Manufacturing Process and Emerging Advantage of Graphene Based Composites in Aerospace- A Review

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Abstract—**The cardinal pillar for this paper is to showcase the composition of Graphene-based composites and reveal the hidden uses of Graphene-based composites in aerospace dominion. This paper briefly discusses the different methods by which graphene-based composites can be synthesized mostly those with functional polymers and inorganic nanostructures and additionally covers a few of the applications of graphene-based composites such as lightweight, fire retardancy, and additive manufacturing.Moreover, this detailed paper also brings up crucial highlights where graphene-based composites have covered long distances from the research lab to commercialization, specifically focusing on aerospace industries.**

Keywords-Graphene based composites, Polymers, Graphene oxide, Nanoparticles, Nanocomposites, Application, Aerospace, Aircraft

I. INTRODUCTION

A massive amount of analysis and experiments have been researched in the past years to prepare inorganic nanostructures without any effects on their shape, size, crystallinity, and functionality further increasing their efficiency. Ex-situ hybridization and in-situ crystallization are the two most common and efficient manufacturing processes for graphene based composites.

Therefore later in this detailed paper, a further discussion about the core applications for graphene-based composites and how can they really be implemented are mentioned. Targeting the key aspects in aerospace industries. In essence to graphene-based composites application such as, if even 1% of lightweight is achieved in any size aircraft it could save us more than 1 billion USD on fuel and in additive manufacturing, it could make the component production more efficient and lastly graphene-based composite plays a vital role on barricading the further burning in an aircraft.

II. GRAPHENE BASED COMPOSITES PREPARATION

A. *EX-SITU HYBRIDIZATION*

The blending of COTS nanocrystals and graphene-based composites in solutions is recognized as ex-situ hybridization. The modification of the nanocrystals and graphene sheets is usually done for better binding through either non-covalent interactions or chemical bonding and all of this is mostly carried out before blending. For example, 2-mercaptopyridine modified Au nanoparticles (NPs)[2] or benzyl mercaptan-capped CdS NPs[3] have been successfully joined to GO or rGO surfaces through the neat arrangement of pi-pi. Similarly, rGO sheets can be further modified with adhesive polymers for binding the NPs, which has already been observed in the Nafion-coated rGO/TiO2 composites. Bovine serum albumin (BSA) protein one of the Amphiphilic bio-polymers also plays a role in Improving the rGO surface through the pi-pi interaction, which correspondingly illustrates as a universal adhesive layer to absorb Au, Ag, Pt, and Pd NPs.[1]

B. *IN-SITU CRYSTALLIZATION*

We know that the ex-situ hybridization has the ability to priorly select the nanostructures with recommended functionalities. However, this may sometimes give undesirable values such as low density and incomplete encapsulation of the nanostructures on the GO/rGO surfaces.[2] Comparing in-situ crystallization with ex-situ hybridization, the in-situ crystallization has static encapsulation of nanocrystals through the surface functionalization by regulating the nucleation points on GO/rGO.[2]

III. TYPES OF IN-SITU CRYSTALLIZATION

A. *SOL-GEL METHODS*

The sol-gel process is a procedure in which solid materials are created from small molecules. This method is widely used in the preparation of metal oxide structures and film coatings, with metal alkoxides or chlorides. Therefore, the process engages in the conversion of monomers into a colloidal solution (sol) that acts as the precursor for the gel of either discrete particles or network polymers. What's more, is that the in-situ sol-gel, this method has a beneficial factor of the OH groups of the GO/rGO sheets, since it plays a vital role at the nucleation sites for the hydrolysis. We also see the chemical bonding of metal oxide nanostructures with the GO/rGO surfaces. Sol-gel methods are used in the in-situ for the preparation of TiO2, Fe3O4, and SiO2 nanostructures

Graduate Research in Engineering and Technology (GRET): An International Journal ISSN 2320 – 6632, Volume-1, Issue-7

14

on FGS (or rGO) sheets. For example, the typical precursors such as TiCl3, titanium isopropoxide, and titanium butoxide, are used for TiO2, which results in nanorods, NPs, or macro–mesoporous framework of TiO2 based on their applied contrasting analysis.

