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# Polaritons in layered 2D materials for novel light-matter interactions

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In recent years, one of the most exciting developments in nano-optics has been the observation of enhanced light-matter interactions through a plethora of dipole type polaritonic excitations in two-dimensional (2D) layered materials. In graphene, electrically tunable and highly confined plasmon-polaritons were observed[1–9], opening up opportunities for optoelectronics[10], bio-sensing[11] and other mid-infrared applications[9]. In hexagonal boron nitride (hBN), low loss infrared active phonon-polaritons acquire a hyperbolic behavior for some frequencies[12–14], allowing for ray-like propagation exhibiting high quality factors and hyperlensing effects[15, 16]. In transition metal dichalcogenides (TMDs), reduced screening in the 2D limit leads to optically prominent excitons with large binding energy[17, 18], and their polaritonic modes were also recently observed with scanning near field optical microscopy (SNOM)[19]. We review recent progress in state-of-the-art experiments, survey the vast library of polaritonic modes in 2D materials, their optical spectral properties and figure-of-merits. Taken together, the emerging field of 2D material polaritonics and their hybrids[14] provide enticing avenues for manipulating light-matter interactions across the visible, infrared to terahertz spectral ranges, with new optical control far beyond what can be achieved through traditional bulk materials.

In most materials, electric dipoles (e.g. phonons, excitons and plasmons) can be excited when illuminated[20–23], producing hybrid quasiparticles with photons called *polaritons*. These polaritons are surface electromagnetic modes at the interface between a positive (e.g. normal dielectric) and negative permittivity material. In the case of plasmon-polaritons (PP), the latter is provided by free carrier motion i.e. Drude conductivity. In the case of exciton-polaritons (EP) and phonon-polaritons (PhP), this is associated with their resonant optical absorption, resulting from a highly dispersive permittivity. These optical resonances can lead to a negative permittivity, albeit over a narrow spectral window. These polaritonic excitations are presented in Fig. 1a, together with their Kramers-Kronig dielectric function pairs. These polariton modes are characterized by two related length scales: the polariton wavelength along the interface and the extension in the perpendicular direction, are both smaller than the free-space wavelength. The associated reduced modal volume presents an extremely large local density of

electromagnetic states at the interface, leading to strong light-matter interactions. Hence, polaritonics provide the necessary mechanism to confine, harness and manipulate light at dimensions smaller than the diffraction limit[24, 25]. This review is devoted to the emerging but rapidly developing field on polaritons in 2D materials.

*From metal to graphene plasmon-polaritons.* The most well-known physical realization of polaritons consists of electromagnetic modes bound to a flat interface between a metal and a dielectric, called surface plasmon-polaritons (SPPs)[25]. The field of metal plasmonics has developed tremendously over the last few decades, which includes interesting effects such as extraordinary transmission through nanoholes in metal[26, 27], single molecule detection[28, 29], compact nanophotonics components[30], and novel optical phenomena with metamaterials[31] and metasurfaces[32]. However, metal plasmonics suffers from the problem of absorption, which traditionally has limited the range of possible materials to metals like silver and gold.

The physical characteristics of SPPs in metals are fixed by the material properties but can be changed by changing geometry. For instance, let's consider a thin metal film, where the SPPs at both interfaces couple in symmetric and antisymmetric combinations. The symmetric mode, also often called the "short-range SPP", has the field concentrated in the metal film as illustrated in Fig. 1b for the case where metal film thickness is smaller than its skin depth. This mode is more strongly confined and propagates a smaller distance than the isolated SPP. Graphene plasmons can be understood as the extreme case of such "short-range SPPs" as the thickness approaches the atomic level, and light is being confined to dimensions 2 – 3 orders smaller than that of the free space wavelength.

*State-of-the-art graphene plasmonics.* Besides the extreme light confinement, graphene presents several advantages as compared to metal plasmonics. First, its carrier density, which determines its plasmonic Drude weight, can be electrically[3], chemically[4], or optically[33] tuned. This is due to the fact that graphene is a semimetal with a small density-of-states, where typical carrier concentrations are less than  $\sim 0.01$  electrons per atom, in contrast to the case of gold. The consequence of this lower carrier concentration is that graphene PPs can be stimulated in the terahertz to mid-infrared frequencies[1–4, 9], and in some cases even into the short-wave infrared[34], while metal SPPs are found in the UV, visible to the near-infrared. Second, the low electronic density-of-states and relatively weak electron-phonon coupling endowed graphene with very high intrinsic carrier mobilities, first achieved by suspending graphene[35]. Recent advances in polymer-free van der Waals assembly technique have produced similar high quality graphene by full encapsulation within hexagonal boron nitride (hBN) multilayers[36].

