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Review

Electrophoretic deposition of carbon nanotubes

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Abstract

Electrophoretic deposition (EPD) has been gaining increasing interest as an economical and versatile processing technique for the production of novel coatings or films of carbon nanotubes (CNTs) on conductive substrates. The purpose of the paper is to present an up-to-date comprehensive overview of current research progress in the field of EPD of CNTs. The paper specifically reviews the preparation and characterisation of stable CNT suspensions, and the mechanism of the EPD process; it includes discussion of pure CNT coatings and CNT/nanoparticle composite films. A complete discussion of the EPD parameters is presented, including electrode materials, deposition time, electrode separation, deposition voltage and resultant electric field. The paper highlights potential applications of the resulting CNT and CNT/composite structures, in areas such as field emission devices, fuel cells, and supercapacitors.

Keywords: Carbon nanotubes; Functional groups; Field emission; Coating; Microstructure

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Contents

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1. Introduction

Although carbon nanotubes (CNTs) were first observed at least 30 years ago [1], Iijima's report in 1991 [2] triggered enormous world-wide interest in these archetypical nanomaterials; over three thousand publications on CNTs appeared in the year 2005 alone [3,4]. Single-walled carbon nanotubes (SWCNTs) consist of one layer of the hexagonal graphite lattice rolled to form a seamless cylinder with a radius of up to a few nanometres. Micron lengths are typical but there is no fundamental limit; the longest examples to date are several centimetres. As synthesised, CNTs are

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capped at their ends by half of a fullerene-like structure. A concentric arrangement of a number of graphitic cylinders is termed a multi-walled carbon nanotube (MWCNT) and diameters can reach up to 100 nm; this limit is somewhat arbitrary but commonly applied. These concentric tubes are held together by van der Waals bonding between the layers, which are separated by approximately 0.34 nm. As the diameter increases, at some point the perfect cylindrical structure is lost and the structure becomes more similar to a vapour-grown carbon fibre. The properties of nanotubes depend on the helicity (the orientation between the graphitic hexagons and the nanotube axis), the diameter and length of the tubes, and the crystalline quality [5].

Many of the remarkable properties of CNTs are now well established [6–11], and their exploitation in a wide range of applications forms a major part of current research and development efforts [11,12]. One of the challenges is to tackle the problem of manipulating CNTs, individually or collectively, to produce a particular arrangement needed for a given application. Moreover, if CNTs are to be combined with other materials to form composites, it is generally important to develop processing methods that disperses the CNTs homogeneously in the appropriate polymer, ceramic or metallic matrix.

One very promising technique being developed for manipulating CNTs is electrophoretic deposition (EPD). EPD is commonly employed in processing of ceramics, coatings and composite materials [13–15]. It is a high-level efficient process for production of films or coatings from colloidal suspensions: electrophoretically deposited materials exhibit good microstructure homogeneity and high packing density. The technique allows the application of coatings, thin and thick films, the shaping of bulk objects, and the infiltration of porous substrates, fibrous bodies and textile structures with metallic, polymeric or ceramic particles [15]. The interest in the EPD technique is driven not only by its applicability to a great variety of materials (and combinations) but also by its simplicity; EPD is a cost-effective method usually requiring simple equipment as well as being amenable to scaling-up to large dimensions [13–15].

EPD is achieved via the motion of charged particles, dispersed in a suitable solvent, towards an electrode under an applied electric field. Deposition on the electrode occurs via particle coagulation. Electrophoretic motion of charged particles during EPD results in the accumulation of particles and the formation of a homogeneous and rigid deposit at the relevant (deposition) electrode. In contrast to many colloidal processes, suspensions with relatively low solids loading can be used; the low viscosity provides processing and handling advantages. The method can be applied, in general, to any solid in particulate form with small particle sizes (<30 μm) and to colloidal suspensions [13,14]. EPD is essentially a two-step process. In the first step, particles suspended in a liquid are forced to move towards an electrode by applying an electric field (electrophoresis). In the second step, the particles collect at the electrode and form a coherent deposit (deposition). Deposition occurs only on conducting surfaces, however non-conductive substrates can be infiltrated by using EPD [15]. Compared with other processing methods, EPD offers advantages of low cost, process simplicity, uniformity of deposits, control of deposit thickness, microstructural homogeneity, and deposition on complex shaped substrates, including the potential to infiltrate porous substrates [13–15]. All these advantages can be also exploited for forming films and coatings of CNTs. The schematic diagram of an EPD cell for electrophoretic deposition of carbon nanotubes is shown in Fig. 1.

