

QUANTUM MATERIALS

The quest for ultrafast plasmonics

Black phosphorous, a van der Waals layered semiconductor, is reported to reveal a plasmonic response that can be initiated by photoexcitation with femtosecond pulses.

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Besides graphene, the family of single- or few-layer crystalline materials today includes members as diverse as semiconductors (MoS₂ and other transition-metal dichalcogenides, black phosphorus), superconductors (NbSe₂, FeSe), wide-gap insulators (hexagonal-BN), topological insulators (Bi₂Se₃) and ferromagnets (CrI₃). Many physical properties of these van der Waals materials (so-called after the weak forces that hold together individual atomic planes in these crystals) can be dynamically controlled by an applied electric field and/or photoexcitation, providing a versatile platform for investigating quantum phenomena and for applications in electronics and photonics.

Of particular interest is the exploration of plasmon polaritons — hybrid light-matter modes involving the collective oscillation of mobile charges¹. In graphene, plasmon polaritons have been exploited to confine and manipulate infrared radiation to length scales as short as tens of nanometres. These compact polaritons can propagate over a micrometre-range distance² and their wavelength can be electrically controlled^{3,4}. Moreover, switching of graphene plasmons with femtosecond pulses has been demonstrated by heating of the electron gas⁵, a process however that is not ideal for practical devices. Writing in *Nature Nanotechnology*, Miriam Vitiello, Tyler Cocker and colleagues, from the Scuola Normale Superiore in Italy and the University of Regensburg in Germany, now report both imaging of compact, long-range propagating plasmon-phonon polaritons and their ultrafast optical switching in black phosphorous⁶. In particular, they present evidence that the plasmonic response in this semiconductor can be initiated by femtosecond pulses through direct excitation of electrons across the bandgap.

Black phosphorous is a direct bandgap semiconductor. The magnitude of the bandgap is determined by the number of atomic layers and can vary between 1.5–2.0 eV (monolayer) and 0.3 eV (bulk)⁷, an important energy range for telecommunications, optoelectronics and energy-harvesting applications. Unlike in

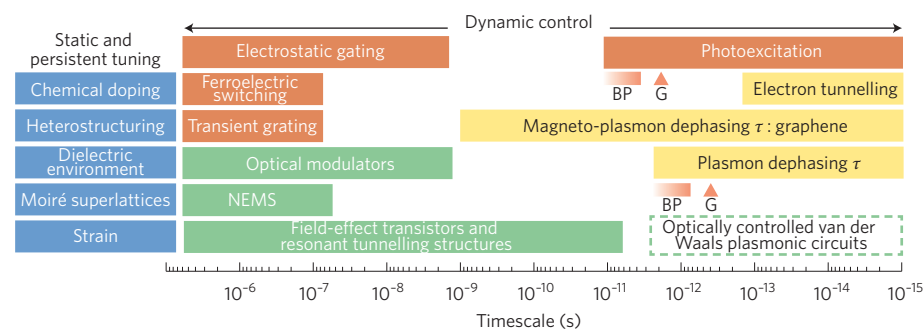


Figure 1 | Methods for controlling plasmons in van der Waals materials and the corresponding timescales. Static and persistent tuning methods are displayed in the blue boxes; dynamical control methods are displayed in the orange ones. The yellow boxes show the dephasing times (τ) of plasmons and magneto-plasmons in van der Waals materials along with characteristic timescales of electron tunnelling in these systems. The green boxes represent timescales pertinent for various photonics technologies. The box with the dashed green outline indicates the desired timescales for future ultrafast plasmonic circuits. NEMS: nanoelectromechanical systems; BP: black phosphorous; G: graphene.

graphene, which is gapless, plasmonic control in black phosphorous can be accomplished via photoexcitation of electron-hole pairs across the bandgap. In the case of Vitiello, Cocker and colleagues' system, a 110-nm-thick black phosphorous sample is sandwiched between two SiO₂ layers. Ultrafast pump-probe spectroscopy data taken before the pump pulses reach the sample show no plasmonic response, with the spectra being dominated by the phonons of the SiO₂ layers. On photoexcitation, however, oscillations in infrared images with spatial periodicity of ~1 μ m emerge. The researchers posit that the oscillating pattern is due to a hybrid plasmon-phonon mode between the plasmons in the black phosphorous and the surface phonons in the SiO₂, given that the frequency range of this photoinduced mode overlaps with that of the SiO₂ phonons. Surprisingly, this photogenerated mode appears to have a very weak dissipation (bottom yellow box in Fig. 1).

The demonstration of *in operando* control of plasmon-phonon polaritons in black phosphorous heterostructures by optical pulses can be an important advance in the quest for ultrafast plasmonics. Notable previous efforts include experiments on aluminium films, which demonstrated

ultrafast control of plasmon amplitude via a transient nonlinear photoresponse^{8,9}. However, real-space propagation of photoinduced plasmons in a semiconductor has remained challenging because it has been difficult to combine nanoscale imaging with ultrafast optical excitations. Vitiello, Cocker and colleagues have now overcome this obstacle and imaged a collective mode produced via photogeneration of carriers in semiconducting black phosphorous.

