



Review

Recent Developments Concerning the Dispersion Methods and Mechanisms of Graphene

Aoyan Liang, Xiaosong Jiang *, Xin Hong, Yixin Jiang, Zhenyi Shao * and Degui Zhu

School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu 610031, China; 2014110095@my.swjtu.edu.cn (A.L.); hongxin@my.swjtu.edu.cn (X.H.); jyx@my.swjtu.edu.cn (Y.J.); dgzhu@home.swjtu.edu.cn (D.Z.)

* Correspondence: xsjiang@swjtu.edu.cn (X.J.); zysao@cdtu.edu.cn (Z.S.); Tel./Fax: +86-28-8760-0779 (X.J.)

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Abstract: Graphene, as a reinforcement for composite materials, has become a focus recently. However, the dispersion of graphene in composite materials is a problem that has been difficult to solve for a long time, which makes it difficult to produce and use graphene-reinforced composites on a large scale. Herein, methods to improve the dispersion of graphene and dispersion mechanisms that have been developed in recent years are reviewed, and the advantages and disadvantages of various methods are compared and analyzed. On this basis, the dispersion methods and mechanisms of graphene are prospected, which lays the foundation for graphene application and preparation.

Keywords: graphene; surface modification; dispersion method; dispersion mechanism

1. Introduction

Since Geim et al. [1] successfully prepared graphene by tape stripping in 2004, the study of graphene has never ceased. Graphene is a two-dimensional network carbon nanomaterial. The carbon atoms in graphene form a unique two-dimensional hexagonal honeycomb lattice structure by sp² hybridization. This monatomic layer structure makes graphene the thinnest and strongest material in the world [2]. Graphene also has excellent physical and chemical properties, such as mechanical properties [3], thermal properties [4], electrical properties [5], and optical properties [6]. Therefore, graphene has a wider value and prospects for practical application compared with other members of the carbon nanomaterials family, namely zero-dimensional fullerenes and one-dimensional carbon nanotubes. In recent years, graphene has often been combined with polymer materials [7–11], ceramic materials [12–16], and metal materials [17–19] to prepare graphene-reinforced composites, which not only makes the physical and chemical properties of the composite materials be greatly improved [20–22], but also expands the application of graphene in the field of optoelectronic materials [23,24], biosensors [25,26], and catalysts [27,28]. Graphene, however, has a poor dispersion and weak interface bonding force in the matrix, which greatly limits the use of graphene as a reinforcement for composite materials.

The poor dispersibility of graphene in composites is due to its insolubility in the matrix, van der Waals forces, and π – π stacking between the graphene lamellae. Typically, graphene is prone to aggregate and precipitate irreversibly in a variety of matrices [29]. The weak bonding strength between graphene and a matrix is mainly caused by the low surface activity of graphene, which makes graphene difficult to bond with the matrix interface [30]. Thus, how to improve the poor dispersibility and weak adhesion of graphene in the matrix of a composite material has become a vital problem. In order to solve this problem, it is necessary to explore the dispersion methods and mechanisms of graphene. At present, the methods for improving the dispersibility of graphene are mainly divided into three categories, namely physical dispersion methods, covalent bonding methods, and noncovalent bonding methods. Physical dispersion methods usually adopt mechanical methods

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to disperse the agglomerated graphene nanosheets. Covalent bonding methods are usually achieved by combinations of graphene oxide and organic small molecules, polymers, or other materials with excellent dispersibility through certain chemical reactions to improve the dispersion of graphene in composite matrices [31,32]. In a sense, graphene oxide is obtained by chemical oxidation. Noncovalent bonding methods are achieved by combinations of graphene and functional molecules through a π - π bond, an ion bond, a hydrogen bond, or other noncovalent bonds to enhance the stability of graphene [33–35]. The reaction condition and operation of the covalent bonding methods are more difficult to achieve than those of the noncovalent bonding methods, but the stability of the functional graphene acquired by a covalent bonding method is better [36]. In addition, other methods that improve the dispersion of graphene have been studied, such as electroless plating.

Graphene owns wide and viable application due to its excellent physical and chemical properties. Graphene has become a focus as a reinforcement for composite materials. However, the dispersion of graphene in composite materials is a problem that has been difficult to solve for a long time, which has made it difficult to produce and use graphene-reinforced composites on a large scale. This paper summarizes a variety of methods to obtain functional graphene that have been developed in recent years and describes its mechanisms. It is expected to deepen the understanding of the graphene dispersion methods and its dispersion mechanisms in order to improve and expand graphene's properties and application areas through surface modification. The future of the graphene dispersion method is also discussed on the basis of the discussion and analysis.

2. Physical Dispersion Methods

The physical dispersion method involves dispersing the agglomerated graphene nanosheets via mechanical methods without chemical reactions [37]. This method can improve the dispersion of graphene by forming graphene sheets with fewer flakes. The cost of the physical method is low, and it can be applied to large-scale production [38]. Physical methods include ultrasonic treatment, stirring, and ball-milling [39,40]. The ultrasonic treatment plays a great role in liquid phase exfoliation and is generally used as an assistant method, which is reviewed in the synthetical method section. The stirring and ball-milling methods are reviewed here.

2.1. Stirring

A stirring treatment can cause shear force that can be utilized to disperse the graphene, and it includes friction stirring and magnetic stirring [41,42]. Friction stir processing (FSP) can effectively disperse graphene nanosheets in a metal matrix, especially in an aluminum matrix. Jeon et al. [37] fabricated Graphene/aluminum metal matrix composites (MMC) by friction stir processing (FSP). The addition of graphene improved the thermal conductivity of the graphene/aluminum MMC by more than 15% in comparison with that of the aluminum matrix. Khodabakhshi et al. [39] used the same method to fabricate a new Al–Mg/graphene nanoplatelets (GNPs) nanocomposite. They applied five cumulative FSP passes on the composite. After that, the graphene showed good dispersion and negligible deterioration of the graphene planar structure. Dixit et al. [41] prepared multi-layer graphene reinforced aluminum via friction stir alloying. The results showed that the strength of the composite was increased two-fold without a loss in ductility due to the dispersion of the graphene in the aluminium.

Graphene/carbon nanotube composites can also be prepared to improve the dispersion of graphene. Carbon nanotubes, like graphene, are nanoscale carbon materials with a large specific surface area, good electrical conductivity, and excellent mechanical properties [43,44]. There is a synergistic effect between graphene and carbon nanotubes, which causes their physical and chemical properties to be significantly improved [45–47]. In 2014, Liang et al. [42] mixed graphene and carbon nanotubes in four different proportions (8:2, 6:4, 4:6, and 2:8) and dispersed them in epoxy resin by simultaneous magnetic stirring and sonication. According to the results, when the ratio of carbon

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nanotubes to graphene is 8:2, the best dispersion effect can be achieved. This method can increase the flexural properties and reduce the electrical percolation threshold of the epoxy composites.

2.2. Ball-Milling

Just like stirring, ball-milling can produce shear force on graphene. The ball-milling apparatus can also cause vertical impact and collisions by adding brittle balls which will fragment the graphene and inhibit its agglomeration. Leon et al. [38] achieved graphene flakes with different sizes by adding commercially available melamine during the process of ball-milling under solid conditions. The prepared graphene can be well-dispersed in organic solvents, water, or culture media. Alinejad et al. [48] obtained graphene nanoflakes of about $50 \times 200 \text{ nm}^2$ by adding NaCl during ball-milling. Because graphene particles are soft, the brittle and hard NaCl particles can serve as milling agents to grind the graphene into thin layers and keep graphene particles away from agglomeration. NaCl can be easily washed away by water after milling.

A ball-milling treatment can help to fabricate graphene composites of many kinds of matrix. Guo et al. [49] fabricated composites of GNPs and epoxy through ball-milling. The obtained graphene/epoxy resin composites had an enhanced thermal conductivity. The results showed that GNPs with high quality (<10 layers) were uniformly dispersed in the matrix. Yu et al. [40] synthesized a ZnO/graphene nanocomposite by high-energy ball-milling. According to the results, graphene was dispersed homogeneously in the ZnO matrix, which greatly improved the lithium storage capability of ZnO. Bastwros et al. [50] fabricated a 1.0 wt.% graphene-reinforced aluminum 6061 (Al6061) composite by hot compaction in the semi-solid regime of the Al6061. Before the compaction, graphene and Al6061 powder were ball-milled, which provides a good dispersion of graphene in Al6061 matrix.

Because of the advantages of physical dispersion, such as simple operation and easy access to the equipment, many scholars have chosen to disperse graphene by physical dispersion methods and synthesize metal matrix composites. However, physical methods will cause damage to the graphene structure and the dispersion rate of graphene is low. For example, the Raman spectra results of graphene in Figure 1 [50] show that the intensity ratio of the D-band to the G-band ($I_{\rm D}/I_{\rm G}$) increased from 1.08 to 1.42 after milling for 5 h. The increase of $I_{\rm D}/I_{\rm G}$ indicates that more defects and disordering were created during the process according to the reference [51]. The number of defects increased mainly because of the physical force applied during the process. The defects caused by these methods are difficult to repair, and the high content of graphene is intractable to obtain. Therefore, physical methods are usually used as assistant methods for other methods.

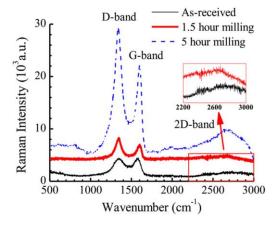


Figure 1. Raman spectra of the milled Al6061-2.0 wt.% graphene powder at different milling times and as-received graphene [50]. (Reproduced from [50] with permission; Copyright 2014 Elsevier).

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3. Covalent Bonding Methods

At present, the covalent functionalization of graphene is the most widely used functional method. Although the main part of graphene is composed of stable hexatomic rings, its edges and defect sites have higher reactivity [52]. Graphene oxide can be prepared by chemical oxidation. Because graphene oxide contains a large number of carboxyl groups, hydroxyl groups, epoxy bonds, and other active groups, the covalent functionalization of graphene can be carried out through a variety of chemical reactions. Graphene oxide is mostly obtained by Hummers.

3.1. Using Small Organic Molecules

Earlier studies of improving graphene's dispersion mainly focused on using small organic molecules to modify graphene by combining small organic molecules and the oxygen-containing functional groups on the surface of graphene oxides through covalent interaction. This is an efficient way to enhance the dispersion and stability of graphene. These small organic molecules include isocyanate [52], 1-ethyl-3-(3-(Dimethyl amino)-1-propylamine)-carbodiimide [53], thionyl chloride [54], and N,N'-Dicyclohexylcarbodiimide [55].

He et al. [56] utilized ethanol amine as dispersant and hydrazine hydrate as reducer to prepare a graphene composite (ETA-RGO: ethanol amine-reducedgrapheneoxide), and a stable and uniform ETA-RGO dispersion solution was obtained. They used the covalent interaction between the carboxyl of graphene oxide and the amidogen of the ethanol amine to disperse graphene in a water solution with good stability. AFM and TEM results showed that graphene was distributed in the form of a single layer, and the maximum width of graphene in the system was about 1µm and the thickness was about 0.8 nm. In addition, the graphene in the ETA-RGO solution rapidly agglomerated when the pH value decreased to less than 6, which shows an obvious pH value response property of the composite. This method is expected to expand the application range of graphene-related materials in the biological field. Mungse et al. [31] utilized octadecylamine (ODA) to modify graphene oxide through the reaction between the amino of the ODA and the carboxyl of graphene oxide. They obtained long alkyl-chains-functionalized graphene. This functionalized alkylated graphene had long-term stability in lube oils. The optimized concentration of alkylated graphene is up to 0.02 mg/mL. Haddon et al. [57] also observed good dispersion of alkylated graphene in some common organic solvents, such as tetrahydrofuran (THF) and carbon tetrachloride.

