h-BN thin flake (thickness information can be found in Figure S2). It can be seen that the SRS image agrees well with the bright-field optical image, presenting the morphological and thickness features of the flake, but with a contrast mechanism based on the E_{2g} vibration (Figure 2A and B). The CARS image looks noisier due to the weak PMT response at the longer wavelength of the anti-Stokes photons (~814 nm), and the thinner parts of the flake appear much darker compared with the SRS image, which could be attributed to the nonlinear dependence of the CARS signal on sample thickness, as will be shown in more detail later in the text. In contrast to CRS, SHG reflects information on structural symmetries that result in extremely different image contrasts and patterns, as shown in Figure 2D. The dark regions in the SHG image do not correspond to the thinner sample, but rather represent an even layer number, particular crystal orientation, or stacking order, which have been well studied in 2D materials including MoS₂ and h-BN.^{14,15,43} Therefore, although SHG is sensitive to lattice symmetry, it could not be used to characterize the absolute thickness of h-BN thin flakes.

Rapid SRS Spectral Imaging of h-BN. Conventional spontaneous Raman is a very weak process and hence limits the sensitivity and mapping speed of confocal Raman microscopy, especially for materials with small Raman

scattering cross sections including 2D h-BN. No decent Raman mapping of h-BN has been reported so far, in contrast to the extensively studied graphene where Raman microscopy reveals the properties of strain, edge states, and so forth.⁴⁴

We compared the imaging results of spontaneous and stimulated Raman scattering microscopy of the same h-BN flake as shown in Figure 3. The spontaneous Raman image was



Figure 3. Spontaneous and stimulated Raman microscopy and spectroscopy. (A) Spontaneous Raman image with 20×30 pixels taken in 40 min. (B) SRS image of the sample with 320×320 pixels taken in 30 s. (C) Spontaneous Raman spectra and (D) SRS spectra of different regions of the sample using pump wavelength of 913 nm. Scale bar: $10 \ \mu$ m.

taken by a commercial confocal Raman spectrometer (XploRA Plus, Jobin Yvon, Horiba Gr, France) pixel by pixel, under 45 mW of 532 nm CW laser excitation. The spectral acquisition time for each pixel is ~ 2 s, and the final signal was averaged twice. A 20 \times 30 μ m² sample area with 1 μ m scanning step size cost ~40 min for spontaneous Raman imaging (Figure 3A), whereas for SRS imaging of the E_{2g} mode, the 42 \times 42 μ m² FOV with 320×320 pixels only cost ~30 s (Figure 3B). The pixel dwell time used in SRS imaging was $\sim 2 \mu s$ with 60 times of averaging, which is $\sim 30\,000$ times faster than that of spontaneous Raman microscopy. Under these conditions, SRS images demonstrated 9-fold higher signal-to-noise ratio (SNR) than spontaneous Raman results (95 versus 10), measured within the same sample area (region 1 in Figure 3A and B). In addition, our SRS system reached a spatial resolution of ~350 nm, which is significantly higher than that of the commercial confocal Raman system (~1 μ m), offering a Raman based contrast with both high speed and resolution. The spatial resolution is determined by several factors. Our SRS microscope uses an objective with higher NA than that of the spontaneous Raman (1.2 versus 0.5), but with longer excitation wavelength (~800 nm versus 532 nm). On the other hand, the performance of confocal Raman relies on the optimization of the confocal pinhole, while SRS gains another factor of $\sqrt{2}$ enhancement of resolution because of the

