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Mechanical Detection and Imaging of Hyperbolic Phonon Polaritons in Hexagonal Boron Nitride

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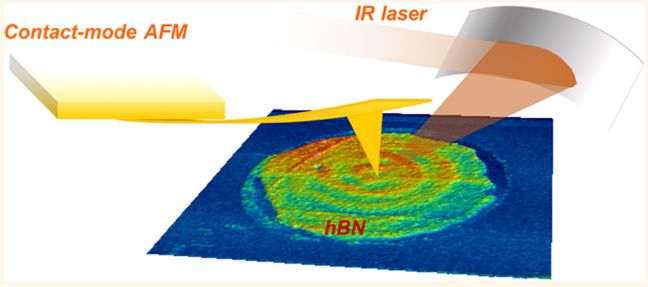
Supporting Information

ABSTRACT: **Mid-infrared nanoimaging and spectroscopy of two-dimensional (2D) materials have been limited so far to scattering-type scanning near-field optical microscopy (s-SNOM) experiments, where light from the sample is scattered by a metallic-coated atomic force microscope (AFM) tip interacting with the material at the nanoscale. These experiments have recently allowed imaging of plasmon polaritons in graphene as well as hyperbolic phonon polaritons in hexagonal boron nitride (hBN). Here we show that the high mechanical sensitivity of an AFM cantilever can be exploited for imaging hyperbolic phonon polaritons in hBN. In our imaging process, the lattice vibrations of hBN micrometer-sized flakes are locally enhanced by the launched phonon polaritons. These enhanced vibrations are coupled to the AFM tip in contact with the sample surface and recorded during scanning. Imaging resolution of Δ/20 is shown (Δ being the polaritonic fringes' separation distance), comparable to the best resolution in s-SNOM. Importantly, this detection mechanism is free from light background, and it is in fact the first photonless detection of phonon polaritons.**



KEYWORDS: *hexagonal boron nitride, photothermal microscopy, phonon polaritons, nanoimaging, atomic force microscopy, scanning near-field optical microscopy*

The first atomic force microscope (AFM) was evocatively labeled "touching microscope" to convey that the microscope "feels" the sample's atoms and can produce an atomically resolved image of the surface. In their first paper "Atomic Force Microscope",[1] Binning, Quate, and Gerber had already envisioned a general-purpose device "that will measure any type of force; not only interatomic forces, but electromagnetic forces as well". Today, the AFM is really a general-purpose device used in many configurations for specific force characterization, including electric force microscopy,[2,3] magnetic force microscopy,[4,5] microwave impedance microscopy,[6,7] multifrequency force microscopy,[8] *etc.* In its most recent applications AFM has also been proposed in different schemes for optical near-field imaging[9−13] and spectroscopy at the nanoscale without detecting any light.[14−19]

In this paper, we show imaging of optically excited hyperbolic phonon polaritons (HP^2) in hexagonal boron nitride (hBN) flakes by monitoring only the mechanical oscillations induced in an AFM cantilever.

Phonon polaritons, as well as surface plasmon polaritons (SPPs), have attracted great interest for many years due to their role as energy carriers.[20−22] In fact, directional control of electromagnetic energy propagation in flat optoelectronic devices needs strong coupling of electromagnetic waves to local material excitations. SPPs are generated by collective excitations of electrons (*e.g.*, at a metal−dielectric interface), while an electromagnetic wave coupled to the lattice vibrations (phonons) of a polar crystal gives rise to the excitation of phonon polaritons.

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Hexagonal boron nitride is of particular interest in terms of phonon polaritons since it has been found to have low-loss phonon polaritons in the upper Reststrahlen band (1370−1610 cm^{-1}). Moreover, in this wavelength (wavenumbers) range (type II band), hBN is hyperbolic, *i.e.* $\varepsilon_z > 0$ and $\varepsilon_t < 0$, where ε_z and ε_t are the axial (normal to the surface) and tangential (in plane) permittivities, respectively.[23−29] In fact, due to the momentum mismatch between the free space illuminating light and the highly confined propagating polaritons, a local scatterer (point of origin) close to the sample surface is needed to launch phonon polariton propagating waves.[30]

