

# Functionalized Graphene/Polymer Nanofiber Composites and Their Functional Applications



Hanan Abdali and Abdellah Aji

**Abstract** Nanofiber composites materials produced by electrospinning may have a very high specific surface area owing to their small diameters, and nanofiber mats can be highly porous with excellent pore interconnection. However, applications using nanofiber composites also require specific properties such as good electrical conductivity, are flame retardant, anti-static and anti-radiative as well. Over the past few decades, the carbon nanomaterial, graphene has been researched widely owing to its intrinsic properties such as large surface area, excellent thermal, electrical, and optical properties in addition to superior chemical and mechanical characteristics needed in specific applications. The chemical functionalization of graphene nanosheet improved its dispersibility in common organic solvents, which is important when developing novel graphene-based nanocomposites. Moreover, graphene may also be functionalized in order to modify its intrinsic characteristics, for example, its electronic properties can be modified to control the conductivity and band gap in nano-electronic devices. Functionalized graphene-based polymer nanofiber composites exhibit a variety of improved, or even new properties such as adsorption performance, anti-bacterial, hydrophobicity and conductivity valued across a wide range of applications in sensors, biosensors, transparent conductive films, high-frequency circuits, toxic material removal, capacitors, spintronic devices, fuel cells, touch screens, flexible electronics and batteries. This book chapter summarizes the recent progress in functionalized graphene-based polymer nanofibers composites, with an emphasis on their applications.

**Keywords** Functionalized graphene · Nanofibers · Nanocomposite · Electrospinning · Electrospun polymers · Applications

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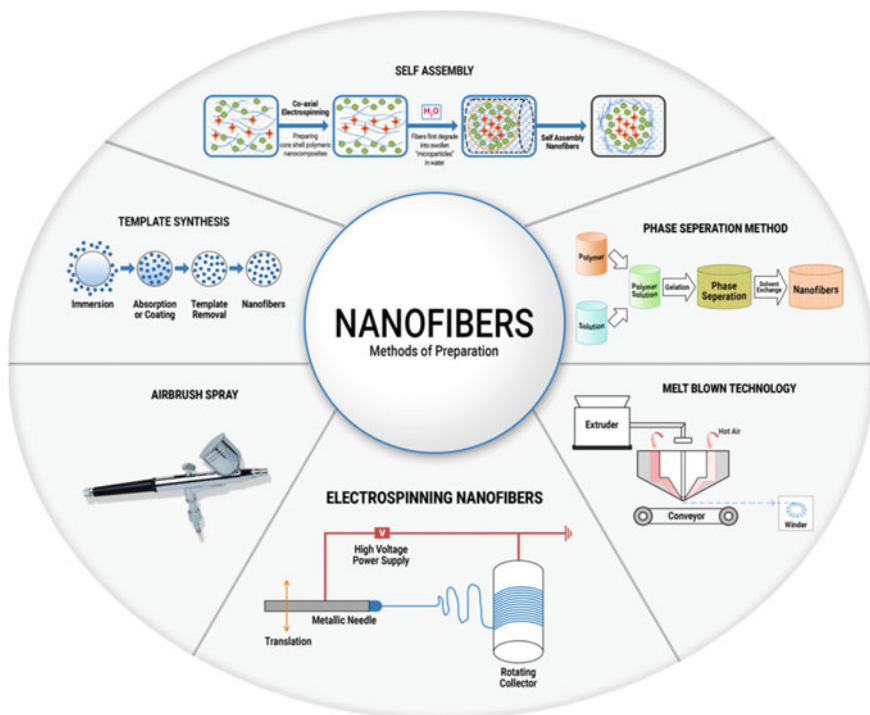
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# 1 Introduction

Materials with nanoscale dimensions, occur in zero, one, two or three dimensions. One dimensional (1D) fibrous nanostructures can be fabricated by various methods such as self-assembly [1, 2], template synthesis [3], phase separation [4], and electrospinning [5–7] (see Fig. 1). Among these methods, electrospinning is a cost-effective, user-friendly and extremely versatile technique, allowing the manufacture of macro/nanofibers in a continuous process and at longer-length scales. There are three phases in the electrospinning process: jet initiation, jet elongation with or without branching, and/or splitting, followed by the solidification of the jet solution into nanofibers [6–8]. Hitherto, more than 100 polymers and numerous inorganic materials have been electrospun into nanofibers. The flexible nature of the electrospinning process allows for easily modifying hierarchical features such as; nonwoven, aligned or patterned fibers, nanoribbons, nanorods, random three-dimensional structures, sub-micron spring and convoluted fibers with controlled diameters when preparing complex nanostructures by changing the solution and processing parameters [6–9] and/or set-up geometries [10–12]. Moreover,



**Fig. 1** Various methods for preparation of nanofibers. With permission from [6]. Copyright © 2017, Elsevier B.V. All rights reserved

electrospinning nanofibers of mixed polymers and carbon particles enhance the mechanical properties of the resultant nanofiber mats and presents structural advantages as it constitutes a nonwoven mesh characterized by large surface area, unit mass and interconnected porosity [13–15]. In particular, graphene is composed of single layers of aromatic carbons and is considered a suitable prospect in the production of functionalized electrospun fibers owing to its remarkable physical and chemical properties, including high fracture strength ( $\sim 125$  GPa), high Young's modulus ( $\sim 1100$  thermal conductivity ( $\sim 5000$  W/mK), rapid mobility of charge carriers ( $\sim 200,000$  cm<sup>2</sup>/Vs GPa), excellent electrical ( $\sim 10^6$  S/cm) and large specific surface area (theoretically calculated value, 2630 m<sup>2</sup>/g) [13–16]. The unique features of graphene surfaces enable easy suspension and mixture with the polymers in powder form for electrospinning solutions. These composites are suitable for producing architected, nanofiber materials for tissue engineering, drug release, sensors, biosensors, batteries and supercapacitors, dye-sensitized solar cells, fuel cells, catalysts, filters, memory devices, and in food applications [14–17]. However, graphene's low dispersibility in common organic and inorganic solutions necessary in such applications, poses a significant challenge that needs to be addressed. In particular, a proficient dispersion of graphene in common solvents is key toward forming homogeneous nanocomposites. Therefore, modifying graphene by tailoring its solubility remains crucial in a multitude of commercial applications. Covalent and noncovalent methods are usually used to modify the surface of graphene. Often, these modification techniques were commonly performed to enhance the dispersion of graphene in a polymer matrix to attain the greatest impact on the fiber materials and correlate the introduced graphene properties to enrich the performance of fibers [13, 18].

In this chapter, the preparation of nanofibers with functionalized graphene and the corresponding effects on the nanofiber composites, while exploring recent research in relevant applications is also discussed. The strategies to functionalize graphene surfaces are also briefly highlighted.

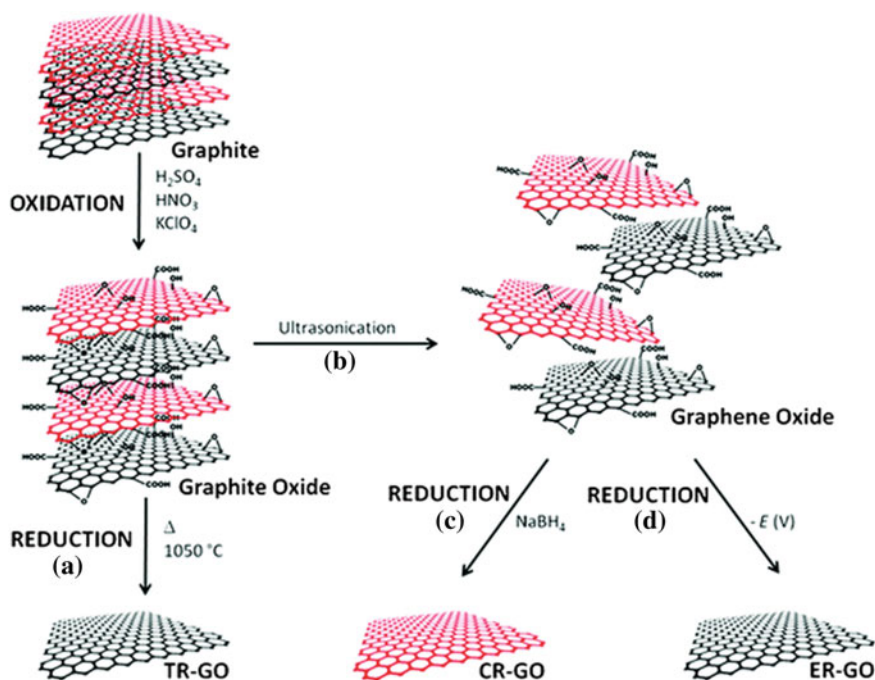
## 2 Chemical Functionalization of Graphene

Graphene, consisting of a single-layer sp<sup>2</sup>-hybridized carbon atom network, is the most intensively studied material in nanotechnology owing to its properties and features. This single-atom-thick sheet of carbon atoms arranged in a honeycomb pattern is the world's thinnest, strongest, and stiffest material, also boasts excellent conductivity, thus graphene is being studied in almost all fields of science, medicine and engineering [19–21]. Despite its potential in various applications, it is also noteworthy that graphene itself possesses a zero band gap including inertness to reaction, that weakens its competitiveness in the field of semiconductors and sensors. Consequently, this remains a significant reason for research in this material paying special attention to its functionalization, reaction with organic and inorganic

substances, as well as the chemical modifications of graphene surfaces including the intensity of covalent and noncovalent interactions with graphene [18–23].

As, the most current and lucrative method for large scale production of graphene-based materials is centered around the oxidation of graphite to graphene oxide (GO) and then reducing the GO to graphene by either thermal, chemical, or electrochemical methods [18, 20] (see Fig. 2). The GO surfaces are highly oxygenated, and carboxyl, diol, ketone, epoxide, and hydroxyl functional groups can alter the van der Waals interactions significantly and enable greater solubility in water and some organic solvents. Yet, owing to the presence of the oxygen functional groups in its structure, GO is electronically insulating and thermally unstable as it undergoes pyrolysis at elevated temperatures [19–21]. Therefore, reducing GO removes most but not all of the hydroxyl, carboxylic acid and epoxy functional groups [19–21].

Usually variations on the Staudenmaier [24] or Hummers [25] methods are used to obtain GO in which graphite is oxidized using strong oxidants such as  $\text{KMnO}_4$ ,  $\text{KClO}_3$ , and  $\text{NaNO}_2$  in the presence of nitric acid or its mixture with sulfuric acid



**Fig. 2** Schematic of the production of CMGs from graphite. Graphite was first oxidized to graphite oxide. Thermal reduction and exfoliation (a) of graphite oxide led directly to TR-GO. Graphite oxide was ultrasonicated (b) to generate graphene oxide, following which the chemical reduction (c) of graphene oxide yielded CR-GO. Alternatively, graphene oxide was electrochemically reduced (d) to afford ER-GO. With permission from [20]. Copyright © 2012, Royal Society of Chemistry

[25]. Gao et al. [26] used a  $K_2FeO_4$ -based oxidation approach instead of  $KMnO_4$  to obtain a single-layer GO at room temperature. Recently, using the Hummers method, Yu et al. [27] have obtained GO that is free of  $NaNO_3$  by partly replacing  $KMnO_4$  with  $K_2FeO_4$  and controlling the amount of concentrated sulfuric acid. The chemical reduction of GO by using reducing agents for example; hydrazine [28, 29], sodium borohydride followed by hydrazine [30], hydroquinone [31], dimethylhydrazine [32], and ascorbic acid [33], etc., provides a streamlined technique for the production of graphene, nevertheless, the cost and hazardous nature of these chemicals utilized during the reduction may limit its application [34]. Conversely, thermally reducing graphene oxide (RGO) is produced by heating dry GO under inert gas and high temperature [34–37], for instance, heating GO in an inert environment at 1000 °C for 30 s results in the reduction and exfoliation of GO generating RGO layers. As such, the thermal reduction produces chemically modified graphene layers without the need for dispersion in a solvent compared with other chemical reduction methods [34]. Accordingly, to obtain functionalized graphene, the chemical modification of graphene oxide followed by reduction was used. It has been demonstrated that both modification techniques are excellent for the preparation of processable graphene, preventing agglomeration and enabling the formation of stable dispersions and was utilized for the fabrication of polymer nanofiber composites in numerous applications [13, 18, 37].

