Nano-Graphene and Its Derivatives for Fabrication of Flexible Electronic Devices: A Quick Review

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Abstract

Along with technology development, the demand for flexible, foldable, and portable electronic devices has grew over the past few years. Successful fabrication of this flexible electronic devices relying on the internal electronic components which are also flexible and lightweight. In this regard, researchers are now working on using nanomaterials which exhibit the desired electronic properties to replace the conventional electronic components. Graphene nanosheet and its derivatives are known for their intrinsic electrical behaviour. Meanwhile, they are lightweight and consume small space in any design. Hence, recent research has been focussing on fabricating flexible and foldable electronic components by attaching the graphene and its derivatives on a thin film/substrate. In fact, this idea has been realized in year 2017 on the first flexible OLED panel that uses transparent graphene-based electrode. In view of the positive impact of this nanomaterial towards future design of electronic devices, the present paper aims to provide a quick review on the current stage of research, the challenges encountered, as well as the future outlook in the use of graphene nanomaterials for designing flexible electronics. Copyright © VBRI Press.

Keywords: Graphene, nanotechnology, flexible, foldable, electronic devices.

Introduction

Flexible electronics are specifically a class of electronic devices which can be bent, folded, twisted, stretched, or even deformed into arbitrary shapes but retain its electrical performances [1]. It is different from the conventional electronic devices which were built of integrated circuit planted on a rigid wafer. The problem with the conventional electronic components is that they are hardly incorporated into an irregular or soft moving object [2]. On the other hand, the current digital and electronic industries have been moving into fabrication of thin and flexible devices for both human and industrial daily usage. This includes the fabrication of E-skin in robotics, biosensing devices, smart-wearable human healthcare, environmental monitoring devices, energy conversion and storage devices, daily communication devices, and various display devices. In fact, along with the competitive growth in smart phones markets, the technologies of thin and flexible smart phones are of big interest in worldwide companies.

Nanotechnology plays an important role in the design of these flexible electronic devices. In particular, nanomaterials with intrinsic electronic properties are employed to replace the conventional rigid electronic components. Graphene and its derivatives (namely graphene oxide (GO) and reduced graphene oxide (rGO) are the nanomaterials that known for electrical characteristic. Graphene, a 2-dimensional nanomaterial, is regarded as the best conductor for electricity [3]. The conductive behaviour of graphene is ascribed to its chemical structure which consisted of many sp² hybridized carbon atoms arranged in honeycomb hexagonal lattice. The π-electrons of the carbon atoms freely mobile within the crystal plane and thus make the graphene an excellent electrical conductor [4]. On the other hand, the GO is an insulator due to disruption of sp² bonding networks by the oxygenated group. To restore the electrical conductivity and recover the honeycomb hexagonal lattice, the oxygenated group shall be removed via reduction method [5-7]. The derivative produced from this reduction is term as rGO; nevertheless, the rGO still retains some of the oxygenated group and thus make it less conductive than the pristine graphene [8]. Fig. 1 illustrates the chemical structure of graphene, GO, and rGO.
Owing to the unique properties, graphene, GO, and rGO have been the centre of research study ranging from fundamental investigation on their physical and chemical properties, synthesis methods, mechanism simulation, application in wastewater treatment processes, application in biomedical field, up to fabrication of electronic devices and etc. Table 1 highlights the several areas of studies on graphene and its derivatives over the past three years.

Table 1. Recent research studies on graphene and its derivatives.