3.2. Using Polymers

In recent years, the research on using polymers to improve the dispersion of graphene has been more extensive than that using small organic molecules. This is because polymer-functionalized graphene has more advantages, and the structural parameters of polymers can be adjusted, such as the monomer type, topological structure, molecular weight, and electric property. Polymer modification can provide graphene with better mechanical properties, including toughness and ductility, and give graphene more useful properties by changing the type and function of the polymer [58]. In general, there are two methods for the covalent modification of graphene by polymers: the grafting-to method and the grafting-from method [32]. The grafting-to method firstly synthesizes polymer chains with active functional groups at the end, and then grafts the chains onto graphene oxide by a coupling reaction. Zhang et al. [59] adopted this method. They used SOCl₂ as an organic coupling agent, and then obtained polyethylene glycol mono-methyl ether 750 (MPEG750)-modified graphene through esterification. The results showed that the graphene oxide (GO)-MPEG750 is dispersible in both polar and nonpolar solvents. Gong et al. [60] adopt the same method. They prepared functionalized graphene oxide (FGO) through an esterification reaction between the carboxyl of graphene oxide and the hydroxyl of polyvinyl alcohol (PVA). FGO shows a good dispersibility in the polyamide6 (PA6) composite matrix. Except for the esterification reaction, Rani et al. [61] prepared FGO through amidation. They treated graphene oxide with aniline, 2-aminothiazole, and 2-aminopyrimidine, Coatings 2018, 8, 33 5 of 23

and then prepared three types of amide-functionalized graphene oxide (AGOs), respectively. Figure 2 shows the processing steps to prepare AGOs. The results showed that AGOs are soluble in water, dimethyl sulfoxide, and dimethyl formamide, and can be stabilized for months.

Figure 2. Schematic processing steps for the preparation of amide-functionalized graphene oxides AGO1, AGO2, and AGO3 [61]. (Reproduced from [61] with permission; Copyright 2014 Elsevier). GO: graphene oxide; AGO: amide-functionalized graphene oxide.

Deshmukh et al. [62] used the colloidal processing method to add graphene oxide into a water-soluble polypyrrole (WPPy)/polyvinyl alcohol (PVA) blend solution and then fabricated WPPy/PVA/GO nanocomposites. The good dispersion in the polymeric matrix of graphene is due to the covalent interaction between GO and WPPy. The composite also has an excellent dielectric property because of the existence of graphene. Noh et al. [63] fabricated polymer composites with excellent graphene dispersibility via using solvent-free powder mixing and in situ polymerization. They also compared the dispersion of graphene nanoplatelets (GNP), graphene oxide (GO), and chemically converted graphene (CCG), respectively. They used the powder-mixing method to mix cyclic butylene terephthalate (CBT) resin powder with three kinds of graphene powder, and then put them into a square mold to prepare three kinds of graphene composite, namely GNP-pCBT, GO-pCBT, and CCG-P-pCBT. The results showed that the graphene in these three composites was highly dispersed. The dispersion of CCG-P in the matrix was the best, followed by GO, which was mainly due to the introduction of a large number of benzene groups in the CCG-P and the fact that the GO contained various oxygen-containing functional groups. The highest content of graphene in the composites reached to 20 wt.%.

The grafting-from method firstly evenly mixes graphene and a polymer monomer, then causes in situ polymerization at the layers of graphene or graphene oxide. Because the polymer "grows" from the surface of the graphene, the amount of grafted polymer on the surface of the graphene can be changed by changing the feed ratio or reaction time. In 2009, for the first time, Ye et al. [64] fabricated amphiphilic polymer-functionalized graphene by in situ living free-radical polymerization. Firstly, they treated graphene with chemical oxidation and ultrasonic exfoliation to prepare GO and the GO was reduced by NaBH4. Then, polystyrene—polyacrylamide (PS-PAM) was covalently grafted onto graphene by using benzoyl peroxide (BPO) as radical initiator, and graphene modified by PS-PAM was obtained. This PS-PAM-functionalized graphene has good solubility and dispersibility in water and dimethylbenzene. However, this traditional polymerization provides poor control

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over the structure of the grafted polymer. In recent years, the rapid development of controlled polymerization has provided an opportunity for regular polymer-functionalized graphene, including nitroxide-mediated polymerization (NMP) [65], atom transfer radical polymerization (ATRP) [66], reversible addition-fragmentation chain transfer polymerization (RAFT) [67], and single electron transfer and living radical polymerization (SET-LRP) [68]. On this basis, Wang et al. [69] obtained a graphene/poly (*N*,*N*-Dimethylacrylamide) (PDMAA) nanocomposite (G-PDMAA) via the single electron transfer and living radical polymerization (SET-LRP) method. Firstly, they used hydrazine to reduce GO and adopted a diazonium addition reaction to give graphene-containing hydroxyls (G-OH), then they obtained graphene with SET-LRP initiating groups (G-Cl) through esterification with 2-chloropropionyl chloride. Finally, they used in situ SET-LRP to grow PDMAA chains from the surface of graphene and obtained G-PDMAA. The G-PDMAA nanocomposite showed excellent dispersion in common organic solvents and water solution. It is expected to be used in polymer modification and biomaterials.

Osicka et al. [70] fabricated GO modified by poly (methyl methacrylate) (PMMA) polymer chains via surface-initiated atom transfer radical polymerization (SI-ATRP). Poly (dimethyl siloxane) (PDMS) containing different amounts of silicone oil and curing agent as matrix was used. The results showed that PMMA could enhance the interaction between GO and the matrix to achieve high dispersion of graphene. Meanwhile, GO can effectively improve the photocatalytic performance of the matrix materials. Jiang et al. [71] also used PMMA to improve graphene dispersion by latex technology and melt blending. They firstly modified GO with hydroxyethyl acrylate (HEA) and simultaneously reduced the GO. The covalent bonding between the GO and HEA resulted in a functionalized graphene oxide (FGO) with double bonds. Then they used emulsion copolymerization between methyl methacrylate (MMA) monomers and FG double bonds for the pretreatment of FGO. Finally, the PMMA/graphene composites were obtained by melt blending. Figure 3 shows the procedures they used. It was found that PMMA on the surface of graphene can effectively prevent graphene agglomeration and obviously improve graphene dispersion in the polymer matrix. Yuan et al. [72] fabricated graphene/polypropylene (PP) nanocomposites through a novel covalent approach. They firstly modified GO with p-phenylenediamine and cyanuric chloride to obtain FGO. Then, they then grafted FGO with maleic anhydride-grafted polypropylene (MAPP). The obtained FGO showed good dispersion and strong interfacial interaction in a PP matrix.

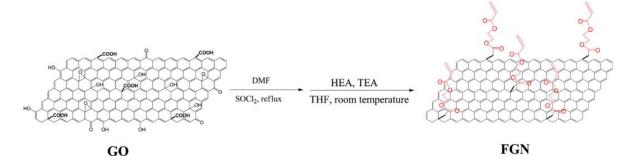


Figure 3. Schematic illustration for the preparation of functionalized graphene oxide (FGO) [71]. (Reproduced from [71] with permission; Copyright 2013 Elsevier).

4. Noncovalent Bonding Methods

Besides the covalent bonding methods, modifying the graphene's surface with functionalized molecules through a π – π interaction, an ionic bond, or a hydrogen bond etc. can also form a stable dispersion of graphene.

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4.1. Using a π - π Interaction

Because of the conjugated structure with hexatomic rings which is formed by the sp² hybrid carbon of graphene, graphene can have π - π noncovalent interactions with other organics which have the same conjugated structure and absorb the organic molecules on the surface of the graphene to improve the dispersibility. Yang et al. [73] found that the π - π structured plane of humic acid (HA) can be absorbed on the surface of graphene, which supplied oxygen-containing groups to graphene sheets to improve the dispersion of graphene in water. Iqbal et al. [74] proposed an approach to improve the dispersibility of graphene in a polyethylene (PE) matrix. They mixed graphene, PE, and oxidized PE (OPE) via a solution blending method. It was found that the dispersion of graphene in a PE/OPE matrix improved a lot. Pyrene and its derivatives are common organic molecules with conjugated structures which can effectively inhibit the agglomeration of graphene by absorbing on graphene [33]. Parviz et al. [75] exploited pyrene derivatives called PMMA to modify untreated pristine graphene and obtained a stable dispersion of pyrene-functional graphene nanosheets in chloroform solution. Through vacuum filtration, they prepared a graphene film with completely different conductivity from the top to bottom. Balasubramaniyan et al. [76] modified highly reduced graphene with PMMA by solution blending, which improved the dispersion of graphene in the PMMA matrix. Graphene quantum dots (GQDs) are a kind of graphene with a single layer or a few layers whose transverse size is less than 100 nm. Because of the unique photoluminescence phenomenon it produces, it has attracted great attention [77]. Besides this, it also has a π - π conjugated structure that provides a new way to improve the dispersion of graphene. He et al. [78] improved the dispersion of graphene in water by using graphene quantum dots as dispersants. The results showed that dispersing 100 mg of graphene powder only needed 7.8 mg of graphene quantum dots. The obtained graphene's highest concentration reached 0.4 mg/mL in water. Moreover, it could maintain a stable dispersion for at least three months.

Melt-blending is the most economical and efficient way to achieve the homogeneous dispersion of graphene in a polymer matrix. Many scholars have used a melt-blending method to prepare graphene/polymer composite materials with good dispersibility, and they have found that the combination of graphene and some polymers occurs mainly through the π - π interactions. This π - π bond can effectively improve the dispersion of graphene. Shen et al. [79] prepared thermally reduced graphene oxide (TRG)/polycarbonate (PC) composites by a melting-blend process. Obtaining the dark supernatant after ultracentrifugation experiments showed that the dispersion of TRG was improved in some solutions. The mechanism is shown in Figure 4. Oyarzabal et al. [80] prepared a pristine graphene (PG)/polycarbonate (PC) nanocomposite by a melt-blending method. The concentration of PG from 1 wt.% to 7 wt.% showed good dispersion. The addition of graphene also enhanced the mechanical properties and barrier properties of the composite. You et al. [81] have successfully prepared highly thermally reduced graphene oxide (TRG) using a melt-blending method. They mixed graphene with a styrene-ethylene/butylene-styrene (SEBS) block copolymer at 225 °C for 25 min. The results showed that the obtained TRG not only achieved a relatively high degree of reduction, but also had good dispersion in the polymer matrix due to the tight combination of SEBS and graphene via the π - π interaction. Istrate et al. [82] prepared a polyethylene terephthalate (PET)/graphene composite via melt-blending at an extremely low graphene loading level. It was pressed into thin film to detect its performance. The results showed that graphene was well-dispersed in the polymer matrix. Moreover, at a nanofiller load as low as 0.07 wt.%, the composite's elastic modulus and tensile strength increased more than 10% and 40%, respectively, compared to pristine PET.