## 2.1 *Non-covalent Functionalization*

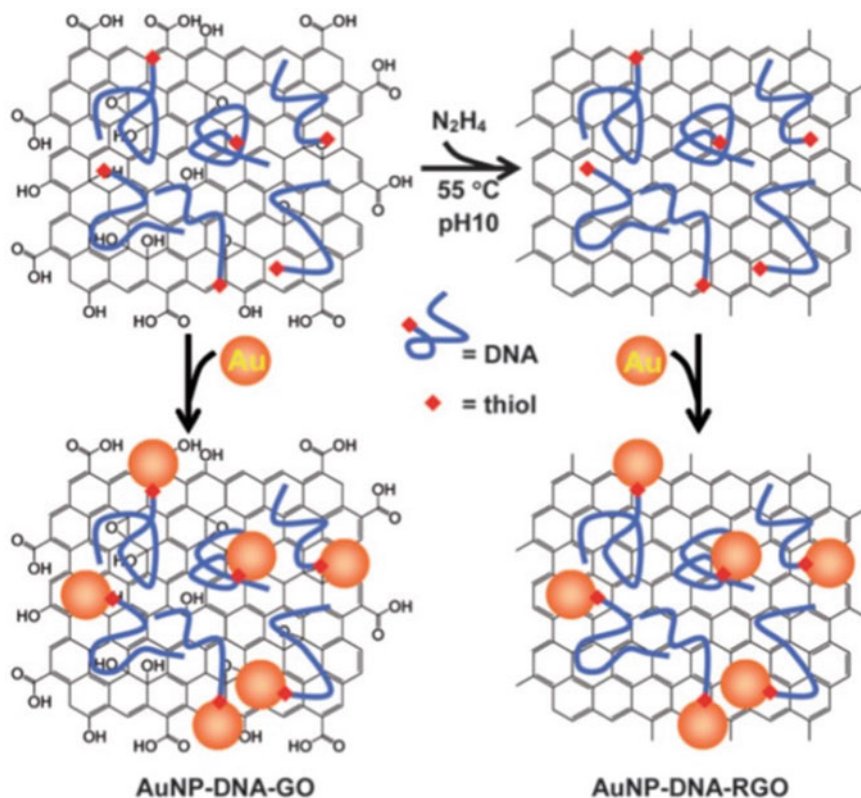
The non-covalent functionalization, which relies on the van der Waals force, electrostatic interaction or  $\pi$ - $\pi$  stacking [38, 39], is easier to undertake without changing the chemical structure of the graphene sheets. Consequently, this is the most effective way of customizing the electronic/optical property and solubility of the nanosheets [40], because, without affecting the electronic network, it offers the possibility of attaching functional groups to graphene [41, 42]. Noncovalent modification is attained by the interaction with polymers, such as poly (3-hexylthiophene) (P3HT), porphyrin, pyren, cellulose derivatives, polyaniline (PANI), poly(sodium 4-styrenesulfonate) (PSS), and porphyrins or biomolecules such as deoxyribonucleic acid (DNA) and peptides, as well as adsorption of surfactants or small aromatic molecules. The first example of non-covalent functionalization of graphene nanosheets using PSS was published by Stankovich et al. [39]. It was found that exfoliation and in situ reduction of GO in the presence of PSS could form non-covalently-functionalized graphitic nanosheets that were extremely stable and dispersible in water (1 mg/ml). It is possible to achieve a stable dispersion of reduced graphene in different organic solvents with amine-terminated polymers through non-covalent functionalization [43]. In this technique, the reduction of GO is first undertaken in an aqueous medium using an ammonia-hydrazine mixture, this is then followed by washing and the removal of aggregated graphene sheets. The amine-terminated polymer is dissolved in organic

solvents for non-covalent functionalization of RGO. Next, the aqueous dispersion of RGO is added to the organic polymer solution. The phial including phase-separated organic and aqueous phases then undergoes a 5 h sonication for the non-covalent functionalization of graphene. Here, the functionalized graphene can easily be dispersed in a variety of solvents and is shown to exhibit electrical conductivity [43]. Liu et al. [44] have successfully functionalized the graphene surfaces with a pyrene-terminated positive charged polymer, poly(2-N,N'-(dimethyl amino ethyl acrylate)) (PDMAEA), and a negatively charged polymer, polyacrylic acid (PAA) via  $\pi$ - $\pi$  stacking. The functionalized graphene polymer composites indicated that the phase transfer behavior between aqueous and organic media occurs at different pH values. The remarkable electrical conductivity of graphene with an extremely high surface area (theoretically 2630 m<sup>2</sup>/g), is combined with the graphene nanosheets is used to construct nanodevices specifically when developing high capacity cathode materials for Li-ion batteries [44]. In other research, gold nanoparticles were deposited on DNA-functionalized graphene presented by Liu et al. [45] (see Fig. 3), where thiolated DNA oligonucleotides were prepared to adsorb on to the GO nanosheets resulting in the DNA-coated GO being reduced by hydrazine to DNA-RGO. Gold nanoparticles were then mixed in aqueous solutions of DNA-RGO and DNA-GO composites respectively. These gold-arrayed DNA-functionalized graphene nanosheets have considerable potential not only in the field of bio detection but also for use in optoelectronics, battery materials, magnetism catalysis, field effect devices [45]. In a subsequent study, Choi et al. [46] have described the functionalization of graphene through self-assembly of a hydrophobic backbone of Nafion (see Fig. 4). The result indicated that the graphene nanosheets were easily dispersible and presented with biosensing properties of good conductivity and electrochemical characteristics for organophosphates.

Functionalization can be used to maximally retain the natural structure of graphene, yet, it must be also be noted that interactions between functionalities and graphene surfaces remain weak and therefore unsuitable applications requiring strong interactions.

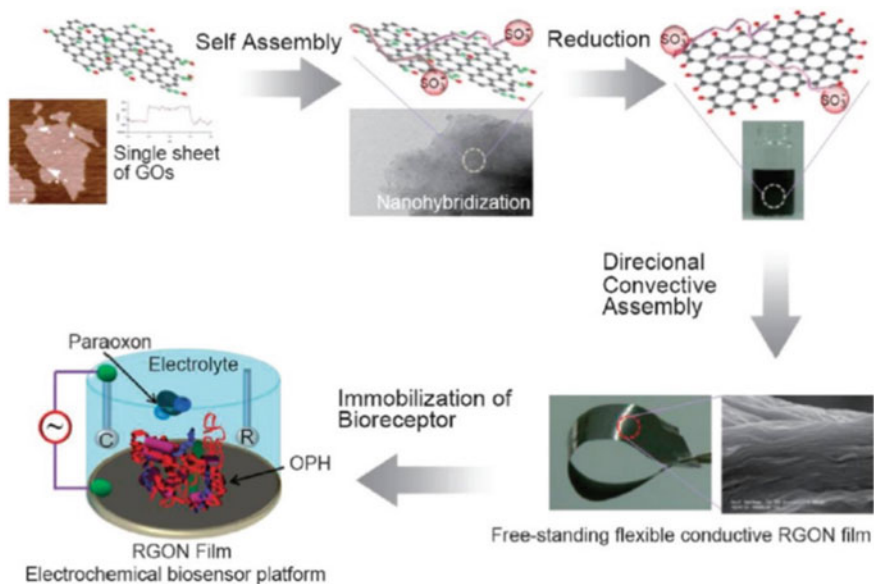
## 2.2 Covalent Functionalization

Reaction between the functional groups of the molecules and the oxygenated groups on GO or reduced GO (RGO) surfaces is the foundation for covalent functionalization of graphene [47, 48], for example, carboxyls on the edges with epoxides and hydroxyls on their basal planes [49]. The abundant surface chemistry of GO/RGO enables a myriad of possibilities during the covalent functionalization of graphene-based sheets when compared with non-covalent functionalization. Covalent techniques are employed to generate composites that have strong interactions between graphene and the modifier [49]. GO or RGO can be grafted onto polymeric chains that have reactive groups like hydroxyls and amines, such as, poly(ethylene glycol), polylysine, polyallylamine, and poly(vinyl alcohol). These



**Fig. 3** DNA coating and aqueous dispersion of GO and RGO, which were then used as two-dimensional bio-nano-interfaces for homogeneous assembly of metal carbon heteronanostructures. With permission from [45]. Copyright © 2010, Royal Society Chemistry

materials are combined together and promise the desired properties of their individual parts, for example; the polymeric part offers dispersibility in certain solvents, mechanical strengthening, and many morphological properties, while the graphene nanosheets exhibits characteristics such as chemical reactivity, electrical conductivity, and reinforcement of the mechanical properties. The poly-L-lysine (PLL) was covalently grafted to RGO through the reaction of epoxy groups on graphene oxides and amino groups on PLL in the presence of potassium hydroxide (KOH) [50] (see Fig. 5). PLL-functionalized graphene is water-soluble and biocompatible, which makes it a novel material promising in biological applications. In an analogous approach, Salavagione et al. [47] successfully prepared the PVA covalently grafted onto GO nanosheets via ester bonds between the carboxylic groups of GO and the hydroxyl groups of PVA. These chemical bonds can be created either by direct formation or after the transformation of carboxylates to the more reactive acyl chlorides. It was shown that the PVA/RGO composite was

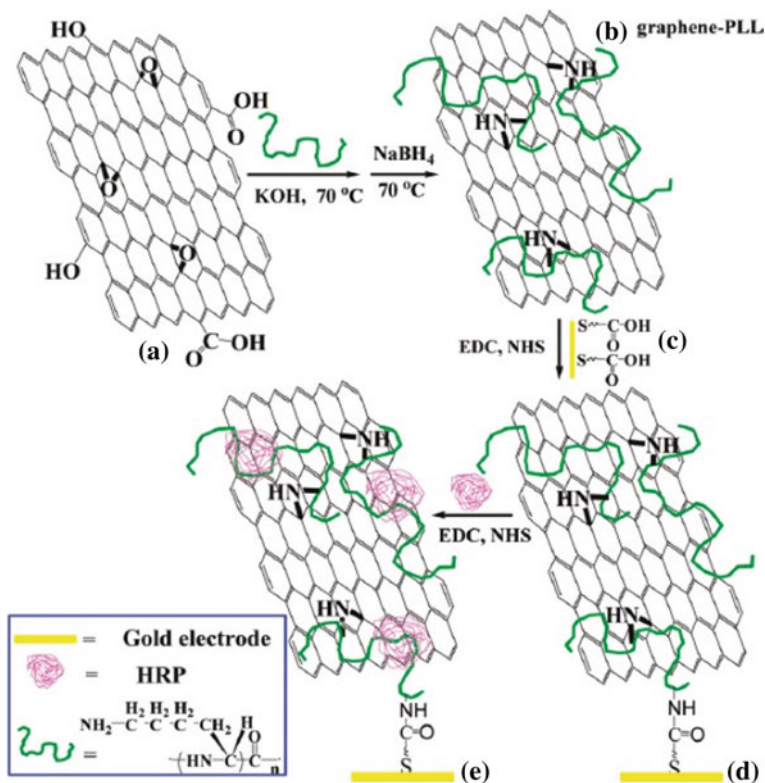


**Fig. 4** Illustration of a procedure to design RGON hybrids and the RGON platform used as an electrochemical biosensor. With permission from [46]. Copyright © 2010, American Chemical Society

generated after partial reduction by hydrazine [47]. Lee et al. [51] have also presented an easily obtained method for covalent attachment of polymer brushes to GO surface utilizing initiated atom transfer radical polymerization (ATRP). The hydroxyl groups formed on the surface of GO were initially functionalized with a common ATRP initiator (α-bromoisobutyryl bromide), and next polymers of styrene, butyl acrylate, or methyl methacrylate were grown directly through a surface-initiated polymerization (SIP).