<table>
<thead>
<tr>
<th>Year</th>
<th>Area of studies</th>
<th>References</th>
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<tbody>
<tr>
<td>2019</td>
<td>Physical and chemical studies</td>
<td>10-18</td>
</tr>
<tr>
<td></td>
<td>Synthesis methods improvement</td>
<td>19-22</td>
</tr>
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<td></td>
<td>Water purification</td>
<td>23-24</td>
</tr>
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<td></td>
<td>Morphology study</td>
<td>25-28</td>
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<tr>
<td></td>
<td>Electronic applications</td>
<td>29-31</td>
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<tr>
<td></td>
<td>Reaction kinetic theory and simulation</td>
<td>32-34</td>
</tr>
<tr>
<td></td>
<td>Biomedical application</td>
<td>35-39</td>
</tr>
<tr>
<td></td>
<td>Energy conversion</td>
<td>40-43</td>
</tr>
<tr>
<td>2018</td>
<td>Physical and chemical studies</td>
<td>44-47</td>
</tr>
<tr>
<td></td>
<td>Biological study</td>
<td>48-51</td>
</tr>
<tr>
<td></td>
<td>Synthesis methods improvements</td>
<td>52-57</td>
</tr>
<tr>
<td></td>
<td>Water purification</td>
<td>58-64</td>
</tr>
<tr>
<td></td>
<td>Morphology</td>
<td>65-67</td>
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<td></td>
<td>Biomaterial synthesis</td>
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<td></td>
<td>Reaction kinetic theory and simulation</td>
<td>69-73</td>
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<td>Electronic applications</td>
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<td></td>
<td>Architected printing</td>
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<td></td>
<td>Power generation</td>
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<td></td>
<td>Biomedical applications</td>
<td>82-88</td>
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<td></td>
<td>Photo-catalysis applications</td>
<td>89-97</td>
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<tr>
<td></td>
<td>Air filtration</td>
<td>98</td>
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</table>

2017

<table>
<thead>
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<th>Area of studies</th>
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</tr>
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<td>99-100</td>
</tr>
<tr>
<td>Biological studies</td>
<td>101-102</td>
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<tr>
<td>Synthesis methods improvement</td>
<td>103-107</td>
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<tr>
<td>Water purification</td>
<td>108-117</td>
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<tr>
<td>Morphology</td>
<td>118-121</td>
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<tr>
<td>Reaction kinetic theory and simulation</td>
<td>122-125</td>
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<tr>
<td>Electronic applications</td>
<td>126-132</td>
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<td>Biomedical application</td>
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<tr>
<td>Energy conversion</td>
<td>135-136</td>
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<tr>
<td>Photo-catalysis applications</td>
<td>137-139</td>
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While for rGO, its electrical conductivity may vary by the synthesis condition and/or by the starting material. Pavoskit et al. 2017 reported that rGO produced from graphite flakes exhibited better electrical conductivity than the one produced from an expanded graphite. This could be due to the many defects formed in the rGO produced from the expanded graphite. More interestingly, few layers of rGO was found to exhibit ten times superior in electrical conductivity than the starting graphite [142].

Phiri et al., 2018 reported that the incorporation of graphene, GO, or rGO into a cellulose material may alter the electrical and thermal properties of the material in different manners. The graphene and rGO-based composites showed highest conductivity value with 1.66 S m⁻¹ and 0.57 S m⁻¹ but as expected, GO-based composite is an insulator. However, in term of the thermal stability, it was found that the graphene-based composite is more stable compared to both GO and rGO-based composites. Such observation may ascribe the oxygen groups in GO and rGO that decompose when temperature increase; the weight loss is higher in GO due to higher oxygen moieties present [143].

### Substrates used for fabrication of flexible electronic film

The unique electronic characteristics of graphene and its derivatives have made them a good candidate for the fabrication of electronic component. Basically, a flexible electronic component consists of a dielectric substrate, an electrical conductor, an adhesive material, as well as a protective layer. The substrate for electronic applications must be highly flexible (i.e. low Young’s Modulus), high thermal stability, high thermal dimensional stability, low water vapour and oxygen transmission rate, and surface smoothness. The flexible substrates are categorized into three main types: polymer films (such as plastic), thin glass, and metal foils. Each material has its own pros and cons as listed in Table 2. Meanwhile, Table 3 provides a summary of substrates used in fabricating graphene-based flexible electronic film.

Table 2. Comparison of plastic, thin glass, and metal-foil substrate [144].

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Advantages</th>
<th>Disadvantages</th>
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<tbody>
<tr>
<td>Polymer film (e.g. Plastic)</td>
<td>Rugged, Bendable and Rollable, Transparent</td>
<td>Poor dimension stability, Low process temperature and chemical resistance, High H₂O and O₂ permeation.</td>
</tr>
<tr>
<td>Thin glass</td>
<td>Conformable, Transparent, Low H₂O and O₂ permeation.</td>
<td>Low mechanical stability, Low process temperature.</td>
</tr>
<tr>
<td>Metal foil</td>
<td>Rugged and Conformable, Low H₂O and O₂ permeation, High process temperature, Good dimension stability</td>
<td>Opaque, Rough surface, Capacitive effect</td>
</tr>
</tbody>
</table>