B. ELECTROCHEMICAL DEPOSITION

Electrochemical deposition of inorganic crystals is directly inscribed on the surface of the graphene-based composites, in the absence of post-synthetic transfer for the composite materials, which is an alluring practice for thin-based applications. ZnO, Cu2O, and CdSe are some of the nanostructures which successfully settle on the surface of the rGO or CVD-graphene films. For example, ZnO nanorods that settle on spin-coated rGO thin films on quartz, with the help of ZnCl2 which is the oxygen-saturated aqueous solution, and KCl that acts as an electrolyte.[4] This type of practice is further extended to deposit nanostructures like Cu2O and Cl-doped n-type Cu2O on rGO films, where uniform thin films are deposited onto the flexible polyethylene terephthalate (PET) flat substrates. A well-maintained sequence of nanostructure patterns can also be cooked by electrochemical deposition using a porous template[6] instead of adding random deposition of nanostructures on rGO films. As the report states that on the CVD-grown graphene sheets a layer of mesoporous silica film was first established by the use of the sol-gel process, and then on the surface of graphene CdSe NPs were electrochemically deposited through the pores of the pre-coated silica film. So, after the removal of the silica film by HF etching a systematized CdSe NPs were disclosed on the graphene. (Fig. 1).
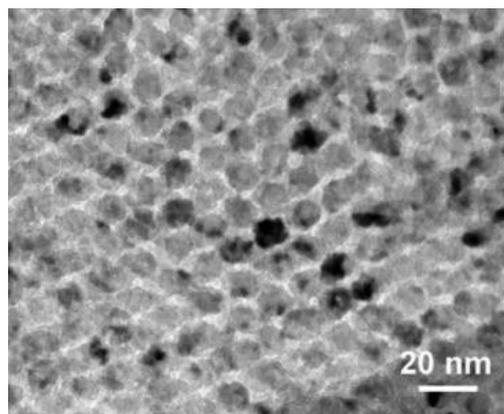

Figure 1. TEM image of ordered CdSe NPs electrochemically deposited on a graphene sheet. Reproduced with permission from ref. 183. Copyright 2010, John Wiley & Sons, Inc.

C. ORDERED METAL OXIDE-GRAPHENE COMPOSITES VIA IN-SITU SELF-ASSEMBLY

A distinguished method has been established to prepare the ordered metal oxide-graphene hybrids by the assisted self-assembly[6] substance that tends to deduce the surface tension of a liquid in which it is dissolved rather than the neat random arranging of graphene-based hybrid nanosheets.

After the mixing of anionic surfactants with rGO sheets which are joined to the hydrophobic domains of the surfactant micelles (Fig. 2A), we observe the introduction of metal cations that will bond to the surfactants which are assembled on rGO, giving an overall ordered structure (Fig. 2B). Then in-situ crystallization takes place by the use of redox or hydrolysis reactions, resulting in the alternating layers of rGO/metal oxides. For example, NiO, SnO2, and MnO2 (Fig. 2C and D).
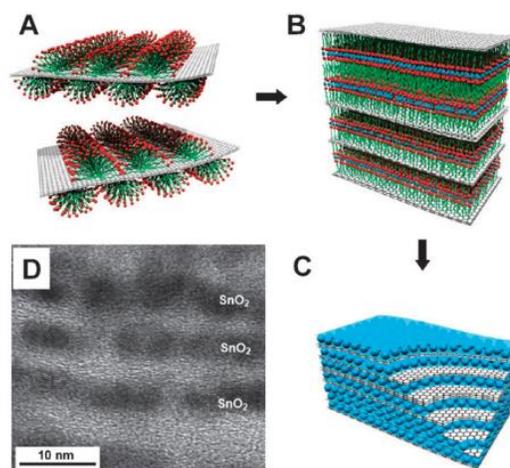

Figure 2. (A–C) Schematic illustrations ofmetal oxide/rGO composites. (A) Absorption of surfactant hemimicelles on the surfaces of the rGO (B) The self-assembly of anionic sulfonate surfactant on the graphene surface (C) Layered metal oxide–rGO composites composed of alternating layers of metal oxide nanocrystals and rGO stacks. (D) High-magnification TEM of SnO2/rGO composites. Copyright 2010, American Chemical Society.

IV. GRAPHENE-POLYMER COMPOSITES

The 3D arrangement and the kind of interaction between graphene sheets and polymers is what graphene–polymer composites are based on and this is further categorized into three types, which are graphene-filled polymer composites, layered graphene–polymer films, and polymer-functionalized graphene nanosheets.

The most common fillers such as amorphous carbon and carbon nanotubes (CNTs) extracted from carbon are used to amplify the electronic, mechanical, and thermal properties of polymer matrices. However, graphene-based fillers are predicted to substitute CNT due to their low cost. The dispersity and its bonding with the polymer matrix are crucial factors to attain optimal properties of the composites while reducing the content of the graphene filler. And with this outlook in our mind, graphene-filled polymer composites are prepared by solution mixing, melt blending, and in situ polymerization.