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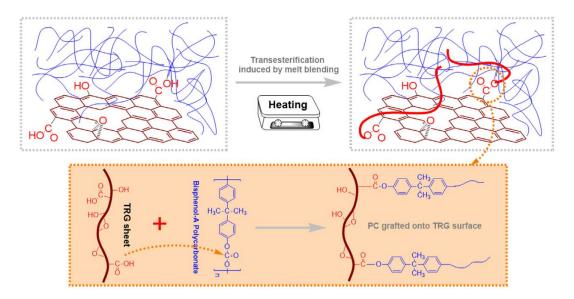


Figure 4. Schematic diagrams of the transesterification between the carbonate groups in PC chains and the carboxyl groups on thermally reduced graphene oxide (TRG) sheets at high temperature during melt-blending [79]. (Reproduced from [79] with permission; Copyright 2013 Elsevier).

4.2. Using Ionic Bonds

In 2008, Li et al. [34] explored the dispersion state and the charge repulsion of ionic bond-functionalized graphene. They found that GO was able to dissolve in water, not only because of the hydrophilic oxygen-containing functional groups on the surface of GO, but also because the surface carboxyl of GO carries a negative charge. These negative charges repel each other, forming a stable colloidal solution. By taking advantage of this discovery, they could remove the hydroxyl group, epoxy bond, and other functional groups of GO, retain the carboxyl anion by controlling the reduction process, and obtain well-dispersed graphene in water. After that, Liang et al. [83] used the charge effect between positive and negative ions. They added an amphiphilic surfactant with positive charges (quaternary ammonium salt) into an aqueous solution that had highly dispersed graphene formed by a negative charge effect. Then, they added organic solvent (trichloromethane). After a simple oscillation, they realized the transformation of graphene between different solvents for the first time. This simple method can broaden the idea of graphene's dispersion modification and application.

Li et al. [84] realized the uniform dispersion of GO in aluminum powder through direct electrostatic adsorption. This type of adsorption did not require any chemical catalyst. Additionally, GO could be reduced to reduced graphene oxide (RGO) during the annealing process. According to the results, the Young's modulus and hardness of the composite increased by 18% and 17%, respectively, with the mere addition of 0.3 wt.% RGO. Ahadian et al. [85] treated graphene with sonication in aqueous bovine serum albumin (BSA). By using the electrostatic interaction between graphene and the amino acids of BSA, they obtained graphene that was well-dispersed in water. It has high application value in the biomedical field. Hassan et al. [86] fabricated graphene/polyaniline (PANI) thin films with an interpenetration network structure by the following steps. Firstly, they prepared PANI nanospheres through microemulsion polymerization. Then, they used the electrostatic interaction between PANI and GO to form a unique layered structure, and finally reduced GO with hydriodic acid. The results showed that the graphene and polyaniline nanosheets can be well-dispersed by electrostatic adsorption, and the electrical properties of the films are greatly improved. Choi et al. [87] fabricated the end-functionalized polymers amine-terminated polymers and used them to modify rGO via ionic interaction. The protonated amine terminal group of polystyrene can improve the graphene's dispersibility in many organic solutions.

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Quaternary ammonium salt can combine with graphene via an ionic bond to inhibit the aggregation of graphene so the dispersion of graphene can be improved [83]. years, many scholars have done experiments and tests on this method. Chen et al. [88] used 2-hydroxypropyltrimethyl ammonium chloride chitosan (HACC)-modified GO via charges interaction between them and reduced GO by hydrazine hydrate to obtain HACC-RGO. They also explored the dispersion and electrochemical properties of HACC-RGO in different pH solutions. Dispersion results showed that HACC-RGO had good dispersion and stability in aqueous solution of pH 2~9, and the average particle size of HACC-RGO decreased with the increase of HACC dosage. Sui et al. [89] introduced quaternary ammonium salt cetyltrimethyl ammonium bromide (CTAB) as a modifier for the noncovalent functionalization of GO, and used GO as reinforcing agent for enhancing the property of olefin block copolymers (OBCs). The results showed that GO had good dispersibility in an OBCs matrix because of the CTAB modification. The tensile strength, elongation, and Young's modulus of the matrix increased 30%, 13%, and 78%, respectively, when adding 1.0 wt.% GO. Some scholars have combined quaternary ammonium salts that bear organics through covalent binding and graphene to improve the dispersibility of graphene in a polymer matrix. Polakova et al. [90] prepared a polymer film with a uniform dispersion of graphene through the ionic bond between graphene and quaternary ammonium salt bearing a polymerizable methacrylamide group. Meanwhile, the thermal conductivity and thermal stability of the polymer film were greatly improved.

4.3. Using Hydrogen Bonds

A hydrogen bond is a strong noncovalent bond. Because the surface of the graphene oxide has a large number of carboxyl and hydroxyl groups, it is easy to form hydrogen-bonding interactions with other substances. Therefore, the dispersion of graphene in a material matrix can be improved by combining organics with graphene oxide via hydrogen bonds. Sayyar et al. [35] uniformly dispersed graphene into a chitosan–lactic acid matrix through the hydrogen-bonding interactions between graphene and the matrix, and then prepared conductive hydrogels. The graphene was homogeneously dispersed and formed a unique three-dimensional network structure, which has high application value in the field of tissue engineering. Polyethylenimine (PEI) has many amine groups, which can absorb to graphene oxide by hydrogen bonding. Roy et al. [91] modified GO with PEI to obtain an FGO. They discovered that the FGO had good dispersibility in nylon 12 composites.

Polyvinyl alcohol (PVA) is a common organic compound. PVA can form hydrogen bonds with GO to produce a strong interfacial binding force, by which graphene can be evenly dispersed in a PVA matrix. Qi et al. [92] successfully used GO as a reinforcement agent and combined GO with PVA to obtain well-dispersed graphene/PVA composites. They found that the graphene addition significantly improved the shape memory properties of the PVA. Yadav et al. [93] fabricated a montmorillonite (MMT)/graphene oxide (GO)/chitosan (CS) composite using a simple solution mixing evaporation method. The results showed that the composites of chitosan, MMT, and graphene oxide were homogeneous in nature. Additionally, they observed a synergistic effect of MMT and GO reinforcing on the chitosan matrix. Graphene is often used as reinforcement in rubber because of the strong hydrogen bond between them. Kang et al. [94] successfully prepared graphene oxide/carboxylated acrylonitrile butadiene rubber (GO/XNBR) composites by using a latex co-coagulation method. Figure 5 shows the procedures and mechanism. The results showed that the tensile strength and tear strength of XNBR are increased by 357% and 117%, respectively, with the addition of 1.9 vol.% GO due to the high degree of dispersion of graphene in the matrix and a strong interfacial adhesion between the GO and the matrix.

Liu et al. [95] dispersed GO in the matrix of thermoplastic polyurethanes (TPU) by solution blending. The graphene distributed uniformly and in an orderly manner in the TPU matrix because of the hydrogen bond. TRG was prepared by an in situ thermal reduction to weaken the hydrogen bonding and improve its dielectric properties. The TRG/TPU composites with good dielectric properties were successfully prepared by this method. She et al. [96] obtained epoxidized natural rubber (ENR) by introducing hydroxyl groups and epoxy groups into natural rubber (NR). The addition

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of these groups could result in strong hydrogen bonds between the GO and the matrix and improve the dispersion properties of the graphene in the NR. The results showed that the GO was uniformly distributed in the matrix. The tensile strength and elastic modulus are increased by 87% and 8.7 times, respectively, with the addition of 0.7 wt.% GO.

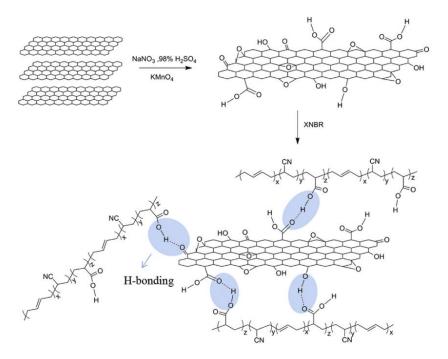


Figure 5. Scheme illustrating preparing procedures and H-bonding interactions between carboxylated acrylonitrile butadiene rubber (XNBR) and GO [94]. (Reproduced from [94] with permission; Copyright 2014 Elsevier).

4.4. Chemical Plating

High strength, high electric conductivity, and high thermal conductivity are the advantages of graphene that differentiate it from other existing reinforcement agents, such as carbon nanotubes. If these performance advantages can be introduced into bulk metal matrix composites, they will have a great influence on the design and performance improvement of metal matrix composites. If we can first coat some metal material on the surface of graphene to form a continuous and high-strength combination of the two and then combine it with the required metal matrix, disadvantages such as the poor bonding and wettability of graphene when the graphene is directly combined with the desired metal matrix can be overcome. Additionally, this will be the key to using graphene to prepare metal matrix composites. The chemical plating of metal atoms on the surface of graphene is an effective solution.

Chemical plating is a kind of wet process in which the metal ions in the solution are reduced to metal atoms and deposits on the surface of materials without the external current [97]. It provides a very important method for the surface modification of graphene. This method is different from the electro deposition technology: First of all, the chemical plating process does not require current. Secondly, not all materials can be chemically plated. It can only plate on the surface of the material with an autocatalytic ability [98]. Because graphene nanosheets do not have catalytic activity, making the chemical plating of graphene possible, they need to absorb some catalytically active films or particles on the graphene's surface. This process is called sensitization and activation [99]. There is no consistent explanation about the principle of chemical plating. At present, there are three theories, called the atomic hydrogen theory, the hydride theory, and the electrochemistry theory. The atomic hydrogen theory is briefly described as follows:

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Nickel sulfate solution contains nickel ions. Sodium hypophosphite must decompose hypophosphite and Na ions. Water will react with hypophosphite to form H⁺ on the surface of some specific materials (called autocatalytic materials):

$$H_2PO_2^- + H_2O \rightarrow HPO_3^{2-} + H^+ + 2H_{ad}.$$
 (1)

The reaction between a nickel ion and absorbed hydrogen on the surface of an autocatalytic material is as follows:

$$Ni^{2+} + 2H_{ad} \rightarrow Ni^{+} + 2H^{+}$$
 (2)

Phosphorus is produced by a reaction between the absorbed hydrogen and hypophosphite, so the coating contains phosphorus.

$$H_2PO_2^- + H_{ad} \rightarrow 2H_2O + P + OH^-$$
 (3)

The more hydrogen is absorbed, the more gas is produced and the faster the deposition process is.

$$2H_{ad} \rightarrow H_2$$
 (4)

"Autocatalytic" means that reaction (4) occurs automatically. The metal elements in the VIIIB group have an autocatalytic effect, such as palladium, rhodium, platinum, iron, cobalt, nickel, gold, silver, ruthenium, and iridium. Some people think that this is because the electronic orbitals of the d layers of these elements are unique and can provide dehydrogenation to hydrogen atoms.

Based on the above theoretical analysis, Gong et al. [100] used TRG to prepare graphene/Ni nanocomposites by chemical plating assisted with ultrasonic treatment. They used sensitization (SnCl₂) and activation (PbCl₂) as a pretreatment before the chemical plating. The samples obtained from sensitization, activation, and chemical plating were analyzed. With the prolonging of plating time, Ni nanoparticles took Pb particles as the catalytic center and gradually attached to the surface of the graphene. The Ni distribution was similar to the distribution of Pb (graphene edges and fold regions). However, Sn made little contribution to the electroless Ni plating, and there were some residues present after the chemical plating that indicated that Sn had no catalytic activity.