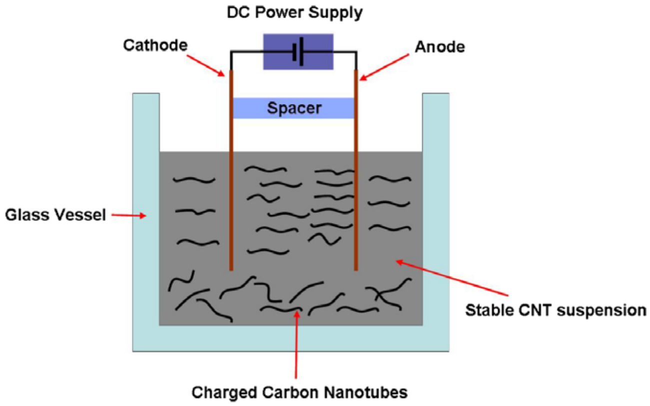

Fig. 1. Schematic diagram of the electrophoretic deposition of CNTs on the cathode of an EPD cell with planar electrodes.

This paper reviews current research and development efforts on the application of the EPD technique for the fabrication of CNT-containing structures. The review includes an overview of investigations dealing with the formation of stable suspensions of CNTs (Section 2) and with the manipulation of CNTs in an external electric field (Section 3). The use of EPD for production of CNT/nanoparticle composite coatings and films is addressed in Section 4, and, finally, the potential applications of the resulting CNT structures and the scope for future work are highlighted in Sections 5 and 6.

2. Preparation and characterisation of CNT suspensions for EPD

As-produced carbon nanotubes are intrinsically inert, often aggregated or entangled, and may contain impurities (such as amorphous carbon or catalytic metal particles) [16–20]. The purification processes that have been investigated usually utilise the differences in the aspect ratio [21] and oxidation rate between the CNTs and impurities [22,23]. A post-synthesis treatment is almost always required to purify and disperse the CNTs in a suitable solvent; a wide variety of approaches have been developed. A typical strategy is to use thermal oxidation, then acid reflux in concentrated HCl, and finally a thermal annealing treatment to purify the raw material; a surfactant can subsequently be used to disperse the CNTs using sonication [24]. A small concentration of dissolved ethyl cellulose, for example, can be added to MWNTs/isopropyl alcohol solution to disperse the CNTs when preparing stable suspensions for electrophoretic deposition of CNTs [25]. However, residual surfactants can be difficult to remove once added and may be detrimental to the performance of the nanotubes in a given application [26].

Alternatively, a mixture of concentrated nitric and sulphuric acids can simultaneously purify, shorten and functionalise CNTs [27,28]. Under such aggressive conditions, defective sites in the CNTs are attacked, resulting in the formation of fragmented CNTs decorated with carboxylic acid and other oxygen-containing groups on their surface. These acidic groups electrostatically stabilise the CNTs in water, or other polar liquids, by developing a negative surface charge. The resulting electrostatic repulsion among the CNTs leads to a remarkable increase in the stability of the colloidal suspension [29]. In addition, functional groups on CNT surfaces can be useful sites for further chemical modification. Titrations indicate that typical concentrations of surface groups are on the order of $\sim 10^{21}$ sites per gram of functionalised CNTs [28].

