Electrophoretic deposition of graphene-based materials: A review of materials and their applications

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**ABSTRACT**

Recently, graphene-based materials have been successfully fabricated by the electrophoretic deposition (EPD) technique and exhibited various extraordinary properties. Here, research progress of the field of graphene-based materials prepared by the EPD process in recent 5 years is reviewed, including graphene films, graphene/non-metal composites, graphene/metal-based nanoparticles composites, graphene/polymer composites. We also summarize the experimental deposition conditions and the applications of the deposited graphene-based materials that have been reported. It can be concluded that EPD is a simple and reliable manipulation technique and promises a bright future for the production of graphene-based materials in the field of advanced nanocomposite materials. Finally the current issues and outlook of the development direction of EPD in future are also proposed.

**Keywords:** Electrophoretic deposition, Graphene, Graphene-based composite materials, Applications

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**1. Introduction**

Electrophoretic deposition (EPD) is a colloidal process where the suspended particles are impelled from the suspension medium to the substrate by an electric field. EPD was discovered by Ruess in...
1808 and was practically applied to deposit thoria particles on a Pt cathode as an emitter for electron tube in 1933 [1]. Afterward, EPD was evolved from being a technique restricted only to traditional ceramics to become an important tool in the processing of advanced materials, such as metals, polymers, carbides, oxides [2,3]. EPD can meet many extreme requirements for the substrates and has plenty of advantages over other membrane fabrication techniques such as moldable nature, uniform and controllable thickness, smooth surface, etc [4]. In recent years, EPD has been widely employed to produce composite materials for coatings, shaping monolithic, laminated and graded free-standing objectives, infiltration of porous materials and woven fiber preforms, and so on [3].

Especially, EPD has been shown to be an effective technique for manipulating graphene layers in liquid suspensions with the aim to produce graphene-related materials including graphene films and graphene-based composite materials [5–9]. Recently, there has been increasing number of publications reporting the research progress of the EPD of graphene and graphene-based composite materials, in which the advantages of EPD is utilized for manipulating graphene to satisfy a variety of applications. The mechanically robust graphene-based nanocomposite coatings, as well as functional nanostructured graphene-based films obtained by the EPD technique, anticipate a promising future for electronic [10], sensing [11–13], biomedical [14], energy harvesting [15], catalytic [16], energy storage [17,18], and environmental applications [19,20].

The intention of this review is to present a comprehensive summary of relevant previous work and describe the application of the EPD technique in the processing of graphene-based materials. The mechanisms and kinetics of graphene-based EPD 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 EPD, the corresponding EPD conditions, as well as their applications such as supercapacitors, solar cells, sensors, coatings, etc.

2. EPD mechanisms and kinetics

2.1. EPD mechanisms

EPD is usually carried out in a two-electrode cell, where the electric field can be either in a direct electric current mode or in a modulated electric current mode (Fig. 1) [21]. EPD can be applied to any colloidal system with the suspended particles size <30 μm. The EPD of graphene-based materials consists of two steps, electrophoresis and deposition [22]. 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.

Theoretical and modeling studies are being carried out to clarify the mechanisms of EPD, including the EPD of graphene. The affects of electrochemical parameters such as conductivity, solvents, zeta potential, electric field, concentration, etc. on the EPD of graphene-based materials are also being studied. EPD relies on the capability of the graphene sheets to acquire an electric charge in the solvent of suspension [2]. A stable graphene suspension is the prerequisite of the EPD of graphene, which means the graphene flakes have to keep dispersed in the solvent and move towards the electrode independently of each other so that the graphene sheets can be deposited without agglomeration and keep opening the possibility of rearrangement of graphene sheets during packing [23].

2.2. EPD kinetics

In order to predict the kinetics of EPD for particulate materials, Hamaker proposed the Hamaker’s law by simply applying the principle of conservation of mass, as shown in the following equation [24,25]:

\[ \frac{dm}{dt} = f \mu \epsilon_{SC} \]  

(1)

where \( m \) is the mass of deposition (g) and \( t \) is the deposition time (s). \( f \) is a factor taking into account that only a fraction of the particles brought to the electrode by electrophoresis is incorporated in the deposit (\( f \leq 1 \)). \( \mu \) and \( E \) represent the electrophoretic mobility (\( \text{m}^2/\text{V}\cdot\text{s} \)) and the strength of electric field, respectively. \( S \) is the surface area of the electrode (\( \text{m}^2 \)) and \( C \) is the concentration of the colloidal suspension (\( \text{g}/\text{m}^3 \)) [24,25]. The Hamaker’s law indicates a way to predict the deposition yield from the strength of electric field. However, regarding to the strength of electric field, it is subject to the EPD conditions, such as the applied voltage, the distance of the electrodes, resistances of the deposit and the suspension, thickness of the deposit, etc.