Hu et al. [101] used NaBH₄ as a reductant to reduce GO and nickel ions and prepared graphene/Ni nanocomposites at room temperature. Unlike chemical plating, this method does not require pretreatment for graphene, such as sensitization and activation. The principle is shown by reaction (5) and reaction (6). The results showed that the mass fraction of Ni atoms on the graphene surface reached a maximum of 32.9% and the Ni atoms were highly dispersed. Its microstructure was characterized by a unique pore structure, which was mainly due to the large specific surface area of GO and the interaction between nickel ions and oxygen-containing functional groups.

$$4Ni^{2+} + BH^{4-} + 8OH^{-} \rightarrow 4Ni + BO_{2}^{-} + 6H_{2}O$$
 (5)

$$-COOH \xrightarrow{[BH_4^-]} -CH_2OH \tag{6}$$

Besides chemical plating Ni onto graphene, some scholars have realized the chemical plating of other metal atoms on the surface of graphene. Zhao et al. [102] successfully plated copper atoms onto a graphene oxide surface, which improved the dispersion of graphene in a copper matrix. They adopted the typical chemical plating process, that is, using sensitization (SnCl₂) and activation (PbCl₂) as a pretreatment before the chemical plating. Then, CuSO₄ was added to provide copper atoms. Finally, the obtained powders were reduced to prepare graphene/Cu composites. The results showed that the copper atoms on the graphene surface effectively inhibited the agglomeration of graphene and made graphene disperse uniformly in the copper matrix. The residual oxygen bond of the functional group on graphene also increased the binding force. This made the tensile strength and Young's modulus of the composites enhance by 107% and 21%, respectively.

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At present, using graphene as a chemical coating on a metal surface to form a composite coating has a very wide range of applications. Uysal et al. [103] successfully plated an Ag/WC/graphene nanocomposite film on the surface of a metal. The dispersed results and mechanisms are shown in Figure 6. The even dispersion of graphene and WC significantly improved the wear resistance of the composites, and the friction coefficient of the composites decreased greatly compared with that of pure silver. Zhang et al. [104] plated an Fe–RGO composite film on a copper surface. The graphene was well-dispersed. Compared with the coating of pure iron, the coating containing graphene had a more compact structure, which significantly improved its corrosion resistance.

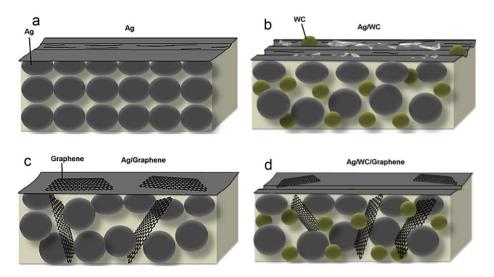


Figure 6. Schematic representation of worn surface: (a) adhesive wear in pure Ag, (b) abrasive grooves in Ag/WC, (c) graphene lubrication in Ag/Graphene, and (d) mixed mode of wear in Ag/WC/Graphene [103]. (Reproduced from [103] with permission; Copyright 2016 Elsevier).

5. Synthetical Methods

The synthetical method involves a combination of a physical method, a covalent method, and a noncovalent method, which can achieve a better dispersion of graphene than a single type of method. In Table 1, the advantages and disadvantages of these three methods are presented. The synthetical method can make use of the benefits of the three methods and effectively avoid their shortcomings. It can realize the homogeneous dispersion of graphene in all kinds of matrix.

Table 1. The advantages and disadvantages of the physical methods, the covalent bonding methods, and the noncovalent bonding methods.

Disper	sion Methods	Mechanism	Advantages	Disadvantages
Physical methods	Stirring	Applying physical force to - separate agglomerated graphene via shear stress.	Simple operation, easy access to the equipment, and low cost.	Low dispersion rate and introducing disordering and defects to the graphene.
	Ball-milling			
Covalent bonding methods	Small organic molecules	Introducing various active groups by chemical reaction on the surface or edge of the graphene.	Making the graphene more workable and operable.	Causing damage to the initial structure of the graphene.
	Polymers			
	π – π interaction		change the graphene's initial	Introducing other components on the graphene's surface (such as a surfactant).
Noncovalent bonding	covalent Ionic bonding Modifying the graphene's sur	Modifying the graphene's surface with functionalized molecules		
methods	Hydrogen bonding	through noncovalent interaction.		
	Chemical plating			

Yang et al. [105] improved the dispersion of graphene by hydrogen passivation and an ultrasonic treatment, and prepared a graphene/epoxy resin composite with well-dispersed graphene. The principle of the method was: $C-C + H_2 \rightarrow 2C-H$. After ultrasonic treatment, the C-C bond between

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graphene weakened and gradually dispersed. Then, it was passivated with hydrogen. A more stable C–H bond was formed, which separated the graphene flakes and enhanced the binding with the matrix material. Zhou et al. [106] prepared pristine graphene/copper matrix composites (PG/Cu) and reduced graphene oxide/copper matrix composites (RGO/Cu) and compared them. To achieve the uniform distribution and dispersion of PG and RGO in the Cu matrix, they proposed a new physical mixing method. The method has five steps: First, polyvinyl pyrrolidone (PVP) is used to modify PG via the π - π interaction. Second, GO that is uniformly distributed in water is prepared. Next, polyvinyl alcohol (PVA) is used to modify copper powder. Then, PG and GO are respectively mixed with the prepared copper powder, and finally the graphene is treated with thermal reduction. According to the results, GO can combine with the PVA on copper by covalent bonds. Compared with the simple mechanical mixing method, this method can make PG and RGO more evenly distributed in the copper matrix, which is mainly due to the effective combination of the hydroxyl groups on PVA and the carboxyl groups on PVP or GO. It was also found that PG/Cu composites had higher yield strength, compressive strength, and electrical conductivity than RGO/Cu composites because the two-dimensional structure of PG could effectively restrict the movement of dislocations.

Perumal et al. [107] prepared poly(4-vinyl pyridine)-block-poly(ethylene oxide) (PVP-b-PEO) and synthesized it with graphene. After ultrasonic and centrifugal treatment, the graphene reached the highest concentration of 2.6 mg/mL in aqueous and ethanolic solution. They compared their results with dispersions stabilized by another surfactant called P123 and poly(styrene)-block-poly(ethylene oxide) (PS-b-PEO) synthesized. They found that graphene would have better dispersion and stability after synthesizing it by PVP-b-PEO. This was because of not only the π - π interactions between VP (vinyl pyridine) and graphene, but also the nitrogen atoms in VP that make the bond between VP and graphene stronger [108]. In the same year, Perumal et al. [109] also prepared other block copolymers with a similar block length, including poly(ethylene oxide)-block-poly(styrene) (PEO-b-PS), poly(ethylene oxide)-block-poly(4-vinylpyridine) (PEO-b-PVP), and poly(ethylene oxide)-block-poly(pyrenemethyl methacrylate) (PEO-b-PPy). Through reversible addition-fragmentation chain transfer (RAFT), they combined them with pristine graphene and RGO. The dispersion illustration in Figure 7 shows that the combination of graphene and PEO-b-PVP had a more stable dispersion and the graphene had fewer defects. The highest concentration of pristine graphene and RGO obtained reached 1.7 mg/mL and 1.8 mg/mL in the ethanol, respectively.

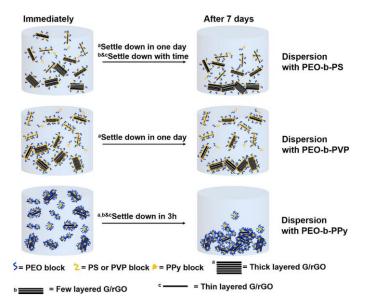


Figure 7. Illustration of the destabilization of graphene dispersions stabilized with PEO-b-PS, PEO-b-PVP, and PEO-b-PPy polymers in ethanol [109]. (Reproduced from [109] with permission; Copyright 2017 Elsevier).

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Achaby et al. [110] studied the influence of melt-blending on the performance of a polyvinylidene fluoride (PVDF)/graphene composite. According to the results, through the synergistic effect of composite additives, high-speed mixing, and melt-forming, the dispersion of graphene in a PVDF matrix can be well-dispersed and a good functional network structure can be formed. The thermal stability and tensile and flexural properties of PVDF are enhanced due to the better dispersion and distribution of graphene throughout the matrix.

Water is an excellent solvent and has no toxicity. However, graphene hardly disperses in it because of the high surface energy of water. An effective way to increase graphene's dispersion in water is to reduce the graphene after oxidation and exfoliation; however, this method will make the graphene obtain a large quantity of structural defects and residual oxygen-containing groups, so that many of the excellent properties of graphene will be weakened [111]. However, the addition of a surfactant can improve the dispersion of graphene in water, and will not destroy the unique structure of graphene. A surfactant is a kind of amphiphilic organic. On one end of its molecular structure are hydrophilic polar groups and on the other end are hydrophobic nonpolar groups. Graphene can be combined with the hydrophobic groups. The hydrophilic groups at the other end can be arranged on the surface of the solution and decrease the surface tension. Therefore, the dispersion of graphene in water can be improved [112]. The use of a surfactant is always assisted by sonication.

Lotya et al. [113] stabilized graphene in water by the surfactant sodium cholate. They treated graphene with long-duration (up to 400 h) and low-power ultrasound followed by centrifugation (at a centrifugation rate between 500 and 2000) to obtain a stable dispersion of graphene in water. The results showed that the concentration of graphene in water can reach to 0.3 mg/mL. More than 80% of the number of graphene sheets was less than five, and more than 10% of the sheets were single layer. This is a simple and economic method to obtain graphene with good quality. In a subsequent study, Ramalingam et al. [114] investigated sodium cholate (SC) and sodium deoxycholate (SDC). They treated graphene with SC and SDC followed by ultrasonic dispersion, and the best dispersion concentration was found to be 0.52 mg/mL and 2.58 mg/mL, respectively. The dispersion effect of SDC was obviously better than that of SC, because the absence of oxygen molecules in the SDC formed a flat hydrophobic surface, which made the surfactant disperse evenly on the surface of the graphene and promoted the exfoliation of the graphene. Sun et al. [115] prepared stable aqueous dispersions of pristine graphene at concentrations of up to 7.1 mg/mL by using the surfactant sodium taurodeoxycholate (STC), of which 8% had a single layer and 82% had less than five layers. Moreover, the dispersion of graphene/STC could be further increased to 12 mg/mL by vacuum evaporation.

Guardia et al. [116] used various surfactants to treat graphene, then compared and summarized the dispersion effect of these surfactants. These surfactants and their acronyms are shown in Table 2. The concentration of each surfactant used in this study was above the critical micelle concentration and was mixed with graphene followed by an ultrasonic treatment. The experimental results estimated from UV–vis absorption measurements are shown in Figure 8. The dispersion effect of all kinds of nonionic surfactants was better than that of the ionic surfactants. When the nonionic surfactant P-123 is at a concentration of 0.5%, the best dispersion of graphene can reach about 1 mg/mL, while the best dispersion of graphene treated by ionic surfactants was only 0.1 mg/mL. Furthermore, the concentration of graphene gradually increased with the extension of ultrasonic dispersion time. The structure of graphene in the water was single layer or a few layers, and the surface barely contained any defects. This study provides a new idea for the large-scale production of graphene with a low cost and good dispersion.