nonlinear optical effect. The spectra of stimulated and spontaneous Raman scattering of the E_{2g} mode from different thickness regions are shown in Figure 3C and D. The SRS spectra were taken by hyperspectral imaging: SRS frequency (delay time) of each image was varied in series (frame by frame, 0.067 ps interval) to create an image stack, and the spectra of regions of interest could be extracted from the threedimensional data. It can be seen that stimulated and spontaneous Raman spectra of the E2g mode appear almost identical, with a single peak centered around $13\overline{70}$ cm⁻¹, and SRS spectra show higher SNR with shorter acquisition time. The SRS peak locates at 1369 cm⁻¹ with fwhm around 13.4 \pm 0.5 cm^{-1} , which is consistent with the spontaneous Raman signals of h-BN measured here (peak position at 1370 cm⁻¹, and fwhm of $\sim 10.7 \pm 0.3 \text{ cm}^{-1}$) and reported before.^{3,45–48} The slightly broader peak width in SRS is caused by the limited spectral resolution of our SRS system (Figure S3), which is primarily determined by the spectral width and chirp of the laser pulses. All spontaneous Raman spectra were fitted with Lorentzian line shapes, while SRS spectra were fitted with Voigt line shapes, which is a Lorentzian function broadened by the Gaussian profile of the system response. A rough comparison between the spectra of different sample thicknesses does not reveal significant variations of line shape or peak position among the samples we have studied (Figure S4). Notice that because the peak width of h-BN is much narrower than the cross-correlation of the two beams (~ 2.6 ps, corresponds to $\sim 140 \text{ cm}^{-1}$), it is unnecessary to correct the line shape with the temporal profile.

Vibrational Resonance of Coherent Raman Scattering Microscopy. A characteristic feature of the CRS process is the vibrational resonance that occurs when the photon energy difference between the pump and Stokes matches with the phonon energy. From Figure S1, it can be seen that the optimum pump wavelength to generate SRS signal of h-BN is ~913 nm. Under the spectral focusing condition, the photon energy difference could be varied by changing the time delay between the pump and Stokes pulses, and the on/off resonance conditions could be easily achieved, as shown in Figure 4. The on-resonance CARS/SRS images offer the highest signal intensities, in contrast to the off-resonance images with minimum signal intensities. Only small detuning of the photon energy difference is needed to tune off the CRS signal because of the narrow spectral width of the E_{2g} Raman peak. Such a sharp resonance feature of CRS microscopy is potentially useful to identify phonon modes with small frequency variations due to heterogeneous sample conditions such as mixed phases, heterostructures, or strains. 2D materials without a CRS feature but detectable TA signals could be easily distinguished because of their broad spectral/temporal responses under the setting of picosecond pump-probe spectroscopy.49-54

Thickness Quantification with SRS Microscopy. The large bandgap of h-BN challenges the thickness determination by optical contrast based on absorption, especially on transparent substrates such as quartz.²¹ The integrated intensity of spontaneous Raman scattering was reported to be proportional to the thickness of few-layer h-BN.²¹ However, the linear relation between the Raman intensity and layer number is only valid for few-layer samples with layer number less than six, and the results lack consistency between different studies of h-BN.⁴⁸ As we have shown above, SHG is not a good candidate for extracting thickness information because of its



Figure 4. Vibrational resonance of coherent Raman scattering imaging. (A–C) Relative positions of pump and Stokes beams in frequency–time space, representing on/off resonance conditions. (D–F) Corresponding SRS images. (G–I) Corresponding CARS images. Scale bar: 20 μ m.

selection rules that results in nontrivial dependence on sample thickness.

We hypothesized that SRS could be a convenient tool for quantitative characterization of h-BN thickness. For each sample, we took SRS, CARS, and AFM measurements for comparison and analysis. AFM results were used to represent the true thicknesses of these samples. A total number of 35 h-BN flakes were measured, with thickness varying from 2.5 to 70 nm. Typical AFM and SRS images are shown in Figure 5A and B. Normalized line-cut profiles across regions of different thicknesses of the two images match very well with each other, indicating the possibility of using SRS to quantify sample thickness (Figure 5C). The slight differences of the line profiles at the flake edges were mainly caused by the different lateral resolutions between the two imaging modalities. In addition, we found that the polarization dependence of SRS intensity is isotropic, which is consistent with the symmetry of the E_{2g} vibrational mode (Figure 5D). This isotropy provides convenience for optical determination of thickness, eliminating the concerns of crystal orientations with respect to light polarizations. More importantly, our results demonstrated the perfectly linear relation between SRS intensity and sample thickness, as shown in Figure 5E. Therefore, it is straightforward to determine h-BN thicknesses by taking SRS images of unknown samples and comparing them with the result of a reference h-BN flake with known thickness: $d = S \times d_0/S_0$, where S and d represent the corresponding SRS signal intensity and thickness, respectively. We also performed CARS measurements, and found that CARS signal intensity follows a quadratic relation to sample thickness, with a slightly distorted spectrum (Figure S5). From these results, we could state that SRS microscopy may become an ideal candidate for nonlinear optical quantification of h-BN thicknesses.