In spite of the deposition yield, if other charged powders are deposited with graphene simultaneously, the Hamaker’s equation can also be used to predict the mass ratio of the graphene-based composite deposits. For example, a method has been reported to calculate the mass ratio of reduced graphene oxide (RGO) and carbon black (CB) in an interleaved RGO/CB film prepared by EPD [26]. Based on the Hamaker’s law, the \( \mu \) can be expressed by the permittivity of the free space and the suspension medium (\( \epsilon_0 \) and \( \epsilon_r \)), the zeta potential of colloidal particles (\( \xi \)), and the viscosity of the suspension medium (\( \eta \)):

\[ \mu = \epsilon_0 \epsilon_r \xi / \eta \]  

(2)

Therefore, the mass of the deposit can be calculated as follow:

\[ m = f C \text{RGO} \xi \text{Et} / \eta \]  

(3)

Assuming the RGO and CB have the same \( f \), the weight ratio of RGO and CB in the deposited film can be estimated only by the concentrations of the RGO and CB suspensions and the zeta potentials of RGO and CB:

\[ \frac{m_{\text{RGO}}}{m_{\text{CB}}} = \frac{C_{\text{RGO}} \xi_{\text{RGO}}}{C_{\text{CB}} \xi_{\text{CB}}} \]  

(4)

In addition, it also indicates that the EPD membrane yield or thickness can be easily controlled by varying the deposition conditions, such as the suspension concentration, pH of the dispersion (or zeta potential), applied voltage, and deposition time. This strategy can be also employed in the other systems, in which the
simultaneous deposition of graphene and other nanoparticles is achieved.

2.3. EPD equipment

Fig. 2(a) represents a typical EPD equipment for graphene deposition. 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 [18]. The substrate can be in an arbitrary shape or be patterned to a certain morphology [12,27,28]. However, this setting has the disadvantage of low yield that can only produce one piece of product at once. Kwon et al. developed an EPD setting with several working and counter electrodes alternately aligned, which greatly increase the yield of EPD (Fig. 2(b)) [29]. In addition, shorten the deposition time can also reduce the side reaction of graphene agglomeration. EPD technique has also been widely used to enhance the mechanical properties of carbon fibers, where the EPD is mostly carried out on the carbon fiber fabrics. However, this technique is limited to the deposition area. Wang et al. proposed an EPD setting, which can achieve the continuous EPD of carbon fibers as presented in Fig. 2(c) [30]. In addition, ultrasonication is applied to the GO suspension during the EPD process to avoid the aggregation of the GO under the loaded voltage. The proposed EPD equipment shows a great potential for the scalable production of graphene-based materials by EPD.

3. Graphene films fabricated by the EPD and their applications

3.1. EPD conditions for depositing graphene-based materials

EPD can be applied to any solid 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 GO) in an aqueous, an organic or a mixer solution stably, the EPD of graphene had become possible. Table 1 presents a summary of the studies reviewed on the graphene materials prepared by EPD, collating the relevant parameters on EPD, including the suspension medium, EPD voltage, EPD time, and applications.

GO and RGO are mostly used as graphene precursor for EPD due to the easy preparation of graphene dispersion derived from the oxygen-containing functional groups. Among them, RGO is mostly reduced from the GO in different approaches: chemically reduced before the EPD process [17], electrochemically reduced during the EPD process [4,5], and post-reduced after the EPD process [11,31–33]. As listed in Table 1, several types of solvents have been used to disperse GO, RGO or modified graphene flakes for EPD, including DI water [34], isopropyl alcohol (IPA) [30], ethanol [35], dimethylformamide (DMF) [36], N-Methyl-2-pyrrolidone (NMP) [13], and acetone/ethanol mixture [37]. Aqueous solutions are more widely used for the EPD of graphene than organic solutions because it has the advantages that lower EPD voltage can be used in an aqueous system and it is more environmentally friendly. Moreover, aqueous solvents also have a faster kinetics and are higher.

Fig. 2. (a), Typical EPD equipment for deposition of GO with a positive and a negative electrodes aligned in parallel [31]. Copyright 2014, American Society of Chemistry. (b), EPD equipment that can produce 16 pieces of GO/CNT coated carbon fabrics simultaneously [29]. Copyright 2017, Elsevier. (c), Equipment of continuous EPD of graphene on carbon fibers [30]. Copyright 2016, Elsevier.
temperature applicable and low cost. Nevertheless, the aqueous suspension also causes problems to the EPD efficiency and the uniformity of the deposit because the electrochemical side reactions often happen along with the EPD such as the electrolysis of water, oxidation of the metal electrodes, etc.