Wan et al. [117] prepared graphene/epoxy composites by a surfactant-assisted method, and the dispersion and interfacial bonding of the graphene were significantly improved. They used polyoxyethylene octyl phenyl ether (POPE) as the surfactant. Firstly, they obtained 100 mg TRG and mixed it with 150 mg POPE, then put them into water treated by ultrasound at 65 °C for 6 h. Finally, the drying process was carried out. The results showed that the agglomeration phenomenon of graphene treated with a nonionic surfactant was obviously reduced, mainly because the treated

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graphene sheet was wrapped by the polymer chain. The dispersion and compatibility of graphene in the epoxy resin matrix were significantly improved and the thermal stability of the composite was also greatly enhanced compared with the epoxy resin.

Table 2. Surfactants and their acronyms used throughout the text [116]. (Reproduced from [116] with permission; Copyright 2011 Elsevier).

	Surfactants Name	Acronym
	Pluronic P-123	P-123
	Tween 80	
	Brij 700	
	Gum arabic from acacia tree	
Non-ionic	Triton X-100	
	Tween 85	
	Brij 30	
	Polyvinylpyrrolidone	PVP
	n-Dodecyl β-D-maltoside	DBDM
	Poly(sodium 4-styrenesulfonate)	PSS
	3-[(3-Cholamidopropyl)dimethylammonio]-1-Propanesulfonate	CHAPS
	Sodium deoxycholate	DOC
T : -	Sodium dodecylbenzene-sulfonate	SDBS
Ionic	1-Pyrenebutyric acid	PBA
	Sodium dodecyl sulphate	SDS
	Sodium taurodeoxycholate hydrate	STC
	Hexadecyltrimethylammonium bromide	HTAB

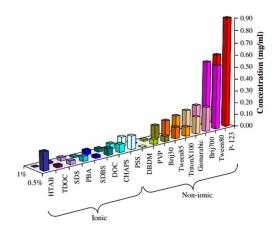


Figure 8. Concentration of graphene in aqueous dispersions achieved by the use of different surfactants (surfactant concentrations: 0.5% and 1.0% wt./vol.) [116]. (Reproduced from [116] with permission; Copyright 2011 Elsevier).

Based on the study of a surfactant, Wang et al. [118] found that adding ethanol into the graphene/surfactant mixture could further increase the concentration of graphene. The experimental results showed that when the surfactant is SDC, the concentration of graphene can be increased by three times, from 0.15 mg/mL to 0.46 mg/mL, by adding 10 wt.% ethanol. Other ionic and nonionic surfactants have the same enhancement effect when adding 10 wt.% ethanol. With the addition of ethanol, the stripping efficiency of graphene in water was five times greater than before, which was up to 9.4%. This was mainly because the addition of ethanol could reduce the mixing enthalpy and improve the stability of the surfactant. A graphene/carbon nanotubes composite can also be prepared by synthetical methods. Fan et al. [119] prepared GO and treated it by ultrasound in water for 30 min. Then, they added Multi-walled carbon nanotubes (MWCNTs) in it with an ultrasonic treatment for 30 min. The MWCNTs-GO film was produced after vacuum filtration. The results showed that the

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dispersibility of MWCNTs-GO was better than that of GO and MWCNTs and the MWCNTs-GO could stabilize for more than 1 month without any precipitation. This was mainly due to the introduction of one-dimensional multi-walled carbon nanotubes between the two-dimensional graphene sheets, which resulted in a three-dimensional network structure. This network structure could effectively inhibit the aggregation of graphene sheets, which made the dispersion of graphene significantly improve.

Yu et al. [120] successfully obtained multi-walled carbon nanotube/graphene (MWCNT/GnP) hybrid materials by a multi-step method, which improved the dispersion of the graphene. The steps are shown in Figure 9. Firstly, pristine graphene was treated with the mixture H_2SO_4/HNO_3 (1:1 v/v) to obtain hydroxylated-graphene (GnP-OH). Secondly, they added poly(acryloyl chloride) (PACl) into the suspension of MWCNT-OH and kept stirring under a nitrogen atmosphere for 48 h. Then, the MWCNT-PACl was washed and filtrated repeatedly with THF followed by the mixing of MWCNT-PACl and GnP-OH at 80°C under a nitrogen atmosphere. Finally, an MWCNT/GnP hybrid material was obtained after cleaning. The results showed that the dispersion of the MWCNT/GnP hybrid material is better than that of graphene and carbon nanotubes. The mechanism is the same as that of graphene. The three-dimensional structure of the graphene and carbon nanotubes was formed by using PACl as a bridge, and the Van der Waals' force between the graphene sheets was successfully suppressed so that the dispersion is improved.

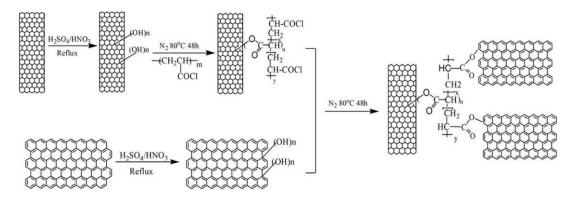


Figure 9. Illustration of the synthesis procedure of multi-walled carbon nanotube MWCNT/graphene (GnP) hybrid materials by the multi-step method [120].

Based on this method, they [121] improved the multi-step method and used a one-step method to fabricate a MWCNT/GnP hybrid material with the same three-dimensional structure. The specific steps are as follows: MWCNT-OH and GnP-OH were obtained via the same process. Then, the MWCNT-OH and the GnP-OH (1:1 m/m) were mixed and PACl was introduced into the suspension of MWCNT-OH and GnP-OH. Finally, the MWCNT/GnP hybrid material was obtained after washing and filtering. According to the results, the obtained dispersibility of the one-step method is better than that of the multi-step method. This discovery mainly lies in the different reaction mechanisms of the preparation process. In the process of the multi-step experiment, carbon nanotubes are easily wrapped by polymer PACl, resulting in the reaggregation of carbon nanotubes. In contrast, the one-step reaction can make GnP-OH and MWCNT-OH have the same opportunity to form a stable three-dimensional structure by covalent bonding with PACl.

6. Summary and Outlook

Graphene has many excellent physical and chemical properties, which provide it with a very wide range of applications in many fields. However, the poor dispersion of graphene and its irreversible aggregation problem have hindered the further application of graphene. In order to make graphene play a more excellent role in the application process, solving the problem of poor dispersion has become particularly important. In recent years, many scholars have done a lot of research to solve

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this problem, which has made the dispersion of graphene improve, and graphene composites have excellent performance. However, how to prepare a large number of low-cost graphene composites is still a difficult problem that needs to be solved. In this paper, the methods and mechanisms of improving the dispersibility of graphene are summarized in detail. There are three main ways to improve the dispersibility of graphene; namely, physical dispersion methods, covalent bonding methods, and noncovalent bonding methods. Physical dispersion owns a simple operation and it is easy to access the equipment, but it will cause damage to the graphene's structure and the dispersion rate of the graphene is low. The defects caused by these methods are difficult to repair and a high content of graphene is intractable to obtain. Therefore, physical methods are usually used as assistant methods for other methods. The covalent bonding methods can be divided into organic small molecule bonding and polymer bonding according to the material that is combined with graphene. Its advantage is to increase the processability of graphene, but it will cause defects and affect the graphene's physical and chemical properties. The noncovalent bonding methods can be divided into π - π bonding, ionic bonding, and hydrogen bonding. The advantages of these methods are their simple operation, mild conditions, and that they will not bring too many defects to the graphene, but will introduce other components (such as surfactants) onto the graphene. With the deeper studies of graphene, some scholars have adopted a combined method of covalent bonding and noncovalent bonding and the method of chemical plating. Chemical plating expands the application of graphene to metal matrix composites.

With the deepening of the theoretical research, there will be more methods of improving graphene dispersion, and these methods show a trend of combining covalent bonding and noncovalent bonding. In order to expand the application scope of graphene, these methods should follow the following points: (1) Minimizing the processing effect on graphene and matrix materials to prepare graphene with high quality; (2) Controlling the amount, type, and position of the binding materials on graphene to improve the controllability of the method; (3) Removing the unwanted components in practical applications to restore the excellent structure and properties of graphene; and (4) Reducing cost to realize the large-scale application of graphene. At the same time, the joint use of graphene preparation and composite preparation should be considered, and a synergistic system of graphene application and research should be constructed. In conclusion, graphene, as a unique two-dimensional material, has excellent thermal properties, optical properties, mechanical properties, and electrical properties, and shows great potential and value both in theoretical research and practical applications. Graphene has a wide range of applications in the fields of electrochemistry, biomedicine, and energetic materials as a reinforcement for composite materials. The key factors affecting the properties of these composites are the dispersion of graphene in the matrix and the interfacial adhesion between the graphene and the matrix. Graphene with excellent dispersibility and strong interfacial bonding can significantly improve the physical and chemical properties of composites, and improve the production efficiency and application range of composites. Along with the future study of graphene, a deeper understanding of the dispersion methods for and mechanisms of graphene will be needed. The properties and applications of graphene will then be further increased, producing more excellent performance from the new graphene material.

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References

- 1. Novoselov, K.S.; Geim, A.K.; Morozov, S.V. Electric field effect in atomically thin carbon films. *Science* **2004**, 306, 666–669. [CrossRef] [PubMed]
- 2. Kim, K.-S.; Lee, H.-J.; Lee, C.; Lee, S.-K.; Jang, H.; Ahn, J.-H.; Kim, J.-H.; Lee, H.-J. Chemical vapor deposition-grown graphene: The thinnest solid lubricant. *ACS Nano* **2011**, *5*, 5107–5114. [CrossRef] [PubMed]

Coatings 2018, 8, 33 18 of 23

3. Akinwande, D.; Brennan, C.J.; Bunch, J.S.; Egberts, P.; Felts, J.R.; Gao, H.; Huang, R.; Kim, J.-S.; Li, T.; Li, Y.; et al. A review on mechanics and mechanical properties of 2D materials—Graphene and beyond. *Extreme Mech. Lett.* **2017**, 13, 42–77. [CrossRef]