Moreover, Lee et al. [51] presented two primary conclusions in their investigation of polystyrene (PS). First, it was suggested that by altering the ratio of initiator modified GO and monomer it was possible to adjust the polymer chain length. Second, it was discovered that the monomer loading changes the molecular weight of the grafted PS, this was produced by gel permeation chromatography (GPC) after detaching by saponification, and it was noted that the polydispersity was low. As such, the authors suggest that the polymerization proceeded in a controlled way. Furthermore, the PS-functionalized GO was shown to increase the solubility in N,N-dimethylformamide (DMF), toluene, chloroform, and dichloromethane significantly, further enhancing the processing capacity of PS-functionalized GO for applications in polymer-based composites [51]. It was found that heating a diazonium salt, resulted in an extremely reactive free radical, which attacks the  $sp^2$  carbon atoms of graphene forming a covalent bond. This reaction has been applied by Niyogi et al. [52] the covalent attachment of





**Fig. 5** Schematic diagram of graphene-PLL synthesis and assembly process of graphene-PLL and HRP at a gold electrode. With permission from [50]. Copyright © 2009, American Chemical Society

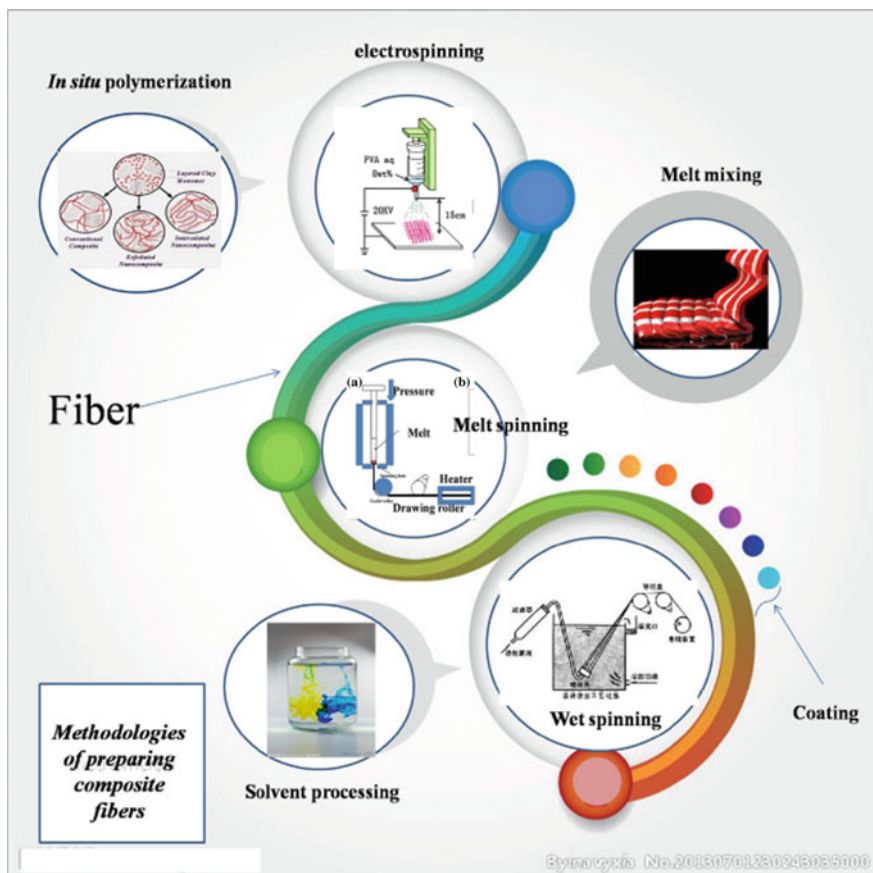
nitrophenyls to graphene sheets introduces a band gap, which can be controlled, making the functionalized graphene potentially useful as semiconducting nanomaterials. Furthermore, the addition of an alternative free radical includes the reaction of benzoyl peroxide with graphene sheets [53]. In another study, Vadukumpully et al. [54] developed a basic yet flexible method for the covalent functionalization of graphene with alkylazides, where the alkyl chains incorporated various functional groups such as hydroxylundecanyl, dodecyl, hexyl and carboxy-undecanyl resulting in improved dispersibility that helped facilitate composite fabrication. This strategy provides a useful platform for the synthesis of functional graphene nanocomposites using gold nanoparticles (the carboxyl groups can trap and immobilize the gold nanoparticles in a selective manner). Moreover, GO could be used as a support for enzyme immobilization in the preparation of biosensing devices. The immobilization of glucose oxidase (GOx) onto GO nanosheets was attained via amide bonding [55].

### 3 Preparation of Functionalized Graphene Based Polymer

#### 3.1 Nanofiber Composites

Graphene's unique electronic, mechanical and thermal properties [14, 15] ensure its role as a promising filling agent for nanofibers composite applications [14]. Graphene has the ability to function as a nanofiller that can potentially enhance the characteristics of polymer-based nanofiber composites at a very low loading. However, several factors can control the characteristics and uses of graphene/polymer nanofiber composites such as the type of graphene utilized, its inherent properties, the manner of dispersion of graphene in the polymeric matrix, its interfacial interaction, the state of wrinkling in the graphene, and the structure of its network in the matrix [13, 56]. Therefore, the functionalization of graphene by covalent and non-covalent modifications promotes the dispersion of graphene in various organic solvents, and this aqueous dispersibility is greatly beneficial for producing graphene sheets, films, fibers composites, etc. Hence, many studies have shown that the chemical modification of graphene alters the graphene microstructure, producing graphene with various functional groups, electrical conductivity, carbon to oxygen atomic ratio (C/O ratio), and solubility in solvents, etc. [13, 43, 57–59]. He and Gao reported a simple and efficient strategy for grafting different functional groups or polymeric chains onto graphene nanosheets using nitrene cycloaddition. This method produced single-layered, functionalized graphene with a variety of functional groups (e.g., hydroxyl, carboxyl, amino, bromine, long alkyl chain, etc.) or polymers (e.g., poly(ethylene glycol), polystyrene) to covalently attach onto the graphene, in a one-step reaction (see Fig. 6) [58]. The modified graphene nanosheets produced are electrically conductive, and have good dispersibility and processability in organic solvents, which advocates their properties as potential contenders not only in future modifications but also in various applications of polymer nanofiber composites. Similarly, Moayeri and Ajji [60] have successfully fabricated a conductive polymer nanofiber composite of 1-pyrenebutanoic acid, succinimidyl ester functionalized graphene/polyaniline/poly(ethylene oxide) (G-PBASE/PANi/PEO). This unique nanostructured composite of PANi/PEO/G-PBASE with small loading of G-PBASE (5 wt% relative to PANi) exhibited increased improvement in the electrical conductivity and good thermal stability in comparison to PANi/PEO nanofibers owing to the homogenous distribution of the functionalized graphene in the polymeric matrix [60]. Moreover, Rafiee et al. [61] have reported that the modified graphene nanosheets are notably effective at intensifying the energy, fracture toughness, fatigue resistance, strength, and stiffness of epoxy polymers at significantly lower loading fractions upon comparison with other additives such as nanoclay, carbon nanotubes (CNTs), and nanoparticles additives. At 0.125% weight of functionalized graphene sheets was remarked to have improved the fracture toughness  $\approx 65\%$  and the fracture energy by  $\approx 115\%$  [61].





**Fig. 7** Schematic illustration of the methods for preparation of fiber composite materials. With permission from [13]. Copyright © 2016, Elsevier Ltd. All rights reserved

polymer matrix remains a considerable challenge as it does in both in situ polymerization and solvent processing [62]. Chatterjee et al. [63] have studied the influence of graphene nanosheets on the structure and mechanical properties of polyamide 12 (PA12) fibers. The PA12 and graphene composite fibers that were fabricated via melt processing were found to help in breaking the agglomerates present in the PA12 and graphene composite fibers during the melt compounding in the micro extruder due to the shear high forces. Although the composite fibers exhibited improved elasticity, yield and tensile strength, the melt spinning process also revealed that there is a high risk of agglomeration [63].

**In situ polymerization** provides strong interaction between the functionalized graphene and the polymeric matrix and enables an outstanding, homogeneous dispersion. Generally, functionalized graphene is mixed with prepolymers or

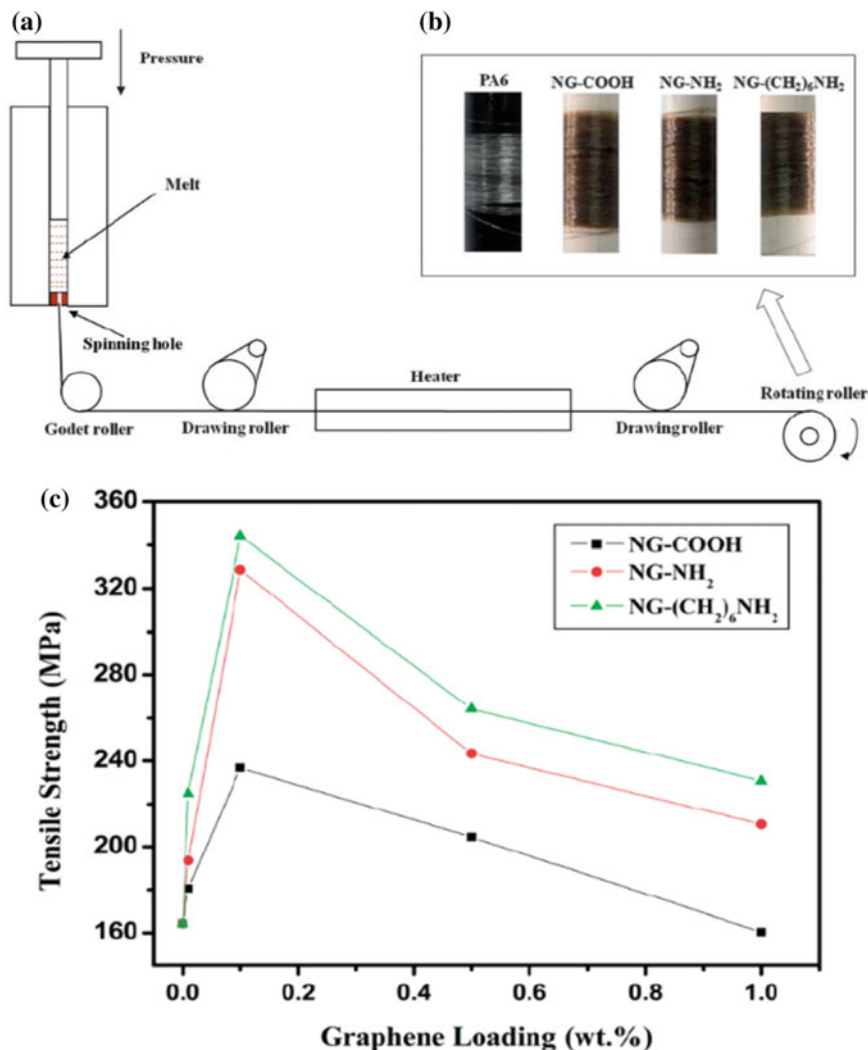
monomers where heat or radiation is then used to initiate the polymerization process [64]. As functionalized graphene can be further functionalized by grafting polymer chains through atom transfer radical polymerization (ATRP) resulting in covalent bonding. Generally, for in situ polymerized nanocomposites, melt spinning which is conducted in a piston spinning machine and hot-roller drawing machine, is commonly used. The research on in situ polymerization of nanocomposites studies not only the effect of the nanofillers on the morphology of the polymer matrix and its final characteristics but also includes the polymerization reaction. Hou et al. [65] successfully prepared nanocomposites of functionalized graphene grafted by polyamide 6 (PA6) by in situ polycondensation of caprolactam (CPL), using the melt spinning and drawing process to produce the nanocomposite fibers. It was established that due to the good distribution of functionalized graphene (0.1 wt%) in the PA6 matrix, the tensile strength of the fibers increased dramatically. Yet, when the functionalized graphene is 0.5 wt% or higher, the graphene agglomerates in the nanocomposite fibers resulting in a reduced tensile strength (see Fig. 8) [65].