Initial experiments[37] probing the highly confined PPs within high mobility encapsulated graphene were performed using scattering type scanning near field optical microscopy (SNOM), with a schematic of the setup presented in Fig. 1c. In this experiment, the metal-coated AFM tip scatters incident free space light into graphene PPs, where the sharpness of the tip provides the needed momentum to overcome the momentum mismatch between free space photons and the confined PPs. The PP propagates away from the tip as circular waves with complex wavevector  $q$ . The PP propagates towards the edge of the graphene flake, and provided this edge is within the polariton propagation length, will be reflected back towards the tip and picks up as out-scattered light. Spatial scanning of the tip near the graphene edge shows characteristic fringes due to interference between the reflected and incident PPs (see Fig. 1d) from which the complex  $q$  can be extracted. Spacing between fringes under such measurement conditions is the PP half-wavelength i.e.  $\pi/\text{Re}[q]$ , while the decay of the fringes goes exponentially

via  $\exp(-\text{Im}[q]x)$ .

Commonly used figure-of-merits for plasmon-polaritons are;  $\gamma \equiv \text{Im}[q]/\text{Re}[q]$ , where  $\gamma^{-1}/2\pi$  gives the number of cycles the PP can propagate before its amplitude decays by  $1/e$ , and the light confinement factor  $\beta$  is obtained by normalizing  $\text{Re}[q]$  to the free-space wavevector. Experiments with hBN encapsulated graphene has achieved  $\beta \sim 150$  and  $\gamma^{-1} > 25$ [37], see Fig. 1e. Hence, the current state-of-the-art in graphene PP has already surpasses performance of SPPs along air-silver interface, which has  $\gamma^{-1} \approx 10$  across the visible spectral range, where  $\beta > 10$ [5]. In these devices, the inverse damping  $\gamma^{-1}$  was found to be dominated by phonons in graphene and hBN[38], rather than that of extrinsic ionized impurities in earlier experiments on  $\text{SiO}_2$  substrates[1, 2, 39] where  $\gamma^{-1} \sim 5$ . We envision that going forward, these high quality graphene PPs can provide an excellent platform for realizing tunable 2D nanophotonics circuits with novel functionalities not previously attainable[40]. Indeed, steps have already been undertaken to develop resonant optical gold rods antennas and spatial conductivity patterns for the launching and control of propagating PPs[41] as illustrated in Fig. 1f and g respectively. We also envision applications of graphene plasmonics in mid-infrared optoelectronics[10], bio-sensing[11], and free-space beam shaping and steering[42, 43] and anticipate that these fields should continue to develop over the next few years.

*Beyond graphene plasmonics.* Graphene has paved the way for the discovery and exploration of other atomic 2D materials with new physical properties[44], among them new types of PPs. For example, Bernal-stacked bilayer graphene has recently received attention as a new plasmonic material, both theoretically[45] and experimentally[46, 47]. It allows for efficient switching of the plasmonic Drude weight with the application of a vertical electric field[46], due to the opening of an electronic band gap[48, 49]. It also accommodates a mid-infrared-active optical phonon mode[50], which can hybridize with the PPs to feature novel effects such as electromagnetically induced transparency and slow light[47]. This, in addition to other new emerging 2D materials such as TMDs[17, 18] and black phosphorus (BP)[51], presents exciting opportunities for exploring new plasmonic effects[52–55].

It will be very instructive to compare the figure-of-merits of PPs in these 2D materials with gold. In the mid-infrared, SPPs in gold has very poor  $\beta$ . However,  $\beta$  can be increased by considering metal films, and utilizing the "short-range SPP" mode (Fig. 1b). To facilitate comparison, we consider the extreme case (most optimal in terms of  $\beta$ ) with thickness of only 0.235 nm (equals to the separation between (111) atomic planes) gold film. Bulk dielectric constants for gold are used[56]. Optical constants for graphene and its bilayer,  $\text{MoS}_2$ , and BP have been obtained from well-known Kubo formula in

