

# Graphene Related Materials Preparation Using EPD

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**Abstract:** In 2008 graphene was one of the most expensive material on the earth. But now graphene was sell in large quantities. This is because of evolution of preparation of graphene methods. Now a days there are many methods are there to prepare graphene and garphene related materials. One of the efficient method is Electro phoretic deposition. In this review we will see how the graphene is prepared using electrophoretic deposition and grapheme related materials are also prepared using electrophoretic deposition.

**Keywords:** Electrophoretic technology and Grapheme.

## 1. Introduction

Electrophoretic deposition [1] is a colloidal processing technique that allows not only to shape free standing object but also allows to deposit thin films and coatings on substrates. Electrophoretic deposition was first used for traditional methods but now it is used for modern technology and research purposes. Electrophoretic deposition method has numerous advantages over the other deposition methods. Graphene related materials are now has many properties and also used in many industrial applications and in reasearch fields and also in emerging technology. The aim of this review is to present advantages of the Electrophoretic deposition technique in the fabrication of graphene related materials. The mechanisms and kinetics of graphene-based Electrophoretic deposition technique are discussed, followed by a summary of the important progress made in recent 5 years. Furthermore, we sum up the graphene-based materials prepared by Electrophoretic deposition, the corresponding Electrophoretic deposition conditions, as well as their applications such as super capacitors, solar cells, sensors, coatings, etc. EPD-processed graphene related material structures have been useful for many industrial appications such as bioelectric sensory devices [2] optical electronics and ultrafiltration processes, photovoltaic cells, energy storage, as well as electromagnetic interference shielding, anti-receptive and corrosion resistant coating. Based on the current trend and the promising potential of the Electrophoretic deposition technique, further applications of Electrophoretic deposition prepared Graphene related materials structures can be anticipated in the near future. For example, Graphene related materials have recently been attracting attention in more biological contexts, such as biomedical

implants, drug delivery and tissue engineering

## 2. Mechanisms of electrophoretic deposition

There are many mechanisms in which the particle come closer and form a rigid structure. Electrophoretic deposition should carry out a two-step process where particle first migrate to the substrate due to the applied electric field and due to the chemical reaction deposition layer is formed [3]. Electrophoretic deposition can be applied to any colloidal system with the suspended particles size <30 mm. The Electrophoretic deposition of graphene based materials consists of two steps, electrophoresis and deposition. Electrophoresis happens when the electric field is applied to the graphene suspension, the charged graphene flakes move toward the oppositely charged electrode driven by the electric force, subsequently, the deposition process occurs on the electrode surface where the graphene flakes accumulate under the electric force.

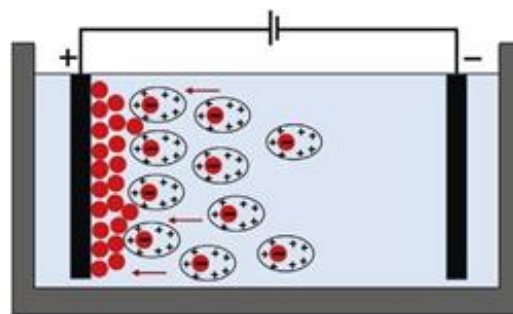


Fig. 1. Grapheme flakes accumulate under the electric force

The process parameters can be easily manipulated to adjust the chemical and morphological conformation of the deposit with considerable flexibility. Electrophoretic deposition in its simplest form requires the application of an electrical potential to electrodes immersed in micro particle dispersion. Two sub-processes take place:

- Colloidal particles suspended in a liquid medium migrate under the influence of an electric field;
- Colloidal particles are deposited onto the electrode and form a stable suspension.

A typical Electrophoretic deposition setup consists of a working and a counter electrode linked to a power supply

providing an electric field between the two electrodes (Fig. 1). The applied electric field can be either produced in direct electric current mode (DC-Electrophoretic deposition) or in a modulated electric current mode.