**Solution processing** is widely used to produce polymer nanofiber composites with uniform graphene dispersion effectively. In this method, functionalized graphene is mixed with a polymer solution after first dispersing in a solvent by using techniques such as magnetic agitation, mechanical mixing, or high-energy sonication [56]. Next, by vaporizing the solvent a composite is produced. Many types of polymer nanofibers have been reinforced by graphene, for instance poly(vinyl alcohol) (PVA) [66–68], polystyrene (PS) [32], Polyethylene (PE) [69], polyvinyl fluoride (PVF) [70], polymethyl methacrylate (PMMA) [57, 60, 71], nylon 6 [72], and chitosan [73–75], etc. However, the specific surface area of the 2D fillers could decrease considerably due to the re-stacking, aggregation and folding techniques of the graphene-based nanosheets. As such, surface functionalization of graphene-based fillers before solution mixing is undertaken to overcome this problem.

Usually, there are three types of spinning techniques to fabricate modified graphene-based polymer nanofiber composites: melt-spinning, wet-spinning and electrospinning. We mainly discuss below the electrospinning technique to fabricate functionalized graphene-based polymer nanofiber composites.

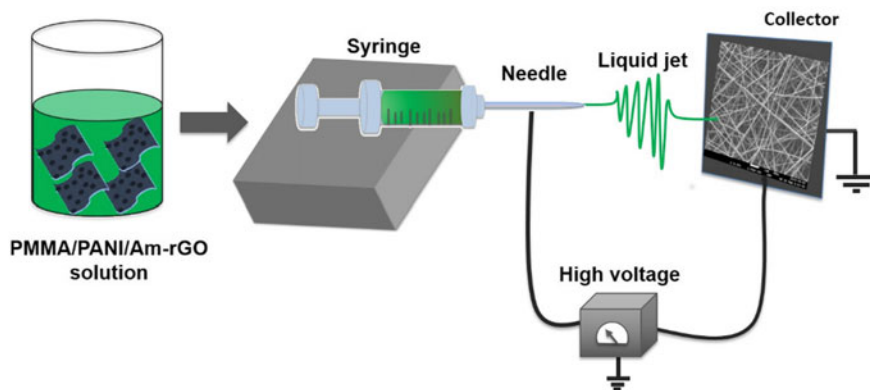
## 4 Principle of Electrospinning

Recently, interest in nanoscale properties and technologies have increased the use of electrospinning technology, owing to its efficient, relatively simple and cost-effective process for producing ultrafine nanofibers or fibrous structures of many polymers with a range of diameters from sub-microns to nanometers [7, 76, 77]. The nanofibers structures obtained using this process result in unique advantages for example, the flexible porosity of the electrospun structure, high surface to volume ration and the ability to spin into different shapes and sizes. These



**Fig. 8** a Melt spinning apparatus used for preparing nanocomposite fibers. b Photographs of neat PA6 and 0.1 NG fibers. c Tensile strength of NG nanocomposite fibers with different loadings of graphene. With permission from [65]. Copyright © 2014, The Royal Society of Chemistry

characteristics exemplified by the nanofibers qualifies their candidacy for applications in filtrations, tissue engineering scaffolds, wound healing, energy storage, sensors, catalyst and enzyme carriers [7]. Technically, electrospinning is a method that employs a strong electric field to draw liquid polymer into fine filaments [12, 78, 79]. The simple electrospinning apparatus made up of a micro-syringe with a needle of small diameter, a nozzle, a high voltage supplier, and an electrode collector, (see Fig. 9) The collector can be fashioned into any shape according to

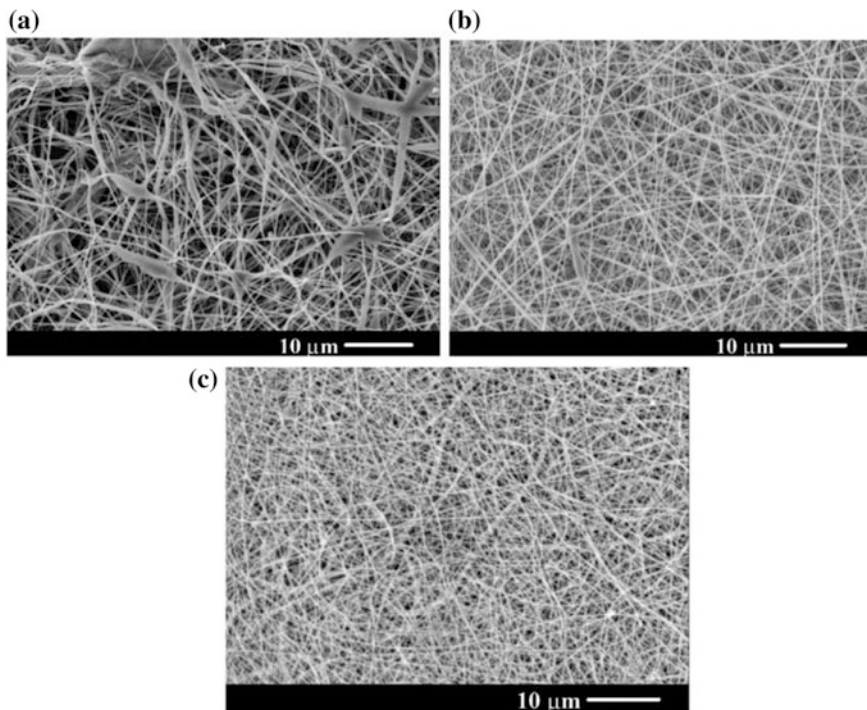


**Fig. 9** Schematic illustration of the electrospinning setup. With permission from [57]. Copyright © 2017, Polymers

the specified product requirements for example; a flat plate, rotating drum, or patterned collector. In most cases, the collector is simply grounded. When a high voltage solution is charged, and the repulsive force within the charged solution is larger than its surface tension and a jet erupts from the tip of the spinneret. This electrified jet then moves counterclockwise towards the electrode, forming a long and thin thread. Subsequently, as the liquid jet is continuously elongated and the solvent is evaporated, randomly oriented, nonwoven mat nanofibers with small diameters (micro to nanometers) are deposited on the collector [12, 78, 79].

Electrospinning deals with several conditions that can influence the transformation of polymer solutions into nanofibers through its process. These include; (i) the intrinsic properties of the solution, such as viscosity, elasticity, conductivity, and surface tension, (ii) the processing parameters for example; the electric potential at the needle, the feeding rate for the polymer solution, and the distance between the syringe and the collector screen [78, 79], (iii) ambient conditions such as temperature, humidity and air velocity in the electrospinning chamber [78, 79]. Proper control of these parameters can be tailored to fiber morphologies and diameters of the electrospun fibers. However, researchers usually elect to keep ambient conditions constant in their research.

Zong et al. [80] studied the effects of varying the processing parameters and solution properties on the structure and morphology of the electrospun fibers. It was discovered that the effect of solution conductivity on the fiber diameter are inversely related, for example, the lower solution conductivity resulted in a larger fiber diameter. Zong et al. reported that the addition of different salts to the polymer spinning solutions, resulted in a higher charge density on the surface of the ejected jet exhibiting more electric charges carried by the jet [80]. The results also demonstrated that salts with smaller ionic radii formed fibers with smaller diameters and vice versa. Mainly, it indicated that greater charge densities led to greater mobility of ions with smaller radii which generated increased elongation forces

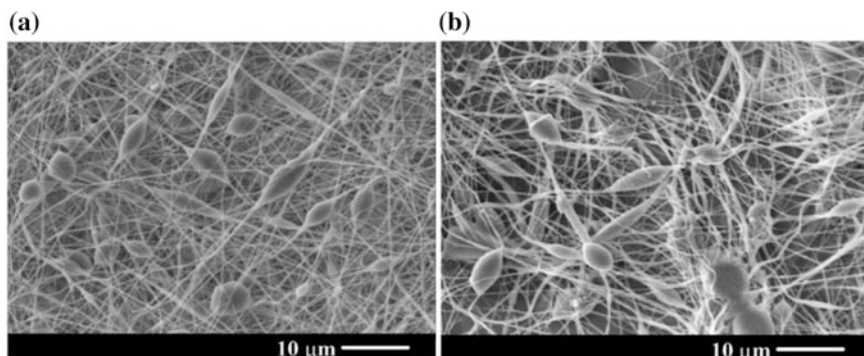


**Fig. 10** SEM images of PDLA membranes fabricated by electrospinning of a 30 wt% solution at voltage of 20 kV, feeding rate of 20 ml/min and with 1 wt% of **a**  $\text{KH}_2\text{PO}_4$ ; **b**  $\text{NaH}_2\text{PO}_4$  and **c** NaCl. With permission from [80]. Copyright © 2002 Elsevier Science Ltd. All rights reserved

exerted on the polymer jet creating a smaller fiber (see Fig. 10) [80]. Moreover, they reported that different fiber morphologies can also be obtained by altering the solution feed rate at a given electric field. They concluded that the droplet suspension at the end of the spinneret is larger with a higher feed rate so the jet of the solution could carry the fluid away at faster velocity. Therefore, this can lead to large beaded fibers as the polymer is not completely dry upon reaching the collector (see Fig. 11) [80]. Additionally, it was demonstrated that higher concentrations and the corresponding higher charge densities of the solution produced uniform fibers with no bead-like textures.

In another study, Ramazani and Karimi investigated the presence of varying amounts of graphene oxide (GO) with different oxidation levels on the morphological appearance, fiber diameter, and structure of poly( $\epsilon$ -caprolactone) (PCL) nanofibers fabricated by the electrospinning method [81]. It was observed that parameters such as GO dispersibility, charge relaxation time, polarity and wettability all of which are used to measure the fiber diameter, improves with oxidation. The surface tension of PCL solution is unchangeable in the presence of GO with different loading and level of oxidation, resulting in diameter variations in





**Fig. 11** SEM images showing the variation of beaded fibers at different feeding rates: **a** 20 ml/min; **b** 75 ml/min. The applied voltage was 20 kV and concentration was 25 wt% with 1 wt%  $\text{KH}_2\text{PO}_4$ . With permission from [80]. Copyright © 2002 Elsevier Science Ltd. All rights reserved

the electrospun fibers. Moreover, they reported that the average fiber diameter decreases in the presence of GO with different loading, owing to the reduction of solution viscosity and increase in the conductivity [81]. Accordingly, researchers have also shown that after GO surfaces were functionalized with poly(ethylene glycol) (PEG), the poly(lactic acid) (PLA)/GO-g-PEG nanocomposite nanofibers exhibited a decrease in diameters when comparing with pure PLA [82]. The plasticizing effect of the grafted PEG molecules on the surface of GO attributed to the decrease in viscosity for PLA/GO-g-PEG electrospinning suspensions, indicating strong interfacial adhesion between GO-g-PEG and PLA and was responsible for the reduction in the average diameter from PLA to PLA/GO-g-PEG [82]. Das et al. [83] indicated that the addition of non-covalently functionalized graphene to the PVA fibers increased the effective fluid charge density, therefore it was necessary to change the flow rate from 0.3 to 15 ml/h. It was shown that a reduction in bead formation resulted with an increase in applied voltage from 10 to 15 kV. An increase in voltage is necessary as the conductivity of the graphene increases the surface charge of the fiber, perpetuating natural bead formation. Furthermore, a higher voltage is required as the elasticity of the jet is increased due to the addition of graphene when compared with the baseline experiment. Increasing the voltage amplifies the repulsive electrostatic force and favors the formation of fibers with smaller diameters [83].