conjunction with their Hamiltonians[45, 52, 53]. In all cases, we have assumed a temperature of 300 K and a n-doped material with a typical doping of  $5 \times 10^{12} \text{ cm}^{-2}$  obtainable with electrical gating[44]. We obtained the free carrier scattering time  $\tau$  from current state-of-the-art experiments[37, 57, 58]. For graphene, its bilayer, and MoS<sub>2</sub>,  $\tau$  is approaching the intrinsic limit determined by their thermal and optical phonons, i.e.  $\tau \sim 1 \text{ ps}$ [38] and  $\sim 0.1 \text{ ps}$ [59] for graphene and MoS<sub>2</sub> respectively. For BP,  $\tau$  can approach  $\sim 1 \text{ ps}$ [60], however, best experiment achieved only  $\sim 0.1 \text{ ps}$ [57]. All calculations are for a configuration where the 2D material is placed on a substrate with dielectric constant of 2.25.

Fig. 2a and b plots the calculated field confinement  $\beta$  and damping ratio  $\gamma^{-1}$  across the far- and mid-infrared frequencies for 2D plasmonic materials and atomic gold film. There is a clear tendency of increasing  $\beta$  with frequency, however, it is only of order 1 for gold even at near-infrared and with hypothetical atomic thickness. On the other hand, 2D materials present much larger  $\beta \sim 100 - 1000$ . This implies 2D materials are clearly better than metals for field enhancement in the mid-infrared. The sudden decrease in  $\beta$  for graphene at around  $3500 \text{ cm}^{-1}$  is due to interband loss, which occurs when the plasmon energy is roughly twice the Fermi energy[61–63]. For bilayer graphene,  $\beta$  degrades drastically in the mid-infrared, but recovers at higher frequency. This behavior is related to the two nested bands in bilayer, separated by  $2400 \text{ cm}^{-1}$  due to interlayer coupling, which transfers the spectral weight to another higher energy plasmonic mode[45]. Here, bilayer provides better  $\beta$  in the far- and near-infrared, while graphene for most of the mid-infrared. Graphene, however, shows better inverse damping ratio of order  $\gamma^{-1} \sim 10 - 100$  across most of the mid-infrared.

Semiconducting TMDs, especially monolayer MoS<sub>2</sub>, have attracted significant attention due to their novel optical dichroic and coupled spin-valley physics [17, 18, 64]. Despite the considerable bandgap of  $\sim 2 \text{ eV}$ , metallic state can still be induced with a vertical electric field if gap trap-states[65, 66] can be sufficiently suppressed. Development of van der Waals heterostructure device platforms where MoS<sub>2</sub> layers are fully encapsulated within hBN represents an important progress in this direction, with a record-high Hall mobility reaching  $34,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for six-layer MoS<sub>2</sub> at low temperature[58]. Interestingly, we found a  $\beta \sim 10^3$ , an order larger than graphene, albeit  $\gamma^{-1}$  is smaller. In addition, pumping with circularly polarized light can lead to a finite transverse conductivity and the appearance of nonreciprocal chiral edge modes as illustrated in Fig. 2c[53, 54]. It should be possible to detect these effects with ultrafast pump-probe SNOM[33] with a small radius of curvature tip of  $\sim 10 \text{ nm}$ .

A new class of anisotropic 2D materials[51, 67, 68] has received considerable attention recently, particularly BP,

which has a bulk gap of 0.3 eV and decent carrier mobility of  $\sim 1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in its thin film state. In BP, the in-plane electronic mass anisotropy can be as large as 10. Due to the anisotropic Drude weights, PPs in BP will be anisotropic[52] as reflected in their  $\beta$  and  $\gamma^{-1}$  as shown in Fig. 2a and b. Anisotropic 2D materials might also host in-plane hyperbolic PP modes[55]. In hyperbolic media, the permittivities along the Cartesian axes are opposite in signs, which fundamentally change how light interacts with matter[69]. The mechanism relies on the interplay between anisotropic intraband and interband motions, which can render capacitive and inductive optical responses along the two axes. In SNOM experiments, these effects could be observed as PP rays launched with an optical antenna as illustrated in Fig. 2c.

