A Inclusive Review of Graphene-Polymer Nanocomposites: Research Position and Developments

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Abstract: For the last decades, graphene-polymer nanocomposites materials have been widely studied in the scientific literature and the fabrication of graphene-based polymer nanocomposites.Graphene has interest because it can produce a dramatic enhancement in properties at very low filler content.The modification of graphene/grapheneoxide and the utilization of these materials in the fabrication of nanocomposites with different polymer matrixes have been discovered. Different organic polymers have been used to fabricate graphene filled polymer nanocomposites by a range of methods. In the case of modified graphene-based polymer nanocomposites, the percolation threshold can be achieved at a very lower filler loading. Herein,the structure,preparation and properties of polymer/graphene nanocomposites are discussed in general along with detailed examples drawn from the scientific literature.as they provide substantial properties enhancements, even at low nanoparticles content.

Introduction

The field of nanoscience has blossomed over the last two decades and the importance of nanotechnology increase in areas such as computing, sensors, biomedical and many other applications. In this regard the discovery of gra- phene [1] and graphene-based polymer nanocomposites is an important addition in the field of nanoscience. Gra- phene, a single-layer carbon sheet with a hexagonal packed lattice structure, has shown many unique properties such as the quantum Hall effect (QHE), high carrier mobility at room temperature ($?10,000cm 2 V ?1 S ?1$) [1], large theoreti- cal specific surface area ($2630m 2 g ?1$) [2], good optical trans- parency ($?97.7\%$) [3], high Young's modulus ($?1$ TPa) [4] and excellent conductivity ($3000–5000$ Wm $?1$ K $?1$) [5]. The superior properties of graphene compared to poly- mers are reflected in graphene-based polymer composites. Graphene-based polymer composites show superior mech- anical, thermal, gas barrier, electrical and flame retardant properties, compared to the neat polymer [6–10]. It was also reported that the improvement in mechanical and electrical properties of graphene-based polymer composites are much better in comparison to that of clay or other carbon filler- based

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polymer composites [6,10]. Although carbon nanotubes (CNTs) show comparable mechanical properties to gra- phene, still graphene is a better nanofiller than CNT in certain aspects such as the rmalan delectrical conductivity [11–33].The physicochemical properties of the nanocomposite depend on the distribution of graphenelayers in the polymer matrix as well as interfacial bonding between the graphene layers and polymer matrix. Pristine graphene is not compat- ible with organic polymers and does not form homogeneous composites. In contrast, graphene oxide (GO) sheets are more compatible with organic polymers [34–39], as a result GO has attracted considerable attention as a nanofiller for polymer nanocomposites. Unlike graphene, graphene oxide is electrically insulating, which makes it unsuitable for syn- thesis of conducting nanocomposites.

Preparation Methods of Polymer Nanocomposites

The preparation method depends on the polarity, mol- ecular weight, hydrophobicity, reactive groups etc. present in the polymer, graphene and solvent [40]. There are three ways for incorporating the polymer at the core of the host-layered materials. In Situ Intercalative Polymerization In this method, graphene or modified graphene is first swollen within the liquid monomer. A suitable initiator is added and polymerization is initiated either by heat or radiation [41,42]. A large number of polymer nanocomposites have been prepared in this method, i.e., polystyrene (PS)= graphene [41–43], Polymethylmethacrylate (PMMA)= expanded graphite (EG) [44], Polystyrene sulfonate (PSS)= layered double hydroxide (LDH) [45], polyimide (PI)= LDH [46], polyethylene terephthalate (PET)=LDH [47], etc. Solution Intercalation In this method, the polymer or pre-polymer is soluble in the solvent system and graphene or modified graphene layers are allowed to swell [6]. Graphene or modified gra- phene is dispersed in a suitable solvent like water, acetone, chloroform, tetrahydrofuran (THF), dimethyl formamide chloroform, tetrahydrofuran (THF), dimethyl formamide (DMF) or toluene then the polymer adsorbs on to the dela- minated sheets and finally the solvent is evaporated [48]. Polymer nanocomposites like polyethylene-grafted maleic anhydride (PE-g-MA)=graphite [49], epoxy=LDH [50,51], polystyrene (PS)=graphene [52], polypropylene (PP)= graphene [53], plyvinylalcohol (PVA)=graphene [11], polyvi- nylchloride (PVC)=CNT [54], ethylenevinyl acetate (EVA)= LDH [55] etc., have been prepared in this method. Melt Intercalation In this method, graphene or modified graphene is mixed with the polymer matrix in molten state. A thermoplastic polymer is mixed mechanically with graphene or modified graphene at elevated temperatures using conventional methods like extrusion and injection molding [52, 53, 56]. The polymer chain are then intercalated or exfoliated to form nanocomposites. A wide range of polymer nanocomposites such as polypropylene (PP)=expanded graphite (EG) [53], High dense polyethylene (HDPE)=EG [57], polyphenylene sulphide (PPS)=EG [58], polyamide (PA6)=EG [59] etc. have been prepared by this method.

Graphene-based Polymer Composites

Polymer nanocomposites based on a range of nanofillers such as expanded graphite (EG), carbon nanotube (CNT), carbon nanofiber (CNF) have been reported [60–87]. This section focuses on the use of graphene as a nanofiller in different polymeric system like epoxy,
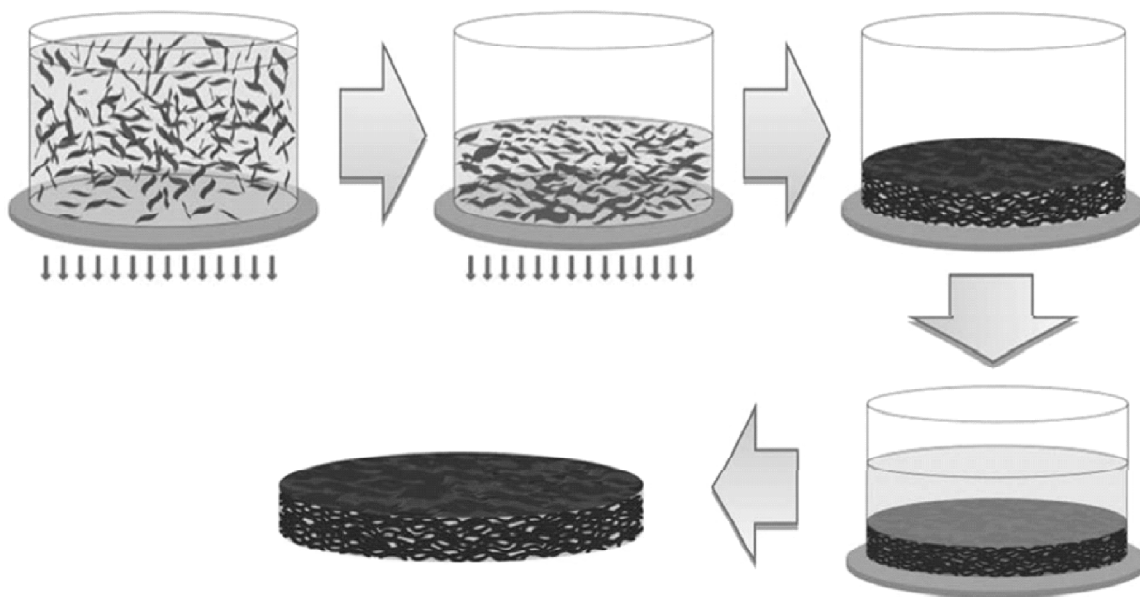
Figure 1: Schematic diagram of the preparation of aligned polymer/graphene [121]