- 4. Fugallo, G.; Cepellotti, A.; Paulatto, L.; Lazzeri, M.; Marzari, N.; Mauri, F. Thermal conductivity of graphene and graphite: Collective excitations and mean free paths. *Nano Lett.* **2014**, *14*, 6109–6114. [CrossRef] [PubMed]
- 5. Cao, M.-S.; Wang, X.-X.; Cao, W.-Q.; Yuan, J. Ultrathin graphene: Electrical properties and highly efficient electromagnetic interference shielding. *J. Mater. Chem. C* **2015**, *3*, 6589–6599. [CrossRef]
- 6. Ozfidan, I.; Korkusinski, M.; Güçlü, A.D.; McGuire, J.A.; Hawrylak, P. Microscopic theory of the optical properties of colloidal graphene quantum dots. *Phys. Rev. B* **2014**, *89*, 085310. [CrossRef]
- 7. Kumar, P.; Yu, S.; Shahzad, F.; Hong, S.M.; Kim, Y.-H.; Koo, C.M. Ultrahigh electrically and thermally conductive self-aligned graphene/polymer composites using large-area reduced graphene oxides. *Carbon* **2016**, *101*, 120–128. [CrossRef]
- 8. Sun, Y.; Shi, G. Graphene/polymer composites for energy applications. *J. Polym. Sci. Part B Polym. Phys.* **2013**, *51*, 231–253. [CrossRef]
- 9. Alam, A.; Meng, Q.; Shi, G.; Arabi, S.; Ma, J.; Zhao, N.; Kuan, H.-C. Electrically conductive, mechanically robust, pH-sensitive graphene/polymer composite hydrogels. *Compos. Sci. Technol.* **2016**, 127, 119–126. [CrossRef]
- 10. Wang, M.; Duan, X.; Xu, Y.; Duan, X. Functional three-dimensional graphene/polymer composites. *ACS Nano* **2016**, *10*, 7231–7247. [CrossRef] [PubMed]
- 11. Boland, C.S.; Khan, U.; Ryan, G.; Barwich, S.; Charifou, R.; Harvey, A.; Backes, C.; Li, Z.; Ferreira, M.S.; Möbius, M.E.; et al. Sensitive electromechanical sensors using viscoelastic graphene-polymer nanocomposites. *Science* **2016**, *354*, 1257–1260. [CrossRef] [PubMed]
- 12. An, Y.; Xu, X.; Gui, K. Effect of SiC whiskers and graphene nanosheets on the mechanical properties of ZrB₂-SiC_w-Graphene ceramic composites. *Ceram. Int.* **2016**, *42*, 14066–14070. [CrossRef]
- 13. Nieto, A.; Bisht, A.; Lahiri, D.; Zhang, C.; Agarwal, A. Graphene reinforced metal and ceramic matrix composites: A review. *Int. Mater. Rev.* **2017**, *62*, 241–302. [CrossRef]
- 14. Zhou, M.; Lin, T.; Huang, F.; Zhong, Y.; Wang, Z.; Tang, Y.; Bi, H.; Wan, D.; Lin, J. Highly conductive porous graphene/ceramic composites for heat transfer and thermal energy storage. *Adv. Funct. Mater.* **2013**, 23, 2263–2269. [CrossRef]
- 15. Zhou, M.; Bi, H.; Lin, T.; Lü, X.; Wan, D.; Huang, F.; Lin, J. Heat transport enhancement of thermal energy storage material using graphene/ceramic composites. *Carbon* **2014**, *75*, 314–321. [CrossRef]
- 16. Liu, J.; Yan, H.; Jiang, K. Mechanical properties of graphene platelet-reinforced alumina ceramic composites. *Ceram. Int.* **2013**, *39*, 6215–6221. [CrossRef]
- 17. Zhuo, Q.; Ma, Y.; Gao, J.; Zhang, P.; Xia, Y.; Tian, Y.; Sun, X.; Zhong, J.; Sun, X. Facile synthesis of graphene/metal nanoparticle composites via self-catalysis reduction at room temperature. *Inorg. Chem.* **2013**, 52, 3141–3147. [CrossRef] [PubMed]
- 18. Wejrzanowski, T.; Grybczuk, M.; Chmielewski, M.; Pietrzak, K.; Kurzydlowski, K.J.; Strojny-Nedza, A. Thermal conductivity of metal-graphene composites. *Mater. Des.* **2016**, *99*, 163–173. [CrossRef]
- 19. Guo, R.; Yue, W.; Ren, Y.; Zhou, W. Hierarchical structured graphene/metal oxide/porous carbon composites as anode materials for lithium-ion batteries. *Mater. Res. Bull.* **2016**, *73*, 102–110. [CrossRef]
- 20. Chuai, D.; Liu, X.; Yu, R.; Ye, J.; Shi, Y. Enhanced microwave absorption properties of flake-shaped FePCB metallic glass/graphene composites. *Compos. Part Appl. Sci. Manuf.* **2016**, *89*, 33–39. [CrossRef]
- 21. Li, P.; Chen, Q.; Lin, Y.; Chang, G.; He, Y. Effects of crystallite structure and interface band alignment on the photocatalytic property of bismuth ferrite/(N-doped) graphene composites. *J. Alloys Compd.* **2016**, 672, 497–504. [CrossRef]
- 22. Ghasemi, F.A.; Ghasemi, I.; Menbari, S.; Ayaz, M.; Ashori, A. Optimization of mechanical properties of polypropylene/talc/graphene composites using response surface methodology. *Polym. Test.* **2016**, *53*, 283–292. [CrossRef]
- 23. Liu, J.; Zhang, Z.; Lv, Y.; Yan, J.; Yun, J.; Zhao, W.; Kou, L.; Zhai, C. Synthesis and characterization of ZnO NWAs/graphene composites for enhanced optical and field emission performances. *Compos. Part B Eng.* **2016**, *99*, 366–372. [CrossRef]

Coatings 2018, 8, 33 19 of 23

24. You, F.; Li, X.; Zhang, L.; Wang, D.; Shi, C.-Y.; Dang, Z.-M. Polypropylene/poly(methyl methacrylate)/graphene composites with high electrical resistivity anisotropy via sequential biaxial stretching. *RSC Adv.* 2017, 7, 6170–6178. [CrossRef]

- 25. Xia, J.; Cao, X.; Wang, Z.; Yang, M.; Zhang, F.; Lu, B.; Li, F.; Xia, L.; Li, Y.; Xia, Y. Molecularly imprinted electrochemical biosensor based on chitosan/ionic liquid–graphene composites modified electrode for determination of bovine serum albumin. *Sens. Actuators B Chem.* **2016**, 225, 305–311. [CrossRef]
- 26. Song, Y.; Luo, Y.; Zhu, C.; Li, H.; Du, D.; Lin, Y. Recent advances in electrochemical biosensors based on graphene two-dimensional nanomaterials. *Biosens. Bioelectron.* **2016**, *76*, 195–212. [CrossRef] [PubMed]
- 27. Ye, J.; Yu, Z.; Chen, W.; Chen, Q.; Ma, L. Ionic-liquid mediated synthesis of molybdenum disulfide/graphene composites: An enhanced electrochemical hydrogen evolution catalyst. *Int. J. Hydrogen Energy* **2016**, 41, 12049–12061. [CrossRef]
- 28. Xu, J.; Wang, L.; Cao, X. Polymer supported graphene–CdS composite catalyst with enhanced photocatalytic hydrogen production from water splitting under visible light. *Chem. Eng. J.* **2016**, *283*, 816–825. [CrossRef]
- 29. Li, J.; Cheng, Y.; Zhang, S.; Li, Y.; Sun, J.; Qin, C.; Wang, J.; Dai, L. Modification of GO based on click reaction and its composite fibers with poly(vinyl alcohol). *Compos. Part Appl. Sci. Manuf.* **2017**, *101*, 115–122. [CrossRef]
- 30. Ma, J.; Meng, Q.; Michelmore, A.; Kawashima, N.; Izzuddin, Z.; Bengtsson, C.; Kuan, H.-C. Covalently bonded interfaces for polymer/graphene composites. *J. Mater. Chem. A* **2013**, 1, 4255–4264. [CrossRef]
- 31. Mungse, H.P.; Kumar, N.; Khatri, O.P. Synthesis, dispersion and lubrication potential of basal plane functionalized alkylated graphene nanosheets. *RSC Adv.* **2015**, *5*, 25565–25571. [CrossRef]
- 32. Salavagione, H.J.; Martínez, G.; Ellis, G. Recent advances in the covalent modification of graphene with polymers. *Macromol. Rapid Commun.* **2011**, 32, 1771–1789. [CrossRef] [PubMed]
- 33. Parviz, D.; Das, S.; Ahmed, H.S.T.; Irin, F.; Bhattacharia, S.; Green, M.J. Dispersions of non-covalently functionalized graphene with minimal stabilizer. *ACS Nano* **2012**, *6*, 8857–8867. [CrossRef] [PubMed]
- 34. Li, D.; Müller, M.B.; Gilje, S.; Kaner, R.B.; Wallace, G.G. Processable aqueous dispersions of graphene nanosheets. *Nat. Nanotechnol.* **2008**, *3*, 101–105. [CrossRef] [PubMed]
- 35. Sayyar, S.; Murray, E.; Thompson, B.C.; Chung, J.; Officer, D.L.; Gambhir, S.; Spinks, G.M.; Wallace, G.G. Processable conducting graphene/chitosan hydrogels for tissue engineering. *J. Mater. Chem. B* **2015**, *3*, 481–490. [CrossRef]
- 36. Yang, H.; Zhang, Q.; Shan, C.; Li, F.; Han, D.; Niu, L. Stable, conductive supramolecular composite of graphene sheets with conjugated polyelectrolyte. *Langmuir* **2010**, *26*, *6708–6712*. [CrossRef] [PubMed]
- 37. Jeon, C.-H.; Jeong, Y.-H.; Seo, J.-J.; Tien, H.N.; Hong, S.-T.; Yum, Y.-J.; Hur, S.-H.; Lee, K.-J. Material properties of graphene/aluminum metal matrix composites fabricated by friction stir processing. *Int. J. Precis. Eng. Manuf.* **2014**, *15*, 1235–1239. [CrossRef]
- 38. León, V.; Rodriguez, A.M.; Prieto, P.; Prato, M.; Vázquez, E. Exfoliation of graphite with triazine derivatives under ball-milling conditions: Preparation of few-layer graphene via selective noncovalent interactions. *ACS Nano* **2014**, *8*, 563–571. [CrossRef] [PubMed]
- 39. Khodabakhshi, F.; Arab, S.M.; Švec, P.; Gerlich, A.P. Fabrication of a new Al-Mg/graphene nanocomposite by multi-pass friction-stir processing: Dispersion, microstructure, stability, and strengthening. *Mater. Charact.* **2017**, 132, 92–107. [CrossRef]
- 40. Yu, M.; Shao, D.; Lu, F.; Sun, X.; Sun, H.; Hu, T.; Wang, G.; Sawyer, S.; Qiu, H.; Lian, J. ZnO/graphene nanocomposite fabricated by high energy ball milling with greatly enhanced lithium storage capability. *Electrochem. Commun.* **2013**, *34*, 312–315. [CrossRef]
- 41. Dixit, S.; Mahata, A.; Mahapatra, D.R.; Kailas, S.V.; Chattopadhyay, K. Multi-layer graphene reinforced aluminum—Manufacturing of high strength composite by friction stir alloying. *Compos. Part B Eng.* **2018**, 136, 63–71. [CrossRef]
- 42. Yue, L.; Pircheraghi, G.; Monemian, S.A.; Manas-Zloczower, I. Epoxy composites with carbon nanotubes and graphene nanoplatelets—Dispersion and synergy effects. *Carbon* **2014**, *78*, 268–278. [CrossRef]
- 43. Jiang, X.; Shao, Z.; Li, J.; Liu, W.; Zhu, D.; Liu, D. Dispersion characteristics of multi-walled carbon nanotubes with gallic acid. *J. Nanosci. Nanotechnol.* **2015**, *15*, 9874–9878. [CrossRef] [PubMed]
- 44. Li, J.; Jiang, X.; Shen, R.; Shao, Z.; Zhu, D.; Liu, D. Dispersion characteristics of multi-walled carbon nanotubes and carbon nanoflakes with oxygen plasma. *Nanosci. Nanotechnol. Lett.* **2015**, *7*, 581–587. [CrossRef]