*Hyperbolic phonon-polaritons in hBN.* While the in-plane anisotropy of BP results in the potential to realize hyperbolic behavior within the plane of the 2D material, the structural anisotropy in all van der Waals crystals results in a strong optical birefringence, which in the polar varieties of these crystals can also result in hyperbolicity[69]. In these cases, the Cartesian axes with opposite sign permittivities tend to be between the in- and out-of-plane directions. Bulk hBN features two sets of infrared active optical phonon modes now referred to as the lower (“LR”;  $\sim 760 - 825 \text{ cm}^{-1}$ ) and upper (“UR”;  $\sim 1360 - 1620 \text{ cm}^{-1}$ ) Reststrahlen bands. As shown in Fig. 3a, its in-plane permittivity is positive (negative) within the LR (UR), while it is opposite in sign along the out-of-plane  $c$ -axis.

The inversion of signs of the permittivity components between these two bands gives rise to a type I and II hyperbolic behavior within the LR and UR respectively[69], which impacts the resultant dispersion relationships of the in-plane transverse ( $k_t$ ) and out-of-plane ( $k_z$ ) hyperbolic modes. Analogous to PP, incident photons can also couple with these charged lattice oscillations to form phonon polaritons (PhPs)[70]. PhP in hBN was first explored within the UR using SNOM[12] through similar interferometric study as previously described for PP in graphene. This initial experiment already recorded  $\beta \sim 25$  and  $\gamma^{-1} \sim 20$ , which further improved to  $\gamma^{-1} \sim 35$  in a subsequent experiment[16]. Such high  $\gamma^{-1}$  is not surprising since PhPs do not suffer from electronic losses, and is mainly limited by crystal structural quality, which should improve with better growth.

Unlike traditional polaritonic materials, hyperbolic PhP modes exhibit multiple branches within the dispersion relationship as shown in Fig. 3b. While the initial work[12] observed only the fundamental, lowest order hyperbolic modes, work using conical-shaped hBN nanostructures experimentally observed up to 7 and 4 branches within the UR and LR, respectively, by varying the aspect ratio of the structures[13]. Unlike the case of SNOM, where the higher order branches exhibit higher in-plane wavevector,  $k_t$ , for the resonators, the modes increased

in  $k_z$ . As the aspect ratio for these nanostructures is directly proportional to the out-of-plane  $k_z$ , this gives rise to the apparent inversion of the dispersion relationships between Fig. 3b (SNOM) and 3c (nanostructures). Subsequent work using SNOM was able to further map out the first few orders of the  $k_t$  dispersion as well[16].

*Slowing light and imaging within hBN.* The PhP dispersions reported in Ref. [16] and [13] suggest negative (positive) group velocity for the  $k_z$  ( $k_t$ ) modes within the UR, and the opposite sign for the LR. Interestingly, recent time-resolved SNOM measurements were able to demonstrate that it is instead the phase velocity which exhibits negative values[71, 72]. Fig. 3c depicts the launching of PhP from the edge of a gold pad, and visualizing its propagation in the time-domain for PhP in the UR (Fig. 3d) and LR bands (Fig. 3e). By tracing its wave envelope, one can discern that the PhP moves with a positive group velocity regardless of the Reststrahlen band. However, by monitoring the fringe velocity, the sign of the phase velocity can be identified as being negative in the LR, while positive in the UR. Such a negative phase velocity necessarily implies that  $k_t$  is negative. Presumably, for modes where  $k_z$  is changing (e.g. 3D confined resonators), the opposite behavior would be anticipated. These experiments also allowed for direct measurement of the hyperbolic PhP modal lifetimes, recorded to be 1.8 and 0.8 ps in the LR and UR, respectively. The aforementioned measurements found corresponding group velocity for the polaritons of 0.027 and 0.002 times that of light. Such slow moving modes are not appropriate for waveguide applications, however, the long residence times associated with these long modal lifetimes and slow velocities can be extremely beneficial for enhancements of local emitters, molecular vibrational modes and applications where strong-light matter interactions are desired.

Another highly promising application for hyperbolic media that has received a lot of attention is the direct imaging of deeply sub-diffractive objects via the so-called “hyperlens”[73]. Originally demonstrated using hyperbolic metamaterials[74] in the visible, the high optical losses associated with the metal plasmonic constituents and the fabrication complexities have limited its imaging capabilities and resolution to the smallest meta-atom. On the contrary, hyperbolic materials based on hBN are homogeneous, ideally infinite, and low-loss by nature of PhP. Proof-of-principle hyperlens experiments were recently demonstrated[15, 16], as illustrated in Fig. 3f-h. In both works, sub-diffractive metal objects were fabricated on a substrate surface using electron beam lithography (Fig. 3g) and covered with a flat slab of hBN (on the order of 100 nm thick) and imaged using a SNOM (Fig. 3h). Multiple rings result from the PhP modes launched from the edges of the metal nanoparticles at angles dictated by the hyperbolic nature of the PhPs(Fig. 3f). This propagation angle (with respect to the surface normal) results from the fact

