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**Strong and tunable interlayer coupling of infrared-active phonons to excitons in van der Waals heterostructures**

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I. INTRODUCTION

Van der Waals (vdW) heterostructures stacked from atomically thin two-dimensional (2D) crystals provide a new paradigm for a cornucopia of intriguing physics and novel device applications [1–5]. Hexagonal boron nitride (hBN), a paradigm for a cornucopia of intriguing physics and novel 2D crystals, provides a new opportunity for nanophotonics [13,18]. However, the control of localized at subdiffractional length scales, opening up opportunities for nanophotonics [13,18]. However, the control of infrared active phonons has remained challenging, impeding strongly their practical applications [19]. Therefore, it is highly desirable and potentially important to combine the fascinating infrared phonons in hBN with other quasiparticles, offering an unprecedented platform to realize tunable hyperbolic polaritons. Recently, hybridizations of infrared active phonons or hyperbolic phonon polaritons in hBN, enabling another way to generate tunable hyperbolic polaritons. Recently, hybridizations of infrared active phonons or hyperbolic phonon polaritons in hBN with electrons in graphene have been uncovered and create tunable hyperbolic plasmon-phonon polaritons [19–24].

Transition metal dichalcogenides (TMDCs), another elemental building block for vdW heterostructures, harbor extraordinary excitation properties, such as valley selection rules [25–28], electrical control of Coulomb-bound many-body states [29–31], and robust exciton polaritons [32–35]. In principle, excitons in TMDCs would couple to exotic infrared active phonons or hyperbolic phonon polaritons in hBN, enabling another way to generate tunable hyperbolic polaritons [16,17]. Recently, interlayer exciton-phonon coupling (EPC) associated with optically silent $B_{1g}$ phonons in hBN and excitons in TMDCs has been revealed in WSe$_2$/hBN [36–38] and WS$_{0.6}$Se$_{1.4}$/hBN [39] heterostructures, making the optically silent hBN vibration become Raman active and giving rise to an electronic transition. However, quantum layer-layer interactions between excitons in TMDCs and infrared...
active phonons in hBN have remained elusive. Understanding such interlayer exciton-infrared active phonon coupling in TMDCs/hBN heterostructures could be of greater relative importance than the interlayer EPC associated with optically silent $B_{1g}$ modes and provide a firm basis for engineering the tunable hyperbolic exciton-phonon polaritons [12–14,16,17].

In this paper, we identify the interlayer coupling between infrared active $A_{2u}$ phonons and excitons in WS$_2$/hBN vdW heterostructures at room temperature. Moreover, our experiments reveal that the interlayer EPC between the excitons in WS$_2$ and infrared active $A_{2u}$ phonons in hBN is strongly dependent on the hBN thickness. For WS$_2$/few-layer hBN heterostructures, the intensities of infrared active $A_{2u}$ phonons drop sharply with a descent of the hBN thickness, in stark contrast to the $B_{1g}$ modes that show a weak increase.

II. SAMPLE PREPARATION AND CHARACTERIZATION

WS$_2$/hBN heterostructures were obtained via a combination of chemical vapor deposition (CVD) growth and dry transfer. High quality monolayer triangular WS$_2$ ($\sim$100 $\mu$m) were first grown on 300-nm SiO$_2$/Si substrates through a CVD process [40]. Atomically thin WS$_2$ layers were first visually identified by their interference color under the optical microscope and then confirmed by the out-of-plane $A_{1g}$(\Gamma) mode under excitation on resonance with $A$ exciton (see the Supplemental Material [41]). A polydimethylsiloxane stamp was then used to place hBN flakes on monolayer WS$_2$ in a vacuum chamber, forming the WS$_2$/hBN heterostructures. This vacuum transfer method greatly improves the interface quality and minimizes the amount of amorphous carbon or trapped air at the interfaces [42]. The heterostructures were then annealed at 280 °C in an Ar/H$_2$ atmosphere to further clean the interface and improve the layer-layer interactions. Figure 1(a) presents an optical microscope image of the WS$_2$/hBN heterostructures highlighted by red lines. The height image obtained from a tapping mode atomic force microscopy scanning of the square region in Fig. 1(a) is presented in Fig. 1(b). The flat morphology of the heterostructures display very low root-mean-square (RMS) surface roughness of 0.42 nm (see the Supplemental Material [41]), demonstrating that the WS$_2$/hBN heterostructures obtained via vacuum transfer can possess very larger clean and smooth regions (lateral size $>15$ $\mu$m) devoid of bubbles. The height line scan profile indicates that the thickness of hBN is 3.6 nm. The photoluminescence (PL) spectra of WS$_2$ and WS$_2$/hBN heterostructures are shown in Fig. 1(c). Both the WS$_2$ and WS$_2$/hBN heterostructures harbor a single narrow $A$ exciton feature centered at 1.963 eV, indicat-
EPC of WS$_2$/hBN heterostructures at room temperature, the measuring the interlayer EPC. To derive the interlayer exciton of monolayer TMDCs brings much inconvenience.