As reported in the literature, several types of solvents have been used to prepare CNT suspensions for EPD, including distilled water [30–32], mixtures of acetone and ethanol [33], and pure organic solvents such as ethanol [34], isopropyl alcohol (IPA) [25,35–38], *n*-pentanol [39], ethyl alcohol [40], tetrahydrofuran (THF) [41–44], dimethlyformamide (DMF) [26,45] and deionised water with pyrrole [46,47]. A summary of the suspensions prepared for EPD experiments, according to the literature, is given in Table 1. As discussed previously, dispersing CNTs homogeneously in a suitable solvent is a necessary step for controlled manipulation of CNTs. Purified/functionalised CNTs can be dispersed, to some extent, in all of the solvents mentioned above. However, Du et al. [29] demonstrated the importance of the quality of the dispersion on the nature of the deposited film. They carried out a comparative analysis on solubility of CNTs in different solvents for producing thin CNTs films on silicon wafers. As shown in Fig. 2, they found that the packing density of CNTs was higher in films obtained from CNTs/distilled water solutions (which had a degree of local alignment) than in those obtained from CNTs/ethanol suspensions,; the difference can be attributed to a varying degree of agglomeration in the suspension; indeed, gels from unagglomerated and unentangled nanotube suspensions are known to produce dense, locally ordered films [28]. It is worth noting that the majority of CNT EPD films have an isotropic appearance with a degree of orientation onto the surface (ie approaching a random planar distribution of CNTs), most likely generated during drying of the gel-like initial deposit. Since electric fields can align individual nanotubes, it is possible to obtain perpendicular orientations; however, special techniques are required to preserve the orientation during drying [38], as will be discussed in more detail below.

Preparation of a stable dispersion of CNTs in a suitable solvent is a necessary prerequisite for successful EPD. The most common strategy is the production of an electrostatically stabilised dispersion, which, in general terms, requires the preparation of a solvent medium in which the particles have a high ζ-potential, while keeping the ionic conductivity of the suspensions low. The stability of CNT suspensions, determined by ζ-potential measurements, has been studied mainly in aqueous and ethanol-based suspensions [30,48–50]. As-produced CNTs have a small and positive ζ-potential in the acidic region with an isoelectric point in the pH range 5–8. After oxidation, the presence of surface acid groups dramatically shifts the isoelectric point to values often below pH 2. Interestingly,

Table 1
Overview of suspension preparation for CNT EPD, according to the literature

CNT type	Suspension properties	Reference
MWNTs	Aqueous solutions of 0.25 and 0.55 mg/mL (CNT/H_2O)	[31]
SWNTs	10 mg of SWNTs mixed with 0.13 g of tetraoctylammonium bromide (TOAB) were dried and resuspended in 25 mL of Tetrahydrofuran (THF) + quaternary ammonium salt	[28]
SWNTs	10 mg of SWNTs with 100 mg of tetraoctylammonium bromide (TOAB) or Nafion in 25 ml of Tetrahydrofuran (THF)	[42]
MWNTs	Ethanol with EPI-Rez resin and EPI-CURE curing agent (aliphatic amine)	[34]
MWNTs	Mixtures of acetone and ethanol in different volume ratios	[33]
MWNTs	0.125 mg/ml (CNT/isopropyl alcohol) and small amount of bezalkonium chloride	[35]
SWNTs	Isopropyl alcohol with $NiCl_2$	[36]
MWNTs	Isopropyl alcohol solution containing $Mg(NO_3)_2$; ethyl cellulose was also added to improve dispersion	[25]
SWNTs	De-ionised water mixed with pyrrole and lithium perchlorate	[46]
SWNTs	Ethyl alcohol with $MgCl_2$	[40]
SWNTs	Tetraoctylammonium broamide (TOAB) in tetrahydrofuran (THF)	[43]
SWNTs	Tetraoctylammonium broamide (TOAB) in tetrahydrofuran (THF)	[44]
Not Specified	Isopropyl alcohol (IPA) with $Mg(NO_3)_2 \cdot 6H_2O$	[37]
SWNTs	Methanol or dimethylformamide (DMF) with <1 wt% concentrated sodium hydroxide	[26]
SWNTs	Distilled water with $Mg(NO_2)_2 \cdot 6H_2O$	[32]
MWNTs	Isopropyl alcohol (IPA)	[38]
MWNTs	2g of CNTs mixed with 500 ml *n*-pentanol with a small amount of anhydrous $Mg(NO_3)_2$.	[39]
Not Specified	0.5 mg CNT/1 mL dimethylformamide (DMF) solution	[45]