that while hyperbolic materials can support very high  $k$  modes, they can only be supported at an angle given by  $\theta = \sqrt{\text{Re}[\epsilon_t]/\text{Re}[\epsilon_z]}$ . As in both the UR and LR of hBN, either  $\epsilon_t$  or  $\epsilon_z$  is negative and dispersive, while the other is positive and nominally constant.

*Natural hyperbolic layered 2D materials beyond hBN.* To this point, research in this area has focused on the natural hyperbolic properties of hBN. However, the natural optical anisotropy associated to van der Waals crystals, and the polar nature of many should in principle offer a broad range of naturally occurring hyperbolic materials covering a very broad spectral range[75–77]. Strong anisotropy in electron motion along the in-plane (metallic) and out-of-plane (insulating) layered materials can lead to hyperbolicity for specific frequency bands, e.g. in graphite and magnesium diboride[76, 78]. Ruthenates have different Drude weights[76] along the in- and out-of-plane axes, and are hyperbolic between the two plasma frequencies. High quality semiconducting TMDs, such as MoS<sub>2</sub>, also accommodate far-infrared anisotropic polar optical phonons, which similar to hBN should result in hyperbolic bands in the Reststrahlen frequencies[79]. Tetradymites, such as Bi<sub>2</sub>Se<sub>3</sub> and Bi<sub>2</sub>Te<sub>3</sub>, should also host such hyperbolic polaritons, albeit in the terahertz regime[80]. In addition, it was recently found that tetradymites can also be hyperbolic in the near-infrared to visible, due to different highly resonant interband transition energies along the in-plane and out-of-plane axes[81]. Lastly, the high T<sub>c</sub> superconducting cuprates are highly metallic in-plane, but with an out-of-plane dielectric response typical of insulator characterized by several Lorentzian type resonances[76].

In Fig. 4, we have compiled representative materials from the above-mentioned layered 2D materials. Their hyperbolicity spectral range, type, and inverse damping ratio  $\gamma^{-1}$  are plotted. Here, we have used the quasistatic approximation and consider only the lowest order mode. In quasistatic limit, the finite thickness does not enter  $\gamma^{-1}$ , thus this allows us to characterize a broad class of materials on equal footing. Among the listed materials, only hBN and Bi<sub>2</sub>Se<sub>3</sub> whose hyperbolicity are phonon in origin, show  $\gamma^{-1} > 10$ .

*Strong excitons in 2D semiconductors.* Over the past few years, a plethora of photoluminescence (PL), absorption, and reflectance experiments have been performed and reported in the literature for several 2D materials, such as TMD monolayers[82–87] (including the distorted 1T phase ReS<sub>2</sub>[88]), BP mono and multilayers[89–92], and, more recently, monolayer organic-inorganic perovskite (OIP) crystals[93], namely (C<sub>4</sub>H<sub>9</sub>NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>. By probing the formation (absorption and reflectance) and recombination (PL) of electron-hole pairs, these experiments have provided us information not only about their optical gaps, which are found to be significantly far from the theoretical quasi-particle bandgaps, but also about the excitonic Rydberg series. Fig. 5a summarizes the ex-

perimentally observed optical gaps (full symbols), which cover a wide range of wavelengths from blue, for monolayer OIPs, all the way to the near-infrared, for BP multilayers. All observed experimental optical gaps are in good agreement with theoretical predictions (open stars) obtained either within Wannier-Mott theory or by Bethe-Salpeter equation (BSE) (see Supp. Info). Our model also suggests possible extension into the mid-infrared with arsenene, a stable analogue of BP but with arsenic atoms.