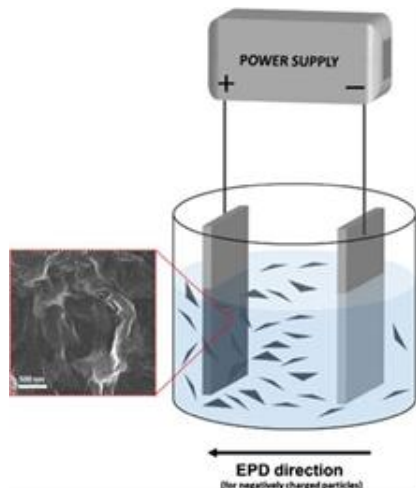


Fig. 2. EPD direction

The modulated current mode can be in the forms of alternating current (AC-Electrophoretic deposition) or pulsed-direct current (pulsed-DC Electrophoretic deposition). Generally, positively charged particles deposit on the cathode (cathodic Electrophoretic deposition) and negatively charged particles on the anode (anodic Electrophoretic deposition). 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. In Electrophoretic deposition processes, the quantity and quality of deposits can be accurately controlled by the Electrophoretic deposition parameters, which can be broadly divided into two groups related to the electric field and suspension. Despite this increasing interest in the Electrophoretic deposition of Graphene related materials, a comprehensive treatment of the subject covering the fundamentals and practical aspects of this field is not available. While a previous review paper covered Electrophoretic deposition of Graphene related materials from the applications point of view, this review paper is intended to provide an overview of the fundamentals and specific technical aspects, including information on Graphene related materials suspensions, Electrophoretic deposition 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 Electrophoretic deposition, there is a distinction between the originally suspended materials and the final deposit, including after any post-processing. The literature can, therefore, often be confusing or difficult to compare. Nevertheless, an agreed common nomenclature for the initial Graphene related materials is a useful starting point.

### A. EPD apparatus

A typical Electrophoretic deposition equipment for graphene deposition [4]. A stable colloidal suspension was prepared and two electrodes are immersed in the suspension in parallel. When deposition on both side of the plate (working electrode) is needed, two counter electrodes can be used, where the two counter electrodes and one working electrode are aligned in parallel with the working electrode in the middle. The substrate can be in an arbitrary shape or be patterned to a certain morphology. However, this setting has the disadvantage of low yield that can only produce one piece of product at once. Kwon et al. developed an Electrophoretic deposition setting with several working and counter electrodes alternately aligned, which greatly increase the yield of Electrophoretic deposition. In addition, shorten the deposition time can also reduce the side reaction of graphene agglomeration technique has also been widely used to enhance the mechanical properties of carbon fibers, where the Electrophoretic deposition is mostly carried out on the carbon fiber fabrics. However, this technique is limited to the deposition area. Wang et. al. proposed an Electrophoretic deposition setting, which can achieve the continuous Electrophoretic deposition of carbon fibers. In addition, ultrasonication is applied to the Graphene oxide suspension during the Electrophoretic deposition process to avoid the aggregation of the Graphene oxide under the loaded voltage. The proposed Electrophoretic deposition equipment shows a great potential for the scalable production of graphene-based materials by Electrophoretic deposition.

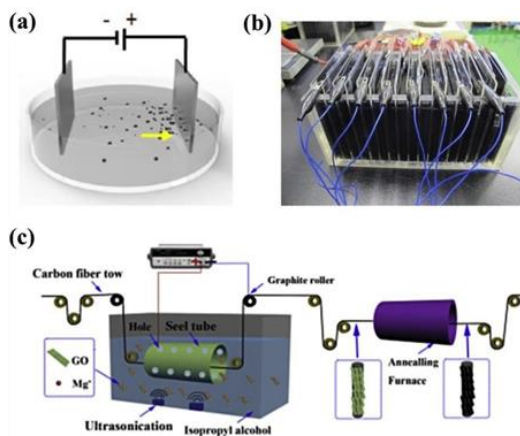


Fig. 3. (a), Typical Electrophoretic deposition equipment for deposition of Graphene oxide with a positive and a negative electrodes aligned in parallel (b), Electrophoretic deposition equipment that can produce 16 pieces of Graphene oxide/CNT coated carbon fabrics simultaneously. (c), Equipment of continuous Electrophoretic deposition of graphene on carbon fibers

