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Functionalization of carbon nanomaterials for advanced polymer nanocomposites: A comparison study between CNT and graphene

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ABSTRACT

The allotropes of carbon nanomaterials (carbon nanotubes, graphene) are the most unique and promising substances of the last decade. Due to their nanoscale diameter and high aspect ratio, a small amount of these nanomaterials can produce a dramatic improvement in the properties of their composite materials. Although carbon nanotubes (CNTs) and graphene exhibit numerous extraordinary properties, their

Abbreviations: AIBN, azobisisobutyronitrile; APS, 3-aminopropylsilane; ATRP, atom transfer radical polymerization; AuNPs, gold nanoparticles; B-GOX, biotinylated glucose oxidase; BHJ, bulk heterojunction; CB, carbon black; CCG, chemical converted graphene; CD, β-cyclodextrin; CFRP, carbon fiber-reinforced polymer; CNF, carbon nanofiber; CNMs, carbon nanomaterials; CNTs, carbon nanotubes; CPT, camptothecin; Cs, specific capacity; CVD, chemical vapor deposition; DCC, dicyclohexylcarbodiimide; DFT, density functional theory; DMAP, 4-dimethylaminopyridine; DMSO, dimethyl sulfoxide; DOX, doxorubicin; DSC, differential scanning calorimetry; dsDNA, double stranded DNA; DT, dodecanethiol; ECSA, electrochemical active surface area; EHO, 3-ethyl-3-hydroxymethyloxetane; EO, ethylene oxide; FA, folic acid; FA-NGO, folic acid nanoscale graphene oxide; FGS, functionalized graphene sheets; FI, fluorescein isothiocyanate; f-MWCNT, functionalized multi-walled carbon nanotube; FT-IR, Fourier transform infrared spectroscopy; GFRP, glass fiber reinforced plastics; GH, hydrogel; GNC, gold nanoparticle clusters; GNP, graphene nanoplatelets; GNRs, graphene nanoribbon; GO, graphene oxide; GNs, graphene nanosheets; GS, graphene sheet; HBPU, hyperbranched polyurethane; HDPE, high density polyethylene; HOMO, highest occupied molecular orbital; HPAE, hyperbranched poly(amine-ester); HPEKs, hyperbranched poly(etherketone)s; HPU, poly(urea-urethane); ITO, indium tin oxide; LA, lactide; LCP, liquid crystalline polymer; LIBs, Lithium ion batteries; LOFX, levofloxacin; LUMO, lowest unoccupied molecular orbital; MDI, 4,4′-methylenebis(phenylisocynate); MEA, membrane-electrode-assemble; MGP, multi graphene platelets; MNPs, magnetic nanoparticles; MWCNTs, multi-walled carbon nanotubes; NGO, nano graphene oxide; NHC, *N*-heterocyclic carbene; NMRP, nitroxide mediated radical polymerization; NPs, nanoparticles; oGCTF@PDAA, organic foam-supported poly(1,5-diaminoanthraquinone); OPV, organic photovoltaic; P3HT, poly(3-hexylthiophene); P3OT, poly(3-octylthiophene); PA6, polyamide-6; PAA, poly(acrylic acid); PAM, poly(acryl amide); PAMAM, poly(amidoamine); PANI, polyaniline; PC71BM, [6,6]-phenyl C71 butyric acid methyl ester; PCBM, 6,6-phenyl C60 butyric acid methyl ester; PANI-NFs, polyaniline nanofibers; PCE, power conversion efficiency; PCL, poly(ε-caprolactone); PCL-diol, poly(ε-caprolactone)diol; PDA, polydopamine; PDDA, poly(diallyldimethylammonium chloride); PDMAEMA, poly[2-(dimethylamino) ethyl methacrylate; PDMS, polydimethylsiloxane; PEDOT, poly(3,4-ethylenedioxythiophene); PEHO, poly(3-ethyl-3-hydroxymethyloxetane); PEI, polyetherimide; PEMFC, polymer electrolyte membrane fuel cell; PEN, poly(arylene ether nitrile); PEO, poly(ethylene oxide); PHT, polythiophene; PI/CNT, poly(3,4,9,10-perylenetetracarboxylic dianhydride ethylene diamine)/carbon nanotubes; PLA-PEG, poly(lactide)-poly(ethylene glycol); PMMA, poly(methyl methacrylate); PMPCS, polymer-poly(2,5-bis[(4 methoxyphenyl)oxycarbonyl]styrene); PMT, poly(3-methylthiophene); PNIPAm, poly(N-isopropylacrylamide); POSS, polyhedral oligomeric silsesquioxane; PPDX, poly(*p*-dioxanone); PPS, polyphenylene sulfide; PPy, polypyrrole; PS-b-PNIPAm, polystyrene-block-poly(N-isopropylacrylamide); PS-g-MWCNT, polystyrene-grafted-multi-walled carbonnanotubes; PSS, poly(styrenesulfonate); Pt, platinum; PTB7, polythieno[3,4-*b*]thiophene/benzodithiophene; PTHF, poly((9H-fluorene-9,9-diyl) dibenzenamine); PTCDA/CNT, 3,4,9,10-perylenetetracarboxylic dianhydride/carbon nanotubes; PU, polyurethane; PV, photovoltaic; PVA, poly(vinyl alcohol); PVC, poly(vinyl chloride); PVDF, poly(vinylidene fluoride); RAFT, reversible addition fragmentation chain transfer polymerization; RGO, reduced graphene oxide; ROP, ring-opening polymerization; S/PPy/GNS, sulfur/polypyrrole/graphene nanosheets; Si/GNs, Si- graphene nanosheets; SEBS, poly(styrene-b-(ethylene-co-butylene)-b-styrene); Sn(Oct)2, tin(II) 2-ethylhexanoate; SIS, poly(styrene-b-isoprene-b-styrene); SPF-Graphene, solution-processable functionalized graphene; SPVA, sulfonated poly(vinyl alcohol); SQUID, superconducting quantum interference device; SWCNTs, single walled carbon nanotubes; TMEG, (tetrabutylammonium hydroxide) stabilized microwave-exfoliated graphene; TNO, $Ti_2Nb_{10}O_{29}$; TPU, thermoplastic polyurethane; TSPs, tetrahedron-structured probes; ZnP, zinc porphyrins; ZCO, $ZnCo_2O_4$; ZMO/NG, $ZnMn_2O_4$/N-doped graphene.