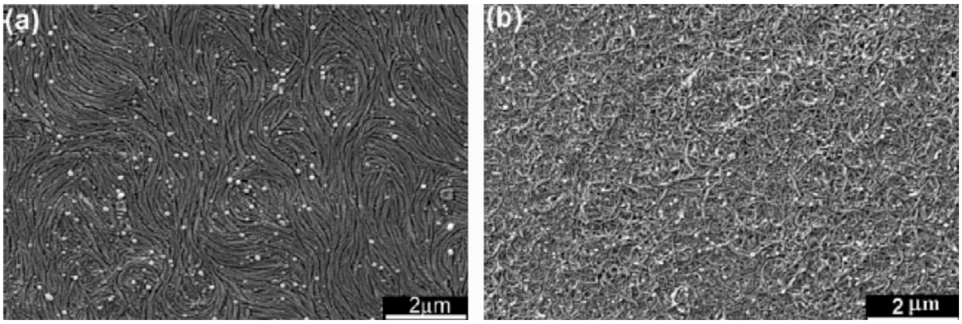

Fig. 2. SEM images showing the surfaces of CNT films prepared from suspensions using different solvents: (a) distilled water, (b) ethanol. [29] – Reproduced by permission of The Royal Society of Chemistry.

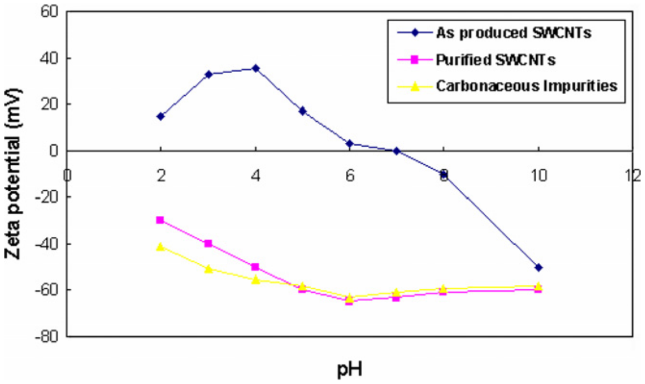

Fig. 3. ζ-potential of as-produced SWCNTs, SWCNTs purified by acid treatment, and associated carbonaceous impurities (modified after [51]).

ζ-potential measurements on SWCNTs suggest that carbonaceous impurities on CNTs can be isolated from the SWCNTs due to their greater ζ-potential at low pH values; this behaviour is illustrated in Fig. 3 [51].

It has been shown that the presence of charger salts can play an important role in improving the adhesion of CNTs to substrates and in increasing the deposition rate in the EPD process [24,35–37,40]. The salts can also contribute to the stability of the suspensions by associating a charge with the CNT surface in suitable solvents. The migration direction of CNTs in suspension during EPD is controlled by the surface charge; for example, oxidised nanotubes are typically negatively charged and attracted to the positive electrode (anode) [31]. More subtle control can be achieved by using different types of charger salts. As can be seen in Table 1, a great variety of salts have been employed in CNT suspensions including quaternary ammonium salts [41–44], benzalkonium chloride [35], $NiCl_2$ [36], $Mg(NO_3)_2$ [25,39], $MgCl_2$ [40] and NaOH [26]. CNTs were deposited on the anode when benzalkonium chloride or metal charger salts were used, while the deposition on the negative electrode (cathode) was observed for quaternary ammonium salt and sodium hydroxide containing suspensions. The effect can be understood in terms of ion adsorption; for example, Mg^{2+} ions are adsorbed by the suspended CNTs, encouraging the formation of an electric double layer [26]. The migration and resultant deposition of CNTs under the influence of a DC field has been attributed to preferential absorption of ions in the solution by the nanotubes [26]. Thus a suitable charger salt can be selected depending on whether deposition is required at the anode or the cathode.

