

Theoretical Studies of Graphene, Superconductors And Metals As Conductors For Metamaterials And Plasmonic Systems

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ABSTRACT:

Among various 2D materials, graphene has received extensive research attention in the last 2-3 decades due to its fascinating properties. The discovery of graphene provided an immense boost up and new dimension to materials research and nanotechnology. The multidisciplinary characteristics of graphene have a wide range of applications from health to aerospace. Modern graphene research has been directed towards the exploration of new graphene derivatives and their utilisations for fabrication of products and devices. The enhancement of graphene properties by functionalization or surface modification is another innovative approach. However, like other 2D materials, graphene research also needs amendments and up-gradation in the light of recent scientific output. In this contribution, we have reassessed the recent research output on graphene and graphene-based materials for applications in different fields. For the reader's comfort and to maintain lucidity, first, some fundamental aspects of graphene are discussed and then recent overviews in graphene research are explored in a systematic manner. Overall, this review article provides an outline of graphene in terms of fundamental properties, cutting-edge research and applications.

Keywords: *Graphene, 2D materials, Graphene oxide, Engineering application of graphene*

INTRODUCTION

Our world is full of materials and these are the backbone of our modern society. Among these materials, carbon-based materials are popular and play a crucial role in human civilization. In the present situation, it is not an overstatement by saying that without carbon materials, our life is impossible on the planet earth. Since 2004, graphene is treated as one of the most wonderful achievements in the field of science and technology [1]. The hexagonal crystalline single layer of graphite (the simplest form and one of the most important crystalline allotropes of carbon atoms having a CeC bond distance of 0.142 nm) has received massive attention in the field of sensors, biomedical, composite materials and microelectronics [1e3]. A wide range of applications such as transparent conductive films, ultra sensitive chemical sensors, thin-film transistors, quantum dot devices and anti-corrosion coverings has been tested and is well established [1e5]. However, industrial-scale production of graphene for these overwhelming applications strongly depends on the easypath of graphene production which was a bottleneck in the past and which, fortunately, has been improved recently.

Graphene is the only allotrope of carbon in which every carbon atom is tightly bonded to its neighbours by an unique electronic cloud that raises several exceptional questions to quantum physics [3,5]. Along with the unique quantum hall phenomenon, graphene itself exists in several forms like graphene nanoribbons, nano-sheets, nanoplates and 3D graphene. Each of them displays amazing applications. As mentioned above, the electronic and quantum properties of graphene are still a matter of fundamental studies. Each carbon atom in graphene is sp^2 hybridised, having three bonds, related to different neighbour carbon atoms (Fig. 2). The sp^2 hybridisation is a combination of s, p_x , and p_y orbitals [1e3]. In the hexagonal phase, three distinct carbon atoms fortify covalently to each carbon atom and all of them are essentially sp^2 hybridised, resulting for each carbon atom in one free electron. The p_z orbital holds this free electron and this p-orbital lies above the plane and forms the pi bond [1e3]. Interestingly, the p_z orbital of graphene plays a vital role in the chemical and physical behaviour of this miraculous material [1e3]. The presence of a zero bandgap is a drawback and unique feature of graphene, which opens several new opportunities to develop artificial humanmade materials with tunable bandgaps that can be of use for the next-generation of computing.

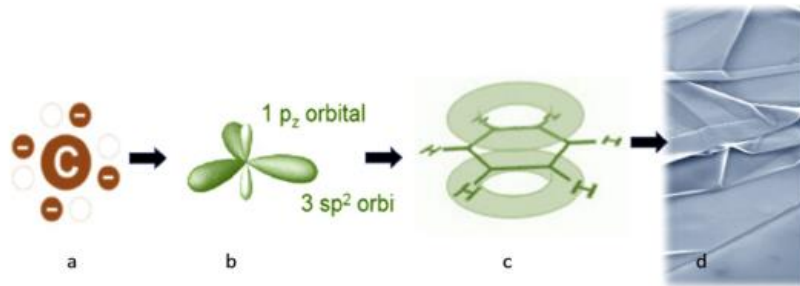


Fig. 1. (a–c) Fundamental aspect of graphene bonding properties and (d) SEM image of single-layer graphene.

