Braz J Phys (2014) 44:278–282
DOI 10.1007/s13538-013-0156-8

SOCIEDADE BRASILEIRA DE FÍSICA

CONDENSED MATTER

News and Views: Perspectives on Graphene and Other 2D Materials Research and Technology Investments

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Received: 9 August 2013 / Published online: 4 September 2013

Abstract With the actual experimental realization of graphene samples, it became possible not only to exploit the special physical properties of graphene but also to exploit its technological applications. As the field developed, the discovery of other 2D materials occurred and this opened up access to a plethora of combinations of a large variety of electrical, optical, mechanical, and chemical properties. Now there are large investments being made around the world to develop the graphene research area and to boost graphene use in technology. Here, we discuss current research and some future prospects for this area of layered nanomaterials.

Keywords Graphene · Transition metal dichalcogenides · Technological applications · 2D materials prospects

The recent work of Novoselov, Geim, and colleagues on the separation and characterization of graphene [1], the atomically thin layer of hexagonally arranged carbon atoms, has attracted exceptional attention from the scientific community because of the implications of graphene and other 2D layered materials on both basic science research and applications possibilities. The Nobel Prize winners of 2010, Geim and Novoselov, opened unlimited new possibilities for graphene, and recently, heavy investments have been made around the world to introduce graphene-related materials technology to many industries. Within this exciting scenario, the path taken by graphene investigators is currently being hastened by the increased research interests in the 2D world beyond carbon atom arrangements, including other layered materials like ionic solids (Ruddlesden-Popper perovskite-type structures like $KLn_2Ti_3O_{10}$, $KLnNb_2O_7$, and $RbLnTa_2O_7$ (Ln denotes the lanthanide ion) and metal oxides (like $LiCoO_2$ and $Na_2Ti_3O_7$), van der Waals solids like hexagonal boron nitride (h-BN), Bi_2Te_3, Sb_2Te_3, and transition metal dichalcogenides like MoS_2 [2]. The transition metal dichalcogenides, for example, form a set of more than 30 layered solids with large varieties of optical, thermal, mechanical, and electronic properties, offering even more possibilities for technological applications.

From a scientific standpoint, the reduction of the sample size in terms of one or a few 2D layers in graphite, reaching graphene in the monolayer limit, opened the possibility to explore many new physical phenomena, such as the study of Dirac-like particles in condensed matter systems [3] and the quantum Hall effect which is observed when electrons (here behaving like Dirac fermions) are under the influence of a magnetic field [4, 5]. This two-dimensional form of organization of carbon atoms with sp^2 hybrid bonds has been studied theoretically since 1947, when Wallace proposed the linear dispersion relation (E(k)) for monolayer graphene [6]. Nevertheless, evolution of the synthesis and characterization of carbon materials (on both microscopic and nanoscopic length scales) went through several stages, during the last

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50 years to reach their present level of sophistication [7]. As principal developments, we can cite the studies on graphite intercalation compounds in the 1970s [8], carbon fibers in the 1980s [9, 10], the fullerene discovery in 1985 [11] by Kroto, Curl, and Smalley (the first time that a molecular level carbon nanostructure was discovered), the single wall carbon nanotube identification in 1993 by Iijima [12], and, finally, the single layer graphene separation by Novoselov and Geim in 2004 [4, 13]. Graphene is the basic building block of several carbon nanomaterials. Graphite can be seen as the piling up of many graphene layers; fullerenes and nanotubes can be considered as the cutting and rolling up of graphene. In viewing nanocarbons broadly, we can say that developments in understanding graphene have generated major advances in other nanocarbonaceous materials research.

Properties like high in-plane mechanical strength, optical transparency, high thermal and electrical conductivity, and the miniaturization possibility due to graphene's 2D character have attracted significant attention for technological applications. Furthermore, the carrier mobility in suspended graphene reaches values higher than 200, 000 cm^2/V s [14], but the mobility is reduced to 10, 000 cm^2/V s on SiO_2 [1], due to defects and scattering through interaction with the substrate. Large area graphene can be synthesized by chemical vapor deposition or by epitaxial growth on the Si face of a SiC wafer, but in such materials the mobilities are reduced to 1, 500 cm^2/V s [15] due to materials processing defects and grain boundary scattering. Even with these difficulties in graphene–substrate integration, the mobilities are still high enough to be attractive for device applications, so that, for example, wafer-scale epitaxial graphene has been used to produce 100-GHz transistors [15]. Other examples of graphene's capabilities are its use as transparent conductors in touch-screens, solar cells, and light-emitting diodes, where its high transparency and low sheet resistance are exploited [16]. Despite these advantages, the lack of a natural bandgap in graphene has promoted efforts to prepare other ultrathin 2D layered materials which do have bandgaps convenient for optoelectronic applications.

