

# Why all the fuss about 2D semiconductors?

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Graphene is no longer alone; a family of atomically thin 2D semiconductors has emerged. Optoelectronics and photonics applications are in their experimental infancy but the future holds much promise.

The isolation of mechanically exfoliated graphene in 2004<sup>1</sup> sparked research on 2D materials that is growing at a tremendous rate. It is often argued that the success of this research field is sustained by the potential of these materials to have a disruptive impact in different technological areas such as electronics and optoelectronics. However, at this stage most of the works on these systems are still focused on addressing fundamental questions and thus we might run the risk of selling empty promises and creating expectations in society that might not be fulfilled in the near future. One of the real key factors behind the rise of this research field is that mechanical exfoliation has democratized materials science as high-quality samples, showing an interesting plethora of physical phenomena, can be prepared in almost any laboratory even without specialized and expensive equipment. Just with a piece of a bulk, layered material, a roll of tape and an optical microscope any trained researcher can isolate atomically thin layers of many different 2D materials ranging from wide-bandgap insulators to superconductors. Since 2010–2011 this relatively young field has experienced a new boost, originating from the works on the semiconducting ‘cousins’ of graphene, that is, atomically thin, or 2D, semiconductors<sup>2–4</sup>. Are we just entering a new ‘hype’ phase, or are there intrinsic and profound reasons to justify the excitement of the scientific community.

One can analyse the surge of interest in 2D semiconductors as being motivated by the limited success in opening a sizeable bandgap in graphene. Indeed, soon after the isolation of graphene, a big part of the scientific community realized that although graphene shows a remarkably high carrier mobility, is flexible (and

tough) and almost transparent, its lack of a bandgap can be a severe limitation for its use in certain applications.

Therefore, from 2007–2008 great efforts were made to open a sizeable bandgap in graphene by patterning graphene into nanoribbons<sup>5</sup>, by hydrogenation<sup>6</sup> or by applying a perpendicular electric field<sup>7</sup>, none of which were entirely successful. Another part of the community focused on finding semiconducting counterparts to graphene rather than modifying it to open a bandgap.

So far, more than ten different 2D semiconductors (with bandgap values spanning from a few millielectronvolts up to several electronvolts) have been experimentally isolated and there are potentially hundreds more that could be isolated in the near future. Because of this broad catalogue of materials, it is always possible to find a 2D semiconductor that is optimal for a certain application (Fig. 1). Table 1 shows a comparison of some relevant properties of the most studied 2D semiconductors for optoelectronics and photonics applications. Moreover, most of the 2D semiconductor families studied so far have also shown interesting phenomena, some of them observed for the first time in these 2D systems. In the following, the most relevant families of 2D semiconductors will be introduced, highlighting the aspects that make them especially interesting.

## Transition metal dichalcogenides

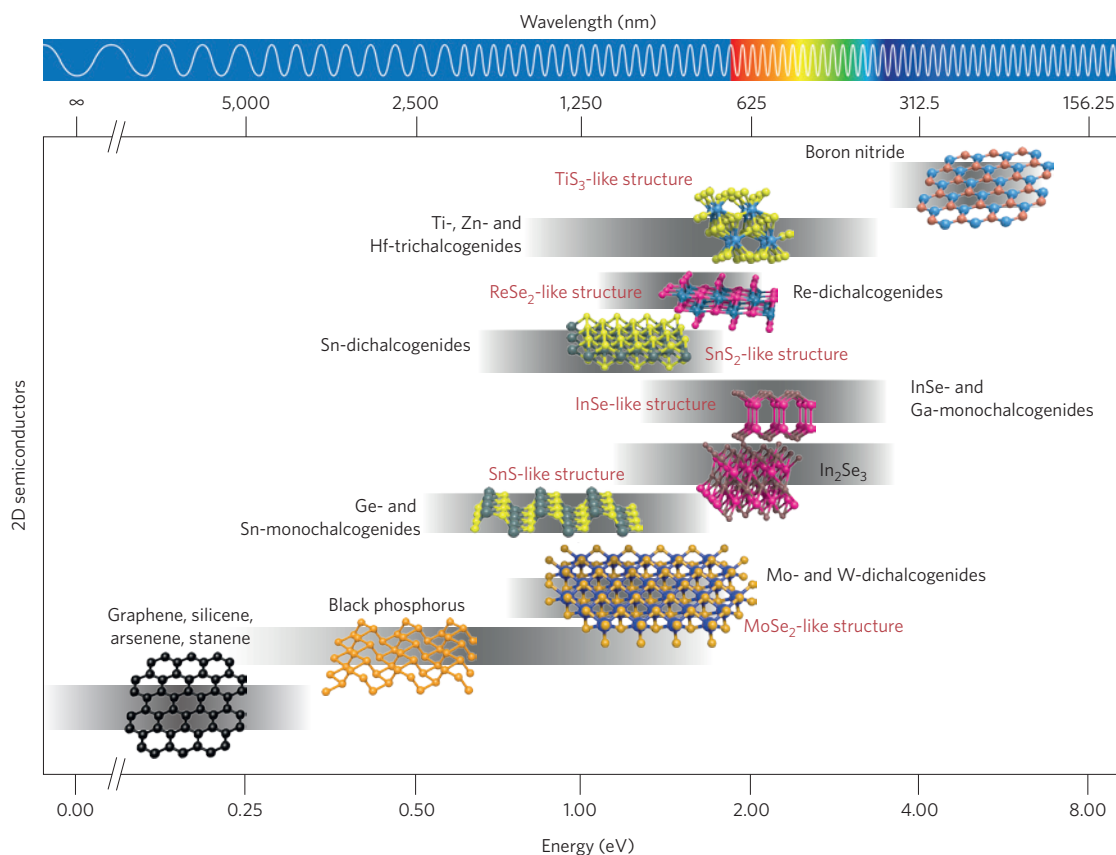
With a general formula  $MX_2$  (M being a transition metal and X a chalcogen) this family of 2D materials is, after graphene, probably the most studied. These materials have an intrinsic bandgap within the visible part of the spectrum. Owing to quantum confinement in the out-of-plane direction, the bandgap strongly changes with the number of layers and