A. FABRICATION METHODS

Solution mixing is the most accessible method for the preparation of polymer composites. GO can directly be mixed with water-soluble polymers, such as poly(vinyl alcohol) (PVA), at copious concentrations, because of the residual oxygen-containing functional groups. However, the

Graduate Research in Engineering and Technology (GRET): An International Journal ISSN 2320 − 6632, Volume-1, Issue-7

15

polymer and the filler are bad solvent compatibility which makes them bad at achieving dispersion. Thus, non-polar solvents and other forms of graphene in particular expanded graphite (EG) and rGO, in which GO does not dissolve, represent the limited solubility in both organic and inorganic solvents. Sonication is used to produce metastable dispersions of graphene derivatives, which is then further mixed with polymer solutions like poly(methyl methacrylate) (PMMA), polyaniline (PANi), polycaprolactone (PCL), and polyurethane (PU), to cure the above problem. To mix graphene-based fillers and the polymer matrices high-speed shearing combined with the ice-cooling method is practiced. During the two processes mentioned above re-stacking, aggregation, and folding of the graphene-based nanosheets are inescapable which ultimately reduces the specific surface area of the 2D fillers. To provide graphene-based fillers with good solubility in various kinds of solvents is only possible when solution mixing is done prior to surface functionalization. For example, we have observed phenyl isocyanate-modified GO sheets to have better dispersity in polystyrene (PS) solution in DMF. The polymer matrix resists the re-aggregation of rGO sheets to retain a homogenous suspension in the course of the wake of in-situ reduction of GO.[7]

To blend the filler and matrix materials, it is necessary for melt compounding to have both high-shear forces and high melting temperature. Therefore, for graphene filler and the polymer matrix, it is not compulsory to have a similar solvent. By applying the melt compounding, Polylactide (PLA)-exfoliated graphite (EG) composite and PET–rGO graphene composite are successfully prepared. The breakage of the filler materials, such as CNTs and graphene nanosheets, can be observed during the use of high shear forces in melt compounding.

To develop graphene-filled polymer composites, such as those with epoxy and polyaniline (PANi). In-situ polymerization technique is used which is yet another conventional method of preparing it. The graphene-based filler is blended with epoxy resins under high-shear forces, in the presence of a curing agent which begins the polymerization, is the classic process used for preparing graphene-epoxy composites. An oxidative agent like ammonium persulfate is used to ease the polymerization for PANi since it is an oxidative process. On the other hand, in-situ electro polymerization can be used for the preparation of graphene-PNAi composite. For example, the working electrode made from graphene paper in a three-electrode cell the deposition of PANi is observed along with the solution which contains aniline monomers as the electrolyte. Graphene is successfully monitored being absorbed in other polymer matrices, like silicone, and poly(vinyl chloride/ vinyl acetate) copolymer, additionally to the epoxy and PANi through the in-situ polymerization.

B. LAYERED GRAPHENE-POLYMER FILMS

Graphene derivatives can also be composited with polymers in layered structures that are fabricated for the directional load-bearing membranes, and thin films for photovoltaic applications. Whereas in graphene-filled polymer composites we observe that the graphene fillers are non-uniformly distributed in the polymer matrices. For instance, the Langmuir-Blodgett (LB) technique is used to deposit GO sheets onto the films of polyelectrolyte poly(allylamine hydrochloride) (PAH) and poly (sodium 4-styrene sulfonate) (PSS) multi-layers (Fig.3 A)[8], by assembling them in layer-by-layer. The outcome produced is that the directional elastic modulus of the composited membrane is from 1.5 to 20 GPa with 8 vol% loadings of the graphene (Fig.3 B) which is good and highly escalating.[1]
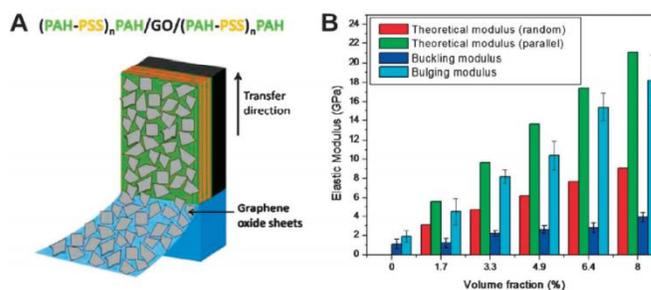

Figure 3. (A) Schematic illustration of fabrication and assembly of the free-standing GO-LbL film. (B) Plot showing the variation of elastic modulus calculated theoretically (under parallel and random orientation) and obtained experimentally (using buckling and bulging measurements) with the volume fraction of GO. Reproduced with permission from ref. 215. Copyright 2010, American Chemical Society.

