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Electrophoretic deposition of graphene-related materials: A review of the fundamentals

Mani Diba^{a,†}, Derrick W.H. Fam^{b,†}, Aldo R. Boccaccini^{c,}, Milo S.P. Shaffer^{b,*}*

^aDepartment of Biomaterials, Radboud University Medical Center, Philips van Leijdenlaan 25, 6525 EX, Nijmegen, the Netherlands.

^bDepartments of Materials and Chemistry, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom.

^cInstitute of Biomaterials, University of Erlangen-Nuremberg, Cauerstrasse 6, 91058 Erlangen, Germany.

[†]These authors contributed equally to this work.

* Corresponding authors. E-mail addresses: aldo.boccaccini@ww.uni-erlangen.de (A.R. Boccaccini), m.shaffer@imperial.ac.uk (M.S.P. Shaffer).

Abstract

The Electrophoretic Deposition (EPD) of graphene-related materials (GRM) is an attractive strategy for a wide range of applications. This review paper provides an overview of the fundamentals and specific technical aspects of this approach, highlighting its advantages and limitations. Since obtaining a stable dispersion of charged particles is a pre-requisite for successful EPD, the strategies for suspending GRM in different media are discussed, along with the resulting influence on the deposited film. Most importantly, the kinetics involved in the EPD of GRMs and the factors that cause deviation from linearity in Hamaker's Law are reviewed. Side reactions often influence both efficiency and the nature of the deposited material; examples include the reduction of graphene oxide (GO) and related materials, as well as the decomposition of the suspension medium at high potentials. The microstructural characteristics of GRM deposits, and their degree of reduction, strongly influence their performance in their intended function. These factors will also determine, to a large extent, the commercial potential of this technique for applications involving GRM, and are therefore discussed here.

Keywords: Electrophoretic deposition, graphene, graphene oxide, graphene related materials

1. Introduction

Graphene-related materials (GRM), including graphene, few layered graphene (FLG), graphene oxide (GO) and reduced graphene oxide (rGO), are multifunctional nanostructured building blocks with extraordinary properties which may contribute to many fields of science and technology [1]. However, in order to exploit GRM properties for the production of functional devices, controlled processing methods are essential. Electrophoretic deposition (EPD) is an attractive technique for manipulation and deposition of nanomaterials, in general, and also for GRM specifically. The process parameters can be easily manipulated to adjust the chemical and morphological conformation of the deposit with considerable flexibility [2, 3]. EPD in its simplest form requires the application of an electrical potential to electrodes immersed in nanoparticle dispersion (Figure 1). Two sub-processes take place: (1) electrophoretic movement of suspended charged particles in a liquid phase toward an electrode under the effect of an electric field; (2) collection of the particles at the electrode surface and formation of a deposit [4].

A typical EPD setup consists of a working and a counter electrode linked to a power supply providing an electric field between the two electrodes (Figure 1). The applied electric field can be either produced in direct electric current mode (DC-EPD) or in a modulated electric current mode. The modulated current mode can be in the forms of alternating current (AC-EPD) or pulsed-direct current (pulsed-DC EPD). Generally, positively charged particles deposit on the cathode (cathodic EPD) and negatively charged particles on the anode (anodic EPD). There is considerable flexibility about the nature, shape, and scale of the working electrode, as well as the sequence of deposition, leading to the formation of hybrid or composite materials as discussed in Section 2.3.

Indeed, as summarised in Table 1, EPD offers numerous advantages for the deposition of GRM. Nevertheless, challenges also exist which limit the applicability of this technique under certain conditions or for certain classes of GRM, as illustrated further in the following sections.

In EPD processes, the quantity and quality of deposits can be accurately controlled by the EPD parameters, which can be broadly divided into two groups related to the electric field and suspension characteristics (Table 2). An overview of data summarized from a wide range of studies concerning EPD of GRM, including the specific parameters used, is collated in Table S1 (see the Supporting Information). Typical values for the parameters are indicated in Table 2, and will be discussed in more detail below. The selection of the most suitable configuration and parameters for an EPD process depends on several factors and limitations including suspension/particle properties and desired characteristics of the deposition products. The kinetics of deposition depends largely on the electric field strengths, the stability and concentration of the suspension, the electrophoretic mobility of the particles and the time given for deposition, as summarized quantitatively in the Hamaker's equation [21] which will be discussed in detail in Section 3.

The application of EPD in graphene research goes back before the isolation of single graphene sheets by Novoselov and Geim [22]; in 2001, Affoune et al. [23] produced nano-sized stacked graphene layers (interlayer spacing of 0.35 – 0.37 nm) from the EPD of nano-diamond suspended in an isopropyl alcohol media, followed by subsequent annealing (at 1600 °C in Ar). Nevertheless, the interest in this technique for the production of graphene-based films and coatings has increased significantly during the last 5 years, as documented by recent publication data (Figure 2). Much of this work

draws heavily on earlier research using EPD of other sp^2 -hybridised carbon nanomaterials [2, 24], particularly carbon nanotubes [25], as well as other nanomaterials (including metals [26], oxides [27] and other functional quantum dots [28]); many of the issues are common, but some factors, most notably the tendency for restacking, in situ reactions, and planar orientation are particularly relevant to GRMs, as will be discussed.

In an EPD process, GRM particles, alone or in combination with other particle types, can be used as input materials. Based on the EPD setup, coatings, films or fibres can be produced, and depending on the EPD conditions, various side-reactions can occur during the deposition process (Figure 3).

EPD-processed GRM structures (mainly films and coatings) have been shown to be promising candidates for a wide range of applications [7], including solar cells [31-33], energy storage [34-36] and other electrochemical devices [37, 38], field emission devices [32, 38, 39], bio-/electrochemical- sensors [40-45], electromagnetic interference shielding [46] anti-reflective [47] and corrosion resistance coatings [48, 49]. Based on the current trend and the promising potential of the EPD technique, further applications of EPD-prepared GRM structures can be anticipated in the near future. For example, GRM have recently been attracting attention in more biological contexts [11], such as biomedical implants [50, 51], drug delivery and tissue engineering [52, 53].

Despite this increasing interest in the EPD of GRM, a comprehensive treatment of the subject covering the fundamentals and practical aspects of this field is not available. While a previous review paper has covered EPD of GRM from the applications point of view [7], this review paper is intended to provide an overview of the fundamentals and

specific technical aspects of the EPD process of GRM, including information on GRM suspensions, EPD parameters, and a discussion of the mechanisms involved. There is ambiguity in the definition of graphene and its related materials in many publications, with varying nomenclature for materials of different thickness and chemical history. In the case, of EPD, there is a distinction between the originally suspended materials and the final deposit, including after any post-processing. Nevertheless, an agreed common nomenclature for the initial GRMs is a useful starting point [54].

2. GRM Suspensions for EPD

The key precondition for successful EPD of particulate materials is the formation of a stable suspension of charged particles. The stability of the suspension, its concentration, and the size of the suspended species affect the quality (uniformity, density, and roughness) of the resulting deposits. Both aqueous and non-aqueous suspensions have been used for the EPD of GRMs. This section provides an overview of the essential considerations required to be taken into account when preparing GRM suspensions for EPD, highlighting systems involved, technical aspects and their advantages and disadvantages. In general, suspensions for EPD have to at least remain stable during the entire deposition process even in the presence of an electric field. This requirement is also a major challenge in the context of GRM, as pristine graphene is hydrophobic and generally does not disperse easily. The most common strategy employed for EPD is the use of GO as the starting material in suspension. GO has oxygen-containing functional groups that aid in stability in polar solvents. However, the in-situ reduction of GO can compromise the stability of the dispersion during deposition (see Section 5). An alternative strategy that will be discussed in Section 2.3 involves the use of charging salts that adsorb onto the surface of the GRM and improve the suspension stability

electrostatically. In addition, the effective charge on the GRM surfaces, and hence the type of deposition (anodic or cathodic), can be determined by the choice of charging salt used. Organic dispersions are less commonly applied in EPD, but offer some advantages especially for more pristine, unoxidised FLGs (see Section 2.2). In all cases, the nature of the graphite used to form the suspensions has a strong effect on the efficiency of the exfoliation process, as well as the size, thickness, shape, and crystallinity of the dispersed layers [55].

Generally, there is no specific particle size requirement for electrophoretic deposition but larger GRM particles tend to settle more quickly due to gravity and may produce non-uniform film properties. However, larger graphene sheets ($> 5\mu\text{m}$) are also seen to deposit more rapidly due to their higher mobilities as discussed in more detail in Section 3. Typical lateral flake sizes used for EPD are around $1\mu\text{m}$, although considerable variation is possible; particularly large GO flakes have been successfully exfoliated (up to millimetre [56]) though not yet used for EPD. Large flakes may improve properties such as barrier performance and electrical transport of EPD deposits, but may also sediment or wrinkle more easily. For functionalised GRMs in aqueous media, especially those based on GO, typical suspension concentrations of around 1 mg mL^{-1} [49, 57, 58] are used. Higher concentration offers faster deposition (see Section 3), but risks suspension instability, restacking, or even electrical shorting if percolation or electrical field induced agglomeration occurs [59]. Typically, suspensions of unfunctionalised GRM are prepared at lower concentrations and oftentimes, a charging additive for stabilisation is needed [11] (see Section 2.2).

2.1 Aqueous suspensions of GO-derived GRM for EPD

EPD using aqueous suspensions is considered an environmentally friendly and low-cost processing method and is usually preferred over EPD from organic solvents. It is readily applied to hydrophilic GO-based materials; however, from an environmental point of view it should be kept in mind that the production of GO itself produces large volumes of acidic waste [60].

i. Oxidative Chemical Exfoliation

Chemical exfoliation of graphite flakes is a common method for production of GO for EPD; GO is usually produced via the Hummer's method or a modified Hummer's method using graphite as the starting material [61, 62]. Typically, the chemical oxidation of the graphite flakes uses strong oxidants (usually KMnO_4 and H_2SO_4) which results in an expanded graphite oxide. Water can be intercalated and bound in between the graphite oxide layers via hydrogen bonding before a physical agitation step is applied to separate the sheets to form GO [61].

The unzipping of carbon nanotubes [30] and nanofibers [63] is a specific variant of the graphite oxidation process that has been used to prepare suspensions of GRM with specific shapes for EPD.

ii. Structure and Properties of GO

GO suspensions generally consist of solvated single layers and highly oxidised carbon-based sheets. These oxygen groups can take the form of epoxies, carboxyls and hydroxyls. In addition, the oxidative moieties are typically found randomly attached to both sides of the GO sheets. This phenomenon results in a primarily amorphous surface structure with a surface roughness of around 0.6 nm [64]. X-ray photoelectron

spectroscopy (XPS) data reveal that typically, hydroxyls and epoxies are found on the basal plane of GO while carboxyls, phenols and ketones are found on the edges. The oxygen content from these moieties make up between 16.6 – 33 at% [65], and the groups are thermally unstable, decomposing in air from around 100°C to give off CO₂, CO, and adsorbed H₂O. There continues to be some ambiguity over the exact structure of GO, due to the variation in graphite feedstock and production routes, as well as the heterogeneity of the product. One problem is that many GO samples, particularly commercial materials produced in large batches, consist of 2 fractions: large sheets with oxygen containing groups that are covalently functionalized, termed as base-washed GO (bwGO) and small and highly oxidized fragments which are termed as oxidative debris (OD) or carboxylated carbonaceous fragments (Figure 4). The OD plays a major role in the stability of GO in aqueous media. These two GO parts can be separated, albeit irreversibly with a base washing step (hence with the resultant large sheets being termed as bwGO, which has a higher C:O content of 4:1); this step may convert acid surface groups to conjugate bases, increasing surface charge, but potentially altering the composition of the material via the introduction of counter-ions. bwGO is not stable in water on its own, forming a (re)stacked structure. However, there have been studies reporting that bwGO forms a more exfoliated, metastable suspension in N-methyl-2-pyrrolidone (NMP) [66].

iii. Chemical reduction of GO

In order to obtain rGO, and partially recover the desirable properties of pristine graphene, GO can be treated with a suitable reducing agent. In situ reduction is popular and discussed further in Section 5(i). However, in several studies, chemical reduction is employed as a post-EPD step. Many reducing agents like vitamin C (ascorbic acid),

hydrazine and hydriodic acid have been explored [67], although hydrazine is particularly effective and popular for simplicity and cleanliness [68, 69]. Chemical reduction before EPD is also possible but additional measures are required to avoid aggregation and restacking, which can occur due to the loss of stabilizing hydrophilic groups. Chemically-reduced GO sheets usually cannot form stable aqueous suspensions without using stabilizing additives, although partial reduction of GO can produce stable dispersions, depending on ionic strength, pH and rGO concentration [69]. In several studies, partial reduction of GO has been reported as an effective way to produce stable and negatively charged rGO aqueous suspensions for EPD [10, 15, 70-72].