The EPD of graphene can be divided into two types: cathodic EPD and anionic EPD. When graphene sheets are positively charged, the EPD happens on the cathode and the process is cathodic EPD. The EPD of negatively charged graphene sheets on the anode is called anodic EPD. Due to the negatively charged nature of GO and RGO, EPD of GO (or RGO) is mostly an anodic process. However, during the EPD, some metal ions are introduced in the suspension through the addition of salts such as LiClO4, Mg(NO3)2, La(NO3)3, Y(NO3)3, MgCl2, AlCl3 [3,5,36,38]. The graphene flakes are charged positively by adsorption of metal ions on their surface. For example, Mg2+ has been used to modify the negatively charged graphene flakes to positively charged Mg2+-graphene for a cathodic EPD (Fig. 3(a)) [36,38]. When a current is passed through solutions of these salts, the formation of a hydroxide has been observed [3]. However, it has also been disclosed that the additive Mg salts may break the stability of the electrolyte and even weaken the tribological performance of the EPD graphene film [39]. In addition, polymer has also been used to modify the surface charge of the graphene flakes owing to their abundant positively charged functional groups (Fig. 3(b)) [40].

3.2. EPD prepared graphene materials

Owing to the advantages of EPD technique that the deposit can occur on substrate with arbitrary shape and surface, the graphene deposit can be in different forms, including continuous in-planar film on the plate substrate [17], fibers or other irregular substrates [10], porous deposits, vertical-aligned graphene deposits [12], non-continuous decoration on the electrodes [41], patterned graphene deposits [42], etc. Hence, the EPD graphene sheets can exhibit different morphologies depends on the deposition conditions such as substrate morphology, graphene precursor for EPD, post-treatment techniques, etc. Mostly, the graphene deposits obtained from EPD are layer-by-layer aligned graphene film (Fig. 4(a)) [17,31,43], while in some cases the modified graphene sheets can have a vertically aligned morphology due to the charge modification on the GO surface (Fig. 4(b)) [11,12]. Other morphologies of graphene deposits with porous nanostructure have also been reported with a freeze-drying process after the EPD of graphene (Fig. 4(c)) [5]. Besides, Dryfe et al. revealed that the morphology and porosity of the EPD graphene also depend on the size of the graphene sheets [44]. When the fine-size graphene is applied as the precursor for the EPD, a highly porous deposit layer can be obtained while a non-porous surface is obtained using the large-size graphene precursor (Fig. 4(d) and (e)). By a detachment process, the deposited graphene film can become a freestanding and flexible membrane. A chemical and an electrochemical methods have been developed to detach the graphene deposit from the substrate and obtain the RGO free-standing membrane with large-area and good electrical conductivity [31].

Table 1
Overview of graphene films prepared by EPD process in recent 5 years.