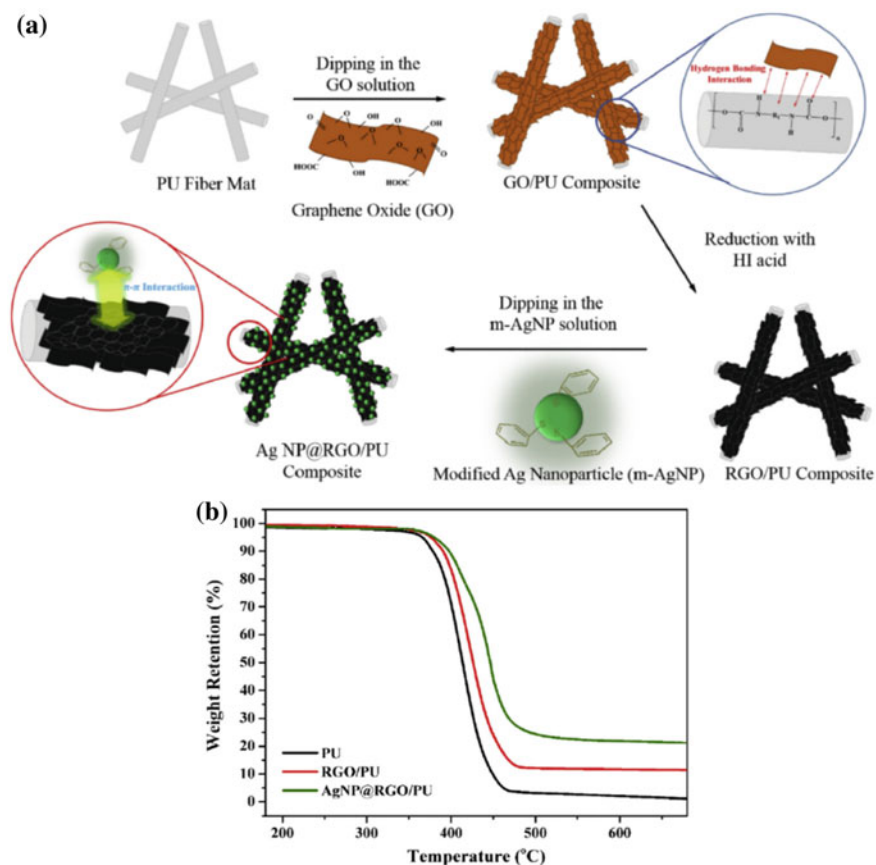
Overall, it was considered that preparing an optimized suspension of functionalized graphene in the solution improved the applicability of the resulting nanofibers. Therefore, many experiments are still needed to produce electrospun functionalized graphene/polymer nanofibers for morphological modification, necessary to meet specific requirements for applications.

## 5 Properties of Functionalized Graphene Based Polymer

### 5.1 Nanofibers Composite

Surface functionalization of graphene showed significant improvement in dispersibility/processability in solvents, as well as in polymer matrices [49, 56, 84]. These in turn, exhibit excellent enhancement in mechanical, electrical, optical and thermal properties of host polymers at very low loading levels. Numerous studies on the properties of functionalized graphene based polymer nanofiber composites have been reported [14, 56, 84]. For instance, Young's modulus, tensile strength, thermal stability, conductivity, and hydrophobicity. Hsiao et al. [85] advocated a basic yet effective method to decorate silver nanoparticles (AgNPs) and RGO on the surface of polyurethane (PU) fibers to fabricate AgNP@RGO/PU fiber composites. This technique provided an effective way of producing lightweight, highly flexible electronic products that have excellent electrical properties. The surface of PU fiber mat was decorated with GO by dipping the PU fiber mats into the GO aqueous solution (GO/PU) and then the GO/PU fiber composite was reduced in hydriodic acid (HI). After that, the AgNPs were deposited on RGO/PU to fabricate AgNP@RGO/PU fiber composites (see Fig. 12a) [85]. They found that the decorated AgNP@RGO restricts the PU fiber mat from thermal decomposition resulting in a notable improvement in thermal stability of composite (see Fig. 7b). Moreover, the AgNP@RGO/PU fiber composites showed superior improvement in electrical properties ( $<10$  U/sq), because the deposited m-AgNPs effectively facilitate the charge transfer ability of RGO [85].

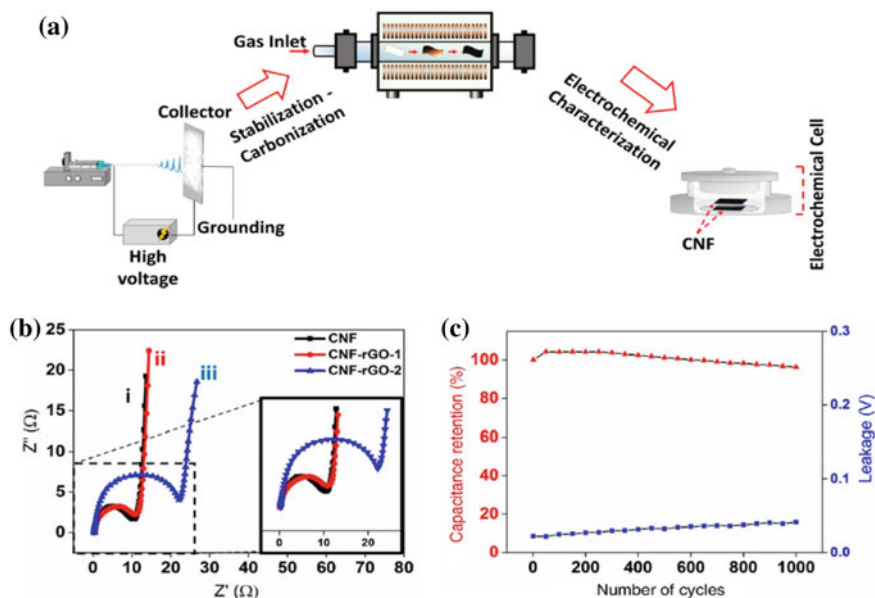
Chee et al. [86] reported a new, non-covalent surface functionalization technique of GO via a UV-sensitive initiator embedded via  $\pi$ - $\pi$  interactions on the graphene nanosheets, followed by the polymerization of hydrophobic polymeric chains along the surface of the graphene. Thereafter, the functionalized GO/Polyacrylonitrile (PAN) nanofibers were produced by the electrospinning technique and then the nanofibers underwent thermal treatments that converted the polymeric chains into a CNF structure as shown in Fig. 13a. The results revealed that functionalized GO was readily dispersed in different solvents, and in the hydrophobic polymeric solution. Furthermore, the functionalized GO-reinforced CNF (CNF/fGO) exhibited an extraordinary ability by showing a specific capacitance of 140.10 F/g, approximately three times higher than that of neat CNF, coupled with a high stability capacitance retention of 96.2% after 1000 times of charge/discharge cycles at 1 A/g (see Fig. 13b and c) [86]. In a further study, Moayeri and Ajji [87, 44] have produced core-shell structured CNF embedded with non-covalently modified graphene by single-nozzle electrospinning setup utilizing phase separated solutions of PAN and polyvinylpyrrolidone (PVP) in DMF solution, followed by the calcination and carbonization processes. Electrochemical assessment of CNF/graphene (G) nanofibers revealed a maximum specific capacitance of 265 F/g after addition of 10 wt% graphene nanosheets. Furthermore, based on the Brunauer-Emmett-Teller (BET) results, the specific surface area and pore volume were increased, directly proportional from



**Fig. 12** **a** Schematic representation of the procedure for preparing the AgNP@RGO/WPU composites; **b** The TGA curves for PU, RGO/PU and AgNP@RGO/PU. With permission from [85]. Copyright © 2015, Elsevier Ltd. All rights reserved

CNF/G0 to CNF/G10 samples and then showed a decreased amount for CNF/G15 sample, which further supports the outcomes generated from the electrochemical tests. The larger pore volume and surface area can be attributed for affecting ion diffusion with high speed at high loading current density and allows for more efficient utilization of specific surface area [87].

Scaffaro et al. [88] investigated the reaction of GO-g-PEG on the mechanical and wettability characteristics of polycaprolactone (PCL) electrospun scaffolds. The contact water angle measurements of PCL/GO-g-PEG composite nanofiber showed better performance with lower water contact angles. The Young moduli of the composite nanofiber mats were significantly improved by adding a low concentration of GO-g-PEG, owing to the grafted PEG chains, which enhanced the filler dispersion. Additionally, the primary proliferation rate results were studied, to



**Fig. 13** **a** Schematic diagram illustrates the synthesis of functionalized CNF/fGO for electrochemical measurement in a two-electrode configuration; **b** Nyquist plots of pure (i) CNF, (ii) CNF/fGO-1, and (iii) CNF/fGO-2. The inset magnified the high frequency region of the spectra; **c** capacitance retention and voltage drop of CNF/fGO-2 as the function of continuous charge/discharge cycles. With permission from [86]. Copyright © 2017, Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by Elsevier B.V. and Science Press. All rights reserved

examine the capability of MC3T3-E1 osteoblastic cells to proliferate on the surfaces of PCL and PCL/GO-g-PEG nanocomposite scaffolds. The preliminary biological assay indicated that PCL/GO-g-PEG improved the ability of cell growth and attachment, owing to the increased hydrophilicity and the resulting degree of cell affinity for the substrate, when compared with the electrospun PCL scaffold [88]. Other research showed significant improvements in thermal, mechanical, and wettability properties of PLA electrospun nanofibers upon addition of GO-g-PEG was published [82]. These studies found that the PLA/GO-g-PEG demonstrated better wettability with lower water contact angles than PLA and PLA/GO as well as the TGA results, that exhibited the GO-g-PEG had a prominent influence than GO in enhancing the thermal stability of PLA electrospun nanofibers. Besides, a significant enhancement of tensile strength of PLA/GO-g-PEG composite nanofibers was reported [82]. In addition, the initial tests of cytocompatibility with Swiss mouse NIH 3T3 cells of PLA, PLA/GO, and PLA/GO-g-PEG nanofibers, were examined. The results indicated the PLA/GO and PLA/GO-g-PEG composite nanofiber scaffolds were non-toxic to NIH 3T3 cells and able to support cell attachment and growth [82, 88].

It can be generally regarded that these electrospun functionalized graphene/polymer nanofibers are capable of supporting various applications in different fields such as sensors, biosensors, electrodes, energy storage or conversion (supercapacitors, fuel cells, solar cells, and batteries), conductive wires, and biomedical materials.