The fast developments in research and applications of graphene and other layered materials have recently triggered a wave of investments around the world, heading toward a new technological revolution. In January, 2013, the European Commission elected graphene to be one of Europe's 10-year 1 billion euro Future Emerging Technology flagships. The first 30-month-budget of 54 million euro will be distributed between 126 academic and industrial research groups (from 17 European countries), and more groups will be included in a second phase of this Graphene Flagship Program [17]. With the aim of developing new batteries and synthesis methods as well as other layered materials and fast and flexible electronic and optical devices, these efforts constitute a considerable mobilization of research activity and resources to bring one specific technology from the laboratory to industry. As another example, South Korea has invested US$ 200 million in graphene research since 2012 [18], where significant contributions come from private industries like Samsung. As yet another example, the United Kingdom has invested a more modest amount (50 million euro) at the beginning of 2012 [19]. Singapore already has its Graphene Research Centre [20], and is becoming a significant graphene research player in this international activity.

In Brazil, the efforts in graphene research are included in the proposal for establishing a national institute of science and technology for carbon nanomaterials, the *INCT de Nanomateriais de Carbono*. Created in 2008, this initiative has the Physics department of the Federal University of Minas Gerais as the base institution and incudes 19 other institutions around the country [21]. The goal of this institute is to develop synthesis methods for carbon materials, research on fundamental physical phenomena, application in electronic devices and sensors, and possibly also toxicity studies of the materials under investigation.

It is also important to cite the involvement with graphene of the Brazilian National Institute of Metrology, the *Instituto Nacional de Metrologia, Qualidade e Tecnologia* [22] with graphene, where nanometrology and applications research are both developed with a view towards providing a scientific base for nanomaterials standards. Figure 1 is based on a literature research taken from the Web of Science about Brazilian publications in the field of graphene, showing the most productive Brazilian institutions in this research area. Using the theme "Graphene" and the address "Brazil", a

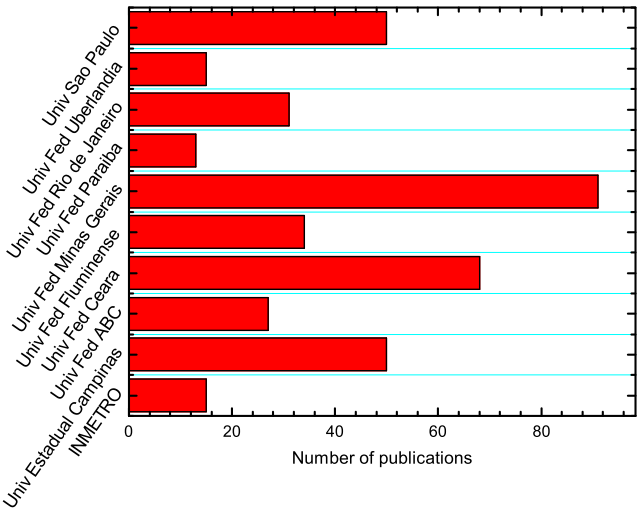

Fig. 1 Principal Brazilian institutions where graphene research is concentrated. The data were obtained from the Web of Science using as theme the term "Graphene" and "Brazil" as the address. Data acquired on July 30, 2013

total of 412 publications are found, the majority published by these 10 principal centers, and the distribution of publications among these Centers shows the prospect for where scientific advances in graphene research are likely to happen in Brazil.