Hyperbolic phonon polaritons have been previously imaged in hBN by means of scattering-type scanning near-field optical microscopy (s-SNOM).[31,32] In this configuration, as reported in ref 31, an hBN flake is usually shaped in a triangle by electron beam lithography and reactive ion etching (Supporting Information). The local scatterer that allows overcoming the momentum mismatch is the metal-coated tip of the s-SNOM microscope illuminated by mid-IR light at an angle.[33−35] The presence of sharp edges like in hBN flakes with a well-defined geometric shape of several micrometers is important since hyperbolic phonon polaritons have low losses, and, by reflecting at the edges, they create standing waves that are then visualized during the imaging process.[36−39] Described more explicitly, (1) the tip launches the phonon polariton; (2) the polariton propagates and is reflected at the edges of the flake, creating a standing wave that may have a minimum, a maximum, or any intermediate amplitude at the tip position; and (3) the tip scatters the radiation to open air for far-field detection by means of a mid-IR detector. Figure 1a and b show the amplitude and phase of the near-field scattered light (s-SNOM signal) from the surface of a 67 nm thick hBN flake on 285 nm thick SiO_2. The phonon polariton standing wave is clearly visible. The s-SNOM microscope used here is the same as that in ref 31 (Neaspec GmbH).

RESULTS AND DISCUSSION

The detection scheme presented here is still based on an atomic force microscopy platform, but no radiation is detected. Imaging of the HP^2 is obtained by monitoring only the mechanical oscillations of the microscope cantilever (Figure 1c). This detection is then free from light background. The detection scheme is similar to both photothermal microscopy and photoinduced force microscopy, where a light-driven local surface−tip interaction (local heating or optical forces) is monitored as induced mechanical oscillations on an AFM cantilever.[17] Also, while this paper was under review, we were informed of a recent work achieving chemical imaging by combining mid-IR illumination with peak force microscopy.[40]

In our microscope (Anasys Instruments) an infrared laser beam from an optical parametric oscillator (OPO) is focused onto the tip−sample region by means of a low numerical aperture parabolic mirror (Figure 1c). The laser is pulsed (10 ns pulse width, 1 kHz fixed repetition rate) and can be wavelength tuned in the upper Reststrahlen band of hBN (1370−1610 cm^{-1}). The microscope operates as an AFM in contact mode. That is, the tip (gold coated; nominal spring constant in the range 0.07−0.4 N/m; nominal resonance frequency of 13 kHz) is then not oscillated by an external dithering piezo; rather it is in "contact" with the sample surface. When the sample is illuminated, some oscillations on the microscope cantilever appear at around 170 kHz (one of the mechanical modes of the cantilever). Similarly to multi-frequency force microscopy,[8] operating on a secondary mechanical mode of the cantilever increases the quality factor of the cantilever and helps to improve the signal-to-noise ratio of the detected signal. Figure 1d shows the image ("photothermal" signal) that we obtained for the polariton standing