Electrostatically stabilized rGO aqueous suspensions can also be produced by sequentially treating GO with potassium hydroxide before reducing it with hydrazine. However, there is also a possibility that functional groups will form in the presence of a strong base. Upon reduction, a stable suspension of rGO is produced due to the strongly bound K^+ ions. However, it is important to note that the rGO suspensions prepared by this method contain high concentrations of K^+ ions, which increase the ionic conductivity of the suspension and may be incorporated within electrophoretic deposited films [73, 74]. Interestingly, highly alkaline solutions have also been applied, without using hydrazine, to produce partially stable reduced GO suspensions, with a retained negative charge through conjugate base formation (see section 2.1ii), suitable for anodic EPD [75].

iv. Preparation of GO-based aqueous suspensions

Due to its hydrophilic nature, unreduced GO can be suspended relatively easily in aqueous media with zeta potential values reported between -2 to -70 mV, as a function of pH [15, 34, 74, 76-78]. For both acidic and basic conditions, GO exhibits net

negative surface charge when suspended in water. In order to obtain a stable suspension, a net zeta potential higher than about -30 mV is usually required which can be obtained across a broad range of pH for GO [15, 16, 79]. Recently, ultrasonicated ozone-modified and electrochemically-exfoliated graphene oxide has been proposed as a route for preparing stable GRM suspensions suitable for EPD [80].

2.2 Organic suspensions of GRM for EPD

The preparation of suspensions of GRM for EPD in organic media is less common due to the difficulty in stabilizing GRM sheets in many solvents. However, unlike aqueous systems, organic media avoid the tendency to evolve gases at the electrodes when high voltages are applied. In a defining work by Hernandez et al. [81], the suspension properties of physically exfoliated graphite were obtained in several organic solvents (NMP, γ -butyrolactone and 1,3-dimethyl-2-imidazolidinone). In this study, sieved graphite powder (0.5 mm mesh) was dispersed in the various solvents at a loading of 0.1 mg mL⁻¹ by physical agitation. A stable suspension was obtained for a subset of solvents with surface tension around 40-50 mJ m⁻²; the behaviour is generally attributed to physical solvent characteristics although solvent degradation may play an important role. In the solvents investigated, up to 28 % of the graphene-layered flakes obtained in NMP were found to be monolayers (overall yield of approx. 1 % which can be increased to 12 % by recycling the sediments). In any case, long periods of physical agitation for exfoliation can reduce the sizes of the graphene layers, and lead to contamination by degraded solvent [82]. However, even in this case, the surfaces of the FLG or graphene must still be charged in order to perform EPD [83], generating particles with different surface charges, through electron transfer, as indicated by zeta potential (Figure 5). The graphene's zeta potential was found to be positive in solvents with lower electron donor

numbers and negative in solvents with higher electron donor number. These results are interesting for preparation of GRM suspensions for EPD in further studies.

An alternative approach simply disperses GO-derived GRMs in polar solvents, in a manner analogous to aqueous systems, exploiting the oxygen containing surface functional groups. Some common polar solvents used in EPD of carbon-based materials are mixtures of acetone, ethanol [84], dimethylformamide (DMF) [37] and isopropyl alcohol [39, 68, 85, 86]. In one example, rGO powder was directly dispersed in anhydrous 1-ethyl-2-pyrrolidinone and, after 1 h of sonication, the suspension obtained was seen to remain stable for more than one month. However, upon EPD, the resultant film again appears to be multi-layered rGO [87].

2.3 GRM suspensions prepared with additives and chemical modifications

Due to the lack of stability of GRM in many solvents, various types of additives and treatment methods have been applied for production of stable suspensions of charged GRMs. However, additives and chemical modifications can change the original properties of GRM sheets and might negatively affect the final film properties. Therefore, optimization of GRM content, electrolyte concentration, and pH, to maximise electrostatic stabilisation for minimal contaminant addition, is a critical first step for obtaining stable GRM-based suspensions suitable for EPD [69, 88]. Electrostatic stabilisation of suspensions is generally covered by DLVO theory [89], although the application to GRMs is complicated by their anisotropy and their heterogeneity in size and chemistry; however, generally, a high net-surface charge and a modest bulk electrolyte strength are most effective conditions to achieve stable GRM-based suspensions.

i. Additives

The choice of charging additive for EPD of GRM is at an exploratory stage. In the light of current experiment evidence, it is not possible to identify an additive as “the best” for the EPD of GRM and the choice depends on both suspension properties and electric-field-related parameters. Nevertheless, there are two important criteria that must be considered when selecting an additive: (i) it should provide high zeta potential and electrophoretic mobility to the suspended particles, (ii) it should enable the formation of a deposit on the working electrode (e.g. through charge neutralization). Fulfilling these criteria can lead to good suspension stability, high deposition rate, and uniform deposit formation during EPD.

Metal ions, which adsorb onto GRM, are commonly used as additives to produce suspensions of positively-charged GRM particles. However, high concentrations of these ions can destabilize the suspensions, whilst, their electrophoresis and accumulation on the electrode's surface can have negative effects on the deposition of the desired GRM [90] as described in Section 5. iv. Typical metal salts that are used for charging GRM for EPD are nitrates of aluminium [91-94], nickel [95-97], zinc [98], cobalt [99], manganese [63, 100], magnesium [17, 20, 31, 39, 68, 85, 86, 101-108] and magnesium chloride [109], although, copper sulfate has been used recently [110]. The performance of these ions, however, may be pH dependent. For example, one study [97] reported that Ni^{2+} ions do not interact effectively with GO sheets if the suspension's pH exceeds 6 when adding KOH into the solution [97]. In addition, metal ions may preferentially adsorb to specific sites rather than distributing uniformly, as illustrated by the selective adsorption of Mg^{2+} to the protonated edges of rGO sheets [107].

Aurintricarboxylic acid ammonium (Aluminon) is an organic salt that has been used as a charging additive for suspensions of graphene layers, producing negatively charged graphene layers for anodic EPD. Aluminon attaches to graphene layers via π - π stacking and its carboxylic groups provide sufficient negative charge for suspension stabilization for EPD. Aluminon solubility and charging effects are pH-dependent and can offer good deposit formation ability (see Section 4 on deposition mechanisms). By similarly exploiting π - π interactions, several dye molecules including hexamethylpararosaniline chloride (CV) [111], methyl violet (MV, which contains CV) [112] and safranin [113] have been used as additives to produce electrostatically-stabilised GRM suspensions.

One report [114] has claimed that a relatively mild chemical doping process can be used to induce positive charges on GRM and increase GRM electrical conductivity without introducing severe defects into the sheets. Thermally expanded graphite (e-graphite) fluorinated by the intercalation of chlorine trifluoride (ClF_3) [115] was treated with acids before being re-dispersed in acetonitrile as positively charged graphene suspensions for EPD. The doping process occurs via adsorption of acid molecules onto the graphene-layers and the type of acid can affect both the doping effectiveness and EPD process. However, this method involves relatively dangerous ClF_3 and also the evolution of CF_4 , a greenhouse gas, making it environmentally problematic.

Apart from metal ions, and organic salts, other organic compounds have also been used as a stabilizing additive for GRMs. One example is the use of p-phenylene diamine (PPD) as both a reducing agent and a stabilizing additive for rGO [90, 116]. Another example is polydiallyldimethylammonium chloride (PDDA), which is a polymer used to stabilise rGO. However, PDDA does not attach to rGO only via cationic adsorption, like the metal ions. Rather, being a strong polyelectrolyte with a hydrophobic backbone, its

amphiphilic character leads to a more complete coverage of the basal plane of rGO compared to Mg^{2+} , which is shown to stabilize only the protonated edges of rGO [107].

Surfactants are widely used to stabilise nanoparticle suspensions, usually in aqueous media [69]. In the context of GRMs, surfactants can assist the exfoliation step that is needed, in combination with ultrasonication or other high shear treatment [117]. Graphene sheets of 300 – 800 nm were exfoliated from graphite in NMP using sodium cholate (NaC) as a surfactant, at a shear rate of $>10^4 \text{ s}^{-1}$. This approach potentially produces sheets that are negatively charged and possibly suitable for EPD. Another approach is to intercalate phenol and methanol into graphite via sonication [118]. On adding cetyltrimethylammonium bromide (CTAB) further intercalation and exfoliation was reported leading to dispersion in a water and methanol mixture. At pH 3 the resulting graphene layers (approx. 5-15 μm in diameter) were positively charged and therefore able to be deposited using cathodic EPD.

In many instances, additives are included both for stabilizing the GRM suspension and for their function in the application of the resulting film. Some examples include the deposition of GO/chitosan films for drug release [53], $\text{CoFe}_2\text{O}_4/\text{rGO}$, Ni/GO and Sn nanoparticle/rGO films for energy storage [119-121], CdSe quantum dot/rGO for energy harvesting [122] and Ni -graphene layers for corrosion resistant coatings [123].

It is also interesting to note that GO has been used as charging additive for the EPD of carbon nanotubes (CNTs), producing GO-CNT composite films [124]. It was reported that in the absence of GO in the suspension, the non-functionalized CNTs could not be successfully deposited [124]. Similarly, GO has also been reported to be an effective additive for the reduction of agglomeration in hydroxyapatite suspensions [50].

ii. Chemical modification

Covalent-linking of chemical moieties to GRMs is another potential method for production of suitable suspensions for EPD; a wide range of GRM chemistry has been explored and may be exploited in this context [62]. One example is the preparation of porphyrin-linked rGO suspensions for subsequent EPD [125, 126]. Although the main aim of the study was to investigate the photophysical and photoelectrochemical properties, the chemical modification provided stability in common organic compounds like o-dichlorobenzene (ODCB) and toluene, with the stability presumably from the hydrophobic interactions between the solvent and the grafted molecules. Although non-covalent modification is often simple, covalent modification of GRM provides more stability and more defined interaction between the linked molecule and the GRM sheet; although the site of attachment in principle acts as a defect in the otherwise sp^2 hybridised layers, the degree of modification can be adjusted to balance the desired effects with any loss of intrinsic properties. Furthermore, with covalent modification, there is no requirement for an excess concentration in solution to maintain equilibrium of adsorbed species, reducing the degree of contamination in the system. Therefore, with the current improving understanding of the precise structure and reactivity of many GRMs, there is a considerable potential for exploration in this area, particularly if the grafted species adds a desired functionality.