<table>
<thead>
<tr>
<th>Graphene precursor</th>
<th>EPD substrate</th>
<th>Suspension medium</th>
<th>Voltage</th>
<th>Time</th>
<th>Application</th>
<th>Year of Publication</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO nanowalls</td>
<td>graphite rod</td>
<td>aqueous Mg(NO3)2 solution</td>
<td>30 V</td>
<td>10 min</td>
<td>single-DNA electrochemical biosensing</td>
<td>2012 [11]</td>
<td></td>
</tr>
<tr>
<td>GO</td>
<td>Au</td>
<td>aqueous LiClO4 suspension</td>
<td>–1.2 V</td>
<td>1 h</td>
<td>solid lubricant for MEMS/NEMS devices</td>
<td>2013 [39]</td>
<td></td>
</tr>
<tr>
<td>Graphene</td>
<td>stainless steel foil</td>
<td>aqueous methyl violet solution</td>
<td>30 V</td>
<td>2 min</td>
<td>supercapacitors</td>
<td>2013 [45]</td>
<td></td>
</tr>
<tr>
<td>GO</td>
<td>carbon cloth</td>
<td>water</td>
<td>6 V</td>
<td>10 h</td>
<td>solid-state supercapacitor</td>
<td>2013 [44]</td>
<td></td>
</tr>
<tr>
<td>Graphene quantum dots (QGds)</td>
<td>ITO glass</td>
<td>aqueous Mg(NO3)2 suspension</td>
<td>70 V</td>
<td>2 min</td>
<td>food toxin detection</td>
<td>2013 [46]</td>
<td></td>
</tr>
<tr>
<td>GO</td>
<td>GO carbon fibers</td>
<td>water</td>
<td>5 V</td>
<td>1 min</td>
<td>sizing agent</td>
<td>2013 [32]</td>
<td></td>
</tr>
<tr>
<td>GO</td>
<td>GO graphite rod</td>
<td>distilled water</td>
<td>30 V</td>
<td>10 min</td>
<td>electrode for electrochemical detection</td>
<td>2014 [12]</td>
<td></td>
</tr>
<tr>
<td>RGO</td>
<td>GO nylon</td>
<td>NMP suspension</td>
<td>3 V</td>
<td>–</td>
<td>gas sensing</td>
<td>2014 [13]</td>
<td></td>
</tr>
<tr>
<td>GO</td>
<td>GO carbon steel</td>
<td>water</td>
<td>4 V</td>
<td>10 s</td>
<td>anti-corrosion</td>
<td>2014 [20]</td>
<td></td>
</tr>
<tr>
<td>RGO</td>
<td>RGO TiO2 nanotube</td>
<td>water</td>
<td>4 V</td>
<td>30 min</td>
<td>Li-ion battery</td>
<td>2014 [28]</td>
<td></td>
</tr>
<tr>
<td>Sulphonated RGO</td>
<td>RGO carbon fiber cloth</td>
<td>ethanol/acetone mixture</td>
<td>20 V</td>
<td>30 min</td>
<td>capacitive deionization</td>
<td>2014 [37]</td>
<td></td>
</tr>
<tr>
<td>RGO</td>
<td>RGO SS</td>
<td>DI water</td>
<td>3 V</td>
<td>5 min</td>
<td>supercapacitor</td>
<td>2015 [17]</td>
<td></td>
</tr>
<tr>
<td>GO</td>
<td>GO carbon felt</td>
<td>water</td>
<td>1.5 mA/cm²</td>
<td>10 min</td>
<td>dye pollutants removal</td>
<td>2015 [19]</td>
<td></td>
</tr>
<tr>
<td>GO</td>
<td>GO SS</td>
<td>DI water</td>
<td>4 V</td>
<td>5 min</td>
<td>supercapacitor</td>
<td>2015 [47]</td>
<td></td>
</tr>
<tr>
<td>GO</td>
<td>GO glass fibers</td>
<td>water</td>
<td>10 V/cm</td>
<td>5 min</td>
<td>fibre/matrix bond</td>
<td>2016 [48]</td>
<td></td>
</tr>
<tr>
<td>GO</td>
<td>GO carbon fibers</td>
<td>IPA</td>
<td>160 V</td>
<td>1 min</td>
<td>mechanical strength enhancement</td>
<td>2016 [30]</td>
<td></td>
</tr>
<tr>
<td>GO</td>
<td>GO carbon fibers</td>
<td>aqueous NaOH solution</td>
<td>20 V</td>
<td>20 min</td>
<td>interfacial strength enhancement</td>
<td>2016 [43]</td>
<td></td>
</tr>
<tr>
<td>RGO</td>
<td>RGO carbon fibers</td>
<td>NH4NO3 solution</td>
<td>15 V</td>
<td>–</td>
<td>electromagnetic interference shielding</td>
<td>2016 [10]</td>
<td></td>
</tr>
<tr>
<td>GO</td>
<td>GO Ti foil</td>
<td>water</td>
<td>10 V</td>
<td>10 s</td>
<td>photocatalyst</td>
<td>2017 [41]</td>
<td></td>
</tr>
<tr>
<td>GO</td>
<td>GO carbon steel</td>
<td>DI water</td>
<td>3–4 V</td>
<td>4–10 min</td>
<td>corrosion protection coating</td>
<td>2017 [34]</td>
<td></td>
</tr>
<tr>
<td>GO</td>
<td>GO copper</td>
<td>DI water</td>
<td>2.3 V</td>
<td>90 min</td>
<td>anticorrosive coating</td>
<td>2017 [7]</td>
<td></td>
</tr>
<tr>
<td>RGO-Mg²⁺</td>
<td>RGO-Mg²⁺ micro-crystalline diamond</td>
<td>ethanol</td>
<td>15 V</td>
<td>20 min</td>
<td>tribological enhancement coating</td>
<td>2017 [35]</td>
<td></td>
</tr>
<tr>
<td>GO</td>
<td>GO carbon fiber</td>
<td>water</td>
<td>15 V</td>
<td>30-150 min</td>
<td>in-tube solid-phase microextraction</td>
<td>2017 [50]</td>
<td></td>
</tr>
<tr>
<td>GO</td>
<td>GO copper</td>
<td>DI water</td>
<td>5 V</td>
<td>10 s</td>
<td>anti-corrosive coating</td>
<td>2017 [51]</td>
<td></td>
</tr>
</tbody>
</table>
3.3. Applications of EPD prepared graphene materials

On account of the excellent electrical conductivity, optical transparency, large specific surface area and desirable mechanical properties of graphene, EPD graphene has been increasingly employed as the material to various applications such as supercapacitors, sensors, anti-corrosive coatings, mechanical enhancement agent, and so on, as listed in Table 1. Among the applications, supercapacitors and anti-corrosive coatings are more reported than others according to the publication records in recent 5 years. Graphene has been confirmed to be a desirable material to be used in supercapacitor electrode [52–54]. By the EPD process, it is reported that the RGO electrode fabricated by EPD contains an in-plane layer-by-layer alignment, desirable electrical conductivity, and a moderate porosity that accommodate the aqueous electrolyte ions [17]. Based on the EPD graphene electrode, the all-solid-state supercapacitor exhibits high specific volumetric capacitance (108 F/cm³) and excellent energy and power densities (7.5 Wh/cm³ and 2.9 W/cm³, respectively) (Fig. 5(a)). Impressively, the supercapacitor is also demonstrated to have a long cyclic stability for as long as 180 days (335,000 cycles) (Fig. 5(b)). The simple fabrication and the excellent performance of the device support the application of EPD graphene as large-area, portable, and long-life supercapacitors.