An overview of data summarised from a wide range of studies concerning EPD[5] of Graphene related materials, including the specific parameters used, is collated in Table S1 (see the Supporting Information) 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 resulting deposit. 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 summarised quantitatively in the Hamaker's equation. Much of this work draws heavily on earlier research using Electrophoretic deposition of other sp<sup>2</sup>-hybridised carbon nanomaterials, particularly carbon nanotubes, as well as other nanomaterials (including metals, oxides and other functional quantum dots); 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 Graphene related materials,

*B. Structure of graphene oxide*

Graphene oxide suspensions generally consist of solvated single layers and highly oxidized carbon-based sheets. The oxygen-containing groups are typically epoxies, carboxyls and hydroxyls [6], found randomly attached to both sides of the Graphene oxide sheets. This phenomenon results in a primarily amorphous surface structure with a surface roughness of around 0.6 nm. X-ray photoelectron spectroscopy (XPS) data reveal that typically, hydroxyls and epoxies are found on the basal plane of Graphene oxide while carboxyls, phenols and ketones are found on the edges. The oxygen content from these moieties is between 16.6 and 33 at%, and the groups are thermally unstable, decomposing in air from around 100 LC to CO<sub>2</sub>, CO, and adsorbed H<sub>2</sub>O. There continues to be some ambiguity over the exact structure of Graphene oxide, due to the variation in graphite feedstock and production routes, as well as the heterogeneity of the product. One problem is that many Graphene oxide samples, particularly commercial materials produced in large batches, consist of 2 fractions: large sheets with oxygen-containing groups that are covalently functionalized, and smaller highly oxidised fragments which are termed as oxidative debris (OD) or carboxylated carbonaceous fragments. Electrophoretic deposition can be applied to any solid [7] with certain particle surface charges in a stable colloidal suspension. Since from the scientists developed the way to exfoliate the graphite (or graphite oxide) layers and disperse graphene (or) Graphene oxide in an aqueous, an organic or a mixer solution stably, the Electrophoretic deposition of graphene had become possible. Presents a summary of the studies reviewed on the graphene materials prepared by Electrophoretic deposition, collating the relevant parameters on Electrophoretic deposition, including the suspension medium, Electrophoretic deposition voltage, Electrophoretic deposition time, and applications. Graphene oxide and RGO are mostly used as graphene precursor for Electrophoretic deposition due to the easy preparation of graphene dispersion derived from the oxygen-containing functional groups. Among them, RGO is mostly reduced from the Graphene oxide in different approaches: chemically reduced before the Electrophoretic deposition process, electrochemically reduced during the EPD process and post-reduced after the EPD process. several types of solvents have been used to disperse, RGO or modified graphene flakes for

EPD, including DI water, isopropyl alcohol (IPA) ethanol dimethylformamide (DMF), N-Methyl-2-pyrrolidone (NMP) and acetone/ethanol mixture. Aqueous solutions are more widely used for the Electrophoretic deposition of graphene than organic solutions because it has the advantages that lower Electrophoretic deposition voltage can be used in an aqueous system and it is more environmentally friendly. The OD plays a major role in the stability of Graphene oxide in aqueous media. These two Graphene oxide parts can be separated, albeit irreversibly with a base washing step (hence with the resultant large sheets being termed as base-washed Graphene oxide (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).

