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Grand challenges in graphene and graphite research

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Graphite is known and used by humankind since ancient times. It is composed of sp^2-bonded, two-dimensional, atomically flat, carbon layers called graphene, weakly joined together by van der Waals forces. Through the ages, graphite found many applications, from a refractory material to electrode for batteries, from pencils to lubricants, among others.

In a pioneering calculation, Wallace obtained the electronic structure of graphite and graphene (Wallace, 1947) that revealed the linear dispersion when the bands cross the Fermi level at the vertices K and K' of the hexagonal Brillouin zone, a feature that, many years later, became widely known as the perfect emulation of a two-dimensional massless Dirac fermion (Novoselov et al., 2005). For almost 60 years, this result appeared ellusive to experimental investigation, as the isolation of a single layer of graphene—the ultimate 2D system - was thought to be forbidden by the Mermin-Wagner theorem (Mermin, 1968).

But Nature has it own ways, and graphene research took a dramatic turn when Geim & Novoselov isolated graphene for the first time using the mechanical exfoliation ("scotch tape") method (Novoselov et al., 2004). In 2010, they received the Physics Nobel Prize for this discovery and subsequent studies on this material, which led to a plethora of observations of the truly exquisite properties of 2D massless Dirac fermions to be accessible in tabletop experiments (Geim and Novoselov, 2007).

The discovery of graphene ignited the broader field of 2D materials (Novoselov et al., 2016). Novel layered materials are discovered or predicted in a daily basis, with diverse properties (metals, insulators, semiconductors, magnetic, topological, etc). In addition, the possibility of combining these materials in stacked structures called "van der Waals heterostructures" offers endless possibilities of design engineering of novel structures to meet target functionalities.

These already infinite possibilities can be yet infinitely multiplied by turning the knob that controls the twist angle between neighboring layers. From early theoretical predictions that the electronic structure of bilayer graphene could be tuned by the twist angle (Lopes dos Santos et al., 2007), this possibility evolved to a truly new subfield of graphene and 2D materials research called "twistronics". A turning point was the discovery of superconductivity in twisted bilayer graphene near the so-called "magical angle" (Cao et al., 2018; Lee et al., 2019; Yankowitz et al., 2019), where bands near the Fermi level become flat and give rise to a variety of strongly-correlated phenomena. This discovery sparkled verifications of such effects in similar and promising systems, such as trilayer graphene (Park et al., 2021; Hao et al., 2021). Today, twistronics is a hot topic not only in graphene but in 2D materials research in general. Although the superconductivity in twisted graphene systems appears to be of unconventional type, the underlying theoretical description is still ellusive, representing an important

challenge in graphene physics. The possibility to explore the twist degree of freedom has been extended to other 2D materials and combinations thereof (Devakul et al., 2021). The immense number of possibilities of different structures—combining different materials and twist angles - offers yet another ***challenge***: to predict and design structures for target electronic or optical properties, a daunting task that certainly must be dealt with using artificial intelligence methods (Tritsaris et al., 2021).

The discovery of new phenomena and the use of single and multilayer graphene for selected applications require steady advances in graphene synthesis. From the early works on mechanically exfoliated graphene (Novoselov et al., 2004), synthesis has evolved considerably. Several methods currently exist to synthesize graphene, each having its own advantages and difficulties (Shams et al., 2015; Zhu et al., 2010). Graphene can be synthesized by top-down approaches such as graphite intercalation, pyrolysis, reduction of graphene oxide, electrochemical exfoliation, sonication, *etc.*, as well as bottom-up approaches such as chemical vapor deposition (CVD), epitaxial growth on SiC, and others. Considerable advances have been achieved in CVD growth of large-area monolayer and bilayer graphene (Wang et al., 2021). Novel bottom-up approaches involving precursor molecules were very sucessful in the bottom-up synthesis of atomically-precise graphene nanoribbons and related structures (Cai et al., 2010; Ruffieux et al., 2016), as well as large area graphene sheets synthesized at liquid-liquid interfaces (Lopes et al., 2018). For industrial-scale graphene synthesis, ***challenges*** include improve quality control, uniformity and reproducibility of graphene flakes and, in the case of CVD graphene, increasing production rate and scalability. In general, inconsistent quality over different producers is also an issue, and the need to improve an unified standardization or grading scheme is critical (Lin et al., 2019).