We can see a prominent difference between WS$_2$ and WS$_2$/hBN scattered light polarization are perpendicular to each), respectively. Spectra of WS$_2$ and WS$_2$/hBN heterostructures excited by polarization-resolved PL spectra of WS$_2$/hBN heterostructures at room temperature. Black and red curves present copolarized configuration (incident light polarization $e_i$ and scattered light polarization $e_s$ are parallel to each) and cross-polarized (incident light polarization and scattered light polarization are perpendicular to each), respectively.

Another way is that we can use the laser radiation on resonance with the other excitons, such as $B$ and $A'$ excitons, since the intensity of these excitons is much weaker than that of the $A$ exciton. In fact, clear signals associated with interlayer EPC have been uncovered in WSe$_2$/hBN heterostructures via resonant coupling to the $A'$ exciton of WSe$_2$ [37,38]. In this paper, we take advantage of the $B$ exciton to obtain clear Raman features about interlayer EPC without the PL background.

Figure 3(c) presents the Raman spectra of hBN, WS$_2$, and WS$_2$/hBN heterostructures excited by 2.33-eV excitation, in resonance with the $B$ exciton of WS$_2$ [49]. Compared with the Raman spectra of hBN and WS$_2$, two Raman signals around 800 cm$^{-1}$ emerge in WS$_2$/hBN heterostructures, indicated by the dashed black vertical lines. Through Lorentzian fitting [Fig. 3(d)], it is known that these two Raman modes locate at 767 and 803 cm$^{-1}$, respectively, which should be Raman forbidden hBN phonons activated in WS$_2$/hBN heterostructures via interlayer EPC [36,37,39]. In addition, the intensities of the Raman forbidden hBN phonons are stronger than that of the Raman active $E_{2g}$ phonon at 1367 cm$^{-1}$. This clearly indicates the strong interlayer EPC.

III. RESULTS AND DISCUSSION

Since interlayer EPC is a defining feature of resonant Raman scattering [36,37], the giant PL background from $A$ exciton of monolayer TMDCs brings much inconvenience in measuring the interlayer EPC. To derive the interlayer EPC of WS$_2$/hBN heterostructures at room temperature, the hindrance of the PL background is more pronounced since PL quantum efficiency is very huge ($\sim 1200$ times larger than that of MoS$_2$ [Fig. 2(a)]) and much larger than that at cryogenic temperature due to dark excitons with lower energy [50–52]. There are two ways to avoid the PL background. First, if WS$_2$/hBN heterostructures have null valley coherence, we can derive the interlayer EPC without the PL background by obtaining clear Raman features about interlayer EPC without the PL background in this method via surface protection [44,45]. Figure 1(d) presents the Raman spectra of hBN and WS$_2$, two Raman signals around 800 cm$^{-1}$ [Fig. 3(d)], it cannot be assigned to the LO mode of infrared active mon polaritons [19–24]. From Fig. 3(d), it can be clearly seen that the active Raman mode with lower energy is at 767 cm$^{-1}$. This clearly indicates the strong interlayer EPC.