3. Kinetics involved in EPD of GRM

Understanding the EPD kinetics of GRMs, in principle, allows the prediction of final film characteristics and more efficient selection of EPD parameters. Although numerous qualitative studies have been performed on the EPD of GRMs, limited attention has been paid to the fundamental EPD kinetics involved.

i. Hamaker's Law

Hamaker's law is a well-known mathematical model predicting the EPD kinetics of particulate materials [3, 21]. It predicts that the time-dependent mass of the deposit, $w(t)$, has a direct relationship with the particles' electrophoretic mobility, μ , the strength of electric field, E , the electrodes' surface area, A , the efficiency coefficient of deposition, f (≤ 1 ; that accounts for the fact that only a fraction of the particles that come into contact with the electrode surface are deposited) and the particle concentration in suspension, C , as illustrated in equations (1) and (2):

$$w(t) = \int_{t_0}^t f\mu EAC dt \quad (1)$$

by integrating (1) with respect to time, equation (2) is obtained:

$$w(t) = f\mu EACt \quad (2)$$

This equation indicates a direct relationship between the electric field and the deposition yield. However, in order to achieve deposition, a minimum electric field is required to overcome repulsive interparticle interactions, which at low voltages can cause reduced deposition [111]. If too low a voltage is used, the particles will move to the electrode surface but their interparticle repulsion will not allow them to aggregate and make a deposit. The explicit deposit formation process is complex and different mechanisms have been suggested. For example, as discussed in Section 4 in more detail, charge neutralization of particles at the electrode surface due to local pH variations, originating from EPD-induced electrolysis of water, can modulate the deposition process.

Hamaker's equation can predict [8] the characteristics of the deposited GRM-based films such as mass and thickness (Figure 6 shows an example).

Moreover, interestingly, this equation can be also used to predict the deposition of films prepared by co-EPD of different carbonaceous particles [15]. In this context, for example, the mass ratio of deposited carbon black (CB) and rGO; was directly related to their individual ζ -potential values and their concentration (i.e. Equation (3)), assuming the same f for both materials:

$$\frac{m_{rGO}}{m_{CB}} = \frac{C_{rGO}\zeta_{rGO}}{C_{CB}\zeta_{CB}} \quad (3)$$

However, other factors can indirectly affect the terms in this equation as well. For example, the electrophoretic mobility of the particle, μ , depends on the dielectric constant, ϵ_r , the shear viscosity of the dispersion medium, η and the zeta potential of the particle, ζ , which is dependent on the surface charge of the particle, as traditionally illustrated in the Smoluchowski equation (Equation (4)) for small Debye lengths (smaller than the radius of the particle) and spherical particles:

$$\mu = \frac{\epsilon_0 \epsilon_r \zeta}{\eta} \quad (4)$$

Therefore, a more viscous solvent or a lower surface charge will result in a lower electrophoretic mobility which will in turn give a low rate of deposition. Electroconductive chargers will increase the particle electrophoretic mobility, μ , by increasing the absolute value of the zeta potential, ζ , which can then cause a proportional increase in yield. On the other hand, a high concentration of charging ions adsorbed on graphene flakes can increase the particles mass and size therefore decreasing μ [112]. Whilst the Smoluchowski equation indicates that mobility is independent of size, GRMs are typically of similar thicknesses to the Debye length, implying that size / GRM flake thickness effects are in fact likely to be observed; in addition, in the case of graphene rather than GO suspensions, electrical conductivity

may introduce a size dependent polarisation. Finally, GRM are highly anisotropic particles, and the mobility equation is modified depending on aspect ratio and the degree of orientation. Analysing the true dependence of heterogeneous mixture of irregularly shaped flakes is virtually impossible, but the system can be modelled as circular platelets. In one study, the motion of graphene sheets was calculated using fluid dynamics [108]. Under an applied electric field, E , graphene sheets can move either with their lateral surfaces parallel or perpendicular to the field with velocities $v_{//}$ or $v_{\perp}$ respectively. Given that there are two opposing forces (from E and from the viscosity η), highest (terminal) velocity ($v_{max//}$ and $v_{max\perp}$) reached would be given by:

$$v_{max//} = \frac{\sigma E S_l}{\kappa \eta \sqrt{S_0}} \quad (5)$$

$$v_{max\perp} = \frac{\sigma E \sqrt{S_l}}{\kappa \eta} \quad (6)$$

where σ is the number of charges per unit area, S_l the lateral surface area, S_0 is the cross sectional area, κ is a related constant and η is the viscosity. From equation (5) and (6), it can be seen that the maximum velocity of the GRM sheets increases as the lateral sheet size increases assuming the charge density is the same [108]. Figure 7 illustrates the retardation force, r , and the accelerating force, F , from the electric field, E , exerted on a single charged GRM particle during an EPD process. Since the degree of orientation is expected to be a function of electric field and particle size, the true effective mobility may be complicated to estimate.

Charging additives are often used to increase the charge density of the GRM sheets as described in Section 2.3. However, the electrochemical reaction that some charging additives undergo during EPD at high voltages also changes the kinetics involved [8].

ii. Deviations from Hamaker's Law

At high EPD voltages or long deposition times, deviations from the linearity predicted by Hamaker's law can occur. These deviations are, in many cases, attributed to decreased deposition rates caused by increased thickness of an intrinsically insulating deposit; for example, layers of GO [97, 127], or/and insulating additives [111, 127] used for stabilization (charging) of graphene suspensions, can passivate the working electrode, causing the electric field to drop predominantly within the existing deposit. When the electric field in solution drops below a critical level, further deposition is reduced to a negligible level; the mass of the deposit plateaus and the current drops sharply (Figure 8) [97, 127].

Formally, the effective electric field in solution (E) can be related to the applied voltage (V_{app}), and the voltage drop in the deposit (V_{drop}) (Equation (7)). V_{drop} increases when depositing an insulating layer, resulting in a decrease in the electric field strength E , with deposition time:

$$E \propto V_{app} - V_{drop} \quad (7)$$

Su et al. [111] studied the EPD kinetics of CV dye-decorated graphene sheets using a quartz crystal microbalance. A nearly linear increase of deposition yield was observed as function of EPD voltage, in line with the Hamaker equation. However, at voltages higher than 40 V, increasing deposition of non-conductive CV dye led to deviation of the voltage-deposition yield relationship from linearity. Similar trends have been reported for the EPD of MV dye [112] and safranin dye [113] modified graphene sheets, possibly due to the passivation of the electrodes from the formation of an insulating layer. A wide range of other deviations from linearity are associated with side reactions

enabled at particular voltages (see Section 5), and/or instability of the suspension during the process [8].

iii. Size distribution of suspended graphene related materials

As noted above, size (length) distribution of the GRM sheets in a suspension, and their field-induced orientation, may have a strong effect on mobility and hence deposition. Different types of GRM sheets have been reported to show different size-dependent electrophoretic mobility. The discrepancy may depend, for example, on the nature of the charging involved; preferential charging of sheet edges should raise the mobility of smaller sheets; evenly distributed surface charging should raise the mobility of larger sheets (as outlined in Equations 5 & 6 which assume constant charge density); other factors such as shape or waviness may also play a role. In one report, for GO sheets, larger flakes were reported to have lower electrophoretic mobility [128] which slowed the kinetics of deposition. However, in the case of Mg^{2+} -decorated graphene, larger flakes were reported to deposit more quickly due to the larger charge-carrying lateral surface of larger sheets and hence larger electrophoretic mobility [108]. Specifically, in that study, a comparison was made for deposition times of 30 s, 60 s and 90 s. It was seen that larger sheets ($> 5 \mu\text{m}$) were deposited in the first 30 s and smaller sheets were deposited when the time increased to 60 and 90 s. Therefore, at long deposition times, the dissimilar electrophoretic mobility of different sized sheets may lead to differential depletion, and segregated deposition during different stages of EPD. This phenomenon not only affects the EPD kinetics, but also can result in a GRM sheet size gradient within EPD-prepared films [92, 108]. This GRM size effect on deposit structure could be a potential drawback of the EPD technique as compared to spin coating or vacuum

filtration, but may offer benefits in specific applications where a graded structure is desirable.

4. Mechanisms of deposit formation

Different mechanisms have been suggested for deposit formation during EPD, such as flocculation by particle accumulation, particle charge neutralisation, and electrochemical coagulation of particles [129]. Nevertheless, the mechanisms for the deposit formation of GRM sheets have not been widely studied. Most of the studies have suggested that GRM particle charge neutralisation at the working electrode surface is the core process that leads to deposit formation. For example, GO dispersions are generally stabilised electrostatically by the charge remaining on the conjugate base of ionised acidic surface oxides; during EPD, water electrolysis at the anode can lead to local acidification, (re)protonation of the charged groups and a loss of stabilising repulsion [49]. Depending on the initial pH of the GO suspension (net initial charge of the GO sheets), deposit formation can be induced on either anode or the cathode, with both options attributed to charge neutralization mechanism [79]. In addition, other effects may also contribute specifically for GRMs, including the removal of oxide groups by GO ‘reduction’ processes that may happen at either anode or cathode (see Section 5). A further possible scenario, at the anode, is the dissolution of metallic ions from the electrode, contributing to the charge neutralisation effects and, if multi-valent, cross-linking of GO sheets can occur through multiply coordinated carboxylates [49]. One strategy against electrode dissolution is the use of inert yet conductive carbon-based electrodes [130-132]. The charge neutralisation mechanism has also been reported to govern the deposit formation for GRM sheets decorated with other charged species, similar to the case of GO, including PIHA (polymeric isocyanate crosslinked

with hydroxy functional acrylic adhesive) [127], hyaluronic acid [133], methyl violet dye [112], aluminon [134], safranin [113] and Ni ions [96]. In one instance, however, chemical bonding was shown to occur between the deposit, rGO, and the working electrode, TiO₂ nanotube arrays, [71] during anodic EPD from rGO aqueous suspensions.

In organic dispersion media, electrochemical degradation may lead to the deposition of organic material, trapping or linking GRM particles [135]. Overall, there is still a need for further detailed studies to qualitatively correlate the mechanisms involved in deposition formation with deposition parameters (pH, ξ potential values etc.), and to understand the opportunities for further control.

5. Side reactions

As introduced in section 4, various electrochemical reactions can occur during the EPD of GRM, including ‘reduction’ (de-oxygenation) of GO, dissolution of electrodes, and degradation of suspension media at high voltages. These side reactions can be beneficial or destructive depending on the final application. The examples below describe a few important classes of side reactions in more detail.

i. EPD-based reduction mechanism of GO

Several studies have reported that EPD of GO at high voltages causes a simultaneous ‘reduction’ (more accurately, de-oxygenation) of GO during deposition [8, 9, 79]. This phenomenon may appear beneficial for the production of rGO films, since it potentially avoids the need for a post-EPD GO reduction process, and may prevent the passivation of the growing film due to the insulating nature of the GO. However, as discussed above, the GO-EPD kinetics may vary, leading to an uncontrollable EPD process, as

key parameters like ξ -potential and the particle concentration vary over the course of deposition; the reduction effect may dominate, if f , the deposition efficiency (see Section 3) is low, and partially reduced GO is recycled into the suspension. In addition, for applications that explicitly require GO deposits, the reduced GO sheets will act as impurities.

XPS and Fourier transform infrared (FTIR) spectroscopy are commonly used for evaluating the degree of reduction of GO materials. The peaks at 288.7 eV, 286.7 eV and 284.6 eV are typically associated with the sp^2 C-C, the C-O and the C=O bonds respectively. Figure 9 shows typical XPS and FTIR spectra of EPD-GO film containing significantly fewer oxygen-based groups (at 288.7 eV and 286.7 eV) compared to a control GO paper prepared by filtration [9]; overall the C:O atomic ratio of the EPD-GO film is much greater (6.2:1) than the control (1.2:1). The EPD-GO films were obtained from deposition on a 200 mesh stainless steel with an applied voltage of 10 V (detailed deposition parameters in ESI). After annealing the GO-EPD film at 100 °C, the XPS spectrum becomes very similar to that of a hydrazine-reduced GO, with a C:O (9.3:1) comparable to the chemically (hydrazine) ‘reduced’ GO (CReGO) (10.3:1).

A reduction process in principle occurs on the cathode [58]. However, as seen in the example above, the ‘reduction’ of GO has also been observed to occur on the anode surface during anodic EPD processes, leading to production of reduced GO films [9, 40, 49, 79, 136, 137]. The extent of reduction does not depend on deposition time [49], but is mainly controlled by voltage. At low voltages electrochemical side reactions are generally avoided; below 10 V unmodified GO has been deposited [8], simplifying kinetic studies of EPD. Generally, most studies report greater deoxygenation at higher voltages. However, one report indicates an increase in oxygenation peaking at 35 V; this

result is consistent, however, with a complex anodic mechanism involving a competition between oxidation and apparent ‘reduction’ [76].