Another initiative for graphene development in Brazil will be implemented in a specialized center for graphene-based photonics development at São Paulo's Mackenzie Presbyterian University, in the MackGrafe *Centro Mackenzie de Pesquisas Avanadas em Grafeno e Nanomateriais*. US$ 15 million (in addition to budgets from the São Paulo Research Foundation, FAPESP) [23] will be spent in building the Center and in the development of graphene-based optical fibers and lasers. With expertise in the development of digital systems for TV and communications, the Mackenzie University is an engineering institution with a good reputation and may provide a favorable environment to put Brazil into the international graphene technological race.

Traditionally, Brazilian science is based on academic research with only a small transfer of laboratory technologies to industry. It is ranked as the 13th country in the numbers of research papers [24], but in numbers of patents and patent applications, the Brazilian contribution has less impact (for example, see ref. [25] for an annual comparison of Brazilian patents and those from other countries that are filed under the Patent Cooperation Treaty). The MackGrafe Center's goal is to construct an intellectual property culture in graphene technology and to transfer their technology to the adjacent Technology Park, though this goal yet remains to be implemented. In this way, it is hoped to increase the Brazilian participation in patents issued and in developing an entrepreneurial feeling among its scientists. From this perspective, the graphene development efforts go beyond scientific discovery and into leveraging a new approach to strategic research and technological investment.

After more than 8 years of accumulated knowledge on graphene (synthesis, characterization, transfer processes, and devices applications), this collective experience is now being applied to other forms of two-dimensional materials, such as "van der Waals solids" whose neighboring layers are weakly bonded [2]. Among these new possibilities are the transition metal dichalcogenides (TMDCs). These constitute one class of laminar materials of the form MX_2 (or X-M-X), where "M" stands for the transition metal atoms of groups (IV, V, VI, VII, and X), and "X" represents chalcogen atoms (S, Se, and Te) [26]. In the most common TMDCs, two hexagonal planes of chalcogen atoms are arranged around a plane of intercalated metal atoms, generating different polytypes depending on their stacking order and metal atom coordination [27]. There are more than 30 varieties of TMDCs, and these collectively show a large variety of electrical behaviors, including metal, insulating, semimetal, semiconductor varieties. Unlike graphene, exotic strongly correlated electron phenomena like charge density waves and superconductivity are observed in some metal dichalcogenides [28, 29], thereby increasing interest in basic studies of TMDCs.

The TMDCs show some special characteristics differing from graphene and these characteristics in particular can be used in applications involving several different layered materials, thereby introducing different functional possibilities, especially when different layer thicknesses are considered. The bulk form of molybdenum disulfide (MoS_2) is a semiconductor with an indirect band gap of 1.2 eV. With the decrease in layer number, there is a resulting increase in electron confinement which changes the electronic structure. In the monolayer limit, MoS_2 has a direct gap of 1.9 eV [27]. This generates the appearance of strong photoluminescence in monolayer MoS_2. The direct gap in the monolayer is very interesting for optoelectronics applications, where miniaturized, flexible, and transparent devices can be designed to produce, detect, or control light.

The band structure dependence with thickness is predicted for other MX_2 compounds with M = Mo, W and X = S, Se, Te; besides the number of layers, strain engineering can be used to control the band structure and optical properties [30]. The natural bandgap present in these materials is desirable even for transistor applications. The availability of layered materials with natural bandgaps is important because the procedure of bandgap engineering in graphene reduces mobilities and increases the complexity of the production process, besides the complexity of requiring high voltages for operation.

Other specific characteristics of some of the other TMDCs includes a strong band structure splitting induced by the large spin–orbit interaction and also through a strong spin-valley coupling. The monolayers of these TMDCs lack inversion symmetry, and with the heavy weight of these atoms and their large electron confinement in two dimensions, the resulting strong spin–orbit splitting that is generated allows spin-polarized carrier populations which can be maintained. Such phenomena are not observed in graphene, since this material is centrosymmetric and the carbon atoms have low atomic number, which generate very weak spin-orbit effects. However, TMDC materials open possibilities for spintronic devices and, through the coupling between spin and valleys, thereby new valleytronic technologies have been promoted. The optical excitation of MoS_2 samples with circularly polarized light showed experimental evidence for the possibility of independent control of the carrier populations in different valleys [31], which can give rise to the implementation of future valleytronic devices.