Studies on electronic properties of graphene and its derivatives

Many underlying electronic properties of graphene, GO, and rGO have been disclosed along with research studies. For instance, Kuc et al., 2010 found that the electronic properties of graphene nano flakes is dependent on their size and topology, whereby its Homo-Lumo gap decreased when the size of the flakes increased [140]. On the other hand, Özçekir et al., 2016 reported that GO flakes of larger building blocks normally resulted in three-fold better mechanical and electrical properties [141].
The coating of graphene or its derivatives onto the flexible substrate is commonly done via roll to roll printing methods (inkjet printing). Deposition, gravure, flexographic, flatbed, soft lithography, laser ablation technique are the typical types of roll to roll printing. The advantages of the roll to roll printing method are in-line hot drying, non-vacuum low temperature deposition, and high-volume continuous production [172-176].

**Challenges and future outlook in this research area**

As prescribed, the flexible OLED launched recently is an indication of realization of graphene-based research study into real world application. It is envisaged that the future OLED display will comprise rollable touch screen with unparalleled resolution and contrast. However, the cost associated to the material/substrate, the stacking process, the barriers protection to oxygen and water (encapsulation process), as well as the solvent selection are the main challenges in OLED research and development. Meanwhile, researchers also concern on the thermal and chemical instability of certain substrates [177]. Apparently, more research studies are required to be done in this area.

Stretch ability is another requirement for flexible electronic devices. To achieve this objective, the adhesion force between the conductive layer (nanomaterials) and the underlying substrate need to be enhanced. Unfortunately, the existing graphene sheets and other nanomaterials are weakly bound to the substrate via van der Waals forces [178]. The poor adhesion may subsequently lead to peeling-off of the nanomaterials during the folding or stretching process. Furthermore, such a poor adhesion will develop into cracks or localised rupture upon stretched. The crack network diminishes the electrical properties of the conductive layer [179] and subsequently led to material failure [180]. To cope with this challenge, research study shall venture into the development of chemical bonding to strongly bind these conductive nanomaterials onto the substrate. For instance, Guo et al., (2015) introduced covalent bond between the Au nanoparticles and PDMS substrate [181]. The strength of chemical bonding is at least two order of magnitude stronger than van der Waals forces. Meanwhile, the authors have introduced a pre-strain process to suppress the localized rupture. The resultant flexible films were found to exhibit a better scratch resistance and durability. The same technique may be tested on graphene-based flexible electronics.

Graphene has been a wonder material and a perfect ingredient for the fabrication of flexible electronics. Nevertheless, it is not without limitation, for instance, graphene possesses with no intrinsic bandgap, huge energy barrier, as well as comparatively high sheet resistance [182]. These limitations have hindered its application in electronics industry. To solve this issue, recent studies have utilised doping technique to improve the electronic properties of graphene [27, 182].

More researches are to be done to further disclose and expand the electronic properties of graphene and its derivatives. For instance, introducing magnetization properties onto graphene and its derivatives (via chemical doping, ion irradiation, or by synthesizing graphene nanoribbons with perfect zigzag edge) may expand their applications to the spintronics field [183-185]. Meanwhile, Piao et al., 2017 [186] reported that the amphiphilic GO sheet able to prevent electric short in the electrorheological measurement, thus, it is a suitable candidate for electrorheological applications. Nevertheless, an ideal flexible electrode shall have good resistance to the electrorheological fluid [187]. Hence, future work may venture into the impact of electrorheological fluid on the flexible materials.

While the usage of graphene and its derivatives have grown significantly over the past few decades, people are now concern about their toxicological impact. It was reported that the toxicity of graphenic materials may vary by their production methods and concentration [188, 189]. Wright et al., 2018 reported that GO with high oxygen content contributed to oxidative stress, cytotoxicity, and pulmonary toxicity. In view of this, future study shall focus on the toxicological studies of graphene-based nanomaterials and ways to reduce it [190]. This piece of information is important especially for flexible electronics that are to be implanted in human bodies.
Conclusion
Application of graphene and its derivatives have been a hot topic due to their tiny sizes and unique electronic properties. Despite being a promising candidate for the fabrication of flexible electronic devices, more research studies are needed, in particular, to boost the electronic properties of the graphene-based nanomaterials, to further improve the adhesion strength of these nanomaterials onto the flexible substrate, as well as to optimise the application performance. In addition, toxicological study is needed prior to large scale incorporation of this nanomaterial in human life.

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Review Article

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