The crystal structure of lamellar hBN belongs to the $D_{6h}^1$ ($P6_3/mmc$) group space. According to group theory, the corresponding irreducible representations of phonons at the Brillouin-zone center can be divided into: $\Gamma = 2E_{1u} + 2E_{2g} + 2A_{2u} + 2B_{1g}$ [53–55]. Only the $E_{2g}$ phonon, involving in-plane atomic displacements in the hexagonal layers, is Raman active at 1367 cm$^{-1}$. For the infrared active $A_{2u}$ mode [Fig. 3(a)], the crystal field in hBN gives rise to a splitting between transverse (TO) and longitudinal (LO) optical phonons, located at 767 and 825 cm$^{-1}$, respectively [55]. Due to the presence of electromagnetic fields for the TO mode, it can be strongly coupled with other quasiparticles, such as photon, electron, and plasmon polaritons [19–24]. From Fig. 3(d), it can be clearly seen that the active Raman mode with lower energy is at 767 cm$^{-1}$, matching well with the TO mode of infrared active $A_{2u}$ phonon. While, for the active Raman mode with higher energy [Fig. 3(d)], it cannot be assigned to the LO mode of $A_{2u}$ since the phonon frequency (803 cm$^{-1}$) is obviously different from the LO mode (825 cm$^{-1}$). It makes sense that the excitons in
WS$_2$ do not couple to the LO mode in hBN since the LO mode is accompanied by only an electric field without curl (being akin to an electrostatic field) [56]. In addition, according to theoretical calculations [53], there is another phonon, optically silent $B_{1g}$ [Fig. 3(b)], located around 809 cm$^{-1}$. Despite a little difference, the $B_{1g}$ mode shows qualitative agreement with the active Raman mode with higher energy [Fig. 3(d)]. Recently, Raman forbidden phonons in hBN have been found to be activated in WSe$_2$/hBN heterostructures and locate at 806 and 798 cm$^{-1}$ in Refs. [36] and [37], respectively [57]. We believe that such activated modes in WSe$_2$/hBN heterostructures should be the phonon with higher energy in Fig. 3(d) ($B_{1g}$ mode), since it is quite distinct from both the TO and LO modes of infrared active $A_{2u}$ phonons. The differences between different experimental results may stem from distinct hBN thickness, as will be discussed below. Thus, our results demonstrate the interlayer coupling between the infrared active $A_{2u}$ phonons of hBN and the excitons of WS$_2$, which will shed light on the engineering of hyperbolic exciton-phonon polaritons and chiral phonons [16,17,58–60].
FIG. 4. Raman spectra of SiO$_2$ (black line), WS$_2$/SiO$_2$ (red line), sapphire (blue line), and WS$_2$/sapphire (magenta line) under 2.33-eV excitation.

Figure 3(e) shows the power-dependent Raman spectra of another WS$_2$/hBN heterostructure sample with similar hBN thickness. The Raman intensities increase with the incident power. Figure 3(f) shows the power dependent Raman intensity ratio between the infrared active $A_{2u}$ (optically silent $B_{1g}$) phonon and Raman active $E_{2g}$ phonon at 1367 cm$^{-1}$. It shows that the Raman intensity ratio between the infrared active $A_{2u}$ (optically silent $B_{1g}$) phonon and Raman active $E_{2g}$ phonon is $\sim 2.7$ (1.5) and is independent of the incident light power. In addition, we observe a Raman peak located at 1125 cm$^{-1}$ for WS$_2$ and WS$_2$/hBN heterostructures [Figs. 2(c) and 4]. However, this Raman mode cannot be observed in pristine hBN on SiO$_2$ or WS$_2$ grown on sapphire [Figs. 2(c) and 4]. Therefore, this Raman mode at 1125 cm$^{-1}$ in WS$_2$ and WS$_2$/hBN heterostructures should be the surface phonon mode of SiO$_2$, which resonantly couples to the $B$ exciton of WS$_2$ [12,37,60,61].

Having demystified the interlayer EPC in WS$_2$/hBN heterostructures, we carried out the polarization-resolved Raman spectra to confirm the symmetry of the activated $A_{2u}$ and $B_{1g}$ phonons. Figure 5(a) presents the Raman spectra under copolarization configuration and cross-polarization configuration. It shows that the intensities of both the activated $A_{2u}$ and $B_{1g}$ phonons depend strongly on the polarization configurations and almost disappear in cross-polarization configuration. Figure 5(b) shows the normalized Raman intensity of the $A_{2u}$ and $B_{1g}$ modes as a function of angle $\theta$ between $e_i$ and $e_s$. The black line is the fitting with function of $\cos^2 \theta$.

Figure 6(a) presents the microscopic image of WS$_2$/hBN heterostructures with different thickness of hBN. To rule out extrinsic factors, we focus on such WS$_2$/hBN heterostructures with distinct hBN thicknesses, but fixed twisting angle between hBN, and WS$_2$, and interfacial coupling [65–69]. Figure 6(b) shows the corresponding Raman spectra. It shows that the intensities of activated phonons in WS$_2$/hBN heterostructures strongly depend on the hBN thickness. Figure 6(c) displays the integrated intensities of the infrared active $A_{2u}$ and optically silent $B_{1g}$ phonons in WS$_2$/hBN heterostructures as a function of hBN thickness. With increasing the hBN thickness, the intensities of the infrared active $A_{2u}$ mode are enhanced significantly, while the intensities of the $B_{1g}$ mode decline slowly. Such hBN thickness-driven anticorrelation intensity modulation between $A_{2u}$ and $B_{1g}$ phonons in WS$_2$/hBN heterostructures is fairly amazing since $A_{2u}$ and $B_{1g}$ modes show similar polarization behavior (Fig. 5). Because the interlayer EPC is associated