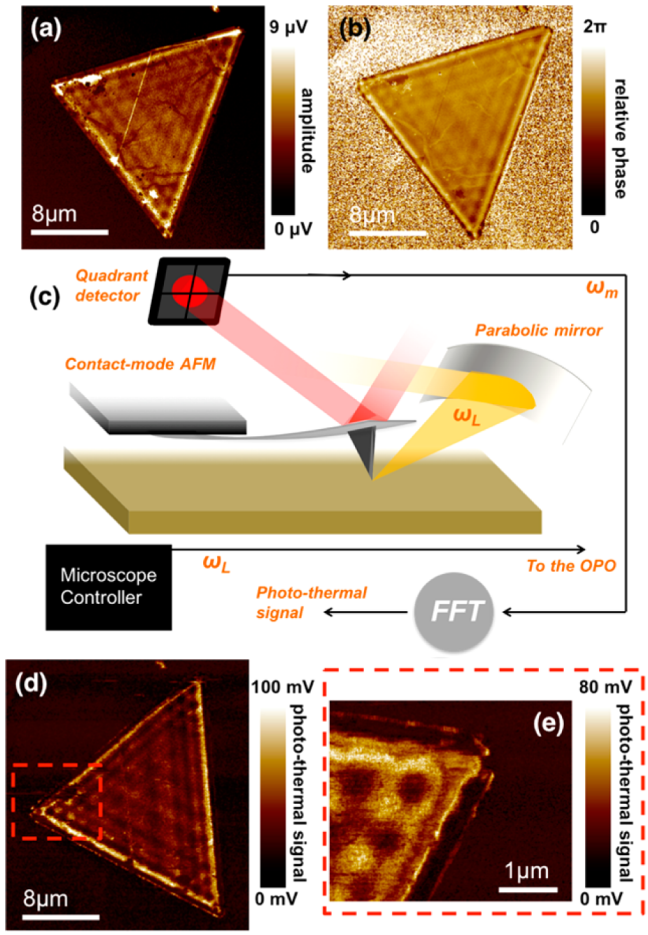

Figure 1. (a) Amplitude (in volts from the detector) and (b) phase (relative phase with respect to a gold-coated surface used as reference) of hyperbolic phonon polaritons imaged using s-SNOM. The hBN flake was shaped in a triangle of dimensions 16 μm × 16 μm × 18 μm using electron beam lithography and is on 285 nm thick SiO_2. The flake thickness is 67 nm, measured with atomic force microscopy in contact mode. (c) Schematic of the experimental setup for photothermal microscopy. A pulsed laser with repetition rate ω_L = 1 kHz (a mid-IR OPO laser) is focused to the tip−sample region by means of a parabolic mirror. In this imaging process, the microscope is operated with a gold-coated tip in contact with the sample surface. The tip launches the phonon polariton; the polariton propagates and is reflected at the edges of the flake, creating a standing wave; the light-induced oscillations at the sample surface are transferred to the tip that starts oscillating on its mechanical modes. Fourier transform of the tip oscillations, monitored through the quadrant detector, is performed to analyze the spectral content. The oscillation amplitude (in volts from the quadrant photodetector) at a specific frequency ω_m is then chosen (with a bandwidth of about 50 kHz) to be monitored and recorded. This frequency is usually around 170 kHz for the AFM cantilever we used. The recorded oscillation amplitude at ω_m is the "photothermal" signal used to generate figures (d) and (e). (d) Photothermal image of the hyperbolic phonon polariton pattern at the surface of the same flake of (a) and (b). (e) Zoomed-in photothermal image of one of the corners of the flake. The illuminating light has a wavenumber of 1440 cm^{-1}.

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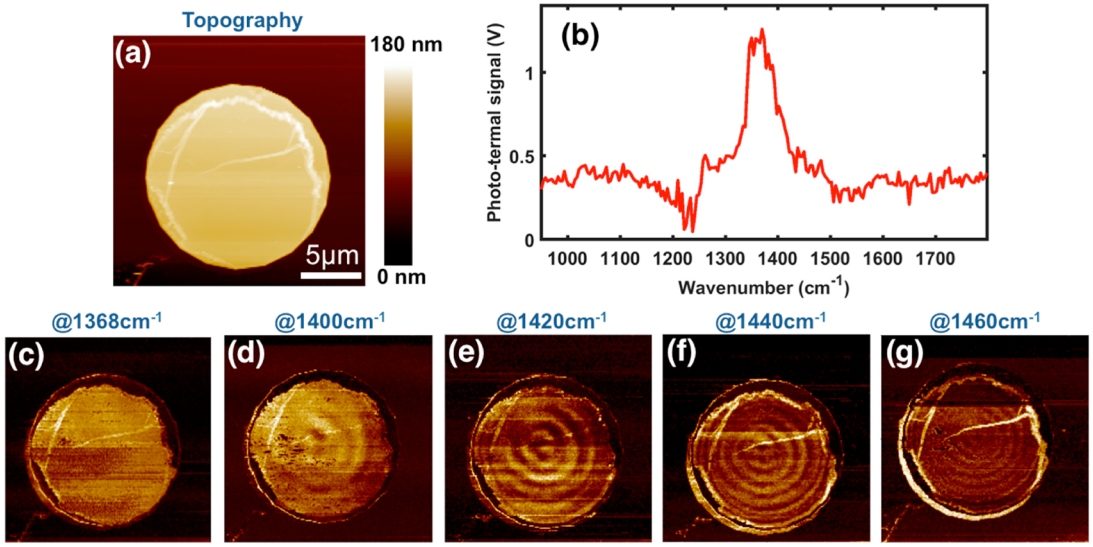

Figure 2. (a) Topography image of an hBN flake cut in the shape of a disk. The flake is on a Si substrate and is 140 nm thick. The flake diameter is 15 μm. (b) Photothermal signal as a function of the laser wavenumber. The position of the AFM tip in this case is in the central part of the flake. Signal is present in the type II band (1370−1610 cm^{-1}) with a peak around 1368 cm^{-1}. (c−g) Photothermal image of the hyperbolic phonon polariton pattern at different wavelengths (wavenumbers) of the illuminating light. The periodicity of the pattern decreases by increasing the wavenumber. Note that the patterns are concentric to the edges of the flake.

wave in the hBN flake. This image is then not obtained by detecting scattered light but by monitoring the amplitude of the induced oscillations on the cantilever at 170 kHZ (with a bandwidth of 50 kHz and a typical scanning rate of 0.1 Hz). There is complete superposition between the s-SNOM patterns shown in Figure 1a and b and that in Figure 1d (see also Figure S1). Figure 1e shows instead a zoomed-in image of the polariton pattern in a corner of the shaped flake. This figure clearly shows the possibility to visualize features only a couple of hundred nanometers wide (resolution of $\Delta/20$, Δ being the fringes' spacing), comparable to the best resolution achieved in mid-IR s-SNOM.