Binding energies of excitonic states can be obtained by  $E_n = E_{Xn} - E_{QP}$ , where  $E_{Xn}$  and  $E_{QP}$  are the  $n$ -th exciton state energy and quasi-particle band gap, respectively, and are shown in Fig. 5b. Unlike bulk semiconductors, excitons in 2D materials are strongly confined to a plane and experience a reduced screening from its surrounding dielectric environment[94], which modifies the character of the Coulomb interaction potential, leading to non-hydrogenic Rydberg series of exciton states[95]. Excited exciton states within the Rydberg series (i.e.  $2s$ ,  $3s$ ,  $4s$ ... states) have been observed in OIPs[93] and TMDs[95–99], using different methods such as reflectance and absorption spectroscopy, as summarized by circles in Fig. 5b. Triangles in Fig. 5b are excited states with  $p$  symmetry, observed by two-photon luminescence experiments in  $WS_2$  and  $WSe_2$ [96–99]. Notice that, as a consequence of the non-Coulombic electron-hole interaction potential, the degeneracy between  $s$  and  $p$  states is lifted, so that two-photon experiments exhibit peaks in the PL spectra that do not match those of the Rydberg series states[97]. In general, binding energies in 2D materials are about an order of magnitude higher than those of bulk semiconductors,[100, 101] such as Si, Ge and III-V or II-VI alloys, being comparable only to exciton binding energies observed in carbon nanotubes[102] and conjugated polymer chains [103]. Such strong electron-hole interaction makes these materials a playground for investigating excitons and their complexes (trions and biexcitons), which are usually harder to observe in conventional bulk semiconductors. In Fig. 5b, we summarize the recently experimentally observed trions and biexcitons binding energies in 2D materials, which ranges from tens to a hundred meV. All these high binding energies for excitons and their complexes as observed are consistent with theory within the generalized Wannier-Mott model described elsewhere[104]. Such unprecedented tightly bound exciton complexes brings the exciting perspective of realizing efficient energy transfer by driving charged excitons through applied electric fields.

Another important consequence of tightly bound excitons in layered 2D materials is a large spatial overlap of the respective electron- and hole-wavefunctions in the exciton, with the corresponding Bohr radius being on the order of only 1 nm[95, 97, 105]. This leads to a particularly strong coupling of excitons to photons[106], resulting in both large absorption coefficients and effi-

cient emission of the radiation in this class of materials. The absolute absorption values at the excitonic transition peak are as high as 10 – 20% [84, 107, 108] for single layers with sub-nanometer thickness, as shown in Fig. 5c. The corresponding area under the resonance (shaded), proportional to the strength of the light-matter coupling[109], is orders of magnitude larger than the respective values in more conventional inorganic semiconductors, such as GaAs[110, 111].

*Excitons polaritons.* EP was first observed in 2D materials within optical microcavities with TMDs[112–114]. Experimentally observed EP branches[114] in monolayer  $MoS_2$  follow anti-crossing paths over the exciton and cavity mode energy lines, with a Rabi splitting as large as  $\sim 46$  meV. The strong coupling regime, typically defined by the rate of the exciton-phonon scattering being larger than the competing dephasing processes of the two particles, was already shown to be attainable even at room temperature[114]. However, real-space observation of EP with SNOM was observed only very recently[19] in an exfoliated 260 nm  $WSe_2$  thin flake. The field of EPs in 2D materials is still at the nascent stage, and we expect exciting future developments.

*Hybrid polaritons and concluding remarks.* Looking forward, perhaps one of the most intriguing prospect associated with 2D van der Waals crystals is the ability to cleave layers from one another to realize heterostructures of arbitrary constituents and thicknesses[115], and possibly new hybrid polaritons and physics[14, 116–118]. Two recent examples are depicted in Fig. 6. By combining graphene with hBN, one can marry the advantage of tunable PP in graphene with high quality, low loss, PhP in hyperbolic hBN. Recent SNOM measurement performed on graphene-hBN heterostructure[119] (Fig. 6a) reveals coupled PP and PhP mode, which no longer confines within the Reststrahlen band (Fig. 6b). Furthermore, new type of atomic-scale heterostructure of polar dielectric 2D materials can also lead to the creation of a new material resulting from hybridized optic phonon behaviour of the constituents[14].

On the EP front, heterostructures of TMDs where electrons and holes are confined to different layers, as illustrated in Fig. 6c, would allow for the formation of “indirect excitons” at an energy lower than that of its single layer constituents. Many pairs of 2D materials are known to be compatible with the type-II band alignment[120] required for such situation. Having a low oscillator strength, but also lower energy, this charge transfer exciton manifests itself as a clear low energy peak in PL experiments that is absent in absorption experiments[116], as shown in Fig. 6d for a  $WSe_2/MoS_2$  hybrid heterostructure[117]. Such long lived excitons are of great importance e.g. for possibly allowing future observation of their superfluidity and exciton Bose-Einstein condensation at relatively high temperatures[118], as well as for future applications in

solar cells and photodetectors[121], where suppression of electron-hole recombination is required.