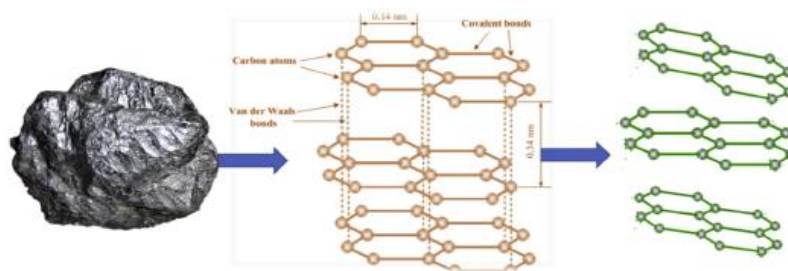


Fig. 2. Schematic depictions about the Origin (presenting the transformation) of graphene from graphite and peculiar structure of graphite and graphene.

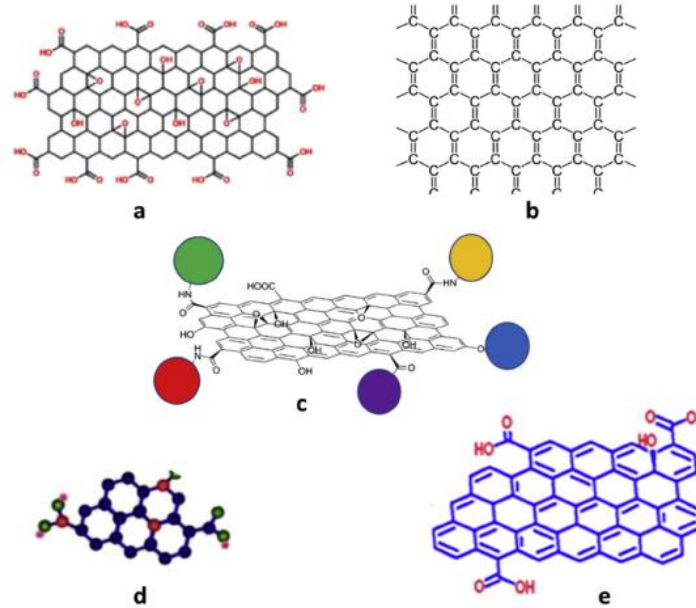


Fig. 3. Different forms of graphene: (a) graphene oxide (b) pristine graphene (c) functionalized graphene (d) graphene quantum dot, and (e) reduced graphene oxide.

The two pi-electrons that are present in every hexagon of the graphene sheets are responsible for the exceptional conductivity of graphene. Due to the tight packing of atoms in the crystal lattice of graphene, it is highly stable, but only in case its size is less than 20 nm, otherwise it is quite unstable thermodynamically except for some specific conditions [2,3]. Due to the gigantic reputation of graphene and its derivatives, several original research articles and reviews have been produced by researchers all over the world [1,4e6]. Now, a timely update on recent progress in graphene research is needed for the academic and industrial scientists. In this aspect, the current review article aims to serve the science community.

STRUCTURE AND PROPERTIES OF GRAPHENE

The electronic structure of graphene's basic unit is presented below (Fig. 1) for a better understanding of the electronic properties of graphene and their derivatives.