Coatings 2018, 8, 33 20 of 23

45. Xu, M.; Futaba, D.N.; Yamada, T.; Yumuda, T.; Hata, K. Carbon nanotubes with temperature-invariant viscoelasticity from -196 °C to 1000 °C. *Science* **2010**, 330, 1364–1368. [CrossRef] [PubMed]

- 46. Geim, A.K. Graphene: Status and prospects. Science 2009, 324, 1530–1534. [CrossRef] [PubMed]
- 47. Yu, M.-F.; Files, B.S.; Arepalli, S.; Ruoff, R.S. Tensile loading of ropes of single wall carbon nanotubes and their mechanical properties. *Phys. Rev. Lett.* **2000**, *84*, 5552–5555. [CrossRef] [PubMed]
- 48. Alinejad, B.; Mahmoodi, K. Synthesis of graphene nanoflakes by grinding natural graphite together with NaCl in a planetary ball mill. *Funct. Mater. Lett.* **2017**, *10*, 1750047. [CrossRef]
- 49. Guo, W.; Chen, G. Fabrication of graphene/epoxy resin composites with much enhanced thermal conductivity via ball milling technique. *J. Appl. Polym. Sci.* **2014**, *131*. [CrossRef]
- 50. Bastwros, M.; Kim, G.-Y.; Zhu, C.; Zhang, K.; Wang, S.; Tang, X.; Wang, X. Effect of ball milling on graphene reinforced Al6061 composite fabricated by semi-solid sintering. *Compos. Part B Eng.* **2014**, *60*, 111–118. [CrossRef]
- 51. Ferrari, A.C.; Robertson, J. Interpretation of Raman spectra of disordered and amorphous carbon. *Phys. Rev. B* **2000**, *61*, 14095–14107. [CrossRef]
- 52. Stankovich, S.; Piner, R.D.; Nguyen, S.T.; Ruoff, R.S. Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets. *Carbon* **2006**, *44*, 3342–3347. [CrossRef]
- 53. Liu, Z.; Robinson, J.T.; Sun, X.; Dai, H. PEGylated nanographene oxide for delivery of water-insoluble cancer drugs. *J. Am. Chem. Soc.* **2008**, 130, 10876–10877. [CrossRef] [PubMed]
- 54. Zhang, X.; Huang, Y.; Wang, Y.; Ma, Y.; Liu, Z.; Chen, Y. Synthesis and characterization of a graphene–C₆₀ hybrid material. *Carbon* **2009**, *47*, 334–337. [CrossRef]
- 55. Veca, L.M.; Lu, F.; Meziani, M.J.; Cao, L.; Zhang, P.; Qi, G.; Qu, L.; Shrestha, M.; Sun, Y.-P. Polymer functionalization and solubilization of carbon nanosheets. *Chem. Commun.* **2009**, 2565–2567. [CrossRef] [PubMed]
- 56. He, S.; Liang, J.; Yuan, J.; Hu, H.; Gao, Y. Preparation of graphene dispersing system stabilized by ethanol amine and its pH-response property. *Fine Chem.* **2016**, 8–13. [CrossRef]
- 57. Niyogi, S.; Bekyarova, E.; Itkis, M.E.; McWilliams, J.L.; Hamon, M.A.; Haddon, R.C. Solution properties of graphite and graphene. *J. Am. Chem. Soc.* **2006**, *128*, 7720–7721. [CrossRef] [PubMed]
- 58. Liu, J.; Yang, W.; Tao, L.; Li, D.; Boyer, C.; Davis, T.P. Thermosensitive graphene nanocomposites formed using pyrene-terminal polymers made by RAFT polymerization. *J. Polym. Sci. Part Polym. Chem.* **2010**, 48, 425–433. [CrossRef]
- 59. Zhang, S.; Song, H. Preparation of dispersible graphene oxide as a filler to increase the thermal stability of a flame retarding polymer. *Carbon* **2013**, *56*, 394. [CrossRef]
- 60. Gong, L.; Yin, B.; Li, L.; Yang, M. Nylon-6/Graphene composites modified through polymeric modification of graphene. *Compos. Part B Eng.* **2015**, *73*, 49–56. [CrossRef]
- 61. Rani, S.; Kumar, M.; Kumar, R.; Kumar, D.; Sharma, S.; Singh, G. Characterization and dispersibility of improved thermally stable amide functionalized graphene oxide. *Mater. Res. Bull.* **2014**, *60*, 143–149. [CrossRef]
- 62. Deshmukh, K.; Ahamed, M.B.; Pasha, S.K.K.; Deshmukh, R.R.; Bhagat, P.R. Highly dispersible graphene oxide reinforced polypyrrole/polyvinyl alcohol blend nanocomposites with high dielectric constant and low dielectric loss. *RSC Adv.* **2015**, *5*, 61933–61945. [CrossRef]
- 63. Noh, Y.J.; Joh, H.-I.; Yu, J.; Hwang, S.H.; Lee, S.; Lee, C.H.; Kim, S.Y.; Youn, J.R. Ultra-high dispersion of graphene in polymer composite via solvent free fabrication and functionalization. *Sci. Rep.* **2015**, *5*, 9141. [CrossRef] [PubMed]
- 64. Shen, J.; Hu, Y.; Li, C.; Qin, C.; Ye, M. Synthesis of amphiphilic graphene nanoplatelets. *Small* **2009**, *5*, 82–85. [CrossRef] [PubMed]
- 65. Hawker, C.J.; Bosman, A.W.; Harth, E. New polymer synthesis by nitroxide mediated living radical polymerizations. *Chem. Rev.* **2001**, *101*, 3661–3688. [CrossRef] [PubMed]
- 66. Kamigaito, M.; Ando, T.; Sawamoto, M. Metal-catalyzed living radical polymerization. *Chem. Rev.* **2001**, 101, 3689–3746. [CrossRef] [PubMed]
- 67. Perrier, S.; Takolpuckdee, P. Macromolecular design via reversible addition–fragmentation chain transfer (RAFT)/xanthates (MADIX) polymerization. *J. Polym. Sci. Part Polym. Chem.* **2005**, 43, 5347–5393. [CrossRef]
- 68. Rosen, B.M.; Percec, V. Single-electron transfer and single-electron transfer degenerative chain transfer living radical polymerization. *Chem. Rev.* **2009**, *109*, 5069–5119. [CrossRef] [PubMed]

Coatings 2018, 8, 33 21 of 23

69. Wang, S.Y.; Guo, G.N.; Yang, D.; Hu, J.H. Preparation of graphene/poly (*N*,*N*-dimethylacrylamide) nanocomposite via Cu-catalyzed single-electron transfer living radical polymerization. *Chin. J. Org. Chem.* **2014**, *34*, 1382–1390. [CrossRef]

- 70. Osicka, J.; Cvek, M.; Mrlik, M.; Ilcikova, M.; Pavlinek, V.; Mosnacek, J. Light-induced and sensing capabilities of SI-ATRP modified graphene oxide particles in elastomeric matrix. In *Proceedings Volume 10164, Active and Passive Smart Structures and Integrated Systems 2017*; International Society for Optics and Photonics: Bellingham, WA, USA, 2017; p. 1016434. [CrossRef]
- 71. Jiang, S.; Gui, Z.; Bao, C.; Dai, K.; Wang, X.; Zhou, K.; Shi, Y.; Lo, S.; Hu, Y. Preparation of functionalized graphene by simultaneous reduction and surface modification and its polymethyl methacrylate composites through latex technology and melt blending. *Chem. Eng. J.* **2013**, 226, 326–335. [CrossRef]
- 72. Yuan, B.; Bao, C.; Song, L.; Hong, N.; Liew, K.M.; Hu, Y. Preparation of functionalized graphene oxide/polypropylene nanocomposite with significantly improved thermal stability and studies on the crystallization behavior and mechanical properties. *Chem. Eng. J.* 2014, 237, 411–420. [CrossRef]
- 73. Yang, S.; Li, L.; Pei, Z.; Li, C.; Shan, X.; Wen, B.; Zhang, S.; Zheng, L.; Zhang, J.; Xie, Y.; et al. Effects of humic acid on copper adsorption onto few-layer reduced graphene oxide and few-layer graphene oxide. *Carbon* **2014**, 75, 227–235. [CrossRef]
- 74. Iqbal, M.Z.; Abdala, A.A.; Mittal, V.; Seifert, S.; Herring, A.M.; Liberatore, M.W. Processable conductive graphene/polyethylene nanocomposites: Effects of graphene dispersion and polyethylene blending with oxidized polyethylene on rheology and microstructure. *Polymer* 2016, *98*, 143–155. [CrossRef]
- 75. Parviz, D.; Yu, Z.; Verkhoturov, S.; Green, M.J.; Hedden, R.C. Gradient films of pristine graphene/pyrene-functional copolymers with janus electrical properties. *ACS Appl. Mater. Interfaces* **2016**, *8*, 31813–31821. [CrossRef] [PubMed]
- 76. Balasubramaniyan, R.; Pham, V.H.; Jang, J.; Hur, S.H.; Chung, J.S. A one pot solution blending method for highly conductive poly (methyl methacrylate)-highly reduced graphene nanocomposites. *Electron. Mater. Lett.* **2013**, *9*, 837–839. [CrossRef]
- 77. Wang, L.; Zhu, S.-J.; Wang, H.-Y.; Qu, S.-N.; Zhang, Y.-L.; Zhang, J.-H.; Chen, Q.-D.; Xu, H.-L.; Han, W.; Yang, B.; et al. Common origin of green luminescence in carbon nanodots and graphene quantum dots. *ACS Nano* 2014, 8, 2541–2547. [CrossRef] [PubMed]
- 78. He, P.; Sun, J.; Tian, S.; Yang, S.; Ding, S.; Ding, G.; Xie, X.; Jiang, M. Processable aqueous dispersions of graphene stabilized by graphene quantum dots. *Chem. Mater.* **2015**, 27, 218–226. [CrossRef]
- 79. Shen, B.; Zhai, W.; Tao, M.; Lu, D.; Zheng, W. Enhanced interfacial interaction between polycarbonate and thermally reduced graphene induced by melt blending. *Compos. Sci. Technol.* **2013**, *86*, 109–116. [CrossRef]
- 80. Oyarzabal, A.; Cristiano-Tassi, A.; Laredo, E.; Newman, D.; Bello, A.; Etxeberría, A.; Eguiazabal, J.I.; Zubitur, M.; Mugica, A.; Müller, A.J. Dielectric, mechanical and transport properties of bisphenol A polycarbonate/graphene nanocomposites prepared by melt blending. *J. Appl. Polym. Sci.* **2017**, 134. [CrossRef]
- 81. You, F.; Wang, D.; Cao, J.; Li, X.; Dang, Z.-M.; Hu, G.-H. In situ thermal reduction of graphene oxide in a styrene–ethylene/butylene–styrene triblock copolymer via melt blending. *Polym. Int.* **2014**, *63*, 93–99. [CrossRef]
- 82. Istrate, O.M.; Paton, K.R.; Khan, U.; O'Neill, A.; Bell, A.P.; Coleman, J.N. Reinforcement in melt-processed polymer–graphene composites at extremely low graphene loading level. *Carbon* **2014**, *78*, 243–249. [CrossRef]
- 83. Liang, Y.; Wu, D.; Feng, X.; Müllen, K. Dispersion of graphene sheets in organic solvent supported by ionic interactions. *Adv. Mater.* **2009**, *21*, 1679–1683. [CrossRef]
- 84. Li, Z.; Fan, G.; Tan, Z.; Guo, Q.; Xiong, D.; Su, Y.; Li, Z.; Zhang, D. Uniform dispersion of graphene oxide in aluminum powder by direct electrostatic adsorption for fabrication of graphene/aluminum composites. *Nanotechnology* **2014**, 25, 325601. [CrossRef] [PubMed]
- 85. Ahadian, S.; Estili, M.; Surya, V.J.; Ramón-Azcón, J.; Liang, X.; Shiku, H.; Ramalingam, M.; Matsue, T.; Sakka, Y.; Bae, H.; et al. Facile and green production of aqueous graphene dispersions for biomedical applications. *Nanoscale* **2015**, *7*, 6436–6443. [CrossRef] [PubMed]
- 86. Hassan, M.; Reddy, K.R.; Haque, E.; Faisal, S.N.; Ghasemi, S.; Minett, A.I.; Gomes, V.G. Hierarchical assembly of graphene/polyaniline nanostructures to synthesize free-standing supercapacitor electrode. *Compos. Sci. Technol.* **2014**, *98*, 1–8. [CrossRef]