Furthermore, EPD has become one of the most used techniques to produce anti-corrosive coatings onto metals [20,34,49,51]. However, for some specific case of carbon steel’s protection, EPD graphene cannot always achieve desirable results. Rangel-Mendez et al. revealed that the reason is the defects (vacancies) involved during the anodic oxidation process and thus a cathodic EPD of GO with the aid of Ca²⁺ was been developed to improve the anti-corrosion of carbon steel [7]. The results show that the cathodic
EPD RGO film could reduce up to three times the corrosion rate of carbon steel, which is proved by the decrease of I_{corr}, the shifting of E_{corr} to more positive values, and the increase of R_{CT} of carbon steel, as shown in Fig. 5(c) and (d).

4. Graphene-based composites prepared by EPD

Out of the preparation of graphene materials such as GO, RGO, and modified GO by the EPD, there have been growing interests in employing EPD to fabricate the graphene-based composite materials, including: (i), Graphene/non-metal nanoparticle composites such as graphene/CNT, graphene/carbon black, graphene/Si; (ii), Graphene/metal-based nanoparticle composites such as graphene/metal, graphene/metal oxide, graphene/mineral, graphene/metal hydroxide; (iii), Graphene/polymer materials.

With the aim of fabricating graphene reinforced composite materials, interleaved porous structures, and nanoparticle spaced graphene films, the co-EPD strategies to fabricate graphene/nanoparticle composite materials can mainly be divided into three types, as presented in Fig. 6. The EPD suspension consists of graphene and one or more other components, which are stably co-dispersed in three types: (I), simultaneous deposition of the separately dispersed graphene flakes and nanoparticles; (II), 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; (III), graphene is compounded with big molecules (polymer chains) before EPD.

4.1. Graphene/non-metal nanoparticle composites and their applications

The reported works based on graphene/non-metal nanoparticle composites are summarized in Table 2. As listed in Table 2, the applications of the graphene/non-metal nanoparticle composites are mainly targeted at supercapacitors [45,55], dye-sensitized solar cells (DSSC) [15,56], and Li-ion batteries [57,58]. As discussed in session 3.2, the EPD 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 EPD graphene are not enough to penetrate the electrolyte ions and thus the surface area of the EPD graphene cannot be fully utilized. On the other respect, the in-plane alignment 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 [26]. Therefore, carbon nanoparticles, including carbon blacks (CB) and carbon nanotubes (CNT) are introduced during the EPD process to enhance the interlayer electrical conductivity and improve the porosity and surface areas.

For example, an EPD dispersion of graphene and CB has been...
prepared with the assistance of anionic surfactant sodium dodecylbenzenesulfonate (SDBS), following the dispersion strategy type I. RGO and CB are stably dispersed with negative zeta-potentials and an anionic EPD process occurs with the simultaneous co-deposition of RGO and CB when an electric field applies to the solution. As shown in Fig. 7, the CB particles are successfully inserted into the interlayer spaces of RGO layers, obviously increasing the interlayer distance and facilitate the diffusion of electrolyte ions. The results indicate that the spontaneous co-deposition of graphene and charged nanoparticles can be achieved by EPD and the contents of the additive nanoparticles can be controlled depending on the target applications.

4.2. Graphene/metal-based nanoparticle composites and their applications

Recent research progress on the EPD of the graphene/metal based nanoparticle composites are listed in Table 3. 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 [16], following the dispersion strategy type I. For example, graphene and Co$_3$O$_4$ nanoparticles are co-dispersed in acetone solvent and migrate together to the Cu foil substrate under the electric field, depositing in a sandwich-like structure, as shown in Fig. 8(a). Contributed from the flexibility of the graphene, the RGO/Co$_3$O$_4$ hybrid films can show excellent flexibility (Fig. 8(b)-(c)). In addition, the RGO/Co$_3$O$_4$ hybrid films can be deposited to the irregular substrate, owing to the advantage of EPD technique (Fig. 8(d)). Applied as a Li-ion battery electrode, the structural integrity and unobstructed conductive network of the RGO/Co$_3$O$_4$ hybrid film can be maintained during cycling, owing to the excellent flexibility of graphene and a large number of voids in this sandwich-like structure. However, in some cases, an electrochemical deposition process simultaneously happens along with the EPD process [65]. When GO sheets are dispersed in a solution containing metal ions, such as Cu$^{2+}$, the positively charged Cu$^{2+}$ ions absorb on the surface of the negatively charged GO sheets automatically and the GO/Cu$^{2+}$ sheets become negatively charged. Followed by a cathodic EPD process, the positive GO/Cu$^{2+}$ sheets deposit onto the cathode and simultaneously, the Cu$^{2+}$ and GO are reduced into Cu nanoparticles.
and RGO, respectively, forming the RGO/Cu nanoparticles composite, as illustrated in Fig. 8(e). The resultant product shows desirable sensitivity and selectivity toward nonenzymatic glucose sensing.