Whilst the exact deoxygenation mechanism is not yet clear, the following reaction steps (8) to (10) have been proposed: [9]:

On electrical contact of GO sheets with the anode surface, some electrons are removed, oxidising carboxylate groups on the GO sheets. Following the Kolbe-like release of CO_2 [138], the radicals that are generated recombine to recover some of the covalent bonds in the original graphene framework. Cross-linking between sheets may also contribute to the deposition process. Although these reactions explain the decarboxylation of GO sheets during EPD, the removal of epoxide oxygen is less explicitly clear, but may follow a similar sequence following additional initial oxidation steps.

Interestingly, Ishikawa et al. [78] used EPD to deposit GO sheets onto a 90 nm thick insulating silicate glass coating on the anode. A higher voltage of around 20 V was required for EPD due to the thickness of the glass substrate, but direct contact between depositing GO nanosheets and the anode surface was avoided. Surprisingly, the resulting EPD deposit was claimed to have a higher degree of GO reduction compared to chemically or thermally reduced GO films, apparently in contradiction to the Kolbe-like mechanism proposed [9]. Similar results have also been reported in a more recent study [139]. However, further investigations are required to clarify the underlying GO reduction mechanism of the EPD technique.

ii. Aqueous electrolysis

Solvent degradation is generally detrimental to the control of film formation in EPD. In protic solvents such as water or ethanol, bubble formation can be problematic at the cathode, due to the evolution of gaseous H_2 by reduction when high voltages are applied. In the case of water-based EPD, electrolysis will also cause O_2 bubble formation at the anode [8, 140]. In one example, gas-formation was claimed to be beneficial as it was used to detach the deposited GRM for the formation of free-standing films [29]. However, bubbles at the working electrode generally disrupt film formation creating a heterogeneous, weaker and excessively porous deposit. The voltage window in which water remains thermodynamically stable shifts as a function of pH, although the width remains constant (Figure 10) [141].

During a constant voltage EPD process, side reactions (e.g. hydrolysis and GO reduction) can lead to instability of the electric current especially at high deposition voltages, and therefore monitoring of the current can be utilized for the detection of side reactions [8].

Applied EPD voltages typically exceed the thermodynamic stability of the solvent, implying that kinetic control is crucial. At low ionic strengths, the electrochemical decomposition reactions are polarised; if the rate of reaction is slowed sufficiently, any hydrogen (or oxygen) generated may diffuse away without bubble nucleation. The critical thresholds for bubble nucleation will vary from system to system, depending on the applied voltage, the nature of the electrodes / deposited material, the composition and concentration of dispersion medium, and so on. This kinetic sensitivity may explain varying reports of bubble evolution in the literature. Low rates of electrolysis may still

be sufficient to adjust local pH, to enable the charge neutralisation mechanisms discussed in section 4.

iii. Degradation of organic solvents

Organic solvents also undergo electrochemical degradation, but it is often more difficult to probe the reactions, as they are typically irreversible, often radical based, and vary from solvent to solvent. Typically cyclic voltammetry is used to determine stable potential windows, as summarised for some common solvents in Figure 11; it's worth noting that contamination (for example with water) can significantly reduce the onset voltages for degradation.

The influence of organic solvent degradation has not, on the whole, been taken into account by previous EPD studies, even though the voltages used normally surpass the potential windows of the solvents. This omission may be because the total volume of solvent degraded as compared to the bulk of the solvent is minimal, and gas evolution is not usually observed in these systems. However, in fact, it is likely that oligomerised/polymerised organic compounds will form if voltages are excessive, at least for certain common GRM solvents such as amides. Even though it may be hard to detect against the background of already functionalised GRMs, such components may play a significant role, for example usefully binding the deposit, or undesirably contaminating it and passivating the EPD process similarly to the way additives contaminate and passivate the working electrode (see Section 2.3 i.); again the kinetics as well as the thermodynamics of the degradation will be important in determining outcome.

iv. Electrochemical reduction of additives

As mentioned in Section 2.3, charging additives can have a detrimental effect on the deposited film by affecting its purity when hydroxides are precipitated and incorporated into cathodic deposits. However, these hydroxides may also improve the deposits' adhesion onto the substrates [142]. Metallic nanoparticles may form within graphene/GO layers either by reduction of the metal ions when they come into contact with the cathode's surface during EPD [63, 96] or during post-EPD annealing or reduction steps [99]. While this phenomenon can be beneficial for production of composite films, care is needed to avoid the unwanted contamination of the deposits.

6. Microstructure

The microstructural characteristics of GRM structures determine their performance in their intended function [7], although requirements differ. For example, electrodes for electrochemical double layer supercapacitors rely on high structural porosity as well as a large interlayer separation of GRM sheets to allow effective electrolyte access and to maximise the active surface area for charge storage [15, 63, 96, 124, 143]. On the other hand, field emission of electrons at low voltages requires a high surface roughness and a predominance of well distributed, individualised GRM edges [39, 85, 91, 92, 101, 144-146]. In contrast, a low surface roughness and high film bulk density are favoured for solid lubricant coatings [76] or barrier layers. A particular strength of EPD-processing of GRM structures is that it can lead to different microstructural features, thin or thick, flat or rough, compact or porous, depending on the processing conditions. However, in order to design GRM structures with specific properties, it is important to understand the relationship between processing parameters and microstructural features, as further discussed in this section.

6.1 Typical microstructural characteristics

Although the EPD technique is mostly used for production of coatings or films, this technique can also be utilized to produce other structures such as fibres (see Figure 12) [9, 30]. The typical film, or coating structures are generally evaluated by the following parameters

i. Thickness

EPD can produce GRM films and coatings with a wide range of thickness, from a single graphene sheet to GRM multilayers hundreds of micrometres thick. Thickness of EPD films can be varied by changing the processing parameters. The thickness has a direct relationship with EPD voltage [8, 37, 76, 147], electric current [9], deposition time [8, 9, 37, 39, 71, 72, 74, 102, 108, 109, 113, 118, 148], particle concentration in suspension [8, 16, 37, 39, 87, 109, 113] and electrophoretic mobility of the depositing particles, as quantified by the Hamaker's equation (see Section 3).

ii. Porosity and bulk density

A wide range of porosities have been reported for GRM deposits processed by EPD, ranging from compact films [8] to membranes with interconnected porosities [142]. Often the microstructure has been characterised only qualitatively by microscopy, but in any case quantification is difficult due to the thin film nature of the deposits and uncertainty about the correct bulk density of the material deposited. Nevertheless, Niu et al. [34] reported a density of 1.26 g cm^{-3} for post-EPD chemically reduced GO films. The reported density was lower than those reported for the GO and rGO films prepared by vacuum filtration and layer-by-layer deposition methods, which had densities of 1.8 g cm^{-3} and 1.6 g cm^{-3} , respectively, indicating a degree of porosity.

iii. Wrinkles, surface roughness, and graphene edges

The presence of wrinkles is a typical characteristic of EPD-processed GRM films and has been reported in several studies [29, 34, 37, 147, 149, 150].

Although the surface area of GRM-based films can be enhanced by the incorporation of additives like CNTs during EPD (Figure 13 A. and B.), the highly wrinkled structure of GO itself can also provide an enhanced surface area. This increase in surface area makes EPD-processed GRM surfaces a good substrate for the nucleation and growth of metal nanoparticles [70, 123, 136, 139, 152], and also allows a better utilisation of the GRM surface area for applications such as supercapacitor electrodes [34].

Reports regarding the surface roughness of EPD-processed GRM films are diverse and correlated with different processing conditions. A similarly wide variation is reported for the presence of protruded graphene edges on the surface of GRM films. Nevertheless, both of these characteristics are related to the orientation of GRM sheets in deposits. Most of the studies [15, 29, 49, 71, 119, 144, 147, 153, 154] have reported that electrophoretically deposited GRM sheets lie parallel to the surface of their underlying electrode which produce a flat surface morphology. However, several studies [39, 68, 91, 103, 105, 106, 136, 146, 155, 156] have reported the EPD of GRM sheets to occur with a perpendicular or random orientation to the electrode surface, leading to a rough surface with protruding graphene edges. Orientation may relate to dynamic effects during electrophoresis, including specific effects of charging salts (see Section 6.2 (v)), but is probably also strongly influenced by capillary effects during drying, and hence, the solvent surface tension and drying method. The nature of any agglomerates present in the suspension, or the agglomeration process inherently associated with the EPD process will also affect the extent of alignment. Re-

agglomeration within partially stabilised suspensions (see Section 2), or due to changes induced during EPD (see Section 5), may cause larger structures to form; the formation of loose agglomerates or more densely restacked layers will influence the final film density. Even if the GRM sheets are predominantly aligned in-plane, a significant number of edges may still protrude normal to the film surface [109]. The alignment of GRM sheets is also an important matter in higher order structures; for example, the rGO sheets are generally aligned in the direction of fibres produced by EPD, under the influence of the electric field and the surface tensions experienced during fibre processing [30].

iv. Conformability

Due to the flexibility of the GRM sheets, EPD processed GRM layers can conform to the deposition surface and copy the pattern of their underlying electrode [144, 157, 158]. This phenomenon not only allows for the production of GRM layers with complex patterns, but also enables 3D coating of porous substrates (e.g. foams) with good interfacial adhesion between coating and substrate [90, 97, 136]. As an example, Maiti et al. [158] reported that when rGO sheets were electrophoretically deposited for short deposition times on carbon fabrics, the deposited rGO layer showed the woven-like geometry of the underlying carbon fabric due to coaxial rGO sheathing over the carbon fibres (Figure 14). Longer deposition times led to production of smoother film surfaces, whilst higher rGO concentrations in the suspension produced a continuous layer with heavy agglomerations on localized areas on the surface.

Several studies have reported successful EPD of GRM on metallic foams [90, 97, 136]. For example, on nickel foam, SEM showed similar surface morphologies between bare

and rGO coated foams at low magnifications (Figure 15 a-d), while high magnifications (Figure 15 e) revealed adhered wrinkled rGO sheets on the foam surface.

Due to the electron transparency of graphene [10, 71, 159-162], thin layers of deposited GRM sheets might not be visible by Scanning Electron Microscope (SEM), particularly when high accelerating voltages are used; instead the underlying electrode structure may appear even in secondary electron images. Nevertheless, when low accelerating voltages (e.g. 1 kV) are used, the incident electron penetration depth into the GRM deposit is decreased and therefore GRM layers can be revealed more clearly in the image, at the expense of spatial resolution (see Figure 16).