In Fig. 1, we summarize some of the common methods for controlling the plasmonic response in van der Waals materials. Although available data pertain predominantly to graphene-based structures, the demonstration of dynamic control of plasmons in black phosphorous gives hope that this may soon be possible in other van der Waals plasmonic materials as well. Desired plasmonic characteristics can be attained by changing the carrier density in the media supporting the plasmons. This task can be accomplished using chemical doping, variation of the dielectric environment, strain and by heterostructuring¹ (blue boxes in Fig. 1).

When the carrier density is varied dynamically, the plasmons acquire a

time-dependent frequency $\omega(t)$, with a rise or fall characterized by the timescale $t_c = \omega|d\omega/dt|^{-1}$. Representative t_c (orange boxes in Fig. 1) span a dynamic range of many decades. Manipulation of plasmons with gating electrodes or transient gratings typically yield t_c no faster than nanoseconds, whereas optical pulses enable access to femtosecond timescales.

The magnitude of t_c is governed by either the excitation or relaxation mechanisms of the electronic system for rising or falling $\omega(t)$, respectively. An example of rising $\omega(t)$ is the creation of the population inversion or hot carriers, which occurs on sub-picosecond timescales; an example of falling $\omega(t)$ is the cooling of hot carriers by emission of acoustic phonons, which leads to t_c of the order of a few picoseconds⁵. In some cases, emission of optical phonons or tunnelling of hot carriers across atomically thin barriers can yield to t_c as short as 10–30 fs (ref. 10).

Another critically important timescale is the plasmon dephasing time τ (yellow boxes in Fig. 1). The dephasing time measures

plasmonic losses originating from three principal factors: (1) carrier relaxation (including tunnelling processes¹⁰); (2) plasmon scattering by defects and inhomogeneities; and (3) dielectric losses in the layers proximal to the plasmonic medium. The propagation of non-equilibrium plasmonic waves can only be observed provided $t_c > \tau$. For highly confined plasmons in graphene, τ can approach a fraction of a picosecond at room temperature⁵ and the propagation lengths reported by Vitiello, Cocker and colleagues seem to imply still longer τ in black phosphorous (the orange triangles and bars, respectively, in Fig. 1).

Plasmon losses in semiconductors can in principle be compensated using optical gain^{9,11} or parametric amplification¹², thus increasing τ . Achieving long plasmon lifetimes in combination with rapid control times will eventually enable ultrafast plasmonic circuits, modulators and switches for a variety of nanophotonic applications.

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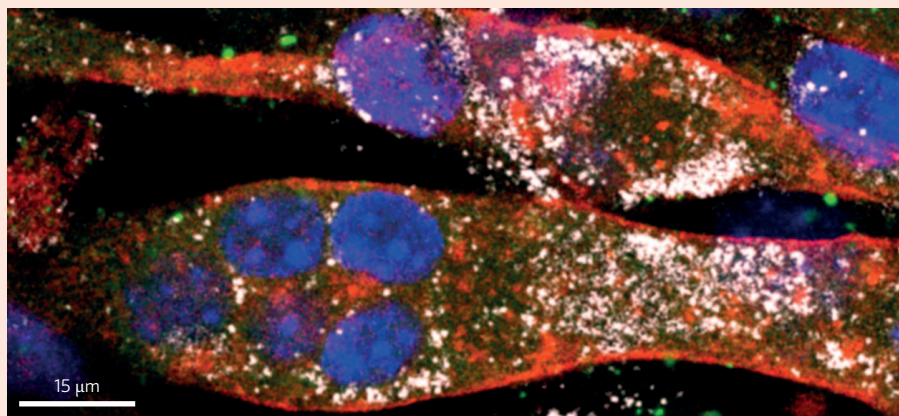
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GOLD NANOPARTICLES

A warm-up for muscle cells

To grow artificial muscles or mend natural tissues it is necessary to stimulate muscle cell contraction and differentiation. *In vitro*, this is typically achieved by electrical stimulation, mechanical stretching or light pulses. Each method, however, presents challenges in terms of generation of toxic by-products, invasiveness or limited applicability. A. Marino *et al.* now show that mild photothermal stimulation can also activate myotube contraction (ACS *Nano* <http://doi.org/bznk>; 2017).

To do so they use silica-gold core-shell nanoparticles that absorb in the near-infrared (the ability to penetrate through deep layers of tissues makes the near-infrared the spectral region of choice for nanomedical applications). When they incubate the myotubes with the nanoparticles and irradiate with near-infrared light pulses, the authors measure a 5 °C increase in the local temperature. Concomitantly, they observe a large increase in myotube contraction compared with control cells subjected to irradiation but with no nanoparticles. In line with previous reports, they demonstrate that the enhanced contraction is related to an increase in the interaction between the two major protein filaments in the myotubes,



actin and myosin. This is a potential advantage over alternative treatments such as electro-stimulation, which works by modulating the cytosolic calcium levels and thus is associated with an increased risk of cell death due to an elevated intracellular concentration of this ion.

Additionally, under an extended heat treatment, during which cells are repeatedly irradiated with near-infrared pulses for five days, Marino *et al.* also observe the overexpression of heat shock proteins, which have been shown to protect tissues from apoptotic damage and to promote

mitochondria biogenesis. The authors suggest that these observations could be used to design a wireless system for switching on muscle contraction *in vivo* while boosting the defences against apoptosis and skeletal muscle loss.

The confocal fluorescence image depicts the cytoplasmic localization of the core-shell nanoparticles (white) in C2C12 muscle cells; cell nuclei are shown in blue, and the actin and myosin filaments in red and green, respectively.

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