C. POLYMER FUNCTIONALIZED GRAPHENE NANOSHEETS

The best thing about Graphene derivatives filler are that they can not only be used as decorations in 2D template polymer but can also be used to nourish or reinforce the properties of polymers using covalent and non-covalent functionalization's. The solubility of the graphene derivatives and the resulting hybrid nanosheets with auxiliary performance can be improved by the polymer coating. The reaction between the functional groups of the polymers and the oxygenated groups on the GO or rGO surfaces is what the covalent functionalization of graphene derivatives is mainly dependent upon. In the preparation of GO-PVA composite sheets, esterification of the carboxylic groups in GO with the hydroxyl groups in PVA is observed. The process to bind the six-armed polyethylene glycol(PEG)-amine stars involves the carboxylic groups on GO in the carbodiimide-catalyzed amide formation. Therefore, at the margin of the GO sheets the carboxylic groups are confined. Amine and chloride groups are some of the non-oxygenated functional groups which are necessary for the grafting of certain polymers. However, before the grafting of polymers more choices of approach are required to amplify GO/rGO surfaces with additional chemical reactions. For example, the fluorene-thiophene-

Graduate Research in Engineering and Technology (GRET): An International Journal ISSN 2320 – 6632, Volume-1, Issue-7

16

benzothiadiazole polymer is been seen grafting covalently onto the rGO surface via Suzuki reaction through the 4-bromophenyl groups, after the 4-bromophenyl groups were coupled on the rGO surface through the diazonium reaction. PS that has been successfully grafted onto the rGO sheet with controlled density is based on which the pre-bonded diazonium group on rGO acts as the initiator for atomic transfer radical polymerization (ATRP). The APTES-modified GO surface can be further bonded with maleic anhydride polyethylene (MA-g-PE) when acyl-chlorinated GO sheets are further reacted and connects to the triphenylamine-based polyazomethine (TPAPAM) and MeOH-terminated p3HT.

The example mentioned previously shows that graphene-based sheets hold the probability of being adaptable due to the rich surface chemistry of GO/rGO because of the covalent functionalization of polymers. However, the van der Waals force, electrostatic interaction, or pi–pi stacking makes it easier to carry out the chemical structure of the capped rGO sheets without being reformed and provides functional means to tailor the electronic/optical property and solubility of the nanosheets, thus being the non-covalent functionalization, which depends upon them. The in-situ reductions of GO with hydrazine in the presence of poly(sodium 4-styrene sulfonate) (PSS) was the first-ever example of the non-covalent functionalization of rGO sheets that were experimented. Whereas the rGO was stabilized by the hydrophobic backbone of PSS and the betterstrewing of the hybrid nanosheets in water was balanced by the hydrophilic sulfonate side groups. Later it was expected to gain good solubility in different kinds of solvents when conjugated polyelectrolytes with various functionalities were used and at the same time, it acquired optoelectronic properties also. The solubility of graphene-polymer nanocomposites can be improved in both high and low polar solvents if amphiphilic coil-rod-coil conjugated triblock copolymer is used. (Fig. 4A shows the chemical structure of PEG-OPE). The basal plane of the in-situ reduced GO can cohere with the conjugated rigid-rod backbone of PEG-OPE using the pi-pi interaction (Fig. 4B), hence an amphiphilic outer-layer surrounding the rGO sheet is formed by the lipophilic side chains and the two hydrophilic coils of the backbone. The uniformly coated polymer layer of the obtained rGO sheets (Fig. 4C) is soluble in both organic flow (such as toluene and chloroform) and water-miscible high polar solvents (such as water and ethanol).[1]
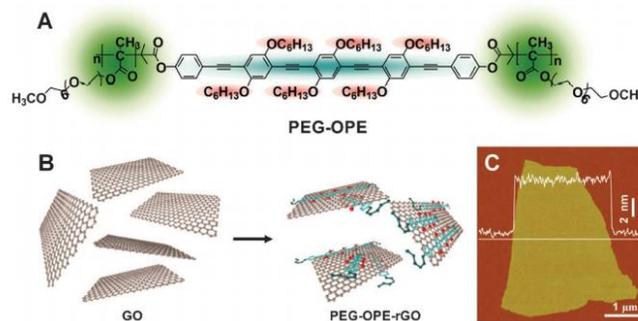

Figure 4. (A) Chemical structure of PEG–OPE. (B) Schematic illustration of fabrication of PEG–OPE stabilized rGO sheets. (C) Tapping mode AFM image and cross-sectional analysis of PEG–OPE–rGO on mica. Reproduced with permission from ref. 14. Copyright 2010, John Wiley & Sons, Inc.