6.2 Effects of EPD parameters

In addition to the basic role of EPD parameters in determining EPD kinetics and deposition yield (films thickness) (see Section 3), they can also affect other microstructural characteristics of GRM deposits:

i. Effects of voltage

Generally, increasing EPD voltage is reported to increase the extent of wrinkling and the film roughness [76], as well as generating porosity and heterogeneity through bubble formation via electrolysis in water (see Section 5.ii. and Figure 17) [8]. Non-uniformity of deposits at high voltages may also originate from the anisotropy of the electric field on the substrate, leading to preferential deposition at the electrode edges [153], the possible formation of aggregates in suspension, or Joule heating effects on relatively insulating deposits [74]. On the other hand, too low a voltage (see Section 3.i.) will not generate a high quality film; so in some ranges, increasing the EPD voltage leads to a reduced porosity. For example, one study [112] reported reduced porosity of

GRM deposits when the EPD voltage was increased from 5 to 20 V. This phenomenon was attributed to the enhanced deposition rate of GRM sheets at the higher voltage leading to a greater packing between depositing particles and consequent void filling between them.

ii. Effects of deposition time

Another parameter that can affect the microstructure of the EPD GRM films is the deposition time [92, 108, 128]. Different types of GRM sheets have been reported to show different size-dependent electrophoretic mobility, leading to graded deposition (see Section 3.iii.) [108]. Longer deposition times have been also reported [8, 92] to lead to higher surface roughness of GRM films, possibly due to agglomeration within the suspension medium during EPD. For similar reasons, an increase of deposition time above a certain level can lead to deposition of non-uniform thick coatings with insufficient attachment to the substrate [8, 49], or with varying porosity [163].

iii. Effects of particle concentration

Increasing the particle concentration in suspension has been reported to enhance the surface roughness of GRM films [8]. Highly concentrated suspensions of GRM sheets tend to suffer from low stability and poor dispersion, leading to greater roughness. For example, one study [153] reported that increasing the concentration of GO sheets in suspension ($\sim 1 \text{ mg mL}^{-1}$) negatively affected the quality of films; the agglomerates in solution disturbed the substrate surface coverage and introduced lumps in the deposit.

iv. Effects of suspension pH

Suspension pH can modify dispersion state, side reactions, and deposition mechanisms, as discussed above. In a study by Hasan et al., the microstructure of GO films was

modulated by using acidic or basic conditions [79]. As illustrated in Figure 18, when basic conditions (pH=11.5) were used, GO sheets were deposited on the anode with a parallel alignment to the electrode's surface. The films had rug-like structure consisting of mainly flat but partially wrinkled GO sheets. On the other hand, in acidic conditions (pH=2.8), the GO sheets formed face-to-face stacked multilayers in the suspension and were mainly deposited on the cathode with a brick-like morphology. When the pH is decreased prior to EPD, the net surface charge of the GO sheets decreases leading to an inferior interparticle electrostatic repulsion. In this condition, a face-to-face restacking of GO sheets is favoured due to their shape (Figure 18). During the EPD experiments, hydrolysis occurs which further decreases the pH of suspensions. The GO sheets in the basic suspension will have a negative net charge, even during EPD, leading to anodic deposition. On the other hand, GO sheets in the acidic suspension will experience a charge reversal during EPD and therefore the deposition occurs mainly on the cathode. The pH-dependent face-to-face stacking of GO sheets has been also reported for GO-chitosan mixed suspensions, leading to formation of rougher deposits during EPD [53].

v. Effects of graphene functionalization and treatment

In an EPD process, the alignment of GRM sheets within a deposit can be altered by functionalization of sheet surfaces [103, 107]. Different functionalization strategies can lead to different characteristics of edge or basal planes of GRM sheets. As explained briefly in Section 2.3, Yang et al. [107] compared the effects of metal ion and polyelectrolyte functionalizations on the EPD of rGO sheets (see Figure 19). During EPD, the positively charged edges of the Mg^{2+} -decorated rGO sheets preferentially moved to and deposited on the cathode. This process led to vertical alignment of the rGO sheets in the deposit and production of a porous deposit with a relatively rough

surface. Similarly, other studies [17, 146] reported that vertically aligned sheets were observed in the EPD of Mg^{2+} -modified GO. In contrast, when the rGO sheets were decorated with a polyelectrolyte like PDDA, an in-plane deposition of the rGO sheets and subsequent production of a relatively smooth deposit were observed due to the presence of PDDA on the basal plane (see Figure 19).

In addition to the effects of chemical decoration already mentioned, other types of treatments can also affect the microstructure. For example, in one study [142], pre-EPD ozonisation of GO was reported to change the interlayer distance between the deposited GO sheets by varying the GO oxygen functionalities. The results suggest that the types of GO functional groups may play a more important role in determining the interlayer distance than the quantity of oxygen groups.

vi. Effects of incorporation of other nanoparticles

In order to produce porous GRM structures, and to limit layer-layer restacking, several studies have used nanoparticles (i.e. carbon black [15], CNTs [151, 164], partially-unzipped carbon fibres [63], ZnS [155], CoFe_2O_4 [119], Ni [96, 120]) as inter-layer spacers between deposited GRM sheets. Lee et al. [165] reported that EPD using mixed suspensions of rGO and layered metal oxide nanosheets led to formation of porous morphologies via a house-of-cards-type stacking. In general, the additional nanoparticles in GRM films also increases the films' surface roughness [15, 50], since GRMs are characteristically thinner/flatter than most other materials, at least if folding, restacking and agglomeration are avoided. It is worth noting that the presence and interaction of secondary non-GRM particles in a suspension can affect the deposition rate. For example, Bae et al. [142] reported that enhanced interaction of functionalized

GO with Sn nanoparticles decreased the GO electrophoretic mobility and the deposition yield.

vii. Effects of post-EPD treatment

Different results have been reported for post-EPD treatment of GRM structures. On the one hand, several studies [8, 30, 68, 150, 166] have reported that post-EPD reduction or thermal annealing of GRM films leads to compaction, surface smoothing and decrease of the interlayer spacing of the deposited GRM films and fibres through removal of trapped water molecules and/or oxygen-containing functional groups. Formation of crevices [96], protruding GRM sheets edges [77, 145], and flaky surfaces [153] have been also reported as the result of post-EPD treatment. On the other hand, some studies [77, 106] have not observed significant microstructural changes after post-EPD treatment of GRM films. For example, Akhavan et al. [106] reported that post-EPD reduction of GRM films with vertically aligned sheets does not alter the films' microstructure. Therefore, it can be concluded that possible effects of any post-EPD treatment on the deposits' microstructure depends on the initial deposit morphology. For example, if the initial film morphology is porous, gases produced by a post-EPD reduction, or simply a rapid drying process, may readily escape without affecting the films' microstructure. In addition, the amount of water (or other solvent / thermally volatile) molecules trapped between the deposited-GRM layers, or the rate of heating during annealing, can determine the degree of microstructural changes induced by post-EPD treatments [9].

viii. Other factors

The EPD mode and type of electrodes used are also important factors. Firstly, in constant-current EPD, the film surface was reported to be significantly smoother

compared to constant-voltage EPD [74]. However, further study would be necessary to deduce the difference in mechanisms involved. Secondly, the type of working electrodes will control electrical conductivity, microstructure and surface roughness [9, 97] which affect the deposition process. These factors can alter the deposition rate and gas evolution at the substrates' surface and therefore affect the deposits' microstructure and thickness.

In recent studies, mechanical properties of carbon fibre-reinforced composites were improved by electrophoretically depositing GO onto carbon fibres [14, 167]. It was also found that ultrasound-assisted EPD produces thicker (160 nm vs 70 nm) and rougher (97.3% vs 37.4%) coatings of GO on de-sized carbon fibres as compared to conventional EPD. In this case, a continuous 60 W at 40 kHz ultrasound was applied onto the EPD bath during the deposition process. [14].

6.3 EPD vs other methods

Relatively few studies have compared the microstructures of GRM films prepared with EPD to films prepared with other methods. Some researchers have reported that films prepared by EPD have a rougher surface [92] and a lower degree of binding. [20], compared to the films prepared by vacuum filtration, whilst others report a similar morphology for the two techniques [9]. On the other hand, EPD deposits were found to be more uniform than rGO films made by drop-casting [87], which consisted of large clusters possibly due to Maragani effects during drying, or by an AC discharge method [98].

7. Discussion and Outlook

This review summarises the fundamentals and specific technical aspects of the EPD process for GRMs. Although there are numerous advantages of EPD as a technique to obtain GRM structures, many aspects have to be addressed to optimize the deposition. These challenges range from the difficulty of suspending GRMs to tailoring the deposition parameters to controlling side reactions during EPD, in order to achieve the desired composition, physical and chemical conformity of the films. However, many promising strategies have already been demonstrated. One of the most popular pathways to achieving the deposition of GRM in an aqueous EPD medium is to chemically oxidize and exfoliate graphite. However, the exfoliation of graphite to form GO sheets induces considerable irrecoverable damage in the sheets, which cannot be entirely reversed even on reduction. Unless the application specifically requires GO, it may be wiser to choose a different dispersion approach to produce higher quality graphene-related deposits. There is still an open question as to the nature of the ideal GRM for a given application, in terms of parameters such as size, thickness, degree of functionalisation, as well as the trade off with what can be practically processed. The most intriguing properties of graphene arise with perfectly crystalline single-layer material, but many real systems compromise this ideal significantly; in any case, any GRM deposit must intrinsically involve restacking of the individual layers to build a larger construct. Much of the literature is rather casual in its use of nomenclature, with the use of the term “graphene” potentially misleadingly applied to thicker graphitic materials; the advice and recommendations provided by the editors of Carbon, provides a useful systematic framework for future publications [54]. In the context of EPD, care

will still be needed potentially to distinguish the nature of the suspension and the final deposit.

It may be that organic exfoliation methods prove to be promising in the long run, if sufficient suspension stability and concentrations can be reliably obtained. Certainly, the type of medium affects the stability of GRM suspensions and the nature of the subsequent deposits. Organic media such as isopropyl alcohol, DMF, anhydrous 1-ethyl-2-pyrrolidinone have been used to produce metastable but useful GRM suspensions. Some of these organic media stabilize the GRM sheets via a charge transfer mechanism between solvent molecules and the GRM surfaces. Depending on the intrinsic ability of the organic medium to donate electrons, the zeta potential of GRM can either be positive or negative; further research on the mechanisms responsible for the stabilization of GRM in organic media would be valuable.

Many suspensions of GRM typically lack the stability that is necessary for EPD, particularly for unfunctionalized FLGs and rGOs that have very few stabilizing functional groups. Therefore, different additives such as metal ions, organic salts, dyes, polymers and covalently-linked molecules are being employed. These additives work by imbuing charge onto GRM surfaces. Metal salts, for example, work by imparting GRM with a positive charge that provides electrostatic stability. However, the presence of a high concentration of metal salts, increases the ionic strength possibly destabilizing the suspensions, contaminates the deposit, and encourages unwanted side reactions. Organic salts and dyes like Aluminon, CV and MV, which attach to the sheets of GRM primarily via π - π stacking, have also been used as charging additives producing charged GRM.

In some applications, co-deposition of other nanoparticles alongside GRM is essential. This hybridisation can be accomplished during EPD, via the deposition of composite particles made up of the GRM and the other nanoparticles in question, by step-by-step (layer-by-layer) EPD of the two materials, or by co-deposition using mixed suspensions. The latter process is of interest as it offers considering flexibility in the composition of the deposited film, however; the mechanisms involved are relatively more complex than in the case of single-component deposition. Typically, the additive used for stabilizing the suspension has to be compatible with all particles. However, in some instances, the co-depositing particles may themselves act as a stabiliser for the GRM [110, 168], for example by forming a relatively stable physical bond with the sheets yet having a high concentration of electrostatically stabilizing side groups. One notable example is the co-deposition of functionalized carbon black particles with rGO. This work illustrated the ease of EPD as a simple one-step technique to co-deposit both the active and conductive component for the fabrication of supercapacitor electrodes. Moreover, by dissolution of charged polymers (e.g. chitosan) in the EPD suspension, EPD can produce composite layers of GRM-polymer [53, 169]. Low voltages are usually applied to reduce unwanted side reactions that may cause the production of gas [8]. This effect must always be considered, as the release of gas from side reactions will reduce the controllability of the deposition and disrupt the desired integrity of the electrophoretic deposits. Although modulated current EPD can be useful to suppress side reactions and gas release at high voltages, this strategy has not been utilized for deposition of GRM yet.

Apart from the mechanisms governing the deposition of GRM films, it is important to look at the kinetics involved, for example using Hamaker's law; although this aspect is not usually discussed in detail in the literature, it provides a predictive framework for

designing EPD processes. Hamaker's law typically describes a linear relationship between the EPD voltage applied and the mass deposited. Deviations at long deposition times or at high deposition voltages are not uncommon, and can indicate changes in deposit conductivity, dispersion composition, dispersion aggregation state, or the influence of side reactions involving either the deposit or the medium. In addition, the thinness of GRMs relative to the Debye length, their variable orientation in an applied field, and in some cases their potential for electronic conductivity, complicate the usual simplifying assumptions about electrophoretic mobility. These factors should be explored in more detail to identify the limits to EPD stability and rate, which may largely determine the commercial viability of EPD of GRM. Low voltages can produce uniform deposits without introducing multiple complex side reactions and are therefore helpful for understanding fundamental behaviour [8].