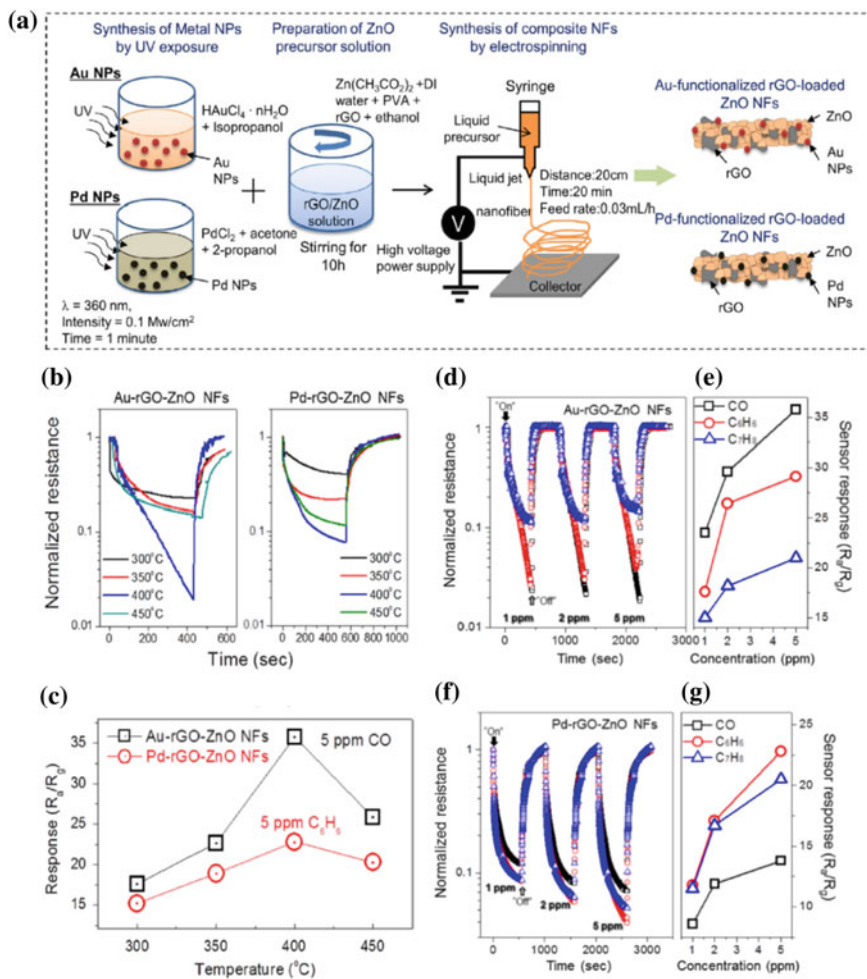
## 6 Application of Functionalized Graphene-Based Polymer

### 6.1 Nanofiber Composites

Various applications can be designed using functionalized graphene/polymer composite nanofibers. For instance, the produced polymer/GO-g-PEG composite nanofiber scaffolds have good cytocompatibility, noncytotoxicity characteristics, superior mechanical, thermal, and electrical properties, which have broad applications in tissue engineering [82, 88]. It was observed that a small amount of GO-g-PEG did not prevent the proliferation and viability of cells, which indicates the high cell affinity of GO-g-PEG. It is expected that the cells will spread on the composite scaffolds and in some cases improve cell growth by having similar rate of cell proliferation to that of tissue culture plates [82, 88].

Advances in sensor technology are in constant demand because of their wide use in various industries, environmental monitoring, space exploration, biomedicine, and pharmaceuticals. Therefore, improving Gas/chemical sensors and biosensors with faster response times, higher accuracies, increased sensitivities and other properties is an important area of research.

The desired features of sensors include small sizes, quicker response times, small sample volumes, selectivity or specificity, stability, longevity, and low costs. Therefore, owing to the unique electronic structures, remarkable mechanical, optical, electrochemical, thermal, magnetic properties, and ease of functionalization with antibodies and other bioreceptors, functionalized graphene has been extensively used in ultrasensitive sensors and biosensor applications [89, 90]. Abideen et al. [91] examined the gas sensing characteristics of gold (Au) or palladium (Pd) functionalized RGO-loaded ZnO nanofibers. The gas sensing tests were carried out at varying temperatures and in the presence of varying concentrations of specific gases (see Fig. 14). It was found that the Au-functionalized RGO-loaded ZnO nanofibers showed higher sensitivity toward 1 ppm of carbon monoxide (CO) gas in the air, while the Pd-functionalized sensors exhibited good performance for 1 ppm of benzene (C<sub>6</sub>H<sub>6</sub>) gas. The high sensing properties of the Au or Pd functionalized RGO loaded ZnO nanofibers was attributed to the RGO/ZnO heterointerfaces, the catalytic effect of Au and Pd nanoparticles, and the large surface area of nanofibers [91]. Li et al. [92] developed a sensor of N-doped, graphene quantum dots decorated with N-doped, carbon nanofibers (NGQDs@NCNFs) composites. The electrochemical sensors for the detection of nitrites found in sausage, pickle, lake water and



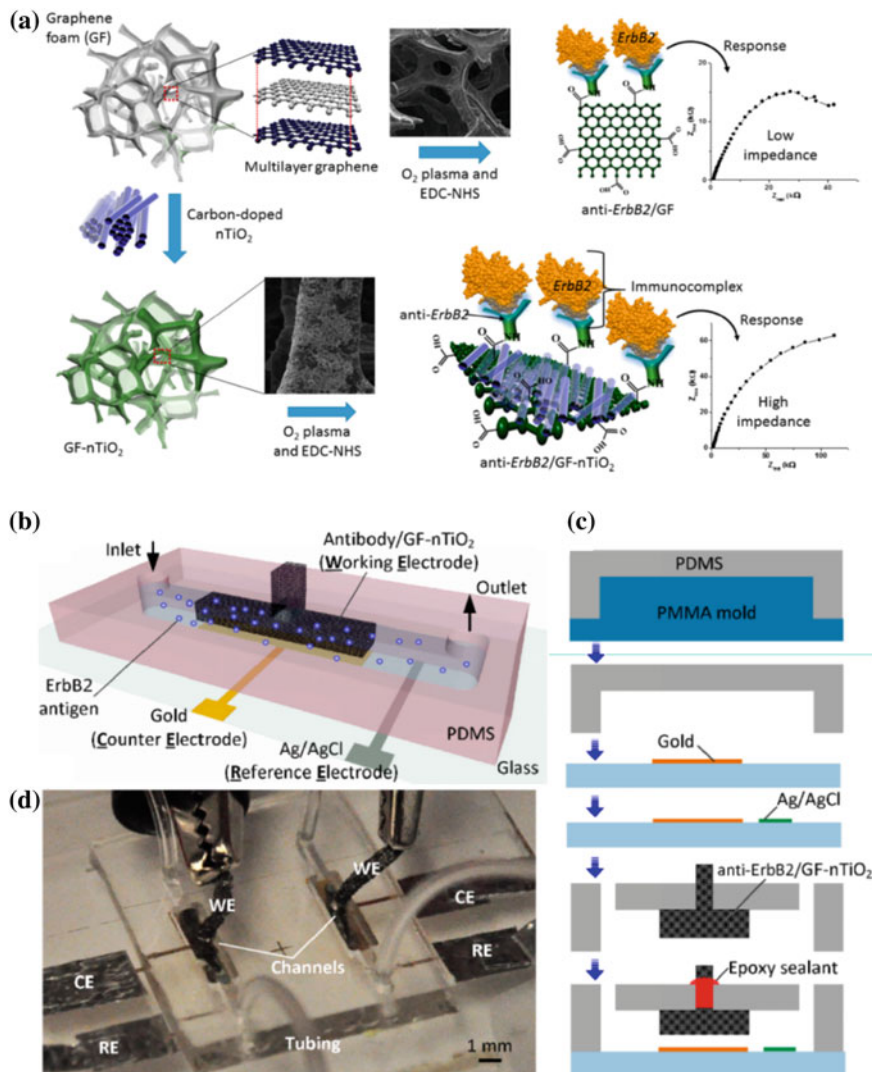
**Fig. 14** a Schematic illustration of the synthesis procedure for Au- or Pd-functionalized rGO-loaded ZnO NF; b Dynamic normalized resistances of the Au-functionalized rGO-loaded ZnO NFs sensor to 5 ppm CO gas at different temperatures and dynamic normalized resistances of the Pd-functionalized rGO-loaded ZnO NFs sensor to 5 ppm  $\text{C}_6\text{H}_6$  gas at different temperatures; c Temperature dependence of the response of the Au-functionalized rGO-loaded ZnO NF sensor and the Pd-functionalized rGO-loaded ZnO NFs sensor to CO and  $\text{C}_6\text{H}_6$  gases; d Dynamic normalized resistances of the Au-functionalized rGO-loaded ZnO NFs sensor to different concentrations of CO,  $\text{C}_6\text{H}_6$  and  $\text{C}_7\text{H}_8$  gases; e Corresponding calibration curves; f Dynamic normalized resistances of the Pd-functionalized rGO-loaded ZnO NFs sensor to different concentrations of CO,  $\text{C}_6\text{H}_6$  and  $\text{C}_7\text{H}_8$  gases; g Corresponding calibration curves. With permission from [91]. Copyright © 2018, Elsevier B.V. All rights reserved

tap water showed wide linear ranges (5–300  $\mu\text{M}$ ,  $R^2 = 0.999$ ; 400–3000  $\mu\text{M}$ ,  $R^2 = 0.997$ ), low detection limit (3  $\mu\text{M}$ ), superior reproducibility and selectivity, and good testing recoveries. In another work, Ali et al. [93] reported the fabrication of a microfluidic electrochemical sensor for the detection and immunodiagnosis of breast cancer biomarkers using a new three-dimensional (3D) immunoelectrodes produced by hierarchical graphene foam (GF) functionalized with electrospun carbon-doped titanium dioxide nanofibers ( $n\text{TiO}_2$ ) and anti-ErbB2 molecules (see Fig. 15). Blending GF with functional  $n\text{TiO}_2$  yields high charge transfer resistance, high surface area, and absorption to the sensor's surface by the analyte, resulting in sensor with remarkable detection of breast cancer biomarkers.

Moreover, functionalized graphene nanosheets are a promising material for flexible, transparent, conductive, thin films, and electronic devices, such as transistors [94], solar cells [95], and field emission displays [96], due to their remarkable, mechanical strength and flexibility. Huang et al. [97] presented a simple yet effective technique to synthesize large silver nanoparticles (AgNps)-graphene nanosheet (GNS) films onto a polyethylene terephthalate (PET), a flexible substrate, by decorating AgNps on GNS surface and enhancing self-assembly of AgNps-GNSs onto the surface of PU nanofibers. They found that the AgNp-GNS (5:1)/PU thin film revealed a considerable rising in transmittance after melting, resulting in a thin film with surface resistance of 150  $\Omega/\text{sq}$  and transmittance of 85% at 550 nm [97]. It has been also reported that the decoration of  $\text{TiO}_2$  with metals such as Pd, Nickel (Ni) and Au with graphene, improve the catalytic and photocatalytic characteristics of  $\text{TiO}_2$  [98–100]. The fabrication of Pd-functionalized graphene nanoparticles merged with  $\text{TiO}_2$  composite nanofibers displayed good photocatalysis to methylene blue [101].

Graphene quantum dots (GQDs) have extraordinary electrical conductivity, good dispersion in various solvents, tunable photoluminescence, high specific surface area, and exhibit low toxicity and good biocompatibility, thus having contributed to energy storage devices applications [102]. For example, the electropolymerization of poly(3,4-ethylenedioxythiophene) (PEDOT) onto polyvinyl alcohol-graphene quantum dot-cobalt oxide (PVA-GQD- $\text{Co}_3\text{O}_4$ ), (PVA-GQD- $\text{Co}_3\text{O}_4$ /PEDOT) nanofiber composite showed a specific capacitance of 361.97 F/g, low equivalent series resistance (ESR) and good stability with retention of 96% after 1000 cycles. The results also inducted a high specific energy and exceptional power ranging from 16.51 to 19.98 W/kg and 496.10 to 2396.99 W/kg, as the current density increased from 1.0 to 5.0 A/g [102]. In another example, GQD/PANi (GQDP) nanofiber exhibited an excellent specific capacitance value of  $\sim 1044$  F/g at a current density of 1 A/g as well as moderate cyclic stability with a retention of life time of 80.1% after 3000 cycles [103].