In the conventional preparation of particulate suspensions for EPD, well-defined quantities of colloidal particles are added to the solvent; the solid content of the suspension is therefore known exactly. However, for EPD of CNTs, preparation of suspensions from dried CNTs typically produces a poor dispersion, or at least a low yield of well-suspended material. Conversely, using oxidised nanotube suspensions without a drying step dramatically improves the dispersion quality but the solid content is less certain. A systematic determination of CNTs concentration is therefore helpful. UV–vis absorbance spectrophotometry has been employed as a simple and fast method to determine the concentration of SWCNT in suspensions [49,51]. The technique has to be calibrated for different types of nanotubes, as extinction coefficients can be expected to vary.

It is worth noting that the high aspect ratio and surface charge of acid-treated CNTs makes them suitable scaffolds for other nanoparticles via adsorption or nucleation at the acidic sites. Metallic and oxide nanoparticles [50,52–57] have been homogeneously deposited on the surface of oxidised CNTs; these particles can be, for example catalytic [58–60], or can contain rare earth metals [48,61]. Moreover, stable suspensions of these CNT/nanoparticle composite assemblies are suitable precursors for production of advanced CNT-based nanostructured composite coatings by EPD. These composite coatings represent attractive nanostructures for a variety of structural, functional and biomedical applications, and some recent examples are discussed below (Section 4).

3. EPD of CNTs

The earliest investigations appear to be those of Du et al. [33], who explored the possibility of using EPD to deposit multi-walled CNTs from ethanol/acetone suspensions on metallic substrates. They observed strong hydrogen evolution at the cathode, leading to a porous film of nanotubes with pore sizes ranging from 1 to 70 μm. In addition, they also showed that the composition (the volume ratio of acetone-to-ethanol) of the solvent itself greatly affected the microstructure of the nanotube film. The same research group reported the fabrication CNT-reinforced resin (type EPI-rez) films by EPD, obtaining relatively large areas [34]; the CNTs were dispersed in, and co-deposited from, an ethanol solution containing both the resin and the curing agent (aliphatic amine) which was sonicated for 30 min to form a stable suspension. A constant deposition voltage of 45 V was used for EPD, with aluminium electrodes placed 50 mm apart. EPD was shown to be a convenient technique to produce relatively homogeneous CNT-reinforced composite polymer coatings with a reasonable content of CNTs [34]. The authors reported that the properties of the final composite films containing two different nanotube weight fractions (55 wt% and 43 wt%) were significantly different. The electrical resistance of the sample with higher nanotube fraction was about 7 kΩ whilst the sample with low CNT content remaining insulating due to the continuous resin layer formed on the nanotubes' surfaces. In principle, the method could be applied to a range of resin matrices and it merits further development for production of CNT/polymer composites.

Thomas et al. [31] successfully deposited homogeneous multi-walled CNT films onto stainless steel substrates using EPD from aqueous suspensions of acid-oxidised nanotubes, without employing additional surfactant, polymer, or stabilizing agents. No hydrogen evolution was observed during this deposition. This result contrasts with that of Du et al. [33] and it may be attributed to the lower electric field strength used by Thomas et al. [31], and/or to the nature of the aqueous medium used as solvent. However, excessively low electric field strengths (<5–10 V/cm) resulted in poor quality, low density, non-uniform coatings, which did not adhere to the substrate. Above around 10 V/cm, the cohesion of CNT films was sufficient to allow the removal of the electrode from the suspension without significant loss of CNTs. At higher electric field strengths (>20 V/cm) or longer deposition times (>5 min) CNT aggregates were deposited rather than individual nanotubes, resulting in a large scatter of the yield and in poorer homogeneity of the CNT films [31,62]. When EPD was carried out at the optimal parameters, very homogeneous CNTs deposits were obtained, as shown in Fig. 4a and b; 3 μm thick CNT coatings were produced in a single deposition step [31]; several successive depositions on the same electrode yielded homogeneous films up to 100 μm thick [62]. It was also found that the lifetime of the CNT suspensions (before agglomeration) could be extended by limiting each deposition step to less than 5 min [62].

EPD has been used only to a limited extent to deposit single-wall CNTs (SWCNTs) [63]. One report describes the production of SWCNT deposits from very dilute SWCNT suspensions in ethanol (1 mg SWCNT in 200 ml ethanol) after the addition of a suitable salt ($MgCl_2$) [40]. Other solvents investigated for SWCNT deposition include dimethylformamide (DMF) and mixtures of distilled water and methanol [25]. Films containing long SWCNT bundles were obtained. Among the solvents used, DMF was found to be the best solvent to prepare high concentration suspensions, followed by distilled water.