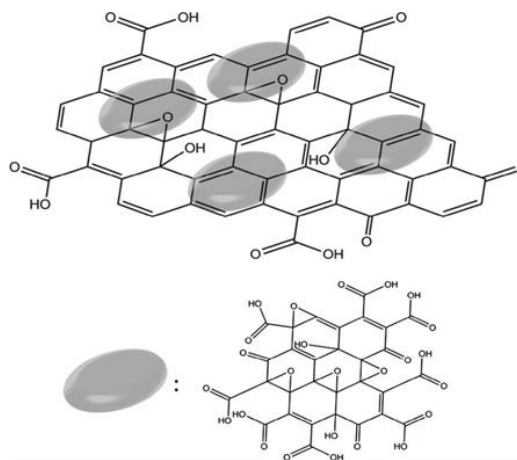


Fig. 4. Structure of graphene oxide

*C. rGo preparation*

In order to obtain rGO [9], and partially recover the desirable properties of pristine graphene, Graphene oxide can be treated with a suitable reducing agent. In situ reduction is popular and discussed further in Section. 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, although hydrazine is particularly effective and popular for simplicity and cleanliness. Chemical reduction before Electrophoretic deposition 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 Graphene oxide sheets usually cannot form stable aqueous suspensions without using stabilizing additives, although partial reduction of Graphene oxide can produce stable dispersions, depending on ionic strength, pH and rGO concentration. In several studies, partial reduction of Graphene oxide has been reported as an effective way to produce stable and negatively charged rGO aqueous suspensions for Electrophoretic deposition.

Electrostatically stabilized rGO aqueous suspensions can also be produced by sequentially treating Graphene oxide 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<sup>+</sup> ions. However, it is important to note that the rGO suspensions prepared by this method contain high concentrations of K<sup>+</sup> ions, which increase the ionic conductivity of the suspension and may be incorporated within electrophoretically deposited PImS. Interestingly, highly alkaline solutions have also been applied, without using hydrazine, to produce partially stable reduced Graphene oxide suspensions, with a retained negative charge through conjugate base formation suitable for anodic Electrophoretic deposition. Out of the preparation of graphene materials such as Graphene oxide, RGO, and modified Graphene oxide by the, there have been growing interests in employing to fabricate the graphene-based composite materials, including:

Graphene / non-metal nanoparticle composites such as, grapheme / CNT, graphene/carbon black, graphene/Si; Graphene/metal-based nanoparticle cposites such graphene/metal, graphene/metaloxide, graphene/mineral, graphene/metal hydroxide; Graphene/polymer materials. With the aim of fabricating graphene reinforced composite materials, interleaved porous structures, and nanoparticle spaced graphene films, the Electrophoretic deposition strategies to fabricate graphene/nano- particle composite materials can mainly be divided into three types, The Electrophoretic deposition suspension consists of gra- phene and one or more other components, which are stably co- dispersed in three types:

- Simultaneous deposition of the separately dispersed graphene flakes and nanoparticles;
- Graphene flakes are dispersed and the nanoparticles with the opposite charges self-assembled on the graphene surface, the overall charge of the colloid depends on which component possesses higher zeta-potential;
- Graphene is compounded with big molecules (polymer chains) before Electrophoretic deposition.

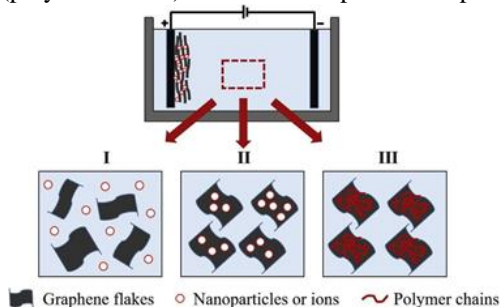


Fig. 5. Graphene flakes

The reported works based on graphene/non-metal nanoparticle composites are summarized, the applications of the graphene/non-metal nanoparticle composites are mainly