Theoretical description of SRS and CARS signal generation and their relations to sample concentration/thickness have been well-presented in previous studies.⁵⁵⁻⁵⁷ Both CARS and



Figure 5. Thickness quantification with SRS microscopy. (A) AFM and (B) SRS images of an h-BN flake. (C) Intensity profiles along the solid lines in AFM (red) and SRS (blue) images. (D) Isotropic polarization dependence of the SRS intensity of the E_{2g} mode. (E) Thickness dependence of SRS intensity shows perfect linearity. (F) Thickness dependence of CARS intensity shows quadratic relationship. Scale bar: 10 μ m.

SRS are coherent Raman scattering processes and can be described by third-order nonlinear optical spectroscopy,^{58,59} with the generated signal fields as

$$E_{\text{CARS}}(\omega_{\text{as}}) = iN\chi^{(3)}E_{\text{p}}^{2}(\omega_{\text{p}})E_{\text{s}}^{*}(\omega_{\text{s}})$$
(1)

$$E_{\rm SRL}(\omega_{\rm p}) = iN\chi^{(3)}E_{\rm p}(\omega_{\rm p})E_{\rm s}^{*}(\omega_{\rm s})E_{\rm s}(\omega_{\rm s})$$
(2)

where $\chi^{(3)}$ represents the third-order optical susceptibility, *N* represents the concentration of chemical bonds or phonons. It is known that in the CARS process, the generated signal at the anti-Stokes frequency ($\omega_{as} = 2\omega_p - \omega_s$) is optically filtered and homodyne detected with a PMT directly. Therefore, the measured CARS signal represents the intensity of the generated light field

$$S_{\text{CARS}} = |E_{\text{CARS}}|^2 = N^2 |\chi^{(3)}|^2 I_p^2 I_s$$
(3)

Whereas in SRL, the generated optical field has the same wavelength as the pump beam and coherently interferes with it. Hence, the final SRS signal is heterodyne detected with the pump light field as the local oscillator. The self-heterodyned SRL signal could thus be written as

$$S_{\text{SRL}} = \text{Re}[E_{\text{SRL}}E_{\text{p}}^*] = N\text{Im}[\chi^{(3)}]I_{\text{p}}I_{\text{s}}$$
(4)

In all the samples we have studied in this work, the thicknesses are much less than the z dimension of the focal spot ($\sim 1 \ \mu$ m); thus, sample thickness is proportional to N. Therefore, the above equations could explain the thickness dependences of both CARS and SRS signals. Note that in 2D materials with strong electronic resonances, these simple linear or quadratic relations could be violated due to strong absorption, interlayer reflection, and multilayer interference. For example, the four wave mixing (FWM) signal intensity of graphene is deviated from the quadratic relation with layer

numbers;⁶⁰ and the pump-probe transient absorption signal might be modulated by Van't Hoff singularity in certain twisted bilayer graphenes.⁶¹ In contrast, h-BN is free from these effects because of the large band gap and weak absorptions at the incident photon energies, providing a near-perfect linear relation of the SRS signal to sample thickness up to ~100 nm.

Imaging monolayer h-BN is challenging at the current stage, mainly due to the intrinsic weak Raman cross section of the atomically thin sample. The thinnest h-BN we have imaged was around 2.5 nm (Figure S6). A rough estimation from the thickness of monolayer h-BN (~0.4 nm)²¹ suggests a SNR of ~0.2. Also, it is difficult to prepare high-quality monolayer h-BN on a quartz substrate without PMMA contamination. However, there are potential means to reach monolayer sensitivity with SRS microscopy. Given that SRS is shot-noise limited,³² and its intensity is proportional to both the pump and Stokes laser power (Figure S7), we may improve the SNR by increasing the incident laser power within the damage threshold, as well as increasing the integration time (by 25 time to reach SNR \sim 1). In addition, Raman sensitivity is expected to be enhanced by using higher energies of pump and Stokes photons, which could be realized by frequency doubling both incident laser beams. Such an enhancement may result from both the wavelength dependent scattering cross section and electronic pre-resonance effect.^{62,63}