To apply EPD of GRMs for large-scale, commercial technological application, other contributions to the costs will need to be considered, particularly the cost of suspension preparation (cost of precursors, additives etc.) and its effective yield in use. However, the use of thin films with a significant technological benefit is likely to be a cost effective route to deploying relatively expensive new materials systems. Although EPD has been successfully utilised for development of ultrathin GRM films [39, 162], the formation of such films is even more sensitive to the quality of GRM stabilisation/exfoliation in the suspension. At very low thicknesses, the continuity of the deposited film will need to be considered, since many applications rely on electron transport. Moreover, in ultrathin layers, the nature of the electrode surface will be especially important in controlling the stability and characteristics of the deposits. Overall, EPD of GRM remains a very attractive route for controlled deposition,

especially for applications that require GRM to be employed as thin films, such as solar cells, corrosion resistant coatings, transparent electrodes, field emission and charge storage devices. One of the particular attractions is that it can be applied to create a wide range of different morphologies adjusted to the contrasting needs of different applications. Many of the same concepts will be applicable to the rapidly growing research field associated with other 2d layered materials, including transition metal dichalcogenides [170], layered double hydroxides [171], and layered nitrides [172], either in isolation, or hybridised with GRMs [84].

In summary, many studies have shown that EPD is a viable process for the deposition of GRMs but the underlying mechanisms are seldom studied. Although some of the main principles involved in conventional EPD processes can also be applied, some of the processes involved in the EPD of GRM are unique and should be studied in detail. These mechanistic studies will aid in the control and optimization of the quality of electrophoretically deposited GRM, and other 2D materials, paving a giant step forwards in translating graphene-based research to commercial products.

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ACCEPTED MANUSCRIPT

Appendix

EPD particles	GRM synthesis method	Dispersion medium	GRM conc. (mg/mL)	Additives	Other particles in suspension	EPD type	Working electrode	EPD voltage or current	EPD time	EPD product	Post-EPD process	Application	Ref.
GO	H	Water	0.6	–	–	Anodic	ITO–glass	150 V	45 s	GO coating	R	Supercapacitors	[77]
GO	H	Water	0.5	–	–	Anodic	Au	6 V	60–240 s	GO coating	R	Supercapacitors	[34]
GO & rGO	H +/– R	Water	1.5	–	CB	Anodic	Stainless steel	6 & 8 V	10 min	GO, rGO & rGO–CB coatings	–	Supercapacitors	[15]
GO	CP	Isopropanol	0.2	Mg(NO ₃) ₂ ·6H ₂ O	Sn	Anodic/Cathodic	Cu	300 V	30 min	Sn–GO coating	R	Latium ion batteries	[142]
G	CP	Water	0–1	CV dyes	–	Cathodic	Stainless steel/Si	10–50 V	0–30 min	Graphene coating	–	NS	[111]
rGO	H + R	Ethylene glycol, NaF, water	NM	–	–	Anodic	Ti	10, 20 & 40 V	1–24 h	rGO coating	–	Photovoltaic devices	[157]
rGO	H + R	Isopropanol, methanol	0.05	Mg(NO ₃) ₂ /PDDA	–	Cathodic	Pt	300 V	3 & 10 min	rGO coating	–	Field emission devices/ biomaterials	[107]
rGO	H + R	Isopropanol	0.1	Mg ²⁺	–	Cathodic	ITO–glass	100–160 V	30–90 s	rGO coating	–	Field emission devices	[108]
GO	H	Water	0.01–0.1	PIHA	–	Cathodic	Cu	10–30 V	5–50 s	GO coating	–	Oxidation & corrosion resistance coatings	[127]
rGO	H + R	Water	1	–	–	Anodic	Carbon cloth +/– CNT coating	2.5 mA/cm ²	10 min	rGO coating	–	Field emission devices	[144]
rGO	H + R	Ethanol	0.2	Al(NO ₃) ₃	CNT	Cathodic	Si	20 V	2.5–10 min	rGO & rGO–CNT coating	–	Field emission devices	[92]

rGO	H + R	Ethanol	0.4	Al(NO ₃) ₃	–	Cathodic	Si	20 V	5–15 min	rGO coating	–	Field emission devices	[91]
GO–Pt	H	Tetrahydrofuran	NM	–	–	NM	Carbon Toray paper	75 V	NM	GO–Pt coating	R	Electrocatalysts	[173]
Graphene	TE+acid treatment+S	Acetonitrile	NM	–	–	Cathodic	PEDOT, Au & graphite	0–10 V	0–10 min	Graphene coating	–	Supercapacitors	[114]
rGO	TE+R	1-ethyl-2-pyrrolidinone	NM	–	CNT	Anodic	ITO-coated PET	1–5 V	30s	rGO & rGO–CNT coatings	–	NS	[87]
GO	H	Ethanol	0.5	–	–	Anodic	TiO ₂	30 V	1 min	rGO coating	R & metal NP deposition	SERRS sensors	[162]
GO	CP	Ethanol, water	0–1.5 wt. %	HY	HA	Anodic	Ti	30 V	1–5	GO–HY–HA coating	–	Biomedical implants	[133]
rGO	H+R	Ethanol	0.1	OPPD	–	Cathodic	Ni foam	50 V	NM	rGO–OPPD coating	Heat treatment	Electrochemical capacitors	[90]
rGO	H+R	Isopropanol	0.1	Mg(NO ₃) ₂ ·6H ₂ O	–	Cathodic	Ti–Si & Si	300 V	5 min	rGO coating	Heat treatment	Field emission devices	[68]
GO	H	Water	0.05	PIHA	–	Cathodic	Cu	10 V	30 s	GO & GO–PIHA coatings	R	Corrosion resistant coatings	[174]
GO	H	Water	1	–	–	Anodic	NdFeB	10 V	1–3 min	rGO coating	–	Corrosion inhibitor coatings	[49]

Graphene	CP	Water	0.1–1	MV dye	CNT	Cathodic	Stainless steel	1–50 V	2 min	Graphene & Graphene–CNT coatings	–	Supercapacitors	[112]
Graphene	CP	Water	0.5	ATA	–	Anodic	stainless steel, Pt & Si	7–10 V	1–10 min	Graphene coating	–	NS	[134]
GO	H	Water	0.1–10 wt. %	–	–	Anodic	SiO ₂ coated Si	1–30 V	1–30 min	rGO coating	Heat treatment	Transparent conductive films	[78]
rGO	CP+R	Water	NM	–	–	NM	TiO ₂ nanotube array	60 V	15–300 s	rGO coating	–	Dye-sensitized solar cells	[71]
rGO	H+R	Water, acetone	NM	Al(NO ₃) ₃ ·9H ₂ O	CNT	Cathodic	Graphite paper	30 V	30 min	rGO & rGO–CNT coatings	–	Dye-sensitized solar cells	[94]
rGCM & rGM	H+R	Isopropanol, HCl	1.25	–	–	Cathodic	Ni	50 V	2 min	rGCM & rGM coatings	–	Pseudocapacitors	[151]
rGO	H+NM	Water	0.25 wt. %	Mg(NO ₃) ₂ ·6H ₂ O	–	Cathodic	FTO–glass	30 V	5–30 s	rGO coating	Heat treatment	Dye-sensitized solar cells	[102]
Graphene	CP	Water	1	Safranin	CNT & pyrrole nanofibers	Cathodic	Ti	30 V	1–10 min	Graphene, graphene–CNT & graphene–pyrrole coatings	–	Supercapacitors	[113]
rGO	H+R	Acetonitrile	50	Mg(NO ₃) ₂ ·6H ₂ O	–	Cathodic	ITO–glass	70 V	2 min	rGO coating	Surface functionalization	Electrochemical biosensors	[103]
rGO	H+R	Isopropanol	0.5	Mg(NO ₃) ₂ ·6H ₂ O	–	Cathodic	Ti	150 V	10 min	rGO coating	–	Field emission devices	[101]

Graphene	Arc discharge	Isopropanol	0.07	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	–	Cathodic	Si	300 V	3 min	Graphene coating	Sn NPs sputtering	Field emission devices	[98]
rGO	H+R	Water	NM	–	–	Anodic	ITO–glass	4 V	10–30 s	rGO coating	EP of a polymer & EPD of Pt NP	Electrochromics & dye-sensitized solar cells	[72]
rGO	H+R	DMF	0.1 wt. %	$\text{Mg}(\text{Cl})_2 \cdot 6\text{H}_2\text{O}$	–	Cathodic	Si	10–40 V	5 min	rGO coating	–	Field emission devices	[109]
GO	H	NM	NM	NM	–	NM	Steel	NM	NM	GO coating	R	NS	[166]
GO, rGO & rGO–CNT	H+R	Water	NM	LAA	–	Anodic	Glassy carbon & ITO– glass	4 V	30–90 s	GO, GO–CNT, rGO, rGO–CNT coatings	R	Supercapacitors	[175]
rGO	Unzipping CNT+R	DMF, Water	NM	–	–	Anodic	Graphitic tip	1–2 V	NM	rGO fiber	Heat treatment/ R	NS	[30]
rGO	H+R	Isopropanol	0.1–0.2	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	–	Cathodic	ITO–glass	100–160 V	1 min	rGO coatings	–	Field emission devices	[39]
Graphene	CVD	Isopropanol	0.005	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	–	Cathodic	Si	100 V	15	Graphene coating	Chemical doping with Au	Field emission devices	[85]
GO	H	Isopropanol	0.4	$\text{Ni}(\text{NO}_3)_2$	–	Cathodic	Stainless steel	60 V	NM	GO & NiO–GO coatings	Heat treatment	Supercapacitors	[96]
Graphene	CP	Water	NM	$\text{Mg}(\text{NO}_3)_2$ & polyacrylic acid	–	Cathodic	Ni Foam	50 V	13 min	Graphene coating	Heat treatment	Supercapacitors	[20]

GO	H	Water, Ethanol	0.25 wt. %	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	–	Cathodic	FTO–glass	10 V	10 s	GO coating	Heat treatment	Dye-sensitized solar cells	[31]
GO	H	Water	4.56	–	–	Anodic	Si	20–45 V	1 hr	GO coating	–	Solid lubricants	[76]
GO	H	NM	1	–	CNT	Anodic	Carbon cloth	6 V	NM	GO & GO–CNT coatings	R	Supercapacitors	[124]
GO	CP	Ethanol	0–5	–	HA NP	Cathodic	Ti	30 V	1–5 min	GO & GO–HA coatings	Heat treatment	Biomedical implants	[50]
rGO	H+R	Water	0.015	–	0	Anodic	Carbon fabric	2.4 mA/cm ²	5–600 s	rGO coating	–	Field emission devices	[158]
Graphene	CP	Isopropanol	NM	$\text{Ni}(\text{NO}_3)_2$	–	Cathodic	Ti	20 V	30 min	Graphene coating	EP of pyrrole	Supercapacitors	[95]
GO	H	Isopropanol	1	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	–	Cathodic	Ti	150 V	4 min	GO coating	Laser treatment & thermal annealing	Field emission devices	[104]
F-rGO	H+R	DMF, acetonitrile	0.8	–	C60, C70, CNT	Anodic	FTO–SnO ₂	200 V	2 min	Binary & ternary composite coatings	–	Optoelectronic devices	[176]
GO & rGO	H+R	Water	1	–	–	Anodic	ITO–glass	0.1–1.0 mA	1–15 min	GO & rGO coatings	–	NS	[74]
rGO	H+R	Water	NM	–	–	Anodic	Stainless steel	3 V	15 min	rGO coating	Etching of rGO film, Heat treatment	NS	[29]

rGO	H+R	Water	NM	–	–	Anodic	ITO–glass	1.25 mA	75 s	rGO coating	CBD of Co ₃ O ₄ , Repetition of the steps	Electrodes for sustained oxygen evolution reaction	[10]
rGO	H+R	Water	0.2	–	–	NM	FTO–glass	0.5 mA/cm ²	NM	rGO coating	EPD of CoS NP. Repetition of the steps.	Dye-sensitized solar cells	[70]
GO	H	Water	0.5	–	–	Anodic	Au–Ti–glass	150 V	20 s	rGO coating	–	Lysozyme detection	[40]
MnO ₂ –rGO	H+R	Acetonitrile, water	NM	Li ⁺	–	Anodic	ITO	25 V	NM	Li–MnO ₂ –rGO coatings	–	Supercapacitors	[165]
GO	H	Water	1.5	–	–	Anodic	Ni foam	10 V	1–10 min	rGO coating	ED of MnO ₂	Supercapacitors	[136]
rGO & rGO–Pt	H+R	Water, DMF	NM	–	–	Anodic	ITO–glass	4 V	5–30 s	rGO & rGO–Pt coatings	EPD of Pt NP	Dye-sensitized solar cells & hydrogen generation	[148]
GO	H	Water	0.4	Ni(NO ₃) ₂	–	Cathodic	Ni foam, ITO, stainless steel & Pt	5–10 V	30–600 s	rGO–Ni(OH) ₂ coating	–	Supercapacitors	[97]
GO	H	Water	3×10 ^{–5} –3×10 ^{–2} wt. %	–	–	Anodic	Carbon fabric	5 V	1 min	GO coating	R	NS	[16]
F-rGO	H	DMF	2	–	–	Anodic	SnO ₂ –FTO	200 V	2 min	Iodophenyl & Porphyrin–functionalized rGO films	–	Photoactive devices	[126]
rGO	H+R	Water	NM	–	–	Anodic	FTO electrode	3 V	60 s	rGO coating	Heat treatment	Dye-sensitized solar cells	[178]