Coatings 2018, 8, 33 22 of 23

87. Ye, X.; Feng, J.; Zhang, J.; Yang, X.; Liao, X.; Shi, Q.; Tan, S. Controlled release and long-term antibacterial activity of reduced graphene oxide/quaternary ammonium salt nanocomposites prepared by non-covalent modification. *Colloids Surf. B Biointerfaces* **2017**, 149, 322–329. [CrossRef] [PubMed]

- 88. Xue, W.; Chen, Y.; Chen, H.; Xia, Y. Mechanical properties and drug release of microcapsules containing quaternized-chitosan-modified reduced graphene oxide in the capsular wall. *J. Appl. Polym. Sci.* **2017**, *134*. [CrossRef]
- 89. Sui, G.; Zhao, Y.; Zhang, Q.; Fu, Q. Enhanced mechanical properties of olefin block copolymer by adding a quaternary ammonium salt functionalized graphene oxide. *RSC Adv.* **2016**, *6*, 54785–54792. [CrossRef]
- 90. Poláková, L.; Beneš, H.; Ecorchard, P.; Pavlová, E.; Sedláková, Z.; Kredatusová, J.; Štengl, V. Nanocomposite preparation via in situ polymerization of quaternary ammonium salt ion-bonded to graphite platelets. *RSC Adv.* **2015**, *6*, 353–357. [CrossRef]
- 91. Roy, S.; Tang, X.; Das, T.; Zhang, L.; Li, Y.; Ting, S.; Hu, X.; Yue, C.Y. Enhanced molecular level dispersion and interface bonding at low loading of modified graphene oxide to fabricate super nylon 12 composites. *ACS Appl. Mater. Interfaces* **2015**, *7*, 3142–3151. [CrossRef] [PubMed]
- 92. Qi, X.; Yao, X.; Deng, S.; Zhou, T.; Fu, Q. Water-induced shape memory effect of graphene oxide reinforced polyvinyl alcohol nanocomposites. *J. Mater. Chem. A* **2014**, *2*, 2240–2249. [CrossRef]
- 93. Yadav, M.; Ahmad, S. Montmorillonite/graphene oxide/chitosan composite: Synthesis, characterization and properties. *Int. J. Biol. Macromol.* **2015**, *79*, 923–933. [CrossRef] [PubMed]
- 94. Kang, H.; Zuo, K.; Wang, Z.; Zhang, L.; Liu, L.; Guo, B. Using a green method to develop graphene oxide/elastomers nanocomposites with combination of high barrier and mechanical performance. *Compos. Sci. Technol.* **2014**, 92, 1–8. [CrossRef]
- 95. Liu, S.; Tian, M.; Yan, B.; Yao, Y.; Zhang, L.; Nishi, T.; Ning, N. High performance dielectric elastomers by partially reduced graphene oxide and disruption of hydrogen bonding of polyurethanes. *Polymer* **2015**, *56*, 375–384. [CrossRef]
- 96. She, X.; He, C.; Peng, Z.; Kong, L. Molecular-level dispersion of graphene into epoxidized natural rubber: Morphology, interfacial interaction and mechanical reinforcement. *Polymer* **2014**, *55*, 6803–6810. [CrossRef]
- 97. Jiang, R.; Zhou, X.; Liu, Z. Electroless Ni-plated graphene for tensile strength enhancement of copper. *Mater. Sci. Eng. A* **2017**, *679*, 323–328. [CrossRef]
- 98. Yaglioglu, O.; Fang, T.; Martens, R.; Eldridge, B. Electroless silver plating and in-situ SEM characterization of CNT-metal hybrid contactors. In Proceedings of the 2014 IEEE 60th Holm Conference on Electrical Contacts (Holm), New Orleans, LA, USA, 12–15 October 2014; pp. 1–5. [CrossRef]
- 99. Song, J.L.; Chen, W.G.; Dong, L.L.; Wang, J.J.; Deng, N. An electroless plating and planetary ball milling process for mechanical properties enhancement of bulk CNTs/Cu composites. *J. Alloy. Compd.* **2017**, 720, 54–62. [CrossRef]
- 100. Gong, W.; Chen, C.; Gao, J.; Kong, Q.; Yang, M.; Wang, M.; Liu, L.; Yang, Y. Preparation of a Ni/grapheme nanocomposite by an electroless plating method. *Carbon* **2015**, *85*, 446. [CrossRef]
- 101. Hu, Q.; Wang, X.; Chen, H.; Wang, Z. Synthesis of Ni/graphene sheets by an electroless Ni-plating method. *New Carbon Mater.* **2012**, *27*, 35–41. [CrossRef]
- 102. Zhao, C.; Wang, J. Fabrication and tensile properties of graphene/copper composites prepared by electroless plating for structrual applications. *Phys. Status Solidi A* **2014**, 211, 2878–2885. [CrossRef]
- 103. Uysal, M.; Akbulut, H.; Tokur, M.; Algül, H.; Çetinkaya, T. Structural and sliding wear properties of Ag/Graphene/WC hybrid nanocomposites produced by electroless co-deposition. *J. Alloy. Compd.* **2016**, 654, 185–195. [CrossRef]
- 104. Zhang, X.; Zhou, Y.; Liang, A.; Zhang, B.; Zhang, J. Facile fabrication and corrosion behavior of iron and iron-reduced graphene oxide composite coatings by electroless plating from baths containing no reducing agent. *Surf. Coat. Technol.* **2016**, 304, 519–524. [CrossRef]
- 105. Yang, Y.; Rigdon, W.; Huang, X.; Li, X. Enhancing graphene reinforcing potential in composites by hydrogen passivation induced dispersion. *Sci. Rep.* **2013**, *3*, 2086. [CrossRef] [PubMed]
- 106. Jiang, R.; Zhou, X.; Fang, Q.; Liu, Z. Copper–graphene bulk composites with homogeneous graphene dispersion and enhanced mechanical properties. *Mater. Sci. Eng. A* **2016**, *654*, 124–130. [CrossRef]
- 107. Perumal, S.; Park, K.T.; Lee, H.M.; Cheong, I.W. PVP-b-PEO block copolymers for stable aqueous and ethanolic graphene dispersions. *J. Colloid Interface Sci.* **2016**, *464*, 25–35. [CrossRef] [PubMed]

Coatings 2018, 8, 33 23 of 23

108. Perumal, S.; Lee, H.M.; Cheong, I.W. A study of adhesion forces between vinyl monomers and graphene surfaces for non-covalent functionalization of graphene. *Carbon* **2016**, *107*, 74–76. [CrossRef]

- 109. Perumal, S.; Lee, H.M.; Cheong, I.W. High-concentration graphene dispersion stabilized by block copolymers in ethanol. *J. Colloid Interface Sci.* **2017**, *497*, 359–367. [CrossRef] [PubMed]
- 110. El Achaby, M.; Arrakhiz, F.Z.; Vaudreuil, S.; Essassi, E.M.; Qaiss, A.; Bousmina, M. Preparation and characterization of melt-blended graphene nanosheets–poly(vinylidene fluoride) nanocomposites with enhanced properties. *J. Appl. Polym. Sci.* 2013, 127, 4697–4707. [CrossRef]
- 111. Allen, M.J.; Tung, V.C.; Kaner, R.B. Honeycomb carbon: A review of graphene. *Chem. Rev.* **2010**, *110*, 132–145. [CrossRef] [PubMed]
- 112. Green, A.A.; Hersam, M.C. Solution phase production of graphene with controlled thickness via density differentiation. *Nano Lett.* **2009**, *9*, 4031–4036. [CrossRef] [PubMed]
- 113. Lotya, M.; King, P.J.; Khan, U.; De, S.; Coleman, J.N. High-concentration, surfactant-stabilized graphene dispersions. *ACS Nano* **2010**, *4*, 3155–3162. [CrossRef] [PubMed]
- 114. Ramalingam, P.; Pusuluri, S.T.; Periasamy, S.; Veerabahu, R.; Kulandaivel, J. Role of deoxy group on the high concentration of graphene in surfactant/water media. *RSC Adv.* **2013**, *3*, 2369–2378. [CrossRef]
- 115. Sun, Z.; Masa, J.; Liu, Z.; Schuhmann, W.; Muhler, M. Highly concentrated aqueous dispersions of graphene exfoliated by sodium taurodeoxycholate: Dispersion behavior and potential application as a catalyst support for the oxygen-reduction reaction. *Chem. Eur. J.* **2012**, *18*, 6972–6978. [CrossRef] [PubMed]
- 116. Guardia, L.; Fernández-Merino, M.J.; Paredes, J.I.; Solís-Fernández, P.; Villar-Rodil, S.; Martínez-Alonso, A.; Tascón, J.M.D. High-throughput production of pristine graphene in an aqueous dispersion assisted by non-ionic surfactants. *Carbon* **2011**, *49*, 1653–1662. [CrossRef]
- 117. Wan, Y.-J.; Tang, L.-C.; Yan, D.; Zhao, L.; Li, Y.-B.; Wu, L.-B.; Jiang, J.-X.; Lai, G.-Q. Improved dispersion and interface in the graphene/epoxy composites via a facile surfactant-assisted process. *Compos. Sci. Technol.* **2013**, *82*, 60–68. [CrossRef]
- 118. Wang, S.; Yi, M.; Shen, Z.; Zhang, X.; Ma, S. Adding ethanol can effectively enhance the graphene concentration in water–surfactant solutions. *RSC Adv.* **2014**, *4*, 25374–25378. [CrossRef]
- 119. Fan, H.; Zhao, N.; Wang, H.; Xu, J.; Pan, F. 3D conductive network-based free-standing PANI–RGO–MWNTs hybrid film for high-performance flexible supercapacitor. *J. Mater. Chem. A* **2014**, *2*, 12340–12347. [CrossRef]
- 120. Jia, Y.; Yu, K.; Qian, K. Facile approach to prepare multi-walled carbon nanotubes/graphene nanoplatelets hybrid materials. *Nanoscale Res. Lett.* **2013**, *8*, 243. [CrossRef] [PubMed]
- 121. Wu, J.; Yu, K.; Qian, K.; Jia, Y. One step fabrication of multi-walled carbon nanotubes/graphene nanoplatelets hybrid materials with excellent mechanical property. *Fibers Polym.* **2015**, *16*, 1540–1546. [CrossRef]



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