In our imaging process, the lattice vibrations are locally enhanced by the launched phonon polariton, spatially modulated by the polariton wave. These enhanced vibrations (on a macroscopic scale this corresponds to local heating and thermal expansion) are what in fact cause the induced tip oscillations (photothermal signal). More precisely, the repetition rate of the illuminating laser is 1 kHz. This results in periodic oscillations of the sample surface upon heating that are transferred to the microscope probe cantilever. The induced oscillations couple to several modes of the cantilever, including the mode around 170 kHz, whose amplitude is monitored during the imaging process. The surface oscillations at 1 kHz are slow with respect to the detection frequency of 170 kHz but fast enough to be not fully compensated by the microscope feedback; they turn then into induced oscillations of the cantilever that is in contact (AFM contact mode) with the sample surface.

Note that other phenomena can in principle contribute to the induced mechanical oscillations of the probe cantilever.

An enhanced radiative heat transfer, mediated by phonon polaritons, between two objects has been studied, for instance.[41,42] However, those experiments need to be carried under vacuum to get reasonable signal-to-noise ratio in the detection. We operated in air. Moreover, the largest enhancement of those experiments has been reported between similar polar crystals that support phonon polaritons at the same wavelength (near-field interaction of the polaritonic field). In our experiment instead, one of the objects, the microscope cantilever, is gold coated. For these reasons, it looks unrealistic that radiative heat transfer is our main sensing mechanism.

Direct forces of optical origin are also possible in principle. According to this picture, the evanescent tail of the phonon polariton in air would couple to the metallic tip, generating a weak optical force depending on the polariton local strength. This would be similar to the working principle of the photoinduced force microscopy technique.[43] However, in our experiment local heating of the sample surface is evident when the laser power approaches 1 mW (Supporting Information). For this, we also exclude optical forces at the sample surface as the main detection mechanism in our experiment.

In a complementary experiment we used an hBN flake, 140 nm thick, deposited on a Si substrate and cut in the shape of a disk (Figure 2). In this case we changed the wavelength of the illuminating light, observing how the polariton pattern periodicity changes (polariton dispersion): smaller wavenumbers result in lager fringe spacing (Figure S2). As shown in Figure 2b, when the microscope probe is on top of the hBN flake, the amplitude of the photothermal signal as a function of the laser wavenumber reflects the type II band with a maximum around 1368 cm^{-1}.[31] However, if the tip is right at the position where one of the bright fringes of the HP^2 standing wave is located for a specific wavelength, the photothermal signal recorded as a function of the illuminating wavenumber (photothermal spectrum) may show peaks at wavenumbers that produce the specific fringe. This case is illustrated in Figure 3c, where the photothermal spectrum shows a peak at 1440 cm^{-1}. In this case the microscope tip is positioned on top of one of the bright fringes produced on the surface when illuminating at 1440 cm^{-1} (Figure 3b red circle). A similar effect is also found in scattering near-field experiments (Figure S7).

All our samples of hBN flakes are on 285 nm SiO_2 (except that of Figure 2, which is on Si), which has a phonon resonance around 1100 cm^{-1}. Our imaging process is able to detect this