polystyrene (PS), polyaniline (PANI), polyurethane (PU), poly (vinylidene fluoride) (PVDF), Nafion, polycarbonate (PC), Poly(ethyl- ene terephthalate) (PET), poly(3,4-ethyldioxythiophene) (PEDOT), etc. (see Figure 1). Polyaniline/Graphene Nanocomposites PANI=graphene composite paper (GPCP) was prepared by the in situ anodic electro-polymerization (AEP) of ani- line on graphene paper [88]. Polymerization was carried out using a three electrode anodic electro-polymerization cell. In this process, a Pt-plate, standard calomel electrode (SCE) and graphene paper were used as the counter, refer- ence and working electrode respectively. 0.05M aniline and 0.5M sulphuric acid were used as the electrolyte, PANI was electropolymerized in situ on the graphene paper at a constant potential of 0.75V for different periods. Wang et al. prepared a high performing PANI=graphene composite electrode using a spin coating method [89]. An aqueous dispersion of purified graphene oxide (GO) film was deposited on a quartz substrate using a deep coating method followed by thermal reduction to obtain graphene film. A dark blue solution of PANI in n-methylpyrrolidone (NMP) was then spin coated on graphene films. The PANI=graphene electrode is more suitable for designing electro chromic devices. The polyaniline=graphene nanosheet=carbon nanotube (PANI=GNS=CNT) composite was prepared by in situ polymerization [90]. The working electrode was fabricated by mixing electro active materials, carbon black and polytetrafluoroethylene (PTFE) in ethanol. The resulting mixture was coated onto a nickel substrate with a spatula followed by drying in an oven. The specific capacitance of the PANI=GNS=CNT composites was much higher than that of pure PANI and PANI=CNT composites [91]. The long-term cycle stability of the PANI=GNS=CNT composites was superior to that of the PANI=CNT and PANI=GNS composites [92]. It was reported that

after 100cycles, the capacitance of the PANI=GNS=CNT composites decreased by only 6% of the initial capacitance compared to the 52% and 67% decrease observed for the PANI=GNS and PANI=CNT composites. Chemically modified graphene and polyaniline (PANI) nanofiber composites were prepared by in situ polymeriza- tion of aniline monomer in presence of graphene oxide in acidic medium [93]. The resulting PANI=graphene oxide composites were reduced to a graphene composite by hydrazine monohydrate followed by reoxidation and reprotonation of the reduced PANI to give PANI=graphene nanocomposite. The conductivity of the PANI=graphene composites (168.7 Sm ?1) was slightly lower than that of PANI=GO composites (231.2 Sm ?1), probably due to a decrease in the degree of doping in PANI, and a change in the morphology of the composites during the reduction, reoxidation and reprotonation process.

Poly (3,4-Ethyldioxythiophene)/Graphene

Poly(3,4-ethyldioxythiophene)[PEDOT]=sulphonated gr-aphene composite prepared by in situ polymerization [9] showed excellent transparency, electrical conductivity, good flexibility as well as high thermal stability and was easily processed in both aqueous and organic solvents. The con- ductivity of PEDOT=graphene film deposited on PMMA is greater than that deposited on quartz. The PEDOT= graphene composites have high thermal stability and show very little mass loss below 297 ? C and ?19% loss below 325 ? C. The PEDOT=graphene composite is thermally more stable than that of PEDOT=PSS composite.

Epoxy/Graphene Nanocomposites

Epoxy=graphene composites were prepared using in situ polymerization and their electromagnetic interference (EMI) shielding were examined [94,95]. Over the entire fre- quency range, the EMI shielding effectiveness increased with increasing graphene loading. Thus epoxy=graphene composites can be used as effective lightweight shielding materials for electromagnetic radiation. Graphene oxide sheet-incorporated epoxy composites were prepared and thermal expansion was examined by a thermo-mechanical analyzer [96]. The epoxy resin showed very poor thermal conductivity but the inclusion of gra- phene sheets showed a significant improvement. A 5wt.% GO-filled epoxy resin showed four times higher thermal conductivity than that of the neat epoxy resin [86,97]. Thus, graphene composites are promising thermal interface material for heat dissipation.

Polystyrene (PS)/Graphene Nanocomposites

PS=isocyanate modified graphene composites were prepared by using solution blending method with DMF as solvent [6]. The composites were coagulated by the drop wise addition of DMF into a large volume of methanol. The composites appeared to be filled almost completely with graphene sheet at a filler loading of only 2.4 volume percent. The conductivity of the composite is directly proportional to filler loading volume percent. Liu et al. [98] prepared PS=ionic liquid functionalized graphene com- posite using similar method, which had higher electrical conductivity than that of neat PS. PS=Functionalized

graphene sheet (FGS) composites were prepared by using a solution blending method [99]. The composites thin films were semi-conducting in nature and exhibited an ambipolar field effect. The conductivity of the thin films decreased with decreasing temperature up to 50K and increased slightly with further decrease in temperature. Such behavior was also observed in graphitic flakes [100] and reduced graphene oxide thin films [40]. Hu et al. [42] prepared PS=graphene nanosheet (GNS) nanocomposites by in situ emulsion polymerization. The compatibility between PS microspheres and GNS is suf- ficient to obtain non-sized dispersion without an additional surface treatment. The thermal stability of the nanocompo- site was 100 ? C higher than that of pure PS. The electrical conductivity of the PS=GNS nanocomposite was much higher than pure neat PS [101].