a transition from direct gap to indirect gap has been observed when the number of layers is increased from monolayer to multilayers<sup>2,3</sup>. Another interesting feature of these materials is that the large spin–orbit interaction in these compounds, due to the heavy transition metals, leads to a splitting of the valence band that strongly affects their optical spectra.

It is also worth mentioning that these materials have a huge exciton binding energy, which makes them ideal for studying excitonic physics through photoluminescence measurements, even at room temperature. These studies revealed interesting phenomena such as the generation of charged excitons (trions)<sup>8</sup> or the valley-polarized photoluminescence emission when one valley is optically pumped with circularly polarized light<sup>9–11</sup>. The recent observations of single-photon emitters in  $WSe_2$  with very narrow emission linewidth ( $\sim 100$   $\mu$ eV), due to localized excitonic states that are related to defects<sup>12–15</sup>, have focused the attention of the optical spectroscopy community on  $WSe_2$ .

## Hexagonal boron nitride

This material has been traditionally considered as a good substrate or encapsulation layer to fabricate nanodevices comprised of other 2D materials<sup>16</sup>. However, since 2014, hexagonal boron nitride has also gained attention in the photonics community because of the recent demonstration of strongly confined phonon–polariton modes — collective oscillations, with frequencies typically in the mid-infrared (IR) wavelength range, resulting from the coupling of light photons with optical phonons in polar dielectrics. Using scanning near-field optical microscopy, polaritonic waves were launched, detected, and imaged in real space in thin boron nitride flakes and their



**Figure 1** | Comparison of the bandgap values for different 2D semiconductor materials families studied so far. The crystal structure is also displayed to highlight the similarities and differences between the different families. The grey horizontal bars indicate the range of bandgap values that can be spanned by changing the number of layers, straining or alloying. This broad bandgap range spanned by all these 2D semiconductors can be exploited in a wide variety of photonics and optoelectronics applications, such as thermal imaging (to detect wavelengths longer than 1,200 nm), fibre optics communication (employing wavelengths in the 1,200–1,550 nm range), photovoltaics (which requires semiconductors that absorb in the 700–1,000 nm range), and displays and light-emitting diodes (requiring semiconductors that emit photons in the 390–700 nm range).

measured dispersion exhibited hyperbolic-dependence<sup>17,18</sup>. This strong confinement of radiation arises from the anisotropy in the permittivity tensor in boron nitride, whose in-plane and out-of-plane components have a different sign. These peculiar materials are known as hyperbolic materials and before these experiments on boron nitride hyperbolic materials were mainly fabricated artificially with nanofabrication techniques. Boron nitride is a natural hyperbolic material that outperforms man-made hyperbolic materials, which tend to suffer from high losses yielding short propagation lengths and broadband resonances. Moreover, while man-made hyperbolic materials have shown confinement values of only  $\lambda/12$  (where  $\lambda$  is the wavelength of the incident light) with poor quality factors,  $Q$ , of  $\sim 5$ , boron nitride nanocones have recently shown strongly three-dimensionally confined ‘hyperbolic polaritons’ (confinements of up to  $\lambda/86$ ) and exhibit high  $Q$  (up to 283)<sup>19</sup>. Therefore, these phonon-polariton modes

in boron nitride can have a strong impact in nanophotonics to confine radiation to a very small length scale (subdiffraction limit), which eventually can result in new imaging applications in the mid-IR part of the spectrum<sup>20</sup>.