V. APPLICATIONS

A. Solving Lightweight using Graphene-based composites

When speaking for lightweight aircraft manufacture, materials utilized for it should have low density and good structural properties. Apparently, materials such as aluminum alloys still hold the problem in weight category, and therefore an airplane frame is mostly comprised of Aluminium.The magnificent outcome can be accomplished in aerospace industries, terminating the redundancy and minimizing weight, if we utilize a certain amount of nanoparticles. Thus providing us with the solution to tackle thelightweight conundrum.The graphene and its based composites in recent studies have proven to show outstanding results such as ultra-high aspect ratio, high stiffness, and surface modification giving reduced weight and enabling us to construct material. Making it an asset in the following industries. Therefore, a certain amount of graphene has the power to corroborate with thermoplastic and thermosetting systems at the matrix interfaces through stress transfer which permits the components to withstand more load [10,11]. CFRP (Carbon Fibre Reinforced Polymer) composites have good mechanical reinforcement since it has splendid interfacial bonding between the fiber and resin.

For example, GF partners Aernnova, Grupo AntolinIngenieria, and Airbus produced a leading edge for an Airbus A350 horizontal tailplane using graphene-based CFRP composite in figure 5.

Graduate Research in Engineering and Technology (GRET): An International Journal ISSN 2320 – 6632, Volume-1, Issue-7

17

Figure 5. Horizontal tailplane using graphene-based CFRP composite

B. Additive manufacturing from Graphene-based composites

The diversified properties of graphene when blended with Advanced thermoplastics will enable humanity to up their game in Additive manufacturing. Additive manufacturing is a technique to produce highly intricate 3D objects layer by layer for many structural and repair applications. Essentially there are two common techniques that are practiced and they are; fused deposition modeling (FDM) and selective laser sintering(SLS).In additive manufacturing, material that manifests superlative mechanical and chemical properties at high temperatures is a semi-crystalline advanced material Polyetheretherketone (PEEK) in situ from the polyaryletherketone (PAEK) family [12-13]. Although PEEK properties already being good, it can further be tailored well with the help of graphene. Which will benefit the aerospace dominion with the wear resistance, mechanical, thermal, and electrical properties.

Using GRM (Graphene and Related Materials) material to print aerospace components will provide us with good efficiency and due to GRM's good thermal properties, it will result in swift manufacture and development and strengthening of mechanical properties which will permit us to use AM plastics for non-critical and, potentially, critical components.

C. Using Graphene-based composites to prevent fire

Our safety concerns with an aircraft to catch fire is increasing as plastics are being used to tackle the lightweight conundrum and they are easy to design.

Therefore in next few years the plastic flame retardant market is going to increase. Essentially, carbon fibre and glass fibre have the capability to brace thermoplastic and thermosetting matrix polymers. Not to mention these reinforced plastics have copious sublime applications such as wings, decks, cabins, kitchens, propulsions systems, bearings, cooling systems, and other critical and non-critical components[14]. The grim fact about the polymer resins used in FRP (Fiber Reinforced Polymer) are that when they catch a fire they release smoke and toxic gases[15,16]. However many flame retardant additives such as halogen, phosphorus, metal oxide and hydroxide based materials are being used to decrease the flammability of the plastics. But still many are cut out from the list due to their toxicity produced when they are burnt and released in the form of gases.

Apparently, the scientists are toiling how graphene can be used within thermoplastics and FRP composites with a mindset of developing materials which have good fire resistance and lower toxic fume release and can be used in aerospace cabin components.

Interestingly, when graphene imbued into a polymer matrix, it can effectively alter the pyrolysis, thermal conductivity and heat absorption [17]. Thus disturbing the combustion process by limiting the heat and fuel sources from ignition [18]. And this full effect is known as synergistic effect, upon graphenes decomposition, char layer is formed on the surface, creating dense barrier leading it to cut off the propagating heat and preventing it from further burning. In addition, the char layer also minimizes the release of toxic gases. With this evidence its safe to manufacture cabin interior components with the above materials.

VI.   CONCLUSION

This article has spotlighted the synthesis techniques for graphene-based composites. In addition to that, this paper has also mentioned the case studies where graphene is motivating the researchers to manufacture graphene-based composites for aerospace industries due to their outstanding performance. However, there are also existing applications such as energy storage technologies (supercapacitors, batteries), energy harvesting (solar, wind), thermal management (cooling for satellites) to name a few.

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Graduate Research in Engineering and Technology (GRET): An International Journal ISSN 2320 – 6632, Volume-1, Issue-7

18

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19