Contaminants such as dyes that contribute to water pollution crisis that has affected agriculture, industries and inevitably economic growth has generated interest in solving this problem. Consequently, the process of adsorption is a commonly used technique owing to its relative easy operation, good performance and cost effectiveness when compared with other approaches. Water-dispersible amine-functionalized graphene ( $\text{G-NH}_2$ ) nanosheets, were blended directly into the



**Fig. 15** **a** Functionalization of anti-ErbB2 molecules on the surface of GF and GF-nTiO<sub>2</sub> electrodes using EDC-NHS chemistry followed by oxygen plasma treatment; **b** Schematic of the microfluidic immunosensor with 3D porous GF electrode modified with carbon-doped TiO<sub>2</sub> nanofibers for the detection of breast cancer biomarkers; **c** Schematic representation of the fabrication of the microfluidic sensor; **d** Photo of two microfluidic immunosensors. With permission from [93]. Copyright © 2016, American Chemical Society



PVA/glutaraldehyde (GA) aqueous solution for crystal violet (CV) adsorption, deemed hazardous to cells and tissues of living organisms and could possibly be cancer-causing upon prolonged exposure in concentrated amounts [68]. The study indicated that the G-NH<sub>2</sub> is a desirable reinforcing filler to promote higher adsorption sites for the PVA fibers, and by that means an greater adsorption of the CV dye from water in composite mats (removal efficiency of 80.85% compared to 66.24% for crosslinked PVA/GA mats) [68].

Additionally, several other studies have concentrated on the application in areas such as antimicrobial agents in food applications, dentistry, drug release, catalysts, recovery of metal ions, medical implants and enzyme carriers [72, 104–106]. Current research and focus on functionalized graphene/polymer nanofiber composites seem to indicate that their use in a variety of industries will be proliferate and long lasting.

## 7 Conclusions and Future Scope

The functionalization of graphene by covalent and non-covalent methods has been discussed briefly in this chapter. The electrospinning process to prepare modified, graphene based polymer nanofiber composites, their properties and applications were also discussed. It has been proven that these modification techniques are extremely successful when preparing processable graphene. However, it must be remarked that a suitable technique for mass producing functionalized graphene has not yet been discovered. In conclusion, it is important that future research in this field concentrate on realizing grand-scale production of functionalized graphene if science and technology in this area remain relevant when concerning environmental safety and security standards, health, and energy production. Numerous researchers have indicated that the functionalized graphene is a suitable and desirable choice as multifunctional nanofiller, which will encourage many industry developments and forge our steps into a new energy and material world. The use of electrospinning to develop functionalized graphene polymer nanofiber composites is an effective choice when obtaining high specific surface area and fibers at a nanoscale level. Moreover, this method offers appreciable improvements in maximizing specific properties out of the electrospun composites. However, research towards commercializing functionalized graphene polymer electrospun nanofibers in applications as well as the refinement of electrospinning machines needs to be further investigated, so that their advantages can be fully realized to a greater extent. Finally, further investigation on fundamental issues such as the homogeneous distribution of individual functionalized graphene nanofillers, their orientation, connectivity, and interface bonding with the polymer matrix are required.

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## References

1. Hassan, M.A., et al.: Fabrication of nanofiber meltblown membranes and their filtration properties. *J. Membr. Sci.* **427**, 336–344 (2013)
2. Ma, P.X., Zhang, R.: Synthetic nano-scale fibrous extracellular matrix. *J. Biomed. Mater. Res.* **46**(1), 60–72 (1999)
3. Martin, C.R.: Membrane-based synthesis of nanomaterials. *Chem. Mater.* **8**(8), 1739–1746 (1996)
4. Nakata, K., et al.: Poly (ethylene terephthalate) nanofibers made by Sea–Island-type conjugated melt spinning and laser-heated flow drawing. *Macromol. Rapid Commun.* **28**(6), 792–795 (2007)
5. Drosou, C., Krokida, M., Biliaderis, C.G.: Composite pullulan-whey protein nanofibers made by electrospinning: impact of process parameters on fiber morphology and physical properties. *Food Hydrocoll.* **77**, 726–735 (2018)
6. Kamble, P., et al.: Nanofiber based drug delivery systems for skin: a promising therapeutic approach. *J. Drug Deliv. Sci. Technol.* **41**, 124–133 (2017)
7. Garg, K., Bowlin, G.L.: Electrospinning jets and nanofibrous structures. *Biomicrofluidics* **5** (1), 013403 (2011)
8. Theron, S., Zussman, E., Yarin, A.: Experimental investigation of the governing parameters in the electrospinning of polymer solutions. *Polymer* **45**(6), 2017–2030 (2004)
9. Bhardwaj, N., Kundu, S.C.: Electrospinning: a fascinating fiber fabrication technique. *Biotechnol. Adv.* **28**(3), 325–347 (2010)
10. Teo, W.E., Ramakrishna, S.: A review on electrospinning design and nanofibre assemblies. *Nanotechnology* **17**(14), R89 (2006)
11. Cavaliere, S., et al.: Electrospinning: designed architectures for energy conversion and storage devices. *Energy Environ. Sci.* **4**(12), 4761–4785 (2011)
12. Reneker, D.H., Chun, I.: Nanometre diameter fibres of polymer, produced by electrospinning. *Nanotechnology* **7**(3), 216 (1996)
13. Ji, X., et al.: Review of functionalization, structure and properties of graphene/polymer composite fibers. *Compos. A Appl. Sci. Manuf.* **87**, 29–45 (2016)
14. Kuilla, T., et al.: Recent advances in graphene based polymer composites. *Prog. Polym. Sci.* **35**(11), 1350–1375 (2010)
15. Geim, A.K., Novoselov, K.S.: The rise of graphene. In: *Nanoscience and Technology: A Collection of Reviews from Nature Journals*, pp. 11–19. World Scientific (2010)
16. Service, R.F.: Materials science. Carbon sheets an atom thick give rise to graphene dreams. *Science (New York, NY)* **324**(5929), 875 (2009)
17. Pan, Y., Sahoo, N.G., Li, L.: The application of graphene oxide in drug delivery. *Expert Opin. Drug Deliv.* **9**(11), 1365–1376 (2012)
18. Kuila, T., et al.: Chemical functionalization of graphene and its applications. *Prog. Mater. Sci.* **57**(7), 1061–1105 (2012)
19. Gao, W.: The chemistry of graphene oxide. In: *Graphene Oxide*, (pp. 61–95). Springer, Berlin (2015)
20. Wong, C.H.A., Pumera, M.: Stripping voltammetry at chemically modified graphenes. *RSC Adv.* **2**(14), 6068–6072 (2012)
21. Szabó, T., et al.: Evolution of surface functional groups in a series of progressively oxidized graphite oxides. *Chem. Mater.* **18**(11), 2740–2749 (2006)
22. Nethravathi, C., et al.: Graphite oxide-intercalated anionic clay and its decomposition to graphene–inorganic material nanocomposites. *Langmuir* **24**(15), 8240–8244 (2008)
23. Tung, V.C., et al.: High-throughput solution processing of large-scale graphene. *Nat. Nanotechnol.* **4**(1), 25 (2009)
24. Staudenmaier, L.: Verfahren zur darstellung der graphitsäure. *Ber. Dtsch. Chem. Ges.* **31**(2), 1481–1487 (1898)

25. Hummers Jr., W.S., Offeman, R.E.: Preparation of graphitic oxide. *J. Am. Chem. Soc.* **80**(6), 1339–1339 (1958)
26. Gao, C., et al.: A green method to fast prepare single-layer graphene oxide. China patent CN104310385A, 28 Jan 2015 (in Chinese)
27. Yu, H., et al.: High-efficient synthesis of graphene oxide based on improved hummers method. *Sci. Rep.* **6**, 36143 (2016)
28. Stankovich, S., et al.: Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon* **45**(7), 1558–1565 (2007)
29. Wang, H., et al.: Solvothermal reduction of chemically exfoliated graphene sheets. *J. Am. Chem. Soc.* **131**(29), 9910–9911 (2009)
30. Si, Y., Samulski, E.T.: Synthesis of water soluble graphene. *Nano Lett.* **8**(6), 1679–1682 (2008)
31. Wang, G., et al.: Facile synthesis and characterization of graphene nanosheets. *J. Phys. Chem. C* **112**(22), 8192–8195 (2008)
32. Stankovich, S., et al.: Graphene-based composite materials. *Nature* **442**(7100), 282 (2006)
33. Zhang, J., et al.: Reduction of graphene oxide via L-ascorbic acid. *Chem. Commun.* **46**(7), 1112–1114 (2010)
34. Kim, H., Abdala, A.A., Macosko, C.W.: Graphene/polymer nanocomposites. *Macromolecules* **43**(16), 6515–6530 (2010)
35. Schniepp, H.C., et al.: Functionalized single graphene sheets derived from splitting graphite oxide. *J. Phys. Chem. B* **110**(17), 8535–8539 (2006)
36. McAllister, M.J., et al.: Single sheet functionalized graphene by oxidation and thermal expansion of graphite. *Chem. Mater.* **19**(18), 4396–4404 (2007)
37. Steurer, P., et al.: Functionalized graphenes and thermoplastic nanocomposites based upon expanded graphite oxide. *Macromol. Rapid Commun.* **30**(4–5), 316–327 (2009)
38. Shen, B., et al.: Melt blending in situ enhances the interaction between polystyrene and graphene through  $\pi$ - $\pi$  stacking. *ACS Appl. Mater. Interfaces* **3**(8), 3103–3109 (2011)
39. Stankovich, S., et al.: Stable aqueous dispersions of graphitic nanoplatelets via the reduction of exfoliated graphite oxide in the presence of poly (sodium 4-styrenesulfonate). *J. Mater. Chem.* **16**(2), 155–158 (2006)
40. Huang, X., et al.: Graphene-based composites. *Chem. Soc. Rev.* **41**(2), 666–686 (2012)
41. Karousis, N., Tagmatarchis, N., Tasis, D.: Current progress on the chemical modification of carbon nanotubes. *Chem. Rev.* **110**(9), 5366–5397 (2010)
42. Tasis, D., et al.: Chemistry of carbon nanotubes. *Chem. Rev.* **106**(3), 1105–1136 (2006)
43. Choi, E.-Y., et al.: Noncovalent functionalization of graphene with end-functional polymers. *J. Mater. Chem.* **20**(10), 1907–1912 (2010)
44. Liu, J., et al.: Synthesis, characterization, and multilayer assembly of pH sensitive graphene-polymer nanocomposites. *Langmuir* **26**(12), 10068–10075 (2010)
45. Liu, J., et al.: Noncovalent DNA decorations of graphene oxide and reduced graphene oxide toward water-soluble metal-carbon hybrid nanostructures via self-assembly. *J. Mater. Chem.* **20**(5), 900–906 (2010)
46. Choi, B.G., et al.: Solution chemistry of self-assembled graphene nanohybrids for high-performance flexible biosensors. *ACS Nano* **4**(5), 2910–2918 (2010)
47. Salavagione, H.J., Gomez, M.A., Martinez, G.: Polymeric modification of graphene through esterification of graphite oxide and poly (vinyl alcohol). *Macromolecules* **42**(17), 6331–6334 (2009)
48. Liu, Z., et al.: PEGylated nanographene oxide for delivery of water-insoluble cancer drugs. *J. Am. Chem. Soc.* **130**(33), 10876–10877 (2008)
49. Park, S., Ruoff, R.S.: Chemical methods for the production of graphenes. *Nat. Nanotechnol.* **4**(4), 217 (2009)
50. Shan, C., et al.: Water-soluble graphene covalently functionalized by biocompatible poly-L-lysine. *Langmuir* **25**(20), 12030–12033 (2009)