4.3. Graphene/polymer composite materials prepared by EPD

EPD has also become an effective approach to fabricate the graphene/polymer composite materials, as listed in Table 4. The methods are mostly in two ways: one-step EPD of pre-prepared graphene/polymer composite particles [9,87] and successional EPD of each component [6,88]. The EPD dispersion for preparing graphene/polymer composites follows the strategy III, which indicates that the graphene flakes and polymer chains are compounded and dispersed in the solvents before EPD. However, in some specific cases, the graphene flakes are compounded with the monomers by chemical bonding or hydrogen bonding, subsequently, the in-situ polymerization happens on the surface of graphene flakes, as presented in Fig. 9. After the polymerization step, the GO is reduced into RGO and the polymer chains are grown all over the surface of the RGO sheets. The RGO/polyaniline composites prepared by EPD have several advantages working as electrode materials 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 EPD 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.

5. Conclusions and outlook

In this review, the fundamentals and research progress on the EPD of graphene-based materials in recent 5 years are comprehensively summarized. EPD 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 EPD. This review literature has indicated that EPD is an effective and versatile technique for the production of graphene and its composite materials for a variety of applications. Especially in the EPD process of graphene-based composite materials, EPD provides a facile and effective way to fabricate the uniform and well-connected composites in one-step, and impressively, the content
of each component is possible to be controlled by controlling the EPD parameters. However, in some specific cases such as EPD of graphene/metal hydroxides, the EPD process happens along with an electrochemical deposition process, which facilitates the process but also makes the mechanism unclear and the process complicated. In addition, it is hard to control the morphology, contents ratio of each component, etc. Even though the EPD has been used in many graphene-based materials and applications, the underlying mechanisms of the EPD of graphene are still unclear. Deeper investigation of the mechanisms of graphene EPD should be carried out in future, which will provide a strong guidance in controlling the parameters of EPD graphene, realize the EPD of more materials, and eliminate the unbene