It is interesting to note that structural holes permit the phonons to go unobstructed, which leads to a significant thermal conductivity in graphene. However, this property has not been observed in graphene oxide and other derivatives of graphene owing to the altered band structure [2,3]. The classification of graphene as metal, non-metal or semimetal is still a matter of debate and requires further research [3]. But, due to the presence of metallic layers with very low bandgaps, it can be treated as a semimetal with an exceptional theoretical background [2,3]. As a whole, it has numerous remarkable characteristics that are not observed for other non-metallic materials as well as for the existing ideal semi-metals. The properties of graphene solely depend on the number of layers and the defects present in the graphene layers. For example, the theoretical surface area of pristine graphene is $\sim 2630 \text{ m}^2/\text{g}$ which is much higher than the surface area of carbon black ($850 \times 10^9 \text{ m}^2/\text{g}$), carbon nanotubes ($100 \times 10^6 \text{ m}^2/\text{g}$), and many other analogues [1e3]. On the otherhand, the surface area of a few layers graphene, graphene oxide, and many other derivatives are much less in comparison

to single-layer graphene [1e3]. Due to these exceptional properties, graphene acts as a perfect material for many modern technologies including electronic applications along with many other materials as substrate or template [3].

GRAPHENE-BASED NANOSTRUCTURES

Pure graphene contains a monolayer of carbon atoms as discussed in the previous section. These monolayer layers commonly exist as an ultrathin film, especially when these are pasted with the help of templates [2,3]. These graphitic layers can be utilized in their solitary form. Further, it can be skimmed off and redeposited onto the substrate for electronic applications [1]. It is notable that including powder form of these nanosystems, graphene can also be seen in other forms as the derivatives of graphite. Different forms of graphene include GO (graphene oxide), GNPs (graphene nano-platelets), GNRs (graphene nanoribbons), rGO (reduced graphene oxide), GQDs (graphene quantum dots) and also graphene empowered items like graphene ink, graphene masterbatches etc. [7] Since the inception of graphene, various methods have been developed for its synthesis. Among them, three synthetic approaches have been adopted frequently: (1) Chemical Vapor Deposition (CVD), (2) Mechanical cleavage from natural graphite, and (3) Chemical methods [7,8]. However, these methods haven't proven to be commercially viable yet [8]. The CVD method is very useful for pure and single-layer graphene production while the oxidation-reduction approach using graphite is one of the simplest and inexpensive approaches for the production of graphene and their derivatives [7,8]. However, the number of layers and defects in graphene can be controlled using the CVD approach, but the same is not possible in the case of Hummer's method (oxidation-reduction using graphite). The different forms of graphene are presented in Fig. 3.

Graphene materials have been explored for solar cell applications too because of their elevated optical transparency, superior mechanical strength, and high carrier mobility. In solar cell devices, graphene materials have been considerably utilized as the transparent electrode, buffer layer, as well as the electron/hole transport materials. In a recent article, Sim et al. used a graphene film as the hole transport electrode for Cu(In, Ga)Se₂ (CIGS) solar cells. In this work, Cu foil was used as the substrate to deposit graphene through the chemical vapour deposition (CVD) technique. The fabricated graphene-based solar cell displayed a power conversion efficiency of $9.91 \pm 0.89\%$, which was better than the reference electrodes. The enhanced conversion efficiency was attributed to the elevated open-circuit voltage and large fill factor. The fabrication technique of the graphene/Cu flexible solar cell and the performance of the device is shown. On the other hand, Ishikawa et al. fabricated a solar cell based on graphene and perovskite (CH₃NH₃PbBr₃), which did not require any hole-transport layer. The vacuum lamination of graphene designed the device. In another recent article, Das et al. demonstrated the current state of the art in graphene research for solar photovoltaics. The authors concluded that the conductivity of graphene increased with increasing the layers; however, the optical transparency is reduced. They also reviewed the utilisation of other 2D materials beyond graphene for solar cell applications. A graphene/Si Schottky junction solar cell was fabricated by Suhail et al., which exhibited a power conversion efficiency of 10%. The chemical doping of graphene further enhanced the efficiency. Moreover, the device also

displayed a efficiency retention of 84% after 9 days of storage in air. In this work, the authors introduced a deep UV treatment to enhance the performance in the solar cell.

