

Spectroscopic signature of interlayer coupling in Black phosphorus-graphite heterostructure

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Abstract: We reveal a pump-polarization-dependent spectroscopic signature of interlayer coupling in a black phosphorus-graphite heterostructure by probing its ultrafast photo-response. The angle-resolved transients provide new insights into the interfacial carrier dynamics in this emerging hybrid system.

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1. Introduction:

Heterostructures are the backbone of modern semiconductor industry and one key concept in solid state science which have been applied for many fields [1]. Due to their atomic thickness and rich optoelectronic properties, two-dimensional (2d) crystals have become important building blocks for forming heterostructures with unprecedented functionalities. Elucidating the interlayer coupling in these van der Waals systems are not only fundamentally important for uncovering new physics, but also are essential for providing important guidelines for engineering heterostructures with desirable photoresponse. Optical characterization methods, such as Raman, photoluminescence (PL) and ultrafast spectroscopies, have been applied for identifying the interlayer coupling in heterostructures [2-4]. For instance, interlayer exciton, a form of electric polarization across van der Waals heterostructures formed by transition metal dichalcogenides (TMDs), is characterized by new photoemission at specific energies [3]. Furthermore, charge transfer induced by interlayer coupling has been observed in MoS₂/WS₂ heterostructure, as evidenced by the photoluminescence quenching and the enhancement of Raman intensity [4]. But for black phosphorus (BP), an emerging 2d materials with unique potential in optoelectronics, investigation on interfacial coupling is still very limited [5-6].

Here we address this issue by using ultrafast spectroscopy to investigate the interlayer coupling in a black phosphorus-graphite heterostructure. The spectroscopic signature of interlayer coupling has been observed in our experiment. Specifically, the interlayer coupling not only reduces the amplitude of ultrafast nonlinear response of the heterostructure, but also induce a polarization-dependent transient in the early stage (within 25 ps) of the decay curves. Our results provide evidence for the existence of interlayer coupling in black phosphorus-graphite heterostructure.

2. Results and discussion

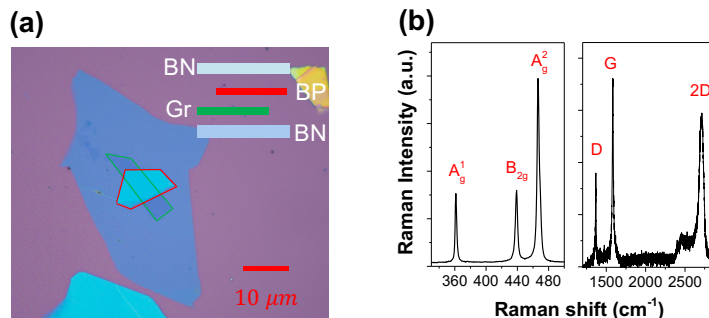


Fig.1 (a) Optical micrograph of an exfoliated few-layer black phosphorus flake on a SiO₂/Si substrate. The inset shows the structure of the sample (BN/graphite/black phosphorus/BN) and the scale bar is 10 μm; (b) Raman spectrum of the graphite/black phosphorus heterostructure, left panel shows three Raman modes of BP and right panel exhibits those of graphene.

The few-layer black phosphorus and graphite are prepared by mechanical exfoliation and are transferred to form a vertical black phosphorus-graphite heterostructure, as shown in Fig. 1(a). The inset of Fig. 1(a) illustrates the detailed multilayer structure within the stack. The top and bottom boron nitride (BN) flakes are used to protect the BP from degradation. In addition, atomic force microscopy (AFM) is performed in this sample and the cross-sectional profiles show that the thickness of black phosphorus is about 10 nm and that of the graphite is about 3 nm. Raman spectroscopy shows not only the three main Raman peaks of black phosphorus: the out-of-plane mode A_g^1 at 361 cm^{-1} , and the in-plane mode B_{2g} and the A_g^2 at 439 cm^{-1} and 466 cm^{-1} ; but also the D, G and 2D peaks of graphene at 1367

cm^{-1} , 1582 cm^{-1} and 2714 cm^{-1} . The Raman shapes and positions are consistent with pristine black phosphorus and graphite, which confirms no significant perturbation to either materials. All characterizations confirm the high quality of the heterostructure.