Polyurethane (PU)/Graphene Nanocomposites

Lee *et al.* prepared water-borne polyurethane (WPU)= functionalized graphene sheet (FGS) nanocomposites by in situ method [8]. The electrical conductivity of the nano-composite was increased 10 5 -fold compared to pure WPU due to homogeneous dispersion of FGS particles in WPU matrix. The presence of FGS also increased the melting temperature and heat of fusion of the soft segment of WPU in the nanocomposites. Liang and his coworkers [102] prepared three types of nanocomposites by solution mixing process. They used isocyanate modified graphene, sulphonated graphene and reduced graphene as nanofiller and thermoplastic poly- urethane (TPU) as the matrix polymer. The rate of thermal degradation of TPU=isocyanate modified graphene nano- composite is much higher than that of TPU=sulphonated graphene and TPU=reduced graphene nanocomposites.

Polyvinyl Alcohol (PVA)/Graphene Nanocomposites

PVA=graphene nanocomposites were prepared by incor- porating graphene oxide (GO) into the PVA matrix using water as the solvent [11]. The mechanical performance of PVA=graphene nanocomposite was superior to that of pure PVA, due to the molecular level dispersion of gra- phene sheets in the PAV matrix because of H-bonding between graphene and PVA [7,97]. Zhao *et al.* [101] prepared fully exfoliated graphene nanosheet=PVA nanocomposites using a facial aqueous solution. The mechanical behavior and tensile strength of the nanocomposite was improved by addition of graphene nanosheets into the PVA matrix.

Polyethylene Terephthalate (PET)/Graphene Nanocomposites

Zhang *et al.* [40] prepared PET=graphene nanocomposites using melt compounding method. The electrical conduc- tivity of PET=graphene nanocomposites increased rapidly with increase in graphene content.Polycarbonate (PC)/Graphene Nanocomposites PC=graphite and PC=functionalized graphene sheets (FGS) nanocomposites were prepared by melt compound-ing method [103]. The tensile modulus of the PC=FGS nano-composites was higher than that of the neat PC. Theelectrical conductivity of PC=FGS was higher than that of PC=graphite nanocomposite.

Poly Vinylidene Fluoride (PVDF)/Graphene Nanocomposites

PVDF=functionalized graphene sheet (FGS) nanocom-posites were prepared from graphene oxide (GO) and expanded graphite (EG) by solution processing and compression molding [104]. The thermal stability of PVDF= FGS nanocomposite was higher than that of PVDF=EG nanocomposite. The mechanical properties of both the composites are higher than the neat PVDF. Nafion/Graphene Nanocomposites Tris (2,2 1 -bipyridyl) ruthenium (II) [Ru(bpy) 3] þ2 = nafion=graphene modified electrodes were prepared by the solution mixing of graphene and nafion [105]. The result-ing electrode was immersed in 1M [Ru(bpy) 3] 2þ solution to get modified electrode. The modified electrode showed good sensitivity, selectivity and stability. Other Graphene-Based Polymer Composites electrical conductivity of PC=FGS was higher than that of PC=graphite nanocomposite.

Poly Vinylidene Fluoride (PVDF)/Graphene Nanocomposites

PVDF=functionalized graphene sheet (FGS) nanocom-posites were prepared from graphene oxide (GO) and expanded graphite (EG) by solution processing and compression molding [104].The thermal stability of PVDF= FGS nanocomposite was higher than that of PVDF=EG nanocomposite. The mechanical properties of both the composites are higher than the neat PVDF.

Nafion/Graphene Nanocomposites

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Other Graphene-Based Polymer Composites

Poly (e-caprolactone) (PCL)=graphenoxide composite was prepared using in situ polymerization [106]. The result-ing nanocomposite show excellent mechanical properties and robustness under bending. Poly (lactic acid) (PLA)= graphene nanocomposites was prepared using response surface method [107], which showed that graphene loading had a significant effect on tensile strength. Liu et al. [108] fabricated graphene oxide (GO) reinforced epoxy resin nanocomposite by transferring GO from water to acetone. Incorporation of ?1wt% of graphene oxide showed a sig- nificant improvement in flexural strength, flexural modu-lus, impact strength and storage modulus.

Mohamadi *et al.* prepared polymethyl methacrylate (PMMA)=graphene nanocomposite by sing in situ polymerization [109]. Liang et al. fabricated polydiacetylene (PDA)=graphene nanocomposite by solution processing method [110]. The resulting nanocomposite showed excellent actuation character with controllable motion, fast response rate and high-frequency resonance. Polyphenylene sulphide (PPS)=graphene composite was prepared by spraying method [111]. The resulting nanocomposite had seven times higher wear life than that of neat PPS. Pang and his co-workers reported a

novel conductive ultrahigh-molecular-weight polyethylene (EHMWPE) composite with a segregated and double percolated struc- ture containing high density polyethylene (HDPE) as car- rier polymer for graphene nanosheets (GNS) [112]. Pan *et al.* prepared polyamide 11=graphene coatings by spray- ing method and the tribiological results showed that the wear life of the composite coating was higher than that of neat polyamide 11 coating [113].

Applications of Graphene-based Polymer Composites

Although numerous challenges remain in developing graphene-based polymer composites, but these materials have already been explored for a range of applications in different fields such as electronic devices, energy storage, sensors, ESD and EMI shielding and biomedical applications (see Figure 2).
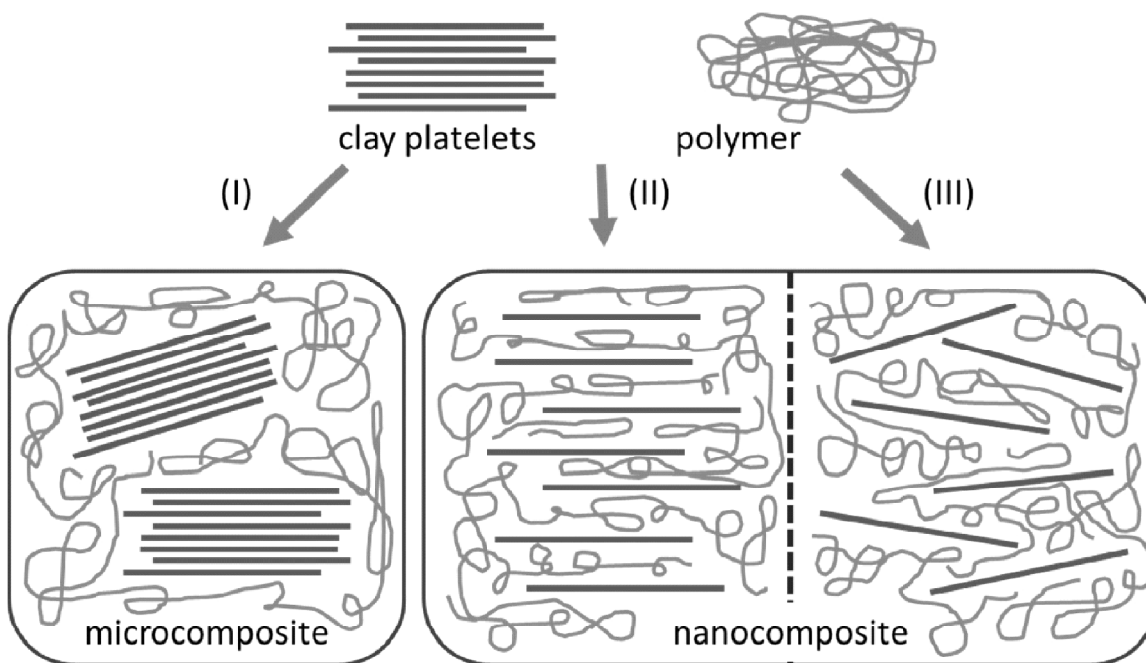
Figure 2: Different types of composites arising from the interaction of layered silicates and polymer. (I) Phase separated microcomposite, (II) intercalated nanocomposites and (III) exfoliated nanocomposites.Adapted from [122]