Our work also indicates the potential applications of SRS microscopy for imaging other large bandgap 2D materials and heterojunctions. With improved spectral resolution of hyperspectral SRS, we may be able to selectively image individual materials and study their interactions in heterostructures. For materials with strong electronic resonances such as graphene and other low bandgap materials, TA signal is overwhelmingly larger than SRS,⁶⁴ hindering the detection of SRS directly. Possible techniques to suppress TA background may include

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using longer wavelengths, multiple laser beams,⁶⁵ and adjusting Fermi levels by gate tuning methods.^{66–69}

CONCLUSIONS

In summary, we have performed multimodal nonlinear optical microscopy on h-BN thin flakes with the combination of SHG, CARS, and SRS imaging. In particular, we have accomplished high-resolution and high-speed SRS mappings for 2D h-BN based on the E_{2g} vibrational mode. Moreover, the intensity of the SRS signal exhibits linear dependence on sample thickness and isotropic response to light polarization, enabling SRS microscopy for quantitative optical determination of h-BN thickness. The enhanced vibrational sensitivity and hyperspectral imaging capability may provide research opportunities in characterizing 2D materials, heterostructures, and devices.

METHODS

Nonlinear Optical Microscopy. In our setup, a commercial femtosecond optical parametric oscillator (OPO, Insight DS+, Newport, CA) was used as the laser source, with the fundamental 1040 nm beam as the Stokes and the tunable output (690-1300 nm) as the pump. Femtosecond laser pulses were linearly chirped through highly dispersive glass rods (SF57). Targeting Raman frequency can be conveniently selected by adjusting the relative time delay between the pump and Stokes pulses. The Stokes beam was modulated at 20 MHz by an electro-optical modulator (EOM), collinearly combined with the pump beam and delivered into a laser scanning microscope (FV1200, Olympus). Then, two beams were raster scanned by a pair of galvo mirrors, focused onto the sample with a water objective lens (UPLSAPO 60XW, NA 1.2, Olympus), transmitted through a high NA condenser (NA = 1.4), passed through an optical filter to block the 1040 nm component, and then directed onto a large-area (1 cm^2) silicon photodiode coupled to a trans-impedence amplifier. The pump and Stokes powers at the sample were ~30 mW and 20 mW, respectively. A polarizer and half-wave plate were inserted before the microscope to control the polarization. A lock-in amplifier was used for the detection of SRS signal. For CARS and SHG measurements, the emission photons were collected through the same objective, filtered by proper optical filters, and detected with PMTs. The spectral resolution of our SRS system is measured to be ~13 cm⁻¹ (Figure S3), with the pump and Stokes pulses chirped to \sim 2.3 ps and ~1.5 ps, respectively. The calculation of the GVD induced by SF57 glass can be found in the Supporting Information.

Spontaneous Raman Measurements. The spontaneous Raman measurements were carried out with a commercial confocal Raman spectrometer (XploRA Plus, Jobin Yvon, Horiba Gr, France) with 45 mW of 532 nm excitation. The NA of the objective lens is 0.5, and the spectral resolution of the system is $\sim 3 \text{ cm}^{-1}$.

Sample Preparation. Golden markers were deposited on the transparent quartz substrate $(1 \text{ cm} \times 1 \text{ cm} \times 1 \text{ mm})$ by photolithography and magnetosputtering in order to locate h-BN flakes. After marker deposition, the substrate was sonicated in acetone and dried with nitrogen gas. The h-BN bulk sample was purchased from Prmart (Shanghai) Technology Co. Ltd. We exfoliated the bulk sample by wafer protective PVC blue film (purchased from Alibaba), and then transferred by PDMS onto the substrate.

Atomic Force Microscopy. AFM measurements were performed with a commercial machine (Dimension Edge, Bruker) in tapping mode.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.9b06337.

SRS and CARS spectra of h-BN; AFM images of the samples shown in Figures 2–4; SRS spectral resolution

characterization; laser power dependences and group velocity dispersion calculation (PDF)

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Author Contributions

M.J. conceived the experiment, J.L. and X.M. prepared the samples and performed the microscopy measurements, Y.S and Z.S. provided help in AFM measurements, Y.F. and L.Z. helped with the spontaneous Raman measurements. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Author Contributions

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Notes

The authors declare no competing financial interest.

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