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## *Two-dimensional crystals: Phosphorus joins the family*

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Subject area: TWO-DIMENSIONAL CRYSTALS

Title: Phosphorous joins the family

Standfirst: Transistor devices can be fabricated from exfoliated layers of black phosphorous.

Hugh O.H. Churchill and Pablo Jarillo-Herrero

Graphene was first isolated by exfoliating single layers from a graphite crystal using Scotch tape<sup>1</sup>. This method was later applied to other materials with layered structures<sup>2</sup>, creating a family of atomically-layered materials which includes insulators such as hexagonal boron nitride, metals such as NbSe<sub>2</sub>, and semiconductors such as MoS<sub>2</sub> and WSe<sub>2</sub>. All of these materials had been studied for decades in bulk form, but their exfoliated, two-dimensional form gave them new life and new properties. Writing in *Nature Nanotechnology*, Xian Hui Chen, Yuanbo Zhang and co-workers have now similarly brought back black phosphorus to the spotlight<sup>3</sup>, which is the most stable and least reactive form of elemental phosphorus, which was discovered in bulk form 100 years ago.

The researchers – who are based at Fudan University and the University of Science and Technology of China – fabricated micron-sized flakes of semiconducting black phosphorus (Fig. 1a) that were only a few nanometres thick and then used them to create field-effect transistors. They show that black phosphorus is the only elemental two-dimensional material, apart from graphene, that is capable of supporting electronic devices. The field-effect transistors demonstrated in this new work highlight attractive characteristics of black phosphorus, with large room-temperature on-off ratios of 10<sup>5</sup> for ultra-thin devices, well developed current saturation, and a peak field-effect mobility near 1000 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for 10 nm thick flakes.

In the context of electronic applications, research in layered materials aims to develop devices built entirely out of ultrathin, flexible and transparent two-dimensional materials. The energy band gap is one of the most important properties in any electronic material and can range from zero (in metals) to several electron-volts (in insulators). Ideally, this range of band gap energies should be available in layered materials in order to develop

the widest possible range of electronic devices. However, so far the values available in such materials range from zero to about 0.3 eV (in graphene and the metallic dichalcogenides), and from 1 to 2 eV (in semiconducting dichalcogenides).

The band gap of semiconducting dichalcogenides increases by about 50% as the material is thinned from bulk to monolayer, and this thickness dependence is predicted to be even more pronounced in black phosphorus<sup>5</sup>. Bulk black phosphorus has a band gap of 0.3 eV, which is expected to increase to between 0.8 and 1.5 eV for an isolated monolayer<sup>5,6</sup>. The band gaps in black phosphorus have values between those of graphene and the semiconducting dichalcogenides, and, as a result, nearly the entire range of between 0 and 2 eV can now be provided by layered materials (Fig. 1b). Furthermore, the band gaps of black phosphorus should make the material useful in a variety of settings, from infrared optoelectronics to high-mobility quantum transport. Unlike semiconducting dichalcogenides, in which multilayers have an indirect band gap, the band gap of black phosphorus is expected to be direct for all thicknesses, a significant benefit for optoelectronic applications.

Black phosphorus layers also have an anisotropic structure, unique among layered materials. Individual layers are buckled (Fig. 1a), with two in-plane, mutually perpendicular directions having armchair and zigzag edges. The structural anisotropy strongly influences the electronic properties in these two directions. The electron effective mass, for example, is several times lighter in the armchair direction than in the zigzag direction<sup>7</sup>, and recent studies have indeed shown a strong angular dependence of the conductivity of few-layer black phosphorus<sup>8,9</sup>.

One intriguing prospect is that in heterostructures created from black phosphorus and other layered materials, the anisotropy of black phosphorus could 'leak' into neighbouring layers and induce new characteristics and capabilities. For example, graphene – which is isotropic – may inherit anisotropic electrical, optical, or mechanical properties when draped over black phosphorus. It is also worth noting that similar buckling also occurs for the layered semiconductors silicene and germanene, but electronic devices have not yet been fabricated with these materials because they have so far had to remain bound to metal growth substrates.