### Table 3
Summary of the graphene/metal-based nanoparticle composites prepared by the EPD.

<table>
<thead>
<tr>
<th>Graphene/metal-based nanoparticle composites</th>
<th>EPD substrate</th>
<th>Suspension medium</th>
<th>Voltage</th>
<th>Time</th>
<th>Application</th>
<th>Year of Publication</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene/Pt nanoparticles</td>
<td>ITO coated glass</td>
<td>DMF</td>
<td>5 V</td>
<td>10/30/60 s</td>
<td>electro-catalytic electrodes</td>
<td>2012</td>
<td>[16]</td>
</tr>
<tr>
<td>Graphene/ZnO</td>
<td>Si wafer</td>
<td>IPA</td>
<td>300 V</td>
<td>3 min</td>
<td>field emission</td>
<td>2012</td>
<td>[67]</td>
</tr>
<tr>
<td>GO/Ni</td>
<td>SS</td>
<td>IPA with NiNO3</td>
<td>60 V</td>
<td>–</td>
<td>supercapacitor</td>
<td>2012</td>
<td>[68]</td>
</tr>
<tr>
<td>RGO/Ni(OH)₂ composite film</td>
<td>Ni foam, ITO, SS, and Pt</td>
<td>water</td>
<td>2-10 V</td>
<td>30-600 s</td>
<td>supercapacitor</td>
<td>2013</td>
<td>[69]</td>
</tr>
<tr>
<td>GO/MnO₂/CNTs</td>
<td>Ni substrate</td>
<td>IPA</td>
<td>50 V</td>
<td>2 min</td>
<td>supercapacitor</td>
<td>2013</td>
<td>[70]</td>
</tr>
<tr>
<td>Ag-hydroxyapatite/graphene</td>
<td>Ti plate</td>
<td>absolute ethanol</td>
<td>60 V</td>
<td>2 min</td>
<td>antibacterial coating</td>
<td>2015</td>
<td>[71]</td>
</tr>
<tr>
<td>Graphene nanosheets/(Co(OH)₂)</td>
<td>TCO</td>
<td>anhydrous IPA</td>
<td>50 V</td>
<td>10 min</td>
<td>dye-sensitized solar cell (DSSC)</td>
<td>2014</td>
<td>[72]</td>
</tr>
<tr>
<td>RGO/Ni(OH)₂</td>
<td>gold substrate</td>
<td>ethanol</td>
<td>50 V</td>
<td>20 s</td>
<td>electrochemical sensing</td>
<td>2014</td>
<td>[73]</td>
</tr>
<tr>
<td>GO-hydroxyapatite</td>
<td>Ti sheets</td>
<td>ethanol</td>
<td>30 V</td>
<td>1-5 min</td>
<td>biological applications</td>
<td>2014</td>
<td>[74]</td>
</tr>
<tr>
<td>GO/Si-Cu quantum dots</td>
<td>Cu foils</td>
<td>absolute ethanol</td>
<td>60 V</td>
<td>400 s</td>
<td>lithium storage</td>
<td>2014</td>
<td>[75]</td>
</tr>
<tr>
<td>Cu(OH)₂/Fe(OH)₃@Graphene</td>
<td>Cu foils</td>
<td>absolute ethanol</td>
<td>5 V</td>
<td>30 s</td>
<td>lithium ion storage</td>
<td>2014</td>
<td>[76]</td>
</tr>
<tr>
<td>GO-Sn</td>
<td>Ni foam</td>
<td>water</td>
<td>5 V</td>
<td>30 s</td>
<td>lithium ion storage</td>
<td>2014</td>
<td>[77]</td>
</tr>
<tr>
<td>GO-hydroxyapatite</td>
<td>Ti plate</td>
<td>absolute ethanol</td>
<td>60 V</td>
<td>2 min</td>
<td>bioactive coating</td>
<td>2015</td>
<td>[78]</td>
</tr>
<tr>
<td>RGO/MoO₃/CNTs</td>
<td>FTO glass</td>
<td>acetonitrile/ethanol mixture</td>
<td>80 V</td>
<td>–</td>
<td>DSSC</td>
<td>2014</td>
<td>[79]</td>
</tr>
<tr>
<td>RGO/Co₃O₄ hybrid film</td>
<td>FTO glass</td>
<td>water</td>
<td>3 V</td>
<td>5 s</td>
<td>DSSC</td>
<td>2015</td>
<td>[80]</td>
</tr>
<tr>
<td>GO/lithium iron phosphate</td>
<td>carbon cloth</td>
<td>IPA with Mg(NO₃)₂</td>
<td>90 V</td>
<td>–</td>
<td>lithium ion batteries</td>
<td>2015</td>
<td>[81]</td>
</tr>
<tr>
<td>GO/Cu</td>
<td>gold</td>
<td>ethanol</td>
<td>50 V</td>
<td>2 min</td>
<td>glucose sensing</td>
<td>2015</td>
<td>[82]</td>
</tr>
<tr>
<td>Co(OH)₂@graphene hybrid film</td>
<td>copper foil</td>
<td>absolute ethanol</td>
<td>60 V</td>
<td>200 s</td>
<td>lithium-ion batteries</td>
<td>2015</td>
<td>[83]</td>
</tr>
<tr>
<td>graphene-iron oxide-chitosan hybrid composite</td>
<td>ITO</td>
<td>water/ethanol mixture with acetic acid</td>
<td>10 V</td>
<td>60 s</td>
<td>pathogen detection</td>
<td>2015</td>
<td>[84]</td>
</tr>
<tr>
<td>CaSO₄/GO</td>
<td>Ti substrate</td>
<td>IPA</td>
<td>60 V</td>
<td>5 min</td>
<td>coatings</td>
<td>2016</td>
<td>[85]</td>
</tr>
<tr>
<td>GO/NiO</td>
<td>nickel foam</td>
<td>IPA</td>
<td>200 V</td>
<td>10 min</td>
<td>supercapacitor</td>
<td>2016</td>
<td>[86]</td>
</tr>
<tr>
<td>GO/TiO₂ hierarchical spheres</td>
<td>Ti threads</td>
<td>acetonitrile</td>
<td>7-20 V</td>
<td>2 min</td>
<td>DSSC</td>
<td>2016</td>
<td>[87]</td>
</tr>
<tr>
<td>Ammonia-doped-porous RGO/CuO</td>
<td>gold</td>
<td>ethanol</td>
<td>30 V</td>
<td>30 s</td>
<td>glucose sensing</td>
<td>2017</td>
<td>[88]</td>
</tr>
<tr>
<td>RGO/MnO₂</td>
<td>ITO substrate</td>
<td>water and acetonitrile mixture</td>
<td>25 V</td>
<td>–</td>
<td>supercapacitor</td>
<td>2017</td>
<td>[89]</td>
</tr>
<tr>
<td>RGO/Co₃O₄ nanocubes</td>
<td>Cu foil</td>
<td>acetonitrile</td>
<td>100 V</td>
<td>25 s</td>
<td>lithium ion battery</td>
<td>2017</td>
<td>[90]</td>
</tr>
</tbody>
</table>