Electronic Devices

With high electrical conductivity, high carrier mobility and moderately high optical transmittance in the visible range of spectrum, graphene-based polymer composites have been used as electrodes for dye-sensitized solar cells [114–116] organic solar cells [117–121] liquid crystal devices [122] organic light emitting diodes (OLEDs) and field emission devices [123,124]. Transparent conducting films are used in many electronic devices as in solar cells, touch screens, flat panel display, etc. Chemical vapor deposition (CVD) grown

gra-phene and chemically modified grapheme (CMG) have been used for the development of such films through different approaches. CVD graphene is synthesized on metal substrates and is then transferred to different transparent films such as polydimethyl siloxane (PDMS) [125] or poly- ethylene terephthalate (PET) [117,124,126]. This approach pro-vides lower film sheet resistances for similar transparency values than CMG and has outperformed the current commercially available technologies. These films have been subsequently tested for solar cell applications [117], field effect transistors [125] and touch screen panels [126]. Graphene-doped conducting polymers such poly (3,4-ethyencdioxy thiophene) poly (styrenesulphonate) (PEDOT:PSS) and poly (3-hexylthiophene) (P3HT) have shown better power consumption efficiency than cells with PEDOT:PSS as counter electrode in dye-sensitized solar cells [127]. Wang *et al.* demonstrated the influence of polymer Poly (3-Hexylthiophene) (P3HT)=fullerene=graphene structure on organic polymer solar devices [128]. Hsu et al. reported a layer-by-layer molecular doping process on graphene for forming sandwiched graphene=tetracyanoquinodimethane (TCNQ)=graphene stacked films for polymer solar cell anodes. Poly(3-hexylthiophene)=Phenyl-C61-butyric acid methyl ester (P3HT=PCBM) bulk hetrojunction polymer solar cells based on this multilayered graphene=TCNQ anodes were fabricated and showed high conductivity and transparency [129].Wang and his co-workers prepared a solution processa-ble functionalized graphene (SPFGraphene) with fuctionalization groups doped with P3HT hybrid thin films based organic photovoltaic cells (OPVCS) [130]. CdS=CdSe quantum dots (QDS) co-sensitized graphene nanocomposites was obtained via polymer brush templated synthesis in which the anodic functional polymer (Polymethyl acrylate cadmium) was grafted via surface initiated atomic transfer radical polymerization (ATRP) for potential photovoltaic application [131]. Liu et al. fabricated a flexible film on PET substrate from large-size graphene oxide for transparent and conducting films for electronics applications [132].

Energy Storage

Li ion battery (LIB) is considered as one of the most promising storage systems because of its high absolute potential against the standard hydrogen cell (3.04V) and its low atomic weight (M¼6.94g mol^{-1}), which leads to the large energy density with a theoretical value up to ?400WhKg ?1[133,134]. Graphene=CNT composites have also been prepared via solution blending in situ CVD growth and have been applied in lithium ion batteries [135]. Z. Song and his co-workers have developed ''green'' cathode by combining graphene with two promising poly-mer cathode materials, poly-(anthraquinonyl sulfide) and polyimide to improve their performance in rechargeable lithium batteries (RLB) [136]. Supercapacitor or Ultracapacitor is another type of electro-chemical energy storage device that provides high power density [10KW.kg^{-1}], short charge=discharge time and along cycling life as compared to battery devices [137]. In terms of their operation mechanism, the super capacitors are generally of two types [138]. The electrical double layer capa-citor which stores energy via electrostatic process and the other is apseudo-capacitor, which is based on the rapid redox reactions of the chemical species present in the electrode. Graphene derivatives and conducting polymers are combined and used as the hybrid

type of supercapacitor, i.e., the combination of EDLC and pseudo-capacitors. Conducting polymers like PANI is one of the most employed polymer to be incorporated with GO and r-GO sheets for super capacitors [139–145]. Furthermore PEI- modified rGo sheets mixed with acid-oxidised multi-walled carbon nanotubes (MWCNTs) to make hybrid carbon films gives an average specific capacitance of 120 Fg ?1 at a high scan rate of 1 Vs ?1[146] (see Figure 3). Microbial fuel cells are of great interest as a promising green energy source to harvest electricity from various organic matters. A macroporous and monolithic anode based on polyaniline hybridized three-dimensional graphene for high-performance microbial fuel cell has been demonstrated by Young and his co-workers [147].
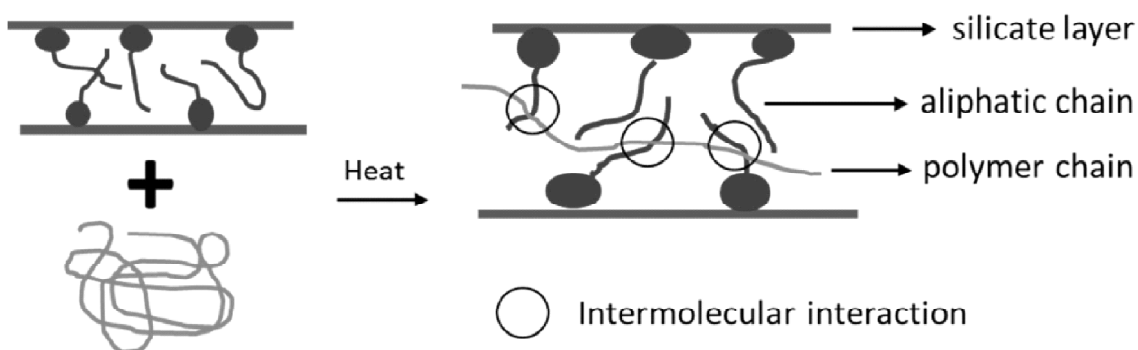
Figure 3: Melt intercalation synthesis of polymer/clay nanocomposite. Adapted from [123]