In sum, we envision the use of 2D polaritons to offer an exciting avenue for engineering light-matter interactions beyond the diffraction limit across the terahertz to visible spectrum. The ability to manipulate polaritons in the vast library of van der Waals 2D materials, in conjunction to nano- and hetero-structuring, allows for on-demand design of new optical properties not possible with conventional materials.

**Figure 1. State-of-the-art graphene plasmonics.**

(a) Illustration of the dielectric function Kramers Kronig pairs ( $\epsilon_1 + i\epsilon_2$ ) for typical metal, dielectric with polar phonon, and semiconductor with exciton resonance. Field distributions of their plasmon-, phonon-, and exciton-polaritons in 2D material systems are depicted. (b) Illustration of the field distribution for the symmetric “short-range surface plasmon-polariton (SPP)” in metal thin film. Graphene plasmons can be understood as the extreme case of such “short-range SPP”. (c) Schematic of the SNOM measurement, where the probe tip is excited with laser source, launching plasmons radially from the tip, and scattered plasmon collected by the tip. Simulated in-plane component of the electric field of a dipole source oscillating at a photon energy of 116 meV couples to graphene plasmon are illustrated in red and blue. (d) Measured optical signal from 2D scan of the tip with SNOM, near the graphene edge (dashed line) at room temperature. Plasmons are reflected off the graphene edge, and appear as interference fringes. (e) Calculated graphene plasmon inverse damping ratios,  $\gamma^{-1}$ , due to graphene acoustic phonons (blue dashed line), substrate phonons of hBN (yellow dashed line), and the combination of these mechanisms.  $\gamma^{-1}$  due to charge impurities at concentration  $1.9 \times 10^{11} \text{ cm}^{-2}$  (green dashed-dotted line) are also displayed. Experimental measured  $\gamma^{-1}$  are shown in solid symbols with error bars representing the 95 % confidence intervals. (f) Experimental SNOM image of a convex Au antenna extremity due to laser excitation at  $11.06 \mu\text{m}$ , demonstrating the possibility of plasmon launching and wavefront engineering in graphene. (g) Similar SNOM image of refraction of graphene plasmon launched from Au antenna due to a graphene bilayer prism as indicated. (c-e) adapted with permission from Ref. [37]. (f-g) adapted with permission from Ref. [41].

**Figure 2. Mid-infrared plasmons beyond graphene.**

Calculated confinement factor,  $\beta$ , and inverse damping ratio,  $\gamma^{-1}$ , for various 2D materials such as graphene, bilayer graphene, black phosphorus (BP), and  $\text{MoS}_2$ , displayed in (a) and (b) respectively. BP exhibits highly anisotropic in-plane electronic dispersion, with effective masses along the two crystal axes differing by a factor of  $\sim 10$ . We displayed results for both the high ( $x$ ) and low ( $y$ ) mass directions. Details of calculation are described in Supp. Info. (c) Illustration of plasmon wavefront launched from a nanodot antenna. In isotropic material like graphene, one expects a circular wavefront. In massive Dirac materials such as  $\text{MoS}_2$ , optical pumping with circular polarized light can induced non-zero chirality, leading to non-reciprocal one-way propagating edge mode[53]. In anisotropic 2D materials like BP, hyperbolic dispersion might be possible at some frequencies[55], leading to plasmon propagation at well-defined directions.