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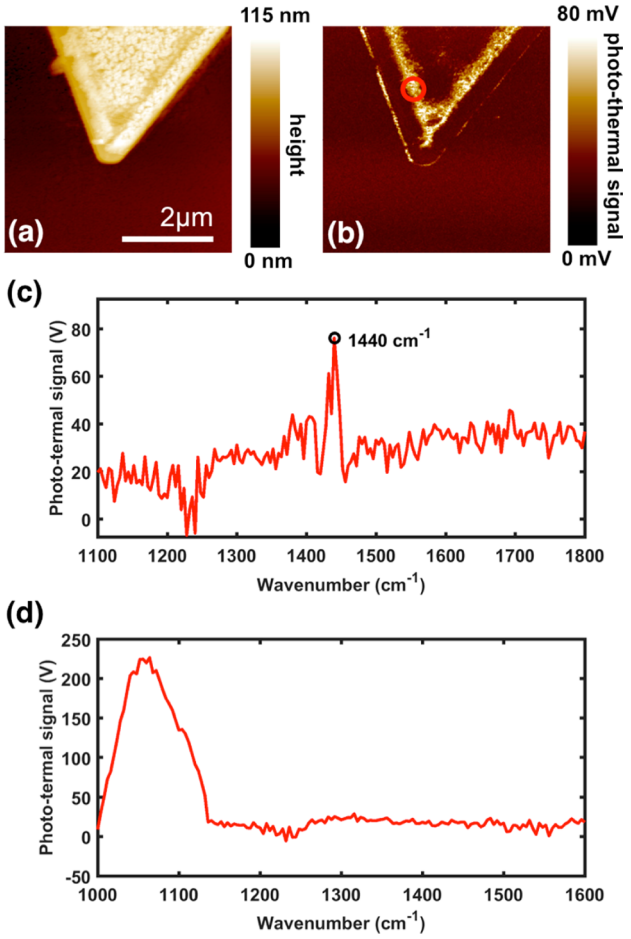

Figure 3. (a) Topography and (b) photothermal image at 1440 cm^{-1} of a corner of a triangle-shaped hBN flake. (c) Spectrum at the tip position highlighted by the red circle in (b). This spectrum is obtained by recording the photothermal signal while swiping the wavenumbers of the illuminating light for a fixed position of the tip. A peak at 1440 cm^{-1} is evident. This only happens when the tip is on top of a maximum of interference of the polariton beam. (d) Photothermal spectrum recorded when the tip is on the SiO_2 substrate. The phonon resonance of SiO_2 is clearly visible around 1100 cm^{-1}.

resonance as well. Figure 3d shows the photothermal spectrum when the microscope tip is on the SiO_2 substrate. High signal around the SiO_2 phonon peak is evident.

CONCLUSIONS

In this work we show that the interference patterns created by phonon polaritons in shaped flakes of hexagonal boron nitride can be imaged with high resolution by monitoring the mechanical oscillations of an AFM cantilever in contact with the sample surface. We show that this imaging process is based on local sample heating mediated by the phonon polariton resonances of hBN, although *ad hoc* experiments should be planned to better quantify contributions from other effects such as optical forces or the specific tip material.

This scheme is similar to photothermal microscopy that has shown the best results so far mainly on soft and easily deformable materials such as polymers.[44] Our imaging process provides the same features obtained in scattering near-field optical microscopy but does not require detecting any light and, as such, is a light-background-free photonless detection of the coupling of light to the crystal lattice oscillations. This result extends mid-IR nanoimaging and spectroscopy *via* mechanical detection based on an AFM probe to crystals, 2D materials, and van der Waals heterostructures.

MATERIALS AND METHODS

Sample Fabrication. Hexagonal boron nitride is mechanically exfoliated onto a 285 nm SiO_2/silicon or a bare silicon substrate with predefined metallic alignment marks. The substrates are then covered with MA-N 2403 (negative e-beam resist) and exposed to an e-beam system with a dose of 1200 $\mu C/cm^2$ using an accelerating voltage of 125 kV. The samples are shaped into triangles, circles, or rectangles. After developing in AZ-726 for 1 min, the samples are prebaked at 100 °C for 10 min. Then hBN is etched by using a reactive ion etching system with $CHF_3/Ar/O_2$ at flows of 10/5/2 sccm, respectively, and an RF generator at 30 W for 2−5 min.[45] After the etching process, exposed MA-N 2403 resist is removed by Remover PG and chloroform; afterward, the samples are rinsed with isopropyl alcohol and dried with nitrogen.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b02323.

Comparison between s-SNOM and photothermal imaging of phonon polaritons in hBN, periodicity trend of phonon polarion fringes in hBN on a Si substrate, description of the apparent change of sample height as an artifact of AFM imaging, comparison of samples before and after thermal annealing, nano-FTIR s-SNOM spectra on an hBN sample (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Benning, G.; Quate, C. F.; Gerber, Ch. Atomic Force Microscope. *Phys. Rev. Lett.* **1986**, *56*, 930−933.

(2) Bohm, C. Electric Force Microscopy: Gigahertz and Nanometer Measurement Tool. *Microelectron. Eng.* **1996**, *31*, 171−179.

(3) Yokoyama, H.; Inoue, T.; Itoh, J. Nonresonant Detection of Electric Force Gradients by Dynamic Force Microscopy. *Appl. Phys. Lett.* **1994**, *65*, 3143−3145.