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reported commercialization is still limited due to their bundle and layer forming behavior. Functionalization of CNTs and graphene is essential for achieving their outstanding mechanical, electrical and biological functions and enhancing their dispersion in polymer matrices. A considerable portion of the recent publications on CNTs and graphene have focused on enhancing their dispersion and solubilization using covalent and non-covalent functionalization methods. This review article collectively introduces a variety of reactions (*e.g.* click chemistry, radical polymerization, electrochemical polymerization, dendritic polymers, block copolymers, *etc.*) for functionalization of CNTs and graphene and fabrication of their polymer nanocomposites. A critical comparison between CNTs and graphene has focused on the significance of different functionalization approaches on their composite properties. In particular, the mechanical, electrical, and thermal behaviors of functionalized nanomaterials as well as their importance in the preparation of advanced hybrid materials for structures, solar cells, fuel cells, supercapacitors, drug delivery, *etc.* have been discussed thoroughly.

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1. Introduction

One of the great achievements of science is the development of techniques which enable us to understand matter and allow us to modify its atomic structure. The modification of different materials and their surfaces at the nano scale has been exploited in recent decades, especially by nano chemists and technologists. The synthesis of carbon nanomaterials (CNMs) and alteration of their surfaces provides an opportunity to bolster scientific efforts in order to create a more resourceful world community capable of confronting its challenges.

Functionalized carbon nanomaterials have unlocked an array of applications across a wide spectrum of fields. Among CNMs, carbon nanotubes (CNTs) and graphene have many superior properties such as low-weight, very high aspect ratio, high electrical conductivity, and extraordinary mechanical, optical, and thermal properties [1–4].

The advantages of CNMs are reflected in the emergence of these materials over the past decade for use in a variety of innovative applications. A screening of the Scopus database in March 2015 was used to find publications containing the words “graphene” and “CNT” and reveals a growing interest in the scientific community for these materials (Fig. 1). The continuous increase in the number of publications containing word “graphene” shows its stature and versatility in the world of material science. Over the past five years, the total numbers of publications focusing on graphene vs. CNTs are approximately equal, though in last two years graphene has been studied more extensively.

The application of carbon nanomaterials to various fields has been assisted by functionalization of their surfaces and the importance of modified nano surfaces is well reflected in scientific work of last decade. The unparalled physiochemical features of these functionalized nanomaterials have been exploited for energy [4], cancer treatment [5–8], antiviral drug development [9], drug transportation in biological systems [10–15], biotechnological applications [16,17] and aerospace [18,19]. In addition, theoretical efforts have been made to analyze and optimize functionalization [20,21]. Non-functionalized carbon nanomaterials possess some drawbacks including the tendency to form stable aggregates or bundles due to very strong intermolecular interactions such as van der Waals