Sensors

Due to the conductance changing as a function of extent of surface adsorption, large specific area and low Johnson noise, graphene has proved to be a promising candidate to detect a variety of molecules such as gases [148–151] to biomolecules [152,153].Furthermore its application extends to pH [154],pressure [155] and temperature sensors [156] (see Table 1). Conductive polymer nanocomposites usually exhibit a positive temperature co-efficient but recent study described the opposite behavior (negative temperature coefficient) in PVDF nanocomposites filled with thermally reduced graphene [156]. This makes it suitable for its use as temperature sensor. Xu *et al.* studied the photo induced electron transfer between tetra-phenyl-porphyrin (TPP) and modified gra- phene materials, hydroxypropyl-b-cyclo-dextrin (HPCD) grafted with GO (HPCD-GO). The HPCD-GO=TPP modified electrode possess an excellent electro catalytic activity towards the reduction and oxidation of hemo- globin (Hb) and showed a detection limit of 5?10 ?9 M revealing high sensitivity [157]. Shan *et al.* constructed the first graphene-based gluscose biosensor using polyvinylpyrrolidone (PVP)–Protected graphene=polyethylemimine (PEI)-functionalised ionic liquid=GOD (glucose oxidase)-modified electrode [158]. Lin's group decorated GCE with GOD=graphene=chitosan film to detect glucose [159]. This biosensor exhibited a wider range from 0.08 to 12mM. Wua et al. prepared a nanacom- posite film consisting of GOD=Pt=graphene=chitosan and the resultant bioelectrode offered fast and sensitive glucose quantification [160]. In another study, Baby *et al.* [161] reported a

GOD=Au=graphene=nafion-based biosensor which exhibited the best sensing performance. Yin *et al.* fabricated graphene=nafion=GC electrode which showed excellent reproducibility, stability and anti- inteference to defect guanine and adenine. [162] Lian and his co-workers designed a highly sensitive uric acid molecularly imprinted electrochemical sensor by using graphene doped chitosan as functional matrix and uric acid as template molecule [163]. Yang *et al.* developed a label-free electrochemical immuno sensor for the measurement of serum thrombonodulin (TM), which is associated with pro- gression and metastasis of tumors by using graphene (dis- persed in nafion solution)=silver-silver oxide nanoparticles as immobilization matrix [164]. Xue *et al.* developed a graphene-nafion matrix modified glassy carbon electrode (Graphene-Nafion=GCE) for the determination of organo- phosphorus pesticides(OPs) [165]. This sensor has been successfully applied in the determination of methyl parathion present in vegetable samples. ESD and EMI Shielding The intrinsic high conductivity and aspect ratio of gra-phene enable the attainment of percolation thresholds at lower loading fractions than carbon black and MWCNTs. This conductivity determines the application of conducting polymer (CP) to electrostatic discharge (ESD) and electro- magnetic interference (EMI) shielding. The surface resis- tivity in case of ESD materials ranges between 1012 to 10 5 X=square, whereas in EMI shielding material it is lower than 10 5 X=square. The applications of ESD and EMI materials extends from carpeting floor mats, electronics packing to telecommunication antenna, mobile phone parts and frequency shielding coating for aircraft and elec- tronics. EMI shielding efficiency in a CMG=epoxy nanocompo-site, achieving a commercially suitable level (around 20dB in the X-band) for 15 weight% loading fraction of hydrazine-reduced GO [166].

Biomedical Applications

The remarkable properties of graphene provide essen-tially infinite possibilities for various applications. One such area is the biomedical applications of graphene-based polymer nanocomposites. The first report on biomedical application of graphene emerged in 2008 [167,168], subse-quently graphene and graphene-based nanomaterials have been utilized in a myriad of bioapplications (e.g., drug and gene delivery, nanomedicine, bioimaging and potential cancer therapies)

Drug Delivery

There has been a surge of interest in developing gra- phene for drug loading and delivery because strong interac-tion exists between hydrophobic drugs and aromatic regions of graphene sheets. Dai's group initially developed NGO-PEG as a nanocar- rier to load variant anticancer drugs via nancovalent physi- sorption and evaluated its in vitro cellular uptake capacity and photoluminescent property [167,168]. Camptothecin (CPT) was successfully loaded onto poly (vinylalcohol) (PVA)-grafted GO and CNTs, and the cancer cell killing capabilities of the obtained GO-PVA-CPT and CNT-PVA- CPT complexes have been compared and evaluated [169]. An efficient approach to functionalized graphene sheets with a well-defined poly (N-isopropyl acrylamide) (PNI PAM) via click chemistry

has been made by Pan and his co-workers [170]. PNI PAM-graphene sheets were proved to be practically nontoxic and possess a superior capability of binding CPT with a high loading ratio of 18.5 weight %. Wen *et al.* engineered redox-responsive PEG detachment mechanism in PEGylated nanographene oxide for intra- cellular drug delivery [171].

Gene Delivery

Gene therapy is a powerful tool for the treatment of both inborn and acquired diseases and to develop nonviral gene delivery vectors with high efficiency of gene transfec- tions [172,173]. Among the polyelectrolytes, PEI has been recognized as a ''gold standard'' because of its strong binding to nucleic acids and excellent proton sponge effects, but on the other hand high cytotoxicity and poor biocompatibility of PEI restricts its further gene therapeutic applications. Liu and Zhang's group fabricated PEI modified GO nanocarriers for pDNA transfection [174,175]. A natural occurring linear cationic polysaccharide, chitosan (CS) has found widespread bioapplications in drug and gene delivery, tissue engineering and as a pharmaceutical ingredient, because of its good biocompatibility, biode- gradability, low immunogenicity and antibacterial pro- perty [173,176,177]. Bao and his co-workers reported the use of the CS-functionalized GO (GO-CS) as a nanocarrier to separately deliver CPT drug and a report DNA into human cancer cell lines [178]. Zhang's group demonstrated that the sequential delivery of therapy siRNA and DOX by the GO-PEI nanocarrier led to the significant enhanced anticancer efficacy [179]. Kim et al. demonstrated the development of GO-based efficient gene delivery carrier through the installation of polyethylenimine (PEI), a cationic polymer which has been widely used as a non-viral gene delivery vector [180].