DOI: 10.1021/acsnano.7b02323
ACS Nano 2017, 11, 8741−8746

(4) Hartmann, U. Magnetic Force Microscopy. *Adv. Mater.* **1990**, *2*, 550−552.
(5) Hartmann, U. Magnetic Force Microscopy: Some Remarks From the Micromagnetic Point of View. *J. Appl. Phys.* **1988**, *64*, 1561−1564.
(6) Seabron, E.; MacLaren, S.; Xie, X.; Rotkin, S. V.; Rogers, J. A.; Wilson, W. L. Scanning Probe Microwave Reflectivity of Aligned Single-Walled Carbon Nanotubes: Imaging of Electronic Structure and Quantum Behavior at the Nanoscale. *ACS Nano* **2016**, *10*, 360−368.
(7) Kundhikanjana, W.; Yang, Y.; Tanga, Q.; Zhang, K.; Lai, K.; Ma, Y.; Kelly, M. A.; Li, X. X.; Shen, Z. X. Unexpected Surface Implanted Layer in Static Random Access Memory Devices Observed by Microwave Impedance Microscope. *Semicond. Sci. Technol.* **2013**, *28*, 025010.
(8) Garcia, R.; Herruzo, E. The Emergence of Multifrequency Force Microscopy. *Nat. Nanotechnol.* **2012**, *7*, 217−226.
(9) Ambrosio, A.; Allegrini, M.; Latini, G.; Cacialli, F. Thermal Processes in Metal- Coated Fiber Probes for Near-Field Experiments. *Appl. Phys. Lett.* **2005**, *87*, 033109.
(10) Ambrosio, A.; Camposeo, A.; Maddalena, P.; Patanè, S.; Allegrini, M. Real- Time Monitoring of the Surface Relief Formation on Azo-Polymer Films Upon Near- Field Excitation. *J. Microsc.* **2008**, *229*, 307−312.
(11) Ambrosio, A.; Cefalì, E.; Spadaro, S.; Patanè, S.; Allegrini, M.; Albert, D.; Oesterschulze, E. Noncontact Tuning Fork Position Sensing for Hollow-Pyramid Near-Field Cantilevered Probes. *Appl. Phys. Lett.* **2006**, *89*, 163108.
(12) Ocelic, N.; Huber, A.; Hillenbrand, R. Pseudoheterodyne Detection for Background-Free Near-Field Spectroscopy. *Appl. Phys. Lett.* **2006**, *89*, 101124.
(13) Gerber, J. A.; Berweger, S.; O'Callahan, B. T.; Raschke, M. B. Phase-Resolved Surface Plasmon Interferometry of Graphene. *Phys. Rev. Lett.* **2014**, *113*, 055502.
(14) Garcia, R.; Herruzo, E. T. The Emergence of Multifrequency Force Microscopy. *Nat. Nanotechnol.* **2012**, *7*, 217−226.
(15) Damircheli, M.; Payam, A. F.; Garcia, R. Optimization of Phase Contrast in Bimodal Amplitude Modulation AFM. *Beilstein J. Nanotechnol.* **2015**, *6*, 1072−1081.
(16) Lozano, J. R.; Garcia, R. Theory of Multifrequency Atomic Force Microscopy. *Phys. Rev. Lett.* **2008**, *100*, 076102.
(17) Dazzi, A.; Prazeres, R.; Glotin, F.; Ortega, J. M. Local Infrared Microspectroscopy with Subwavelength Spatial Resolution with an Atomic Force Microscope Tip Used as a Photothermal Sensor. *Opt. Lett.* **2005**, *30*, 2388−2390.
(18) Lu, F.; Jin, M.; Belkin, M. A. Tip-Enhanced Infrared Nanospectroscopy via Molecular Expansion Force Detection. *Nat. Photonics* **2014**, *8*, 307−312.
(19) Yang, H. U.; Rashcke, M. B. Resonant Optical Gradient Force Interaction for Nano-Imaging and -Spectroscopy. *New J. Phys.* **2016**, *18*, 053042.
(20) Xu, X. G.; Ghamsari, B. G.; Jiang, J.-H.; Gilburd, L.; Andreev, G. O.; Zhi, C.; Bando, y.; Golberg, D.; Berini, P.; Walker, G. C. One-Dimensional Surface Phonon Polaritons in Boron Nitride Nanotubes. *Nat. Commun.* **2014**, *5*, 4782.
(21) Li, P.; Lewin, M.; Kretinin, A. V.; Caldwell, J. D.; Novoselov, K. S.; Taniguchi, T.; Watanabe, K.; Gaussmann, F.; Taubner, T. Hyperbolic Phonon-Polaritons in Boron Nitride for Near-Field Optical Imaging and Focusing. *Nat. Commun.* **2015**, *6*, 7507.
(22) Low, T.; Chaves, A.; Caldwell, J. D.; Kumar, A.; Fang, N. X.; Avouris, P.; Heinz, T. F.; Guinea, F.; Martin-Moreno, L.; Koppens, F. Polaritons in Layered Two- Dimensional Materials. *Nat. Mater.* **2017**, *16*, 182−194.
(23) Yoxall, E.; Schnell, M.; Nikitin, A. Y.; Txoperena, O.; Woessner, A.; Lundeberg, M. B.; Casanove, F.; Hueso, L. E.; Koppens, F. H. L.; Hillebrand, R. Direct Observation of Ultraslow Hyperbolic Polariton Propagation with Negative Phase Velocity. *Nat. Photonics* **2015**, *9*, 674−678.
(24) Basov, D. N.; Fogler, M. M.; Garcia de Abajo, F. J. Polaritons in van der Waals Materials. *Science* **2016**, *354*, 195.