### Black phosphorus

Despite the youth of this 2D material (the first works on atomically thin black phosphorus were reported just two years ago in 2014<sup>21,22</sup>), the number of studies on black phosphorus is growing rapidly. The surge of interest can be due to the combination of several factors: it shows one of the highest charge-carrier mobilities reported for 2D semiconductors (typically  $100\text{--}1,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ ), its bandgap spans a wide range of the electromagnetic spectrum (from mid-IR to visible) and it shows exotic in-plane anisotropy (most 2D semiconductors have a marked anisotropy between the in-plane and out-of-plane directions but are typically isotropic within the basal plane).

Regarding the in-plane anisotropy of black phosphorus, unlike in graphite (where carbon atoms bond with three neighbouring atoms through  $sp^2$ -hybridized orbitals), in black phosphorus each phosphorus atom bonds to three neighbouring atoms through  $sp^3$ -hybridized orbitals, causing the phosphorus atoms to be arranged in a puckered honeycomb lattice formation<sup>23</sup>. This structure is the seed of an anisotropic band structure that leads to highly anisotropic electrical, thermal, mechanical and optical properties. This is in striking contrast with graphene, boron nitride or Mo- and W-based transition metal dichalcogenides that do not present noticeable in-plane anisotropy. Concerning its anisotropic optical properties, black phosphorus has shown a marked linear dichroism<sup>23</sup>, the optical absorption depends on the relative orientation between its lattice and incident linearly polarized light. The dichroism has strong implications for its Raman spectra, plasmonic and screening effects

**Table 1 | Summary of properties of different 2D semiconductors relevant for optoelectronics and photonics applications.**

Material	Mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	Bandgap	Exciton binding energy (meV)	Plasma frequency	Observed phenomena
MoS <sub>2</sub>	1–100 (ref. 4)	1.3–1.9 eV (refs 2,3)	~400 (refs 34,35)	~25 meV (ref. 36)	Charged excitons (trions) <sup>8</sup> Valley polarization <sup>9–11</sup> Strong spin–orbit interaction Quantum confinement <sup>2,3</sup>
Black phosphorus	100–1,000 (ref. 21)	0.3–1.5 eV (refs 22,37)	~400 (ref. 37)	~400 meV (ref. 38)	Anisotropic photoluminescence <sup>25</sup> Quantum confinement
Hexagonal boron nitride	-	5.9 eV (ref. 39)	~150 (ref. 39)	~8 eV (ref. 40)	Hyperbolic material <sup>17,18</sup> Confined phonon–polariton modes <sup>19,20</sup>
Silicene	100 (ref. 33)	2 meV (ref. 29)	-	-	Fairly unexplored <sup>28</sup>

Dash (-) indicates no data are available.

and photoresponse<sup>24,25</sup>. Recently, it has been demonstrated how the photoluminescence yield of black phosphorus always shows a high degree of polarization along the armchair direction of the flake<sup>25</sup>, opening the door for on-chip light polarization manipulation.

Similar to black phosphorus, other 2D semiconductors (Re-based chalcogenides<sup>26</sup> and trichalcogenides such as TiS<sub>3</sub> (ref. 27)) also demonstrated marked electrical and optical in-plane anisotropy.

### Other elemental 2D materials

Just below carbon in group IV of the periodic table we find other elements that (similar to graphene) can also form elemental 2D materials based on silicon (silicene), germanium (germanene) and tin (stanene) atoms, though adopting a buckled structure<sup>28</sup>. Owing to the larger spin–orbit coupling of silicon, germanium and tin with respect to carbon the calculated band structure of these 2D elemental materials differ from that of graphene and thus a bandgap should open (~2 meV for silicene, ~20 meV for germanene and ~300 meV for stanene)<sup>29</sup>.

So far, these narrow-bandgap 2D semiconductors have been epitaxially grown on metallic surfaces<sup>30–32</sup> in ultrahigh vacuum, but their limited environmental stability hampers the study of their properties with *ex situ* techniques. Moreover, it has been shown that the metallic substrates employed for the epitaxial growth strongly modify the electronic properties of silicene, germanene

and stanene. Therefore, experimentally studying the intrinsic properties of these 2D semiconductors (and exploiting them in applications such as mid- and near-IR optoelectronics) seemed impossible. Nonetheless, a method has been reported to encapsulate silicene, to take it out of the ultrahigh-vacuum environment and to fabricate electronic devices out of it<sup>33</sup>. This approach, which overcomes the initial concerns about the environmental instability of this family of 2D materials, opens the door to further studies on them, especially in the context of optoelectronics and photonics where there is still a lack of experimental works. □

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