Raman spectroscopy holds a special place among graphite and graphene characterization techniques (Jorio et al., 2011). It can be used to determine the number of layers in a multilayer sample (Silva et al., 2020), it is quantitatively sensitive to the presence of both linear and point defects (Cançado et al., 2017), doping (Ferrari, 2007) and pressure (Machon et al., 2018). Recent developments on tip-enhanced Raman spectroscopy (TERS) of graphene (Gadelha et al., 2021) have extended the spatial resolution of Raman measurements to unprecedented regimes, alllowing for measurements of localized phonon modes in twisted bilayer graphene. One ***challenge*** in Raman spectroscopy of graphene is to improve even more spatial resolution to measure Raman signals of single defects in graphene in the near future.

The unusual electronic dispersion of graphene gives rise to very attractive optical and plasmonic properties (Grigorenko et al., 2012; Cui et al., 2021), with many possible applications in optoelectronic devices. Plasmons-polaritons in graphene—coupled excitations of photons and electrons—inherit the behavior of 2D massless fermions and can be gate-controlled and imaged (Fei et al., 2012; Chen et al., 2012), enabling the possibility of novel and compact optical devices operating from terahertz to visible frequencies, such as metamaterial and transformation optics devices (Zhao et al., 2016; Vakil and Engheta, 2011; Ju et al., 2011; Lee et al., 2012), photodetectors (Liu et al., 2011); photonic crystals (Xiong et al., 2019), lasers (Chakraborty et al., 2016) and X-ray sources (Wong et al., 2015). ***Challenges*** in plasmonic and optical properties of graphene involve improving the quality and reproducibility of patterned nanostructures, efficient coupling light in and out of graphene, and extending plasmon tunability to the vis-NIR range (García de Abajo, 2014).

From the early days of graphene research, prospects applications of graphene in electronics and spintronics were conceived. Graphene itself does not have a band gap, limiting the possibilities of applications in digital electronics. However, several other applications have been explored, from flexible displays (Ahn and Hong, 2014) to radio-frequency devices (Palacios et al., 2010). In addition, the discovery of graphene opened the door to other 2D materials, many of them semiconductors and holding a greater potential for applications in electronics. Furthermore, from the understanding and control of spin injection, transport and relaxation in graphene, several spintronics applications have been conceived (Han et al., 2014). ***Challenges*** in graphene electronic and spintronic applications rely in devising controlled fabrication protocols that lead to stable and reproducible devices. Scalability and wafer-scale integration are of course important issues as well.

The number of graphene applications is growing steadily every year. Graphene's planar geometry and its sensitivity to the surrounding molecular enviroment make it an ideal material for electrochemical sensors and biosensors (Shao et al., 2010). Graphene and graphene oxide are promising materials for biomedical applications such as drug delivery, biosensing, bioimaging, cancer therapy and theranostics [Shi and Fang, 2018; Song et al., 2020). Applications related to graphene's outstanding mechanical and conductive properties are also promising, such as anti-corrosive coatings (Cui et al., 2019) and various types of composites (with polymers, metals, oxides, and others) (Huang et al., 2012). Graphene and its composites can be used in a variety of applications, such as fuel cells (Liu et al., 2014), Li-ion batteries (Cai et al., 2017), supercapacitors (Velasco et al., 2021), photocatalysis (Li et al., 2016) and photovoltaic devices (Liu Z. et al., 2015). Graphene-based membranes appear to be a great platform for molecular separation and filtration as well (Liu G. et al., 2015). ***Challenges*** in the field of graphene applications involve overcoming the bottlenecks of production cost and volume, in comparison to competing technologies. In addition, to substantially boost graphene penetration in industry, graphene needs to find its "killer" applications, those in which the contributions of graphene are irreplaceable and unique (Lin et al., 2019).

All these applications require careful studies of possible health and environmental impacts of graphene and its

derivatives. Whenever possible, such studies must be incorporated in the very early stages of product and process development ("safety-by-design"). Fortunately, from the whole plethora of nanomaterials, graphene-related materials are one of the most well studied in this aspect (Ding et al., 2022; Fadeel et al., 2018; Bortolozzo et al., 2021). ***Challenges*** in this field are further understanding the structure-activity relationships of graphene materials in health and environment and devising novel methods of mitigation of possible hazardous effects.

In summary, almost 20 years of after its discovery, the study of graphene and graphene-related materials (including graphite, of course) remains a hot topic from both fundamental and applied science. As such, the **Graphite-ene Section** of **Frontiers in Carbon** will be devoted to bring to their readers the latest discoveries in all aspects involving this superlative material.

Author contributions

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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Conflict of interest

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