Fig. 8. (a), EPD fabrication procedures of the RGO/Co₃O₄ hybrid materials. (b), Photographs of RGO/Co₃O₄ hybrid electrode on the surface. (c), Curved RGO/Co₃O₄ hybrid electrode. (d), RGO/Co₃O₄ hybrid film deposited on the irregular substrates [66]. Copyright 2017, American Chemistry Society. (e), Schematic illustration of the preparation of RGO/Cu nanoparticles (Cu NPs) using electrophoretic deposition/reduction [65]. Copyright 2015, Royal Society of Chemistry.
Table 4
Summary of graphene/polymer composite materials fabricated by the EPD.

<table>
<thead>
<tr>
<th>Graphene/polymer composites</th>
<th>EPD substrate</th>
<th>Suspension medium</th>
<th>Voltage</th>
<th>Time</th>
<th>Application</th>
<th>Year of Publication</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene nanosheet/polydiallyldimethylammonium chloride</td>
<td>silicon wafer</td>
<td>methanol</td>
<td>300 V</td>
<td>10 min</td>
<td>field emission and biocompatibility application</td>
<td>2012</td>
<td>[89]</td>
</tr>
<tr>
<td>RGO/polymer</td>
<td>glassy carbon electrode</td>
<td>ultrapure water</td>
<td>0.8 V</td>
<td>–</td>
<td>supercapacitor</td>
<td>2012</td>
<td>[90]</td>
</tr>
<tr>
<td>GO-polymeric isocyanate crosslinked with hydroxyl functional acrylic adhesive</td>
<td>Cu plates</td>
<td>water</td>
<td>10 V</td>
<td>30 s</td>
<td>composite coating</td>
<td>2013</td>
<td>[40]</td>
</tr>
<tr>
<td>GO-hydroxyapatite-hyaluronic acid</td>
<td>Ti substrate</td>
<td>ethanol-water mixture</td>
<td>30 V</td>
<td>1-5 min</td>
<td>anti-corrosive coating</td>
<td>2013</td>
<td>[14]</td>
</tr>
<tr>
<td>RGO/polyethylene</td>
<td>SS</td>
<td>water</td>
<td>2-7 V</td>
<td>5-10 min</td>
<td>electromagnetic interference shielding</td>
<td>2014</td>
<td>[6]</td>
</tr>
<tr>
<td>Graphene/polyaniline composite film</td>
<td>nickel alloy plate</td>
<td>DI water</td>
<td>– 20 V</td>
<td>20 min</td>
<td>supercapacitors</td>
<td>2014</td>
<td>[87]</td>
</tr>
<tr>
<td>Graphene/2nS/polyaniline</td>
<td>ITO glass</td>
<td>IPA</td>
<td>30 V/60 V</td>
<td>10 min/5 min</td>
<td>solar cells</td>
<td>2014</td>
<td>[88]</td>
</tr>
<tr>
<td>GO/chitosan films</td>
<td>Ti foils</td>
<td>aqueous acetic acid solution</td>
<td>10 V</td>
<td>10 min</td>
<td>drug-eluting</td>
<td>2015</td>
<td>[91]</td>
</tr>
<tr>
<td>RGO/polyaniline</td>
<td>titanium</td>
<td>water</td>
<td>30 V</td>
<td>60 s</td>
<td>supercapacitor</td>
<td>2015</td>
<td>[9]</td>
</tr>
<tr>
<td>RGO/polyaniline</td>
<td>Ti sheet</td>
<td>ethanol-water mixture</td>
<td>10 V</td>
<td>30-45 s</td>
<td>orthopedic applications</td>
<td>2016</td>
<td>[92]</td>
</tr>
<tr>
<td>GO reinforced chitosan-hydroxyapatite</td>
<td>Ti substrate</td>
<td>ethanol and water mixture</td>
<td>20 V</td>
<td>3 min</td>
<td>coatings</td>
<td>2016</td>
<td>[93]</td>
</tr>
<tr>
<td>GO/polyethylene</td>
<td>glass/Ti/Au substrate</td>
<td>Milli-Q water</td>
<td>15 V</td>
<td>2 min</td>
<td>lysozyme sensing in serum</td>
<td>2017</td>
<td>[94]</td>
</tr>
</tbody>
</table>

Fig. 9. Schematics of the EPD fabrication process of graphene/polyaniline composite electrodes for pseudocapacitors [87]. Copyright 2014, Royal Society of Chemistry.

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[66] Yang Y, Huang J, Zeng J, Xiong J, Zhao J. Direct electrophoretic deposition of binder-free CoOx/graphene sandwich-like hybrid electrode as remarkable lithium ion battery anode. ACS Appl Mater Interfaces 2017;9(38):32801–11.


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