Figure 2 shows literature research in the ISI Web of Knowledge using the term "transition metal dichalcogenides". The numbers of publications ("a") and citations

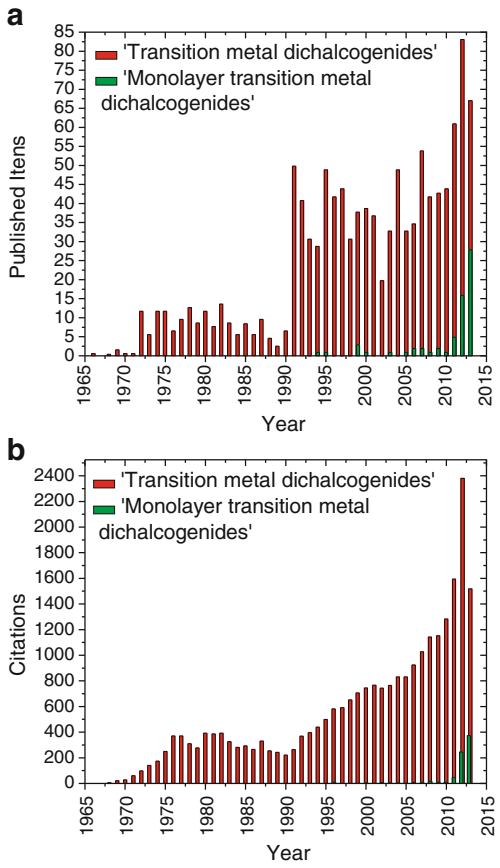

Fig. 2 Literature research in the ISI Web of Knowledge using the terms "transition metal dichalcogenides" and "monolayer transition metal dichalcogenides", in all databases. **a** is the total number of publications and **b** the total citations (per year). The *red bars* are for "transition metal dichalcogenides" and the *green* bars are for "monolayer transition metal dichalcogenides". The *bars* represent publications in a 1-year period. Data acquired on July 09, 2013

("b") in each year are increasing progressively (red in Fig. 2). In the 1970s and 1980s, bulk transition metal dichalcogenide materials were extensively characterized and important advances were achieved by intercalation with lithium and by exfoliation, eventually reaching the single-layer level. The intercalation with other species was developed during the 1990s. From 2010 until now, there has been an increasing interest in the monolayer version of these materials, as can be seen by the green bars of Fig. 2. These data give insight into the tendency of research directions and calls attention to the necessity for specific investments in these materials.

Another example where the application of nanomaterials has had large impact is for thermoelectrics. Thermoelectric materials are those where a temperature gradient can induce a voltage (or a voltage induces a temperature gradient). This possibility is present in quite a few materials, but in some specific materials, this effect can be large enough, for example, to be used to convert waste heat into enough electrical energy to be of potential commercial interest. By inverting the voltage, it is possible to design solid-state coolers. Theoretical predictions dating from 1993 showed that the reduction in dimensionality (generating electron confinement in one or two dimensions) would generate more efficient thermoelectric structures for some of these materials [32–34]. Some metal dichalcogenides are promising thermoelectric materials. Within this encouraging prospect, nowadays, the development of new thermoelectric technological products and thickness scale miniaturization is receiving more substantial funding worldwide.

The recent announcements of investments (in Brazil and worldwide) in graphene are important initiatives to ignite a possible technological breakthrough, but little has been said about increased investments in other 2D material research and technology applications. As an off-shoot of the developments in graphene, these new nanomaterials are now being widely studied, and increasing specific investments in the TMDCs would also be valuable to make this process move faster in Brazil. The scientific discovery process should influence directly where governments make investments, especially in the case of a strategic issue like these layered materials. Some 2D materials share unusual properties with graphene, but since the TMDCs constitute a large variety of atomic species and structural organizations, atypical and specific phenomena not found in graphene can be exploited in TMDCs to generate technologies that can be integrated with graphene, in the emerging van der Waals heterostructures research area. This is the moment to have flexibility to invest in the new possibilities provided by the ensemble of 2D materials so that they can be properly studied, characterized, and incorporated into industrial products, exploiting their own special interesting properties.

Acknowledgments The authors thank Professor Ado Jorio of the UFMG Physics Department for valuable discussions. J.R.S. acknowledges the financial support from CNPq grant 551953/2011-0 and NSF grant DMR-1004147. M.S.D. acknowledges financial support from NSF grant DMR-1004147.

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