targeted at super capacitors, dye-sensitized solar cells (DSSC) [10], and Li-ion batteries . The Electrophoretic deposition graphene has good electrical conductivity and porous structure, however, when the deposited layers are thick or large electrolyte ions such as organic electrolytes are used, the existed pores in the Electrophoretic deposition graphene are not enough to penetrate the electrolyte ions and thus the surface area of the Electrophoretic deposition graphene cannot be fully utilized. On the other respect, the in-plane align- ment of GO or RGO flakes also affects the interlayer electrical conductivity. It has been proven to be effective to combine graphene with the spacers such as carbon black to expose more surface area and increase the interlayer conductivity as well. There- fore, carbon nanoparticles, including carbon blacks and carbon nanotubes are introduced during the Electrophoretic deposition process to enhance the interlayer electrical conductivity and improve the porosity and surface areas. Recent research progress on the Electrophoretic deposition of the graphene/metal based nanoparticle composites Similar with the co-deposition of non-metal nanoparticles, by adjusting the charge of the nanoparticles to be coherent with graphene, some of the metal-based nanoparticles are simultaneously deposited onto the substrate with graphene flakes by the EPD technique , following the dispersion strategy type I. For example, graphene and Co<sub>3</sub>O<sub>4</sub> nanoparticles are co-dispersed in acetone solvent and migrates together to the Cu foil substrate under the electric field, depositing in a sandwich-like structure.

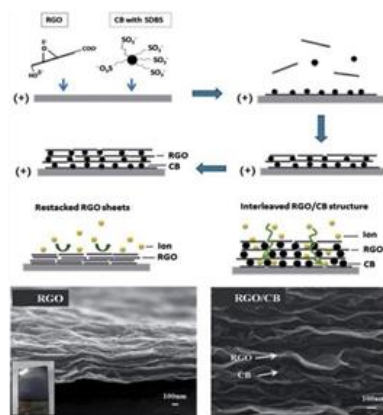


Fig. 5. Electrophoretic deposition

Electrophoretic deposition has also become an effective approach to fabricate the graphene/polymer composite materials. The methods are mostly in two ways: one-step Electrophoretic deposition of pre-prepared graphene/polymer composite particles and successional Electrophoretic deposition of each component. The Electrophoretic deposition dispersion for preparing graphene/polymer composites follows the strategy III, which indicates that the graphene flakes and polymer chains are com- pounded and dispersed in the solvents before Electrophoretic deposition. The Reduced graphene oxide/polyaniline composites prepared by Electrophoretic deposition have several advantages working as

electrodematerials for pseudocapacitors, including short ionic diffusion and full utilization of polyaniline due to the thin polymer layer, good electrical conductivity derived from the graphene conducting backbone, etc. The Electrophoretic deposition of graphene/polymer composite materials may also avoid the problems of graphene agglomeration and difficulty in uniform dispersion of graphene during the fabrication of graphene/polymer composites in traditional processing techniques

### 3. Conclusion

This review has summarized the fundamentals and specific technical aspects of the Electrophoretic deposition process for Graphene related materials. Although there are numerous advantages of Electrophoretic deposition as a technique to obtain Graphene related materials structures, many aspects have to be addressed to optimize the deposition. These challenges range from the difficulty of suspending Graphene related materials to tailoring the deposition parameters to controlling side reactions during Electrophoretic deposition, 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 Graphene related materials in an aqueous Electrophoretic deposition medium is to chemically oxidised and exfoliate graphite. However, the exfoliation of graphite to form Graphene Oxide sheets induces considerable irrecoverable damage in the sheets, which cannot be entirely reversed even on reduction. Unless the application specifically requires Graphene Oxide, it may be wiser to choose a different dispersion approach to produce graphene-related deposits with higher intrinsic crystalline quality. The fundamentals and research progress on the Electrophoretic deposition of graphene-based materials in recent 5 years are

comprehensively summarized. Electrophoretic deposition has been attracting increasing interests in the research area of graphene processing and applications of graphene-based materials, therefore, a review article is necessary for summarizing the newest progress in the area of graphene Electrophoretic deposition. This review literature has indicated that Electrophoretic deposition is an effective and versatile technique for the production of graphene and its composite materials for a variety of applications. Especially in the Electrophoretic deposition process of graphene-based composite materials, Electrophoretic deposition provides a facile and effective way to fabricate the uniform and well-connected composites in one-step.

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