Cancer Therapy

Similar to other nanomaterials used in biomedicine, gra-phene and graphene-based polymer nanocomposites have been used for the treatment of cancer. Lin et al. reported PEG-functionalized GO (NGO-PEG) exhibited negligible in vitro toxicity to various cell lines [167]. In another experi- ment by Liu's group declared that the most radio labeled PEGylated NGO localized in the reticuloendothelial system (RES) including liver and speen after intravenous administration, and could be gradually cleared by both renal and fecal excretion without causing noticeable side effects to the treated female Balb=c mice [181]. Liu's group testified that the PEGylated nanographene sheets (NGS) could also achieve ultra-efficient tumor ablation after intravenous administration and under low-power NIR laser irradiation [182]. NGS-PEG exhibited some interesting in vivo properties including highly efficient tumor passive targeting capability. Markovic et al. reported that graphene-mediated photothermal killing of cancer cells was proposed to involve oxidative stress and mitochondrial membrane depolarization, resulting in mixed apoptotic and necrotic cell death [183]. Tian and his co-workers used the photosensitizer mol- ecule, chlorin e6 (ce6) loaded on PEG-functionlized gra- phene oxide via supramolecular p-p stacking for its potential application in multifunctional cancer therapy [184]. Shen et al. used a multifunctional nanocomposite based on graphene oxide (GO-PEG-FA=Gd=DOX) for in vitro hepatocarcinoma diagnosis and treatment [185].

Other Applications

Die *et al.* have used PEG functionalized nanoscale GO (NGO-PEG) for living cell imaging in near IR (NIR) as NGO was found to be photo luminescent in visible and IR region [168]. Kim *et al.* used graphene oxide-polyethylenimine nanoconstruct as bioimaging tool [180]. Dong and his co-workers utilized graphene as a novel matrix for the analysis of low-molecular-weight com- pounds (such as amino acids, polyamines, anticancer drugs, nucleosides and steroids) using matrix-assisted laser desorption=ionization time-of-flight
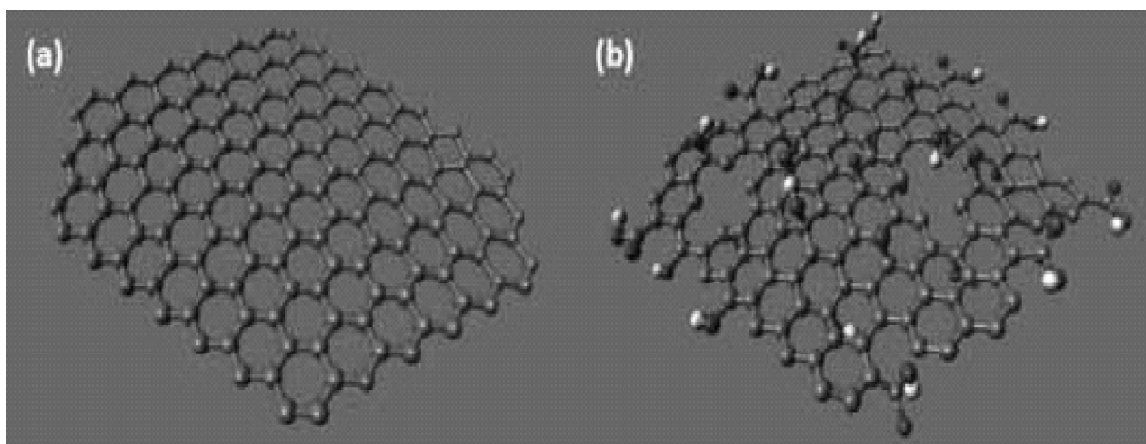