Graphene	Exfoliation of graphite using CTAB	Water	0.1 & 1	–	–	Cathodic	Au–glass	6 V	1–10 min	Graphene coating	–	NS	[118]
GO	CP	Water	0.2 & 0.4	–	–	Anodic	ITO–glass	3–20 V	30–600 min	GO coating	R	NS	[8]
rGO	H+R	Acetone, Ethanol	NM	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	CNT	Cathodic	Graphite paper	30 V	5	rGO & rGO–CNT coatings	–	Supercapacitors	[93]
rGO	H+R	Ethanol	0.2	–	–	Cathodic	ITO–glass	50 V	3 hr	rGO coating	–	NS	[116]
GO	H	Isopropanol	1	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	–	Cathodic	Ti	150 V	4 min	GO coating	R	Field emission devices	[86]
rGO	H+R	Isopropanol	NM	Mg^{2+}	–	Cathodic	Ti–coated Si	300 V	3 min	rGO	Heat treatment	Field emission devices	[105]
GO	H	Water	1.5	–	–	Anodic	Cu, Ni, Al, stainless steel & Si	10 V	1–10 min	rGO coating	–	NS	[9]
GO	H	Water	0.1	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	–	Cathodic	Graphite rod	30 V	10 min	GO coating	R	Single-DNA electrochemical biosensing	[17]
GO	H	Isopropanol	1	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	–	Cathodic	Stainless steel	150 V	2 min	GO coating	R	Antibacterial coatings	[106]
GO	H	Water	0.35	–	–	Anodic/Cathodic	CASL coated stainless steel	3 & 15 V	5–10 min	GO & rGO coatings	Removal of the sacrificial layer	NS	[79]

GO & GNR	H/Unzipping of CNFs	Isopropanol	0.4	$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	–	Anodic/Cathodic	Stainless steel	30 & 60 V	5 & 10 min	GO, GNR, & GNR–MnO ₂ coatings	Heat treatment	Supercapacitors	[63]
GO	H	DMF	0.01	–	–	Anodic	Glassy carbon	120 V	3 min	GO coating	R	Electrochemical platform for TNT sensing	[37]
F-graphene	A self-generating template route	Isopropanol	0.1	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	–	Cathodic	FTO-glass	50 V	10 min	$\text{Co}(\text{OH})_2$ –Graphene coating	Heat treatment	Dye-sensitized solar cells	[99]
GO	H	Water	1.5	–	–	Anodic	Carbon fibre	15 V	40 min	GO-coated carbon fibres	Immersed in water	Electromagnetic interference shielding of cement-based composites	[167]
Graphene	CP	Ethanol	0.01 wt.%	–	Ag-HA NP	Cathodic	Ti	60 V	2 min	Ag–HAP–graphene coating	–	Antibacterial coatings	[51]
Graphene	NM	Water	1.5	Laccase, glucose oxidase	–	Anodic	Glassy carbon 3D micropillar array	10 V	3 min	Enzyme–graphene coating	–	Micro-biofuel cells	[18]
GO	H	Water	0.25	–	–	Anodic	Carbon fibre	20 V	20 min	GO-coated carbon fibres	–	Fibre-reinforced composites	[14]
GO–silica	H	Acetonitrile	0.03	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	–	Cathodic	ITO-glass	120 V	2 min	GO–silica coating	Enzyme Immobilization	Urea biosensing	[41]
GO	H	Water	1.5	–	–	Anodic	Stainless steel	4 V	5 min	GO coating	R, ED of MnO ₂	Supercapacitors	[152]

rGO	H+R	Isopropanol	0.05	–	–	NM	ITO	20 V	5 min	rGO coating	ED of Ag	H ₂ O ₂ electrochemical sensors	[42]
Graphene	CP	Isopropanol	0–15	Polyvinyl butyral	TiO ₂ NP	Cathodic	Stainless steel	5–50 V	30 s	TiO ₂ –graphene coating	–	Photo-generated cathodic protection	[154]
GO	H	Water	0.05–1	Chitosan, vancomycin	–	Cathodic	Ti	10 V	10 min	Chitosan–GO coating	–	Drug delivery	[53]
rGO	H+R	Water	0.1	–	–	Anodic	TiO ₂ nanotube arrays	4 V	1–10 min	rGO coating	–	Photoanodes for water splitting, photocatalysts	[19]
GO	H	Water	1.5	–	–	Anodic	Stainless steel	5 V	10 min	GO coating	R, ED of of Ni–Fe–HCF	Supercapacitors	[140]
GO	H	Water, ethanol	0.5	CuSO ₄	–	Anodic, cathodic	Au	50 V	1–3 min	rGO and rGO–Cu NPs coatings	–	Nonenzymatic glucose sensing	[110]
Graphene	CP	1-methyl-2-pyrrolidone	0.5	–	CNT	Anodic	Al roll	500 V/cm	1.5 cm/s	CNT–graphene coating	–	Lithium ion batteries	[5]
GO	H	Water	1 wt. %	–	–	Cathodic	Glass substrate back covered with Cu tape	30 V	5 min	rGO coating	Annealing, ED of ZnO	Optoelectronics	[139]
Graphene	CP	Ethanol	0.05	Mg(NO ₃) ₂	–	Cathodic	ITO–glass	150 V	15–60 s	Graphene coating	EPD of CNT	Field emission devices	[12]

GO	CP+Sonication	Water	0.1–1	–	–	Anodic	Cu	10–30 V	0–30 min	GO coating	R	NS	[6]
GO	H	Water	0.5	–	–	Anodic	FTO	50 V	30 s	GO coating	Spin coating of ZnO QDs, heat treatment	Ethyl acetate chemical sensor	[43]
rGO	H+R	Water	0.005	Mg(NO ₃) ₂ ·6H ₂ O	–	Cathodic	Transparent conductive oxide-glass	60 V	2 min	rGO coating	Heat treatment, antibody immobilisation	Immunosensor for food toxin detection	[100]
GO	H	Water	1.5	-	-	Anodic	Carbon felt	0.75-6 mA/cm ²	5-40 mins	GO coating	R	Electro-fenton reaction	[130]
GO	H	Water	1	-	-	Anodic	Cu	30 V	30 mins	GO coating	R	rGO synthesis	[58]
rGO	H+R	Water	1	-	-	Anodic	Stainless steel	3 V	5 min	rGO coating	-	Supercapacitors	[143]
GO	NS	Water	2	LiClO ₄	-	Cathodic	Al alloy (Mn/Fe/Cu, forging)	0.6-0.12 V	5-20 mins	GO-Anti-reflective coating	R	Graphene-based anti-reflective coating	[47]
Graphene layers (30-50 layers)	CP	Ethanol	0.01 wt% (of suspension)	-	HA	Cathodic	Ti	60 V	2 mins	Graphene layer-HA composite coating	-	Corrosion stable biocomposites	[11]
GO	H	Water	0.5	-	-	Anodic	TiO ₂ nanotube foil	-1.5-1 V (CV, 50 mV/s)	15 CV cycles	GO coating	SILAR deposition of CdS	Photocatalytic/Photoelectrochemical electrodes	[179]

GO	H	Water	1	FeCl ₂ and FeCl ₃	-	Cathodic	Stainless steel	2.5 V	4 mins	GO-Fe ₃ O ₄ composite coating	R	Supercapacitors	[57]
GO	H	Water	0.25	-	-	Anodic	Carbon fibre tow	20 V	20 min	GO coating	Epoxy infiltration	Carbon fibre composites	[131]
rGO-MWCNT	H+R	Water+Ethanol	0.225 mg (rGO)/mL	Dodecyl benzene sulfonic acid, (Mn(OAc) ₂ ·4H ₂ O)	MWCNT	Anodic	Steel	0.5-1.5 V	Deposited till charges reach 1.6 C/cm ²	MnO _x /rGO-CNT film	-	Supercapacitors	[35]
rGO	H+R	Water	NM	-	-	Anodic	Stainless steel	5-7 V	5 s-10 mins	rGO coating	Cathodic EPD of quarternized polyetherimide	EMI shield	[46]
GO	H	Water	1-4	-	-	Anodic	Cold-rolled carbon steel (0.02% C, 0.01% P, 0.006% S, 0.004% Si, and 0.2% Mn)	4 V (15 mm)	10 s	GO coating	-	Anti-corrosion coating	[48]
GO-Co(NO ₃)·6H ₂ O	H	Absolute ethanol	1 mg (GO)/mL	Co(NO ₃)·6H ₂ O	-	Cathodic	Cu	60 V	200 s	Co ₃ O ₄ @graphene coating	Heat treatment	Li-ion batteries	[168]
GO	H	Isopropyl alcohol	1	Mg(NO ₃)·6H ₂ O	LiFePO ₄	Cathodic	Carbon cloth	90 V (1 cm)	NS	Lithium iron phosphate/reduced graphene oxide Composite coating	Thermal annealing	Li-ion batteries	[132]
rGO	H+R	Isopropyl alcohol	0.05	Mg(NO ₃)·6H ₂ O	-	Cathodic	Ag patterned on glass	30 V (6 mA, 3 mm)	5 mins	rGO coating	Thermal annealing, ZnO quantum	Field Emitter	[180]

											dot decoration		
GO	H	Acetyl acetone	NM	–	TiO ₂	NM	FTO	NS	NS	TiO ₂ –GO coating	Sintering	Dye sensitised Solar cell	[33]
GO	H	Absolute ethanol	1	Fe(NO ₃) ₃ ·9H ₂ O, Zn(NO ₃) ₂ ·6H ₂ O	-	Cathodic	Cu	60 V (1 cm)	300 s	Zn(OH) ₂ –Fe(OH) ₃ –GO coating	Thermal annealing	Li-ion batteries	[181]
GO	H	Water	1.5	-	-	Anodic	3 D Ni foam	10 V	NS	GO coating	Anodic deposition of MnO ₂	Supercapacitors	[36]
rGO	H+R	Isopropyl alcohol	0.5	Zn(NO ₃) ₂ ·9H ₂ O	-	Cathodic	Ti	150 V	600 s	rGO film	-	Field emitter	[38]
rGO	H+R	Acetonitrile	0.02	-	F-Au NP	Cathodic	ITO	NS	NS	rGO–F-Au NP composite	Cholesterol oxidase immobilisation	Free cholesterol biosensing	[44]
Ga–RGO–TiO ₂ nanocomposite	H+R	Water	0.1	-	-	NS	ITO	NS	NS	Ga–RGO–TiO ₂ thin film	-	Photoelectrocatalytic cell	[177]