(25) Shi, Z.; Bechtel, H. A.; Berweger, S.; Sun, Y.; Zeng, B.; Jin, C.; Chang, H.; Martin, M. C.; Raschke, M. B.; Wang, F. Amplitude-and Phase-Resolved Nanospectral Imaging of Phonon Polaritons in Hexagonal Boron Nitride. *ACS Photonics* **2015**, *2*, 790−796.
(26) Dai, S.; Ma, Q.; Liu, M. K.; Andersen, T.; Fei, Z.; Goldflam, M. D.; Wagner, M.; Watanabe, K.; Taniguchi, T.; Thiemens, M.; Keilmann, F.; Janssen, G. C. A. M.; Zhu, S.-E.; Jarillo-Herrero, P.; Fogler, M. M.; Basov, D. N. Graphene on Hexagonal Boron Nitride as a Tunable Hyperbolic Metamaterial. *Nat. Nanotechnol.* **2015**, *10*, 682−686.
(27) Kumar, A.; Low, T.; Fung, K. H.; Avouris, P.; Fang, N. X. Tunable Light−Matter Interaction and the Role of Hyperbolicity in Graphene−hBN system. *Nano Lett.* **2015**, *15*, 3172−3180.
(28) Caldwell, J. D.; Kretinin, A. V.; Chen, Y.; Giannini, V.; Fogler, M. M.; Francescato, Y.; Ellis, C. T.; Tischler, J. G.; Woods, C. R.; Giles, A. J.; Hong, M.; Watanabe, K.; Taniguchi, T.; Maier, S. A.; Kostya, S. Hyperbolic Phonon-Polaritons in Boron Nitride for Near-Field Optical Imaging and Focusing. *Nat. Commun.* **2015**, *5*, 5221.
(29) Giles, A. J.; Dai, S.; Glembocki, O. J.; Kretinin, A. V.; Sun, Z.; Ellis, C. T.; Tischler, J. G.; Taniguchi, T.; Watanabe, K.; Fogler, M. M.; Novoselov, K. S.; Basov, D. N.; Caldwell, J. D. Imaging of Anomalous Internal Reflections of Hyperbolic Phonon-Polaritons in Hexagonal Boron Nitride. *Nano Lett.* **2016**, *16*, 3858−3865.
(30) Dai, S.; Ma, Q.; Andersen, T.; Mcleod, A. S.; Fei, Z.; Liu, M. K.; Wagner, M.; Watanabe, K.; Taniguchi, T.; Thiemens, M.; Keilmann, F.; Jarillo-Herrero, P.; Fogler, M. M.; Basov, D. N. Subdiffractional Focusing and Guiding of Polaritonic Rays in a Natural Hyperbolic Material. *Nat. Commun.* **2015**, *6*, 6963.
(31) Dai, S.; Fei, Z.; Ma, Q.; Rodin, A. S.; Wagner, M.; McLeod, A. S.; Liu, M. K.; Gannett, W.; Regan, W.; Watanabe, K.; Taniguchi, T.; Thiemens, M.; Dominguez, G.; Castro Neto, A. H.; Zettl, A.; Keilmann, F.; Jarillo-Herrero, P.; Fogler, M. M.; Basov, D. N. Tunable Phonon Polaritons in Atomically Thin van der Waals Crystals of Boron Nitride. *Science* **2014**, *343*, 1125−1129.
(32) Li, P.; Yang, X.; Maß, T. W. W.; Hanss, J.; Lewin, M.; Michel, A.-K. U.; Wuttig, M.; Taubner, T. Reversible Optical Switching of Highly Confined Phonon-Polaritons with an Ultrathin Phase-Change Material. *Nat. Mater.* **2016**, *15*, 870−876.
(33) Atkin, J. M.; Berweger, S.; Jones, A. C.; Raschke, M. B. Nano-Optical Imaging and Spectroscopy of Order, Phases, and Domains in Complex Solids. *Adv. Phys.* **2012**, *61*, 745−842.
(34) Govyadinov, A. A.; Mastel, S.; Golmar, F.; Chuvilin, A.; Carney, S. P.; Hillenbrand, R. Recovery of Permittivity and Depth from Near-Field Data as a Step Toward Infrared Nanotomography. *ACS Nano* **2014**, *7*, 6911−6921.
(35) Amenabar, I.; Poly, S.; Goikoetxea, M.; Nuansing, W.; Lasch, P.; Hillenbrand, R. Hyperspectral Infrared Nanoimaging of Organic Samples Based on Fourier Transform Infrared Nanospectroscopy. *Nat. Commun.* **2017**, *8*, 14402.
(36) Gilburd, L.; Kim, K. S.; Ho, K.; Trajanoski, D.; Maiti, A.; Halverson, D.; de Beer, S.; Walker, G. C. Hexagonal Boron Nitride Self-Launches Hyperbolic Phonon Polaritons. *J. Phys. Chem. Lett.* **2017**, *8*, 2158−62.
(37) Xu, X. G.; Gilburd, L.; Walker, G. C. Phase stabilized homodyne of infrared scattering type scanning near-field optical microscopy. *Appl. Phys. Lett.* **2014**, *105*, 263104.
(38) Xu, X. G.; Gilburd, L.; Bando, Y.; Golberg, D.; Walker, G. C. Defects and Deformation of Boron Nitride Nanotubes Studied by Joint Nanoscale Mechanical and Infrared Near-Field Microscopy. *J. Phys. Chem. C* **2016**, *120*, 1945−51.
(39) Gilburd, L.; Xu, X. G.; Bando, Y.; Golberg, D.; Walker, G. C. Near-field infrared pump−probe imaging of surface phonon coupling in boron nitride nanotubes. *J. Phys. Chem. Lett.* **2016**, *7*, 289−94.
(40) Wang, L.; Wang, H.; Wagner, M.; Yan, Y.; Jakob, D. S.; Xu, X. G. Nanoscale simultaneous chemical and mechanical imaging via peak force infrared microscopy. *Sci. Adv.* **2017**, *3*, e1700255.
(41) Shen, S.; Narayanaswamy, A.; Chen, G. Surface Phonon Polaritons Mediated Energy Transfer between Nanoscale Gaps. *Nano Lett.* **2009**, *9*, 2909−2913.