FIG. 5. (a) Raman spectra of WS$_2$/hBN heterostructures obtained in the co-polarized configuration ($e_i//e_s$) and cross-polarized configuration ($e_i\perp e_s$), where $e_i$ and $e_s$ are the polarization vectors of incident light and scattered photons, respectively. (b) Normalized Raman intensity of $A_{2u}$ and $B_{1g}$ modes as a function of angle $\theta$ between $e_i$ and $e_s$. The black line is the fitting with function of $\cos^2 \theta$. The normalized intensities of both the $A_{2u}$ and $B_{1g}$ phonons harbor the same periodical oscillation and can be fitted well with a cosine function (cos$^2 \theta$), indicating that $A_{2u}$ and $B_{1g}$ phonons possess the same symmetry. The same symmetry is because the interlayer coupling between WS$_2$ and hBN lowers the symmetry of the WS$_2$/hBN heterostructures and both the original $A_{2u}$ and $B_{1g}$ modes of hBN become an $A$ mode [36].

Naturally, the dimensionality of a system has profound impact on both phonons and excitons [38,62–64]. To elaborate the influence of hBN thickness on interlayer EPC of WS$_2$/hBN heterostructures, we covered a thin hBN with various thicknesses on monolayer WS$_2$ by a dry transfer method.

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with the out-of-plane electric dipole of a phonon [37], the physical origin for the hBN thickness-induced anticorrelation intensity modulation may stem from the different electric dipole between the $A_{2u}$ and $B_{1g}$ modes. For the $B_{1g}$ mode, there is an in-phase combination between adjacent layers and therefore, it only has an intralayer electric dipole [Fig. 6(f)]. Because the excitons in WS$_2$ are strongly confined to the 2D plane [70,71], the interlayer EPC in WS$_2$/hBN heterostructures is dominated by the phonons of hBN in the immediate vicinity of WS$_2$. Such a layer-layer interaction should...
decrease with increasing the hBN thickness and disappear for bulk hBN [36,37]. This is in good agreement with our results that the intensities of the $B_{1g}$ mode decline with increasing hBN thickness and are absent in WS$_2$/bulk hBN heterostructures (see the Supplemental Material [41]). In stark contrast, the infrared active $A_{2u}$ mode is a lattice vibration with antiphase displacement in adjacent layers and can possess not only an intralayer electric dipole, but also an interlayer electric dipole [Fig. 6(e)]. The interlayer electric dipole can extend the interlayer EPC to a large volume of phonons spread throughout the hBN that do not interact directly with WS$_2$. Due to volume effect, the intensities of infrared active $A_{2u}$ modes in WS$_2$/few-layer hBN heterostructures can increase with increasing the hBN thickness. In addition to the tunable strength of interlayer EPC, the energy of activated phonons can be also tuned via hBN thickness. Figure 6(d) shows the hBN thickness-dependent phonon energies of the activated $A_{2u}$ and $B_{1g}$ phonons in WS$_2$/hBN heterostructures. With increasing the hBN thickness, the infrared active $A_{2u}$ phonon softens, while the $B_{1g}$ mode stiffens. The evolution of phonon energies with hBN thickness may be the reason for the small difference of $B_{1g}$ phonon frequency between our results [Fig. 3(d)] and the results in Refs. [36] and [37].

IV. CONCLUSIONS

In conclusion, we have measured interlayer EPC of WS$_2$/hBN heterostructures through resonant coupling to the $B$ exciton of WS$_2$ at room temperature. We demonstrate that the infrared active $A_{2u}$ phonons in hBN can strongly couple to the excitons in WS$_2$. Moreover, our results demonstrate that the strength of interlayer EPC can be tuned by hBN thickness. The strength of interlayer EPC associated with the infrared active $A_{2u}$ phonon is almost zero for monolayer hBN and increases sharply with increasing the hBN thickness, in stark contrast to the $B_{1g}$ mode that harbors a weak decrease. In addition, we uncover that the energies of activated phonons could be also tuned by hBN thickness. We believe that our observation of the strong and tunable interlayer coupling between infrared active phonons and excitons will shed light on the manipulation of hybrid quasi-particles and polaritons, and the engineering of optoelectronic applications based on vdW heterostructures.

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