Graphene-based screen-printed electrodes (GSPE) are being used for various applications. For example, Jampasa et al. fabricated the GSPE electrode for the electrochemical detection of c-reactive protein in human serum samples. Mainly, the authors developed an electrochemical immunosensor based on graphene through an in house screen-printing technique. Further, a Glucose/ Oxygen Enzymatic Fuel Cell was fabricated by employing Gold nanoparticles modified GSPE. The fabricated bio-device displayed a significant performance when tested for human saliva samples. The GSPE was further assembled with the nano-molecularly imprinted polymer to develop a biomimetic sensor for the detection of acute myocardial infarction (a cardiovascular disease). Ji et al. fabricated a glucose sensor by developing a smartphone-based cyclic voltammetry system with GSPE. The smartphone-based system displayed minimal test errors in comparison with the commercial electrochemical workstations for the electrochemical detection of redox couples, indicating better applicability for electrochemical tests. GSPE was further used to develop an immunosensor for the level-free detection of Cortisol and Lactate. These studies imply that GSPE has been considered as an essential tool for the development of biosensors.

With the rapid progress in graphene research, various kinds of graphene materials have been developed. Among those, graphene-based inks (GI) are significantly utilized for different applications. The printed 3D GI exhibited elevated compressive strength and better electrical conductivity ($> 4 \cdot 10^3$ S/m). The GI was developed through a direct ink wetting process using a single surfactant. Conductive GI was further developed by Liu et al. The conductive ink was prepared by dispersing graphene and MWCNT through the use of polyvinylpyrrolidone in a mixture of ethanol and water. The ink displayed a low sheet resistance and a high optical transmittance of 90%. A facile strategy has been developed to print GI on inert 3D surfaces. The water-insoluble conductive ink was produced by using commercial binders and was used to develop multilayered devices through a conformal printing process. GI based energy storage devices have drawn extensive research interest. Bellani et al. fabricated a micro-supercapacitor (MSC) with GI through a screen-printing technique. The GI was produced through wet-jet milling exfoliation of graphene. The fabricated device exhibited a maximal areal capacitance of 1.324 mF/cm^2 and an energy density of 0.064 mWh/cm^2 . In another work, He et al. fabricated supercapacitor devices through screen-printing of GI on plastic and paper substrates. The printed device displayed a high conductivity of $8.81 \cdot 10^4 \text{ S/m}$ and a better rate capability up to a high scan rate of 200 mV/s . These works significantly demonstrated that the GIs could serve as the potential tool for the fabrication of flexible electronic devices.

CONCLUSION AND FUTURE PROSPECTS

At present, graphene and graphene-based hybrid nano-structures are appealing much consideration as the novel materials for nanotechnology, biomedical engineering, material science, physics, and green chemistry due

to their tunable physical properties, high surface area, elevated electronic, and thermal proper-ties. That is why, within a very short period of time, graphene and its derivatives have shown wonderful commercial applications in the field of composites, nanoelectronics, bioimaging, and nano-medicines. For example, functionalized graphene nanosheets have revealed enhanced interfacial interaction and adhesive properties with mammalian cells, protein and microbial, which make graphene a valuable nanosystem for the next-generation multifunctional bioengineering applications. Similarly, many exceptional applications of graphene in pipelines will dominate our market very soon. However, the production of inexpensive and ultrapure pristine graphene layers are still a matter of deep research. So, an easy and adorable route for graphene production is an inordinate challenge and headache for the materials scientists. In the same line, time-dependent compatibility and interactions of graphene and its derivatives in vivo and in vitro conditions is one of the most challenging tasks for the researchers working on different aspects of graphene. Therefore, we can say, graphene has shown great proficiency in every branch of science and technology but a great support for further research is required from the governments and industries to harness the full potential of graphene and its derivatives for optoelectronics, bio-imaging, frequency multiplier, Hall effect sensors, conductive ink, Spintronics, ultraviolet lens, charge conductor, radio wave absorption, catalyst, sound transducers, waterproof coating, condenser coating, coolant additive, and piezoelectric applications.

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