Black phosphorus is an exciting rediscovery for the material science community and it has quickly become the subject of significant theoretical and experimental investigations. However, it is not yet clear how well thin black phosphorus performs compared with other layered materials such as graphene and MoS<sub>2</sub>. Zhang and colleagues do show that the electronic mobility – a key indicator of device quality – reaches promising values of around 1,000 cm<sup>2</sup>/Vs in multilayer black phosphorus devices, but the mobility drops as the material is thinned down<sup>3</sup>. As a result, an 8-nm-thick film of black phosphorus (about 15 layers) is shown to have a mobility comparable to the best devices made from monolayer MoS<sub>2</sub>. Furthermore, although black phosphorus is the most stable allotrope of phosphorus, it may not be as robust in air as other layered materials<sup>9</sup>. This may partially explain the mobility degradation of thinner films, and could be overcome by exfoliating and encapsulating few-layer black phosphorus while in an inert atmosphere.

Devices based on monolayer black phosphorus – known as phosphorene – have not yet been fabricated, but following the work of Zhang and colleagues on few layer black phosphorus, it is the natural next step for the field.

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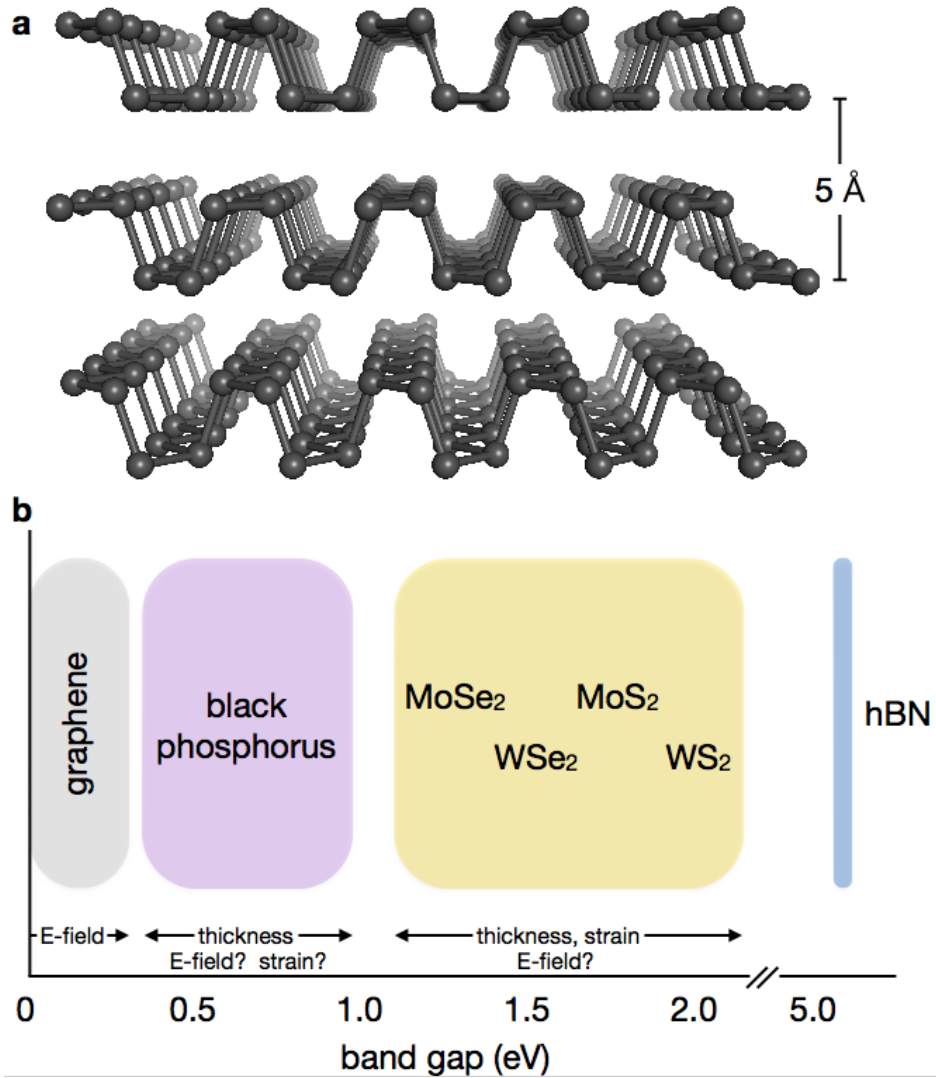


Figure 1 | **a**, The layered and anisotropic crystal structure of elemental black phosphorus. **b**, Band gap energies of several layered materials used for nanoelectronics. The ranges for each material span the values achieved through a variety of means, including perpendicular electric field, film thickness and strain.