ATA: Aurintricarboxylic acid ammonium salt; **CASL:** Cellulose acetate sacrificial layer; **CB:** Carbon black; **CBD:** Chemical bath deposition; **CNT:** Carbon nanotubes; **CP:** Commercial product; **CTAB:** Cetyltrimethylammonium bromide; **CV:** Hexamethylpararosaniline chloride; **DMF:** Dimethylformamide; **ED:** Electrodeposition; **EP:** Electropolymerization; **F-:** Functionalized-; **FTO:** Fluorine-doped tin oxide; **GNR:** Graphene nanoribbons; **H:** (Modified) Hummers' method; **HA:** Hydroxyapatite; **HCF:** Hexacyanoferrate; **HY:** Hyaluronic acid; **ITO:** Indium tin oxide; **LAA:** L-ascorbic acid; **MV:** Methyl violet; **NM:** Not mentioned; **NP:** Nanoparticle; **NS:** Not specified; **OPPD:** p-phenylene diamine **PDDA:** polydiallyldimethylammonium chloride; **PEDOT:** poly 3,4-ethylenedioxythiophene; **PET:** Polyethylene terephthalate **PIHA:** polymeric isocyanate crosslinked with hydroxy functional acrylic adhesive; **QD:** Quantum dots; **R:** Reduction; **rGCM:** rGO–CNT–MnO₂ nanocomposite powder; **rGM:** rGO–MnO₂ nanocomposite powder; **S:** Sonication; **SERRS:** Surface enhanced resonance Raman spectroscopy; **TE:** Thermal expansion.

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Vitae

Mani Diba received a B.Sc. degree (2010) in Materials Engineering from Isfahan University of Technology (Iran) and a M.Sc. (Hons.) degree (2012) in Advanced Materials and Processes from University of Erlangen-Nuremberg (Germany). He performed his M.Sc. thesis at the University of Erlangen-Nuremberg and Imperial College London focusing on the electrophoretic deposition (EPD) of nanomaterials. Since 2013, he has been pursuing his PhD degree in the Department of Biomaterials at Radboud University Medical Centre (The Netherlands). During his PhD studies, he has been a visiting researcher at Harvard University and Max Planck Institute of Colloids and Interfaces. His current research focuses on reversible assembly of nanoparticles.

Derrick Fam received his PhD in 2012 from Nanyang Technological University (NTU, Singapore) during which he worked on transistors based on carbon nanotubes and graphene, and various different deposition techniques like Chemical Vapour Deposition (CVD) and

Atomic Layer Deposition (ALD, in collaboration with Georgia Institute of Technology). Following which, he was a research fellow working with NTU and Hebrew University of Jerusalem (HUJI, Israel). He is currently a postdoctoral fellow from the Agency for Science, Technology and Research (A*STAR, Singapore) in Imperial College London. His research focus is on the fundamentals and electronic applications of carbon nanomaterials including charge storage and semiconducting devices.

Aldo R. Boccaccini is a Professor of Biomaterials and Head of the Institute of Biomaterials at the Department of Materials Science and Engineering, University of Erlangen-Nuremberg, Germany. Previously, he was a Professor of Materials Science and Engineering at Imperial College, London, where he is currently a Visiting Professor. His research activities are in the broad area of glasses, ceramics, composites and porous materials for biomedical, functional, and/or structural applications. He has developed the electrophoretic deposition (EPD) technique for production of nanostructured materials, composites, and functional coatings.

Milo Shaffer is a Professor of Materials Chemistry at Imperial College, London, and Co-director of the London Centre for Nanotechnology. He has extensive experience in carbon and inorganic nanomaterials synthesis, modification, characterization, and application. He has developed and studied a wide variety of nanocomposite systems, including both structural matrices and conducting polymers for electrochemical and photovoltaic applications.

Figure 1. Schematic illustration of a typical EPD setup and an example of a GRM coating. Depending on the surface charges of the GRM, an anodic (if the particles are negatively charged) or cathodic (if the particles are positively charged) EPD occurs.

Figure 2. Number of articles published regarding graphene-based materials and the annual contribution of the EPD technique in this field in the last 5 years (The values were obtained from Web of Science® database in March 2015 using graphene, EPD and electrophoretic deposition as keywords).

Figure 3. An overview of inputs, outputs and possible side reactions for the EPD of GRM (Images are reproduced from Ref. [8], [29] and [30] with permission from Elsevier, American Chemical Society (Copyright 2014), and IOP Publishing Ltd (Copyright 2012), respectively).

Figure 4. Typical structure of A. bwGO with carboxylic acid and ketone groups on the edges and epoxies and hydroxyls located on the basal plane and B. OD which is a highly oxidized fragment that is bound to the surface of the bwGO (reproduced from Ref. [66] with permission from John Wiley and Sons).

Figure 5. Zeta potential values of graphene sheets in different organic solvents; BzCl: benzoyl chloride , DCB:1,2-dichlorobenzene, GBL: 4-butyrolactone, CYC: cyclohexanone, DMF: N,N-dimethylformamide, NMP: N-methyl- 2-pyrrolidone, DMA: N,N-dimethylacetamide, TMU: tetramethylurea, PYR: pyridine, and BzAm: benzyl amine. Sheets derived from graphite with flake size of about 500 μm sonicated in the different organic solvents investigated (initial loading of 5 mg mL^{-1} before sonication for 1.5 hrs and centrifugation). (Reproduced from Ref.[83] by permission of The Royal Society of Chemistry).

Figure 6. Deposit thickness as function of EPD time for GO concentrations of (a) 0.4 mg/mL and (b) 0.2 mg/mL in suspension (EPD voltage 5 V). The dashed lines represent linear regression trend lines, R^2 is the coefficient of determination, d is the film thickness and t is the deposition time (Reproduced from Ref. [8] with permission from Elsevier).

Figure 7. Schematic showing the retardation force (r) and the force from the electric field exerted on a single charged GRM particle. When $F=r$, the particle experiences maximum velocity, $v_{\max}$, as illustrated in Equations (5) and (6) (Redrawn from Ref. [108] by permission from Elsevier).

Figure 8. (a) Deposition yield and (b) electric current as function of deposition time for EPD of graphene oxide-polymer composite coatings (Reproduced from Ref. [127] with permission from Elsevier).

Figure 9. (a) XPS showing GO reduced by filtration (black), EPD-GO film (red), EPD-GO film after annealing at 100 °C in air (blue) and CReGO (green) (b) FTIR spectra of GO films processed via different routes (Reprinted with permission from Ref. [9]. Copyright 2010 American Chemical Society).

Figure 10. Redox potentials (vs the Standard Hydrogen Electrode (SHE)) of water with respect to pH. As the pH becomes higher the reduction potential increases in negativity and vice versa (redrawn from Ref. [141] with permission from John Wiley and Sons).

Figure 11. Potential window for common suspension media (DMSO: Dimethyl sulfoxide, DMF: N,N-Dimethylformamide, ACN: Acetonitrile and NMP: N-Methyl-2-pyrrolidinone used in EPD measured on a bright Pt electrode vs a solvent-independent ferrocene couple) (redrawn from Ref. [141] with permission from John Wiley and Sons).

Figure 12. SEM micrographs showing cross-sections of GRM (a) film and (b) fibre products of EPD (Reproduced with permission from Ref. [9] Copyright 2010 American Chemical Society, and Ref. [30] Copyright 2012 IOP Publishing Ltd).

Figure 13. Some examples of EPD-derived morphologies of GRM composites seen in A. SEM of rGO/MWCNT/MnO₂ (inset is a higher magnification showing the MWCNT with the rGO flakes). B. HRTEM image of the rGO/MWCNT/MnO₂ showing a MnO₂ nanoparticle decorated surface, C. SEM of electrochemically reduced GO with wrinkles and D. SEM showing MnO₂ particles on wrinkled electrochemically reduced GO (Reproduced from Ref. [151] and [152] with permission from Elsevier).

Figure 14. (a) Low magnification SEM micrographs of a graphene coated carbon fabric; High magnification SEM images of a single carbon fibre (b) without and (c) with graphene coating; (d) High magnification SEM micrograph of the surface morphology of a graphene coated carbon fibre (Reproduced from Ref. [158] with permission of The Royal Society of Chemistry).

Figure 15. SEM micrographs of (a, and c) bare and (b, d, and e) rGO coated nickel foams (Reproduced from Ref. [90] with permission of Elsevier).

Figure 16. SEM micrographs of a GRM coated surface obtained at (a) 1 kV and (b) higher SEM accelerating voltages (Reprinted with permission from Ref. [162]. Copyright 2012 American Chemical Society).

Figure 17. SEM micrographs of (a) surface and (b) cross-section of GO films deposited using 15 V EPD voltage. The arrow specifies a possible site of gas evolution (Reproduced from Ref. [8] with permission from Elsevier).

Figure 18. (a) Schematic diagram showing stacking of GO sheets as function of pH. Schematics (b and c) and scanning electron microscopy images (d and e) of films with rug-like (b and d) and brick-like (c and e) microstructures (Reprinted with permission from Ref. [79]. Copyright 2010 American Chemical Society).

Figure 19. (a) Schematic diagram of EPD mechanisms of Mg²⁺ ion and polyelectrolyte functionalized rGO sheets. SEM images of films deposited using suspensions of Mg²⁺ ion (b-d) and polyelectrolyte (e-g) functionalized rGO sheets (Reproduced from Ref. [107] with permission of The Royal Society of Chemistry).

Table 1. Advantages and limitations of EPD for deposition of GRM.

Advantages	Limitations
<ul style="list-style-type: none"> •Cost-effective [3] •Simple equipment [3] •Size-scalability [4-6] •Uniformity of deposit (Section 6) [7] •Dense packing of deposit (Section 6.1) [8] •High and controlled deposition rate (Section 3) [9] •Predictable deposition kinetics (Section 3) [8] •Controlled thickness of deposits (Section 3) (single layer to hundreds of microns) [7] •Deposition at room temperature [5, 8] •Possibility of sequential- and co- deposition of different particles (Section 6.2) [10-12] •Possibility of continuous production [5, 13, 14] •Possibility to produce porous graphene-based deposits (Section 6.1) [15] •Possibility to use flexible and complex substrates.[7, 16-19] •Simultaneous reduction of GO (Section 5.1) [7, 9] 	<ul style="list-style-type: none"> •Need for a stable suspension with sufficient particle surface charge (Section 2) [7] •Need for electrically conductive substrate [7] •Limited thickness of insulating deposits (e.g. GO) (Section 3.2) [20] •Possibility of side electrochemical reactions (Section 5) [8]

Table 2. Overview of key EPD parameters and typical conditions used for EPD of GRM.

Suspension-related		Electric field-related	
Particle type	GO, rGO, pristine graphene, & composite particles	Applied voltage	1-300 V
Particle concentration in suspension	0.01-5 mg/ml	Deposition time	Few seconds to few hours
Particle net charge (zeta potential)	-50 mV to + 50 mV	Electrodes	Stainless steel, ITO, FTO, Si, Au, Pt, Ni, graphite, Ti, Cu, Au, & carbon fabrics
GRM lateral size	1 nm-50 μ m	Inter-electrode distance	Few millimetres to few centimetres
Charging agents	Metal salts, polyelectrolytes, & ionic dyes	Electrode area	Tens of mm ² to tens of cm ²
Co-EPD particles	CNT, HA, Sn, CB, and fullerene		
Medium	Water, ethanol, isopropanol, acetone, acetonitrile, & DMF		

CNT: Carbon nanotube; **HA:** Hydroxyapatite; **CB:** Carbon black; **DMF:** Dimethylformamide; **ITO:** Indium tin oxide; **FTO:** Fluorine-doped Tin oxide.