51. Lee, S.H., et al.: Polymer brushes via controlled, surface-initiated atom transfer radical polymerization (ATRP) from graphene oxide. *Macromol. Rapid Commun.* **31**(3), 281–288 (2010)
52. Niyogi, S., et al.: Spectroscopy of covalently functionalized graphene. *Nano Lett.* **10**(10), 4061–4066 (2010)
53. Liu, H., et al.: Photochemical reactivity of graphene. *J. Am. Chem. Soc.* **131**(47), 17099–17101 (2009)
54. Vadukumpully, S., et al.: Functionalization of surfactant wrapped graphene nanosheets with alkylazides for enhanced dispersibility. *Nanoscale* **3**(1), 303–308 (2011)
55. Liu, Y., et al.: Biocompatible graphene oxide-based glucose biosensors. *Langmuir* **26**(9), 6158–6160 (2010)
56. Du, J., Cheng, H.M.: The fabrication, properties, and uses of graphene/polymer composites. *Macromol. Chem. Phys.* **213**(10–11), 1060–1077 (2012)
57. Abdali, H., Aji, A.: Preparation of electrospun nanocomposite nanofibers of polyaniline/poly(methyl methacrylate) with amino-functionalized graphene. *Polymers* **9**(9), 453 (2017)
58. He, H., Gao, C.: General approach to individually dispersed, highly soluble, and conductive graphene nanosheets functionalized by nitrene chemistry. *Chem. Mater.* **22**(17), 5054–5064 (2010)
59. Jia, L., Liu, J., Wang, H.: Preparation of poly (diallyldimethylammonium chloride)-functionalized graphene and its applications for H<sub>2</sub>O<sub>2</sub> and glucose sensing. *Electrochim. Acta* **111**, 411–418 (2013)
60. Moayeri, A., Aji, A.: Fabrication of polyaniline/poly (ethylene oxide)/non-covalently functionalized graphene nanofibers via electrospinning. *Synth. Met.* **200**, 7–15 (2015)
61. Rafiee, M.A., et al.: Fracture and fatigue in graphene nanocomposites. *Small* **6**(2), 179–183 (2010)
62. Dasari, A., Yu, Z.-Z., Mai, Y.-W.: Electrically conductive and super-tough polyamide-based nanocomposites. *Polymer* **50**(16), 4112–4121 (2009)
63. Chatterjee, S., Nüesch, F., Chu, B.: Crystalline and tensile properties of carbon nanotube and graphene reinforced polyamide 12 fibers. *Chem. Phys. Lett.* **557**, 92–96 (2013)
64. Zheng, W., Lu, X., Wong, S.C.: Electrical and mechanical properties of expanded graphite-reinforced high-density polyethylene. *J. Appl. Polym. Sci.* **91**(5), 2781–2788 (2004)
65. Hou, W., et al.: Preparation and physico-mechanical properties of amine-functionalized graphene/polyamide 6 nanocomposite fiber as a high performance material. *RSC Adv.* **4**(10), 4848–4855 (2014)
66. Jiang, L., et al.: Preparation and characterization of graphene/poly (vinyl alcohol) nanocomposites. *J. Appl. Polym. Sci.* **118**(1), 275–279 (2010)
67. Liang, J., et al.: Molecular-level dispersion of graphene into poly (vinyl alcohol) and effective reinforcement of their nanocomposites. *Adv. Func. Mater.* **19**(14), 2297–2302 (2009)
68. Chailek, N., et al.: Crosslinking assisted fabrication of ultrafine poly (vinyl alcohol)/functionalized graphene electrospun nanofibers for crystal violet adsorption. *J. Appl. Polym. Sci.* **135**(22), 46318 (2018)
69. Chen, Y., et al.: Preparation, mechanical properties and biocompatibility of graphene oxide/ultrahigh molecular weight polyethylene composites. *Eur. Polymer J.* **48**(6), 1026–1033 (2012)
70. Yu, J., et al.: Permittivity, thermal conductivity and thermal stability of poly (vinylidene fluoride)/graphene nanocomposites. *IEEE Trans. Dielectr. Electr. Insul.* **18**(2), 478–484 (2011)
71. Zhang, H.-B., et al.: The effect of surface chemistry of graphene on rheological and electrical properties of polymethylmethacrylate composites. *Carbon* **50**(14), 5117–5125 (2012)
72. Leyva-Porras, C., et al.: EELS analysis of Nylon 6 nanofibers reinforced with nitroxide-functionalized graphene oxide. *Carbon* **70**, 164–172 (2014)

73. Cao, L., et al.: Fabrication of chitosan/graphene oxide polymer nanofiber and its biocompatibility for cartilage tissue engineering. *Mater. Sci. Eng. C* **79**, 697–701 (2017)
74. Hong-Pei, L., et al.: Electrospinning gelatin/chitosan/hydroxyapatite/graphene oxide composite nanofibers with antibacterial properties. *J. Inorg. Mater.* **30**(5), 516–522 (2015)
75. Ardeshirzadeh, B., et al.: Controlled release of doxorubicin from electrospun PEO/chitosan/graphene oxide nanocomposite nanofibrous scaffolds. *Mater. Sci. Eng. C* **48**, 384–390 (2015)
76. Bao, Q., et al.: Graphene–polymer nanofiber membrane for ultrafast photonics. *Adv. Func. Mater.* **20**(5), 782–791 (2010)
77. Ding, B., et al.: Gas sensors based on electrospun nanofibers. *Sensors* **9**(3), 1609–1624 (2009)
78. Doshi, J., Reneker, D.H.: Electrospinning process and applications of electrospun fibers. *J. Electrostat.* **35**(2–3), 151–160 (1995)
79. Feng, L., Xie, N., Zhong, J.: Carbon nanofibers and their composites: a review of synthesizing, properties and applications. *Materials* **7**(5), 3919–3945 (2014)
80. Zong, X., et al.: Structure and process relationship of electrospun bioabsorbable nanofiber membranes. *Polymer* **43**(16), 4403–4412 (2002)
81. Ramazani, S., Karimi, M.: Electrospinning of poly ( $\epsilon$ -caprolactone) solutions containing graphene oxide: effects of graphene oxide content and oxidation level. *Polym. Compos.* **37**(1), 131–140 (2016)
82. Zhang, C., et al.: The surface grafting of graphene oxide with poly (ethylene glycol) as a reinforcement for poly (lactic acid) nanocomposite scaffolds for potential tissue engineering applications. *J. Mech. Behav. Biomed. Mater.* **53**, 403–413 (2016)
83. Das, S., et al.: Electrospinning of polymer nanofibers loaded with noncovalently functionalized graphene. *J. Appl. Polym. Sci.* **128**(6), 4040–4046 (2013)
84. Georgakilas, V., et al.: Noncovalent functionalization of graphene and graphene oxide for energy materials, biosensing, catalytic, and biomedical applications. *Chem. Rev.* **116**(9), 5464–5519 (2016)
85. Hsiao, S.-T., et al.: Preparation and characterization of silver nanoparticle-reduced graphene oxide decorated electrospun polyurethane fiber composites with an improved electrical property. *Compos. Sci. Technol.* **118**, 171–177 (2015)
86. Chee, W., et al.: Functionalized graphene oxide-reinforced electrospun carbon nanofibers as ultrathin supercapacitor electrode. *J. Energy Chem.* **26**(4), 790–798 (2017)
87. Moayeri, A., Aiji, A.: High capacitance carbon nanofibers from poly (acrylonitrile) and poly (vinylpyrrolidone)-functionalized graphene by electrospinning. *J. Nanosci. Nanotechnol.* **17**(3), 1820–1829 (2017)
88. Scaffaro, R., et al.: Electrospun PCL/GO-g-PEG structures: processing-morphology-properties relationships. *Compos. A Appl. Sci. Manuf.* **92**, 97–107 (2017)
89. Latif, U., Dickert, F.L.: Graphene hybrid materials in gas sensing applications. *Sensors* **15**(12), 30504–30524 (2015)
90. Llobet, E.: Gas sensors using carbon nanomaterials: a review. *Sens. Actuators B Chem.* **179**, 32–45 (2013)
91. Abideen, Z.U., et al.: Sensing behavior to ppm-level gases and synergistic sensing mechanism in metal-functionalized rGO-loaded ZnO nanofibers. *Sens. Actuators B Chem.* **255**, 1884–1896 (2018)
92. Li, L., et al.: Quantitative detection of nitrite with N-doped graphene quantum dots decorated N-doped carbon nanofibers composite-based electrochemical sensor. *Sens. Actuators B Chem.* **252**, 17–23 (2017)
93. Ali, M.A., et al.: Microfluidic immuno-biochip for detection of breast cancer biomarkers using hierarchical composite of porous graphene and titanium dioxide nanofibers. *ACS Appl. Mater. Interfaces* **8**(32), 20570–20582 (2016)
94. Sun, Q., et al.: Characteristics of a pentacene thin film transistor with periodic groove patterned poly (methylmethacrylate) dielectrics. *Appl. Phys. Lett.* **96**(10), 41 (2010)

95. Ratcliff, E.L., Lee, P.A., Armstrong, N.R.: Work function control of hole-selective polymer/ITO anode contacts: an electrochemical doping study. *J. Mater. Chem.* **20**(13), 2672–2679 (2010)
96. Yoon, B.-J., et al.: Fabrication of flexible carbon nanotube field emitter arrays by direct microwave irradiation on organic polymer substrate. *J. Am. Chem. Soc.* **127**(23), 8234–8235 (2005)
97. Huang, Y.-L., et al.: Self-assembly of silver–graphene hybrid on electrospun polyurethane nanofibers as flexible transparent conductive thin films. *Carbon* **50**(10), 3473–3481 (2012)
98. Zhang, L., et al.: Electrospun titania nanofibers segregated by graphene oxide for improved visible light photocatalysis. *Appl. Catal. B* **201**, 470–478 (2017)
99. Zhang, H., et al.: P25-graphene composite as a high performance photocatalyst. *ACS Nano* **4**(1), 380–386 (2010)
100. Wu, M.-C., et al.: Enhanced photocatalytic activity of TiO<sub>2</sub> nanofibers and their flexible composite films: decomposition of organic dyes and efficient H<sub>2</sub> generation from ethanol-water mixtures. *Nano Res.* **4**(4), 360–369 (2011)
101. Lee, H.-G., et al.: Facile synthesis of functionalized graphene-palladium nanoparticle incorporated multicomponent TiO<sub>2</sub> composite nanofibers. *Mater. Chem. Phys.* **154**, 125–136 (2015)
102. Abidin, S.N.J.S.Z., et al.: Electropolymerization of poly (3, 4-ethylenedioxythiophene) onto polyvinyl alcohol-graphene quantum dot-cobalt oxide nanofiber composite for high-performance supercapacitor. *Electrochim. Acta* (2017)
103. Mondal, S., Rana, U., Malik, S.: Graphene quantum dot-doped polyaniline nanofiber as high performance supercapacitor electrode materials. *Chem. Commun.* **51**(62), 12365–12368 (2015)
104. De Faria, A.F., et al.: Antimicrobial electrospun biopolymer nanofiber mats functionalized with graphene oxide–silver nanocomposites. *ACS Appl. Mater. Interfaces* **7**(23), 12751–12759 (2015)
105. Ding, X., et al.: Spinning fabrication of graphene/polypyrrole composite fibers for all-solid-state, flexible fibriform supercapacitors. *J. Mater. Chem. A* **2**(31), 12355–12360 (2014)
106. Li, S., et al.: One-step synthesis of graphene/polypyrrole nanofiber composites as cathode material for a biocompatible zinc/polymer battery. *ACS Appl. Mater. Interfaces* **6**(19), 16679–16686 (2014)