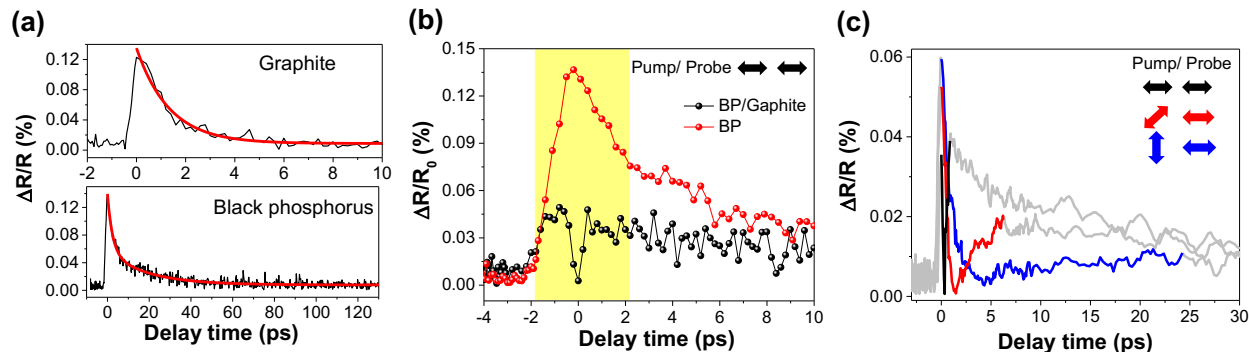


Fig. 2 Photocarrier dynamics in graphite, black phosphorus and their heterostructure. Upper panel in (a) shows differential reflection ($\Delta R/R_0$) measured from a 3 nm-thick graphite and the lower panel exhibits the signal from 10 nm-thick black phosphorus. Red lines are the fitting curves. (b) decay curves of BP and its heterostructure within the first 10 ps; (c) transient reflectance of the heterostructure under different pump polarization (probe is kept parallel to x axis of black phosphorus)

The transient measurements of the heterostructure are carried out with a 76-MHz mode-locked Ti: Sapphire laser, which can generate 100-fs pulses with a center wavelength in the range 790-820nm. The laser is used to pump an optical parametric oscillator (OPO), which outputs 1100 nm pulse as the probe. And the rest part of the laser works as the pump beam to excite electrons into the conduction band. The reflected probe beam is directed to a photodetector, whose output is measured by a lock-in amplifier. A 80X objective is used to focus the pump and probe beams on the samples and the spot size is about $2\ \mu\text{m}$. The use of relatively long wavelength NIR pump (800 nm) and probe (1100 nm) can effectively avoid artifacts from the substrates. The polarization of the probe is kept parallel to x axis in BP.

The representative photocarrier dynamics of few-layer graphite and black phosphorus are summarized in Fig. 2(a). While graphite shows a single-exponential decay with a time constant of 1.3 ps, BP exhibits a bi-exponential relaxation process. The fast time constant of 2.5 ps and the slower time constant of 19.5 ps are attributed to the electron-electron annihilation and electron-hole recombination respectively. The huge difference between the decay curves of the multi-layer black phosphorus (red) and the heterostructure (black), when the pump closely parallels with the x -axis of BP, is shown in Fig. 2(b). Firstly, the amplitude of the transient response in the heterostructure is reduced by at least 60% compared with that of black phosphorus, probably resulting from interlayer charge transfer in the heterostructure. Secondly, a rather abrupt dip appears at the beginning of the decay curves, pointing to rather fast carrier migration across the BP-graphite interface. Interestingly, the dip also shows appreciable polarization dependence, as seen in Fig. 2(c). When the polarization of the pump laser is close to the y axis of black phosphorus, the dip signature is seen to become elongated in time. This means that the interlayer coupling, both in terms of strength and transient, is modulated by the anisotropy of the constituent black phosphorus. Our observation provides new and important evidence for resolving the still elusive photocarrier dynamics at heterostructures involving BP.

3. Conclusion

In summary, we have for the first time investigated ultrafast photocarrier dynamics of black phosphorus-graphite heterostructure and discovered a spectroscopic signature pointing to angle-dependent interlayer coupling. Interestingly, our experimental results suggest pump-polarization may modulate the characteristic time constants of inter-layer charge transfer. Such an interesting phenomenon provides important physical insights into the interfacial carrier dynamics of BP based 2d heterostructures.

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