Figure 4: Atomistic structures of individual sheets of basic graphene (a) and graphene oxide (b). The atoms are color-coded: gray – carbon, red– oxygen, and white– hydrogen. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)
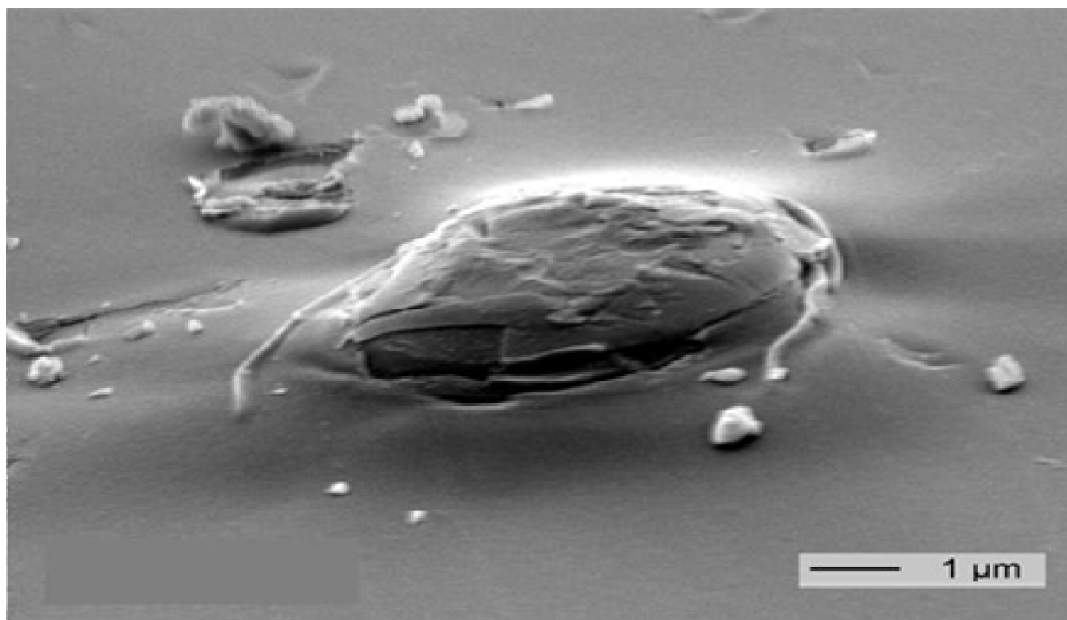
Figure 5: Surface of a polyethylene terephthalate film with particle, partially covered by a SiOx layer (Source: Fraunhofer IVV) [124]
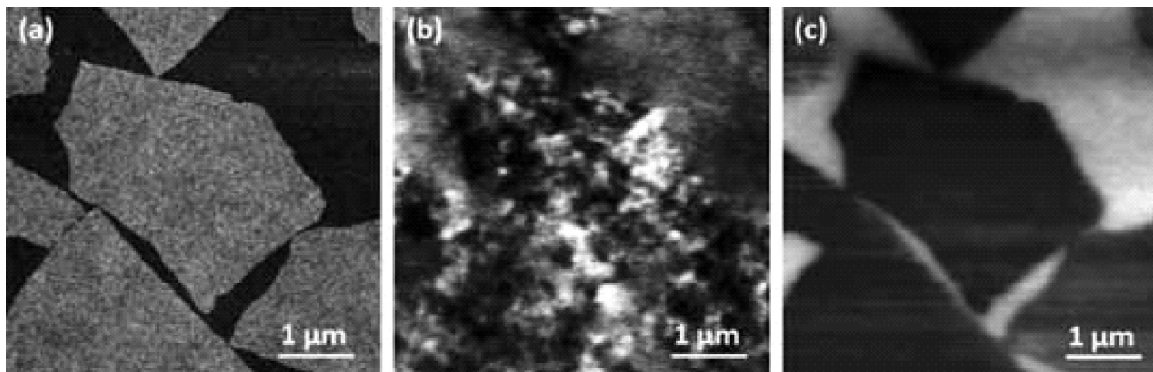
Figure 6: (a) Topography, (b) EFM-phase image before reduction, and (c) after chemical reduction from the same graphene oxide flakes
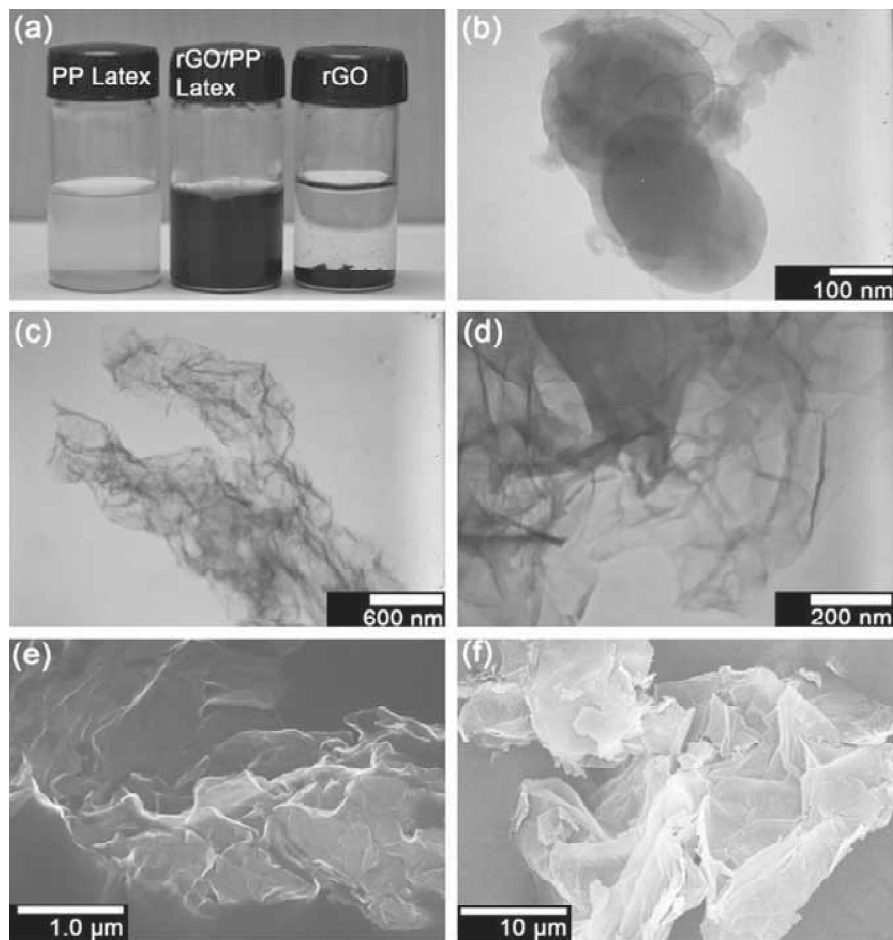
Figure 7: (a) Aqueous suspensions of PP latex and graphene oxide. (b) TEM image of PP latex. (c) and (d) TEM images of the rGO/PP latex composite dispersed in water before filtration. (e) SEM image of fracture surface of the rGO/PP composite (after hot-press molding). (f) SEM of agglomerated GO nanosheets [125]
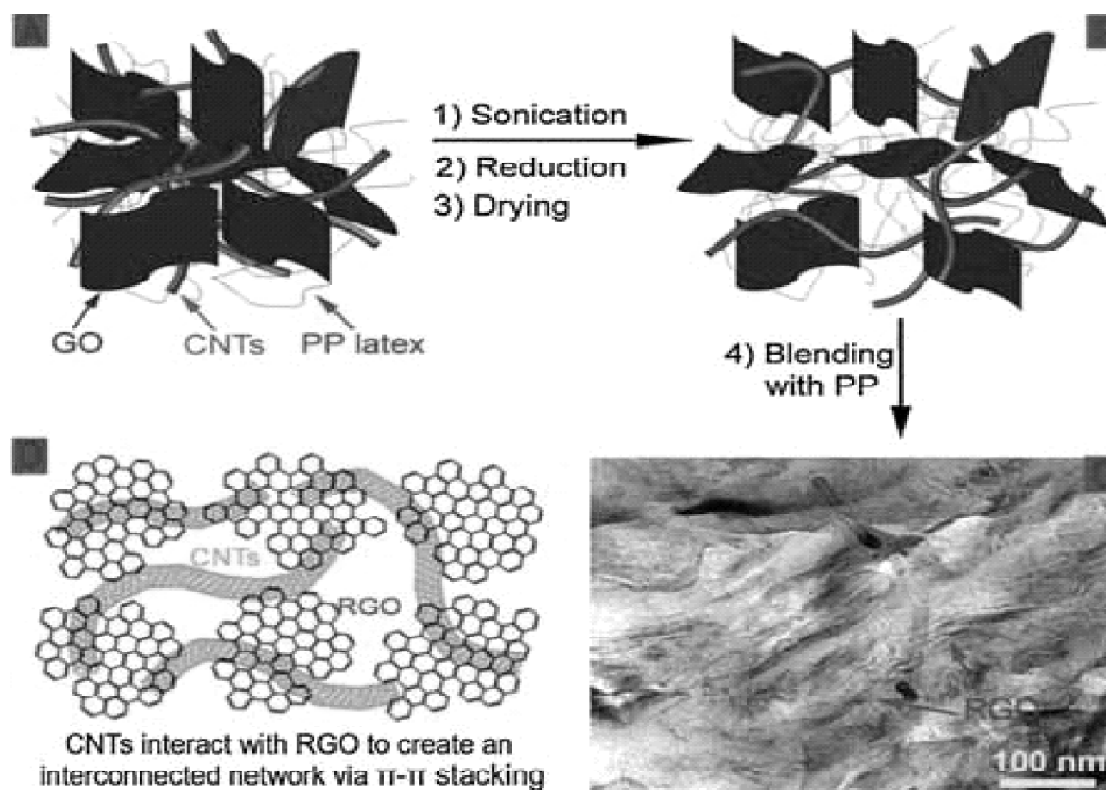
Figure 8: (A) and (B) The formation from interconnected network of rGO and CNTs using PP latex as a dispersing agent. (C) TEM image of PP/RGO/CNTs ternary system. (D) Schematic of strong interactions between RGO and CNTs via stacking [126]
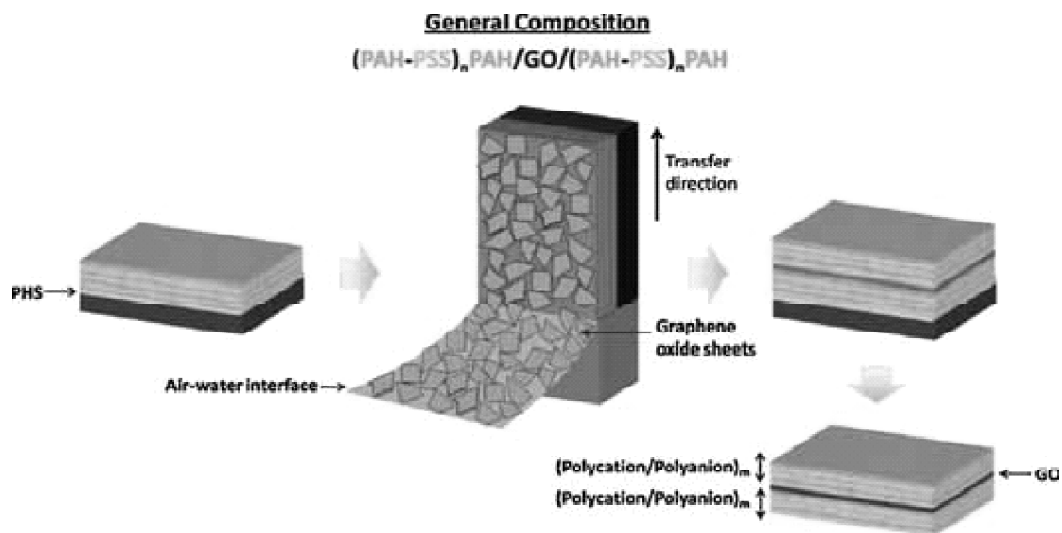