**Figure 3. Hyperbolic phonon-polaritons in hBN.** (a) Real parts of the in-plane ( $\epsilon_t$ ) and out-of-plane ( $\epsilon_z$ ) permittivity tensor components of hBN. Type I lower and II upper Reststrahlen bands are shaded. A schematic of the hBN crystal structure is presented in the inset. (b) Phonon-polariton dispersion within Reststrahlen bands experimentally obtained from the SNOM images near edges of 105 nm thick hBN, versus in-plane momenta  $k_t$  (solid symbols). Solid lines are theory. (c) Hyperbolic phonon polariton dispersion of the out-of-plane wavevector  $k_z$  as determined by the aspect ratio dependence of the resonance frequencies for difference conical shaped nanostructures. This is plotted for both the upper (top) and lower (lower) Reststrahlen band. The solid lines are analytical calculations for ellipsoidal particles, while the various symbols indicate the resonant frequencies for experimental conical nanostructures. (d) Schematic of time-domain SNOM measurement of phonon-polariton in hBN. Incident mid-infrared light incident on the Au antenna launches hyperbolic polaritons in hBN, which propagates away from the Au edge and decay exponentially in amplitude and collected by the nanotip. (e-f) Line scans of the SNOM amplitude taken as a function of the delay time between the incident (on Au) and detected fields (by tip). The polaritons group velocity (measured for frequency within the type II and I Reststrahlen bands respectively) can be extracted from the rate at which the ‘envelope’ of the fields propagate away from the Au edge, while the phase velocity’s sign and magnitude can be determined from the direction and speed of the red/blue fringes with respect to the envelope. (g) Schematic showing the launching of hBN hyperbolic phonon polaritons from edges of Au disc, when it is illuminated with mid-infrared light. (h) AFM image of Au disks defined lithographically on SiO<sub>2</sub>/Si substrate before the hBN transfer. (i) SNOM image of a 395 nm thick hBN at laser frequency  $\omega = 1515 \text{ cm}^{-1}$ , where the observed “rings” produced by the hyperbolic polaritons are concentric with the Au disks. (a,c) adapted with permission from Ref. [13]. (b,g-i) adapted with permission from Ref. [16]. (d-f) adapted with permission from Ref. [71].

**Figure 4. Hyperbolic polaritons beyond hBN.** Frequency chart showing the type I and II hyperbolic range for various naturally occurring hyperbolic layered materials, i.e. cuprates [76] (BSCCO (Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>n-1</sub>Cu<sub>n</sub>O<sub>2n+4+x</sub>), GBCO (GdBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>), LASCO (La<sub>1.92</sub>Sr<sub>0.08</sub>CuO<sub>4</sub>)), ruthenates [76] (SRU (Sr<sub>2</sub>RuO<sub>4</sub>), SR3U (Sr<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub>)), hBN [12, 13], TMDs [79], tetradymites (Bi<sub>2</sub>Se<sub>3</sub>) [80], and graphite [76, 78]. Color map depicts the calculated figure of merit  $\Re\{q\}/\Im\{q\}$  for the lowest polaritonic mode in the quasi-static limit. Dielectric functions of these materials are obtained from

references as cited.

**Figure 5. Excitons in TMDs and beyond.** (a) Survey of experimentally observed optical band-gaps (full symbols) in different 2D materials: OI in both phases (I and II) [93], WS<sub>2</sub>, WSe<sub>2</sub> [95–99], MoS<sub>2</sub>, [82–85], MoSe<sub>2</sub> [86, 87], ReS<sub>2</sub> [67, 88], ReSe<sub>2</sub> [122]; and  $n$ -layers black phosphorus (n-BP). [89–92, 123]. We note that for anisotropic materials like ReS<sub>2</sub>, ReSe<sub>2</sub> and n-BP, the optical spectra is polarization sensitive, and the optical gap is defined by the lowest energy resonance. Open symbols are theoretical calculations based on the Wannier Mott model. Theoretical predictions of quasi-particle (open squares) [124, 125] and optical (blue stars) gaps for  $n$ -As are shown, extending the frequency window into the mid-infrared. (b) Binding energies of exciton states in upper panel, in their Rydberg sequence for s-states (solid circle) and p-states (solid triangle), as well as trions and biexcitons in lower panel. Sketches of the electron-hole structure of these excitonic complexes are illustrated on right. These binding energies can be obtained from the observed optical bandgap and the quasiparticle gaps, see Supp. Info. (c) Measured absorption spectrum of a single WS<sub>2</sub> layer, as sketched in the inset. Adapted with permission from Ref. [126].

**Figure 6. Hybrid polaritonics.** (a) Schematic of SNOM experiment performed on graphene-hBN heterostructure. (b) Experimental dispersions of hybrid plasmon-phonon-polaritons (blue circles) obtained from graphene-hBN heterostructure, compared against phonon-polariton (red triangle) from hBN. Theory are provided as white lines and color map. (a-b) adapted with permission from Ref. [119]. (c) Sketch of a charge-transfer (indirect) exciton in a van der Waals heterostructure with type-II band alignment. (d) Photoluminescence and absorption spectra of WSe<sub>2</sub> and MoS<sub>2</sub> monolayers and their hybrid heterostructure. Reproduced from Ref. [117].



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