DOI: 10.1021/acsnano.7b02323
ACS Nano 2017, 11, 8741−8746

(42) Rousseau, E.; Siria, A.; Jourdan, G.; Volz, S.; Comin, F.; Chevrier, J.; Greffet, J. J. Surface Phonon Polaritons Mediated Energy Transfer between Nanoscale Gaps. *Nat. Photonics* **2009**, *3*, 514−517.
(43) Nowak, D.; Morrison, W.; Kumar Wickramasinghe, H.; Jahng, J.; Potma, E.; Wan, L.; Ruiz, R.; Albrecht, T. R.; Schmidt, K.; Frommer, J.; Sanders, D. P.; Park, S. Nanoscale Chemical Imaging by Photoinduced Force Microscopy. *Sci. Adv.* **2016**, *2*, e1501571.
(44) Dazzi, A.; Prater, C. B. AFM-IR: Technology and Applications in Nanoscale Infrared Spectroscopy and Chemical Imaging. *Chem. Rev.* **2017**, *117*, 5146−5173.
(45) Wang, L.; Meric, I.; Huang, P. Y.; Gao, Q.; Gao, Y.; Tran, H.; Taniguchi, T.; Watanabe, K.; Campos, L. M.; Muller, D. A.; Guo, J.; Kim, P.; Hone, J.; Shepard, K. L.; Dean, C. R. One-dimensional Electrical Contact to a Two-Dimensional Material. *Science* **2013**, *342*, 614−617.

DOI: 10.1021/acsnano.7b02323
ACS Nano 2017, 11, 8741−8746