Figure 9: Fabrication from ordered and hierarchical multilayered graphene oxide-polyelectrolyte nanomembranes via combination from LbL and LB tech-niques [127].

mass spectrometry (MALDI-TOF MS) [186]. Ruoff'sgrouppresentedtheproductionofafree-standing ''Paperlike'' polyoxyethylene sorbitan laurate (TWEEN)= rGO composite, which showed non-cytotoxicity to three mammalian cell lines and biocompatibility, inhibiting non- specific binding of gram-positive bacteria [187]. Fen et al. checked the biocompatibility of graphene=CS composite films using L929 cells [188]. The cell adhesion results showed that the L929 cells can adhere to and develop on the com- posite films as well as on pure CS films. Min *et al.* fabricated graphene=polydimethyl siloxane (PDMS) for their use as electrode for artificial muscles [189].

Conclusion

Graphene-based polymer nanocomposites represent one of the most technologically promising developments to emerge from the interface of graphene-based materials and polymer materials. However, there are still many chal- lenges that must be addressed for these nanocomposites to reach their full potential. We have reviewed the current progress on the production, properties and potential applications of graphene-filled polymer nanocomposites. Although this field is still in an early stage of development, the growing interest and huge potential of this field has become apparent. However, we should learn from the unfulfilled expectations of CNT=polymer nanocomposites and keep in perspective the challenges and fundamental issues that need to be resolved. The first challenge relates to graphene and CMG production. The preparation and transfer of high quality graphene is still not viable in a cost effective manner. Graphene has very high mechanical, thermal and electri- cal properties suitable for thermally and electrically con- ducting reinforced nanocomposites, electronic circuits, sensors, and transparent and flexible electrodes for displays and solar cells etc. Graphene as a nanofiller in polymer matrixes may be preferred over other conventional nanofil- lers (Na-MMT, LDH, CNT, CNF, EG, etc.), due to its high surface area, aspect ratio, TS, thermal conductivity and electrical conductivity. As described before, numerous efforts to prepare useful graphene-based nanocomposites have been made and important improvements achieved. However, in spite of the considerable advances, excitement and promise of exfo- liated graphene-based polymeric nanocomposites, substan- tial fundamental research is still necessary to provide a basic understanding of these materials to enable full exploitation of their nanoengineering potential. Despite the large number of combinations of matrices and potential reinforcing nano-elements with different chemistry, size, shape and properties, all graphene-based nanocomposites share common features with regard to fabrication meth- odologies, processing, morphology characterization and fundamental physics. Thus, the key to prepare advanced graphene-based nanocomposites is the engineering at the polymer-graphene interface. Developing an understanding of the characteris- tics of this interphase region, its dependence on the gra- phene surface chemistry, the relative arrangement of constituents and its relationship to the nanocomposite properties is a current research frontier in nanocomposites that unites the interest of scientists in physical chemistry, materials science and engineering. This review of conducting polymer=graphene nanocom-posites highlighted their potentials applications in the coming years for biomedical application, such as ultra min- iaturized low cost sensors for the analysis of blood and

urine. Conducting polymer=graphene composites can also be used as electrode materials in a range of electrochromic devices. The polymer=graphene flexible electrode has some commercial applications in LEDs, transparent conducting coatings for solar cells and displays. The other commercial applications of graphene polymer composites are: light-weight gasoline tanks, plastic containers, more fuel efficient aircraft and car parts, stronger wind turbines, medical implants and sports equipment. The discovery of graphene as a nanofiller has opened a new dimension for the production lightweight, low cost, and high-performance composite materials for a range of applications. In the very near future, it is expected that a large number of new graphene-based nanocomposites using different polymer hosts (thermoplastic, thermosetting, and especially commodity polymers) and a wide range of graphene nanoe- lements (with different functionalities, size and shape) will be published. For instance the imaginative molecular design of polymeric surfactants has not yet been explored, and can circumvent the problem of solubility, dispersion in poly- mers and the film forming ability of graphene. However, we are far from the end of the tunnel in terms of under- standing the mechanisms of the enhancement effect in graphene nanocomposites.

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