Some work has been also carried out on EPD of oxidised or surfactant-modified SWCNTs. Jin et al. [46] co-deposited pyrrole and SWCNTs on indium-tin-oxide (ITO) from an aqueous suspension, fabricating a 1 μm thick composite film where the CNTs were perpendicularly orientated to the substrate; in this case, the pyrrole polymerises at the surface, electrochemically, producing a composite film; a similar, in situ, deposition and electropolymerisation process was previously reported for MWNTs [47], without alignment. Oh et al. [40] used chemically oxidised SWCNTs to fabricate well adherent and defined CNT patterns exhibiting 20 μm features on ITO-coated and plain glass. The results revealed that the use of functionalised CNTs improves the uniformity of the CNT suspension and significantly enhances the adhesion between the CNTs and the substrate. Girishkumar et al. [41] recently used EPD to deposit a thin film of SWCNTs modified with tetraoctylammonium bromide (TOAB) in tetrahydrofuran (THF) on aminopropyltriethoxysilane (APS) coated optically transparent electrodes (OTE) made of conductive glass. These

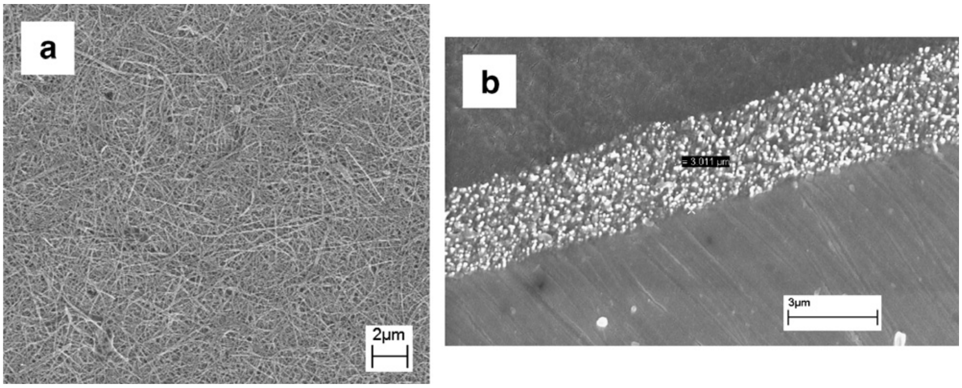

Fig. 4. SEM images of CNT films obtained by EPD on stainless steel substrates showing homogeneous microstructure: (a) surface view and (b) cross section, following the procedure introduced in Ref. [31]. The cross section shows the uniform, thick, CNT layer (bright) embedded in resin.

SWCNT films were designed to be electrodes in portable fuel cells, in particular for methanol oxidation and oxygen reduction. A voltage of 500 V was applied for 1 min to obtain thin deposits of SWCNTs. The tetraoctylammonium bromide (TOAB) binds to the surface of the CNT during sonication by hydrophobic interactions of its alkyl chain, therefore, preventing aggregation and settling of nanotubes. The same group has reported on the fabrication of a membrane electrode assembly for hydrogen fuel cells by using EPD to deposit a SWCNTs support and a Pt catalyst on carbon fibre electrodes [42]. Both the electrophoretically deposited nanotubes and platinum retained their nanostructured morphology on the carbon fibre surface.

Kurnosov et al. [36] suggested introducing a resistive material on top of the conductive cathode in order to improve the adhesion of the CNTs to the substrate and the uniformity of the deposited film. A suspension of SWCNTs in $NiCl_2$/isopropyl alcohol was deposited on an indium tin oxide (ITO) coated aluminium cathode. Oh et al. [40] performed a similar experiment in which functionalised SWCNTs were stabilised in $MgCl_2$/ethanol and deposited on ITO-coated glass. In both cases, the nanotubes strongly adhered to the ITO coating. The adhesion has been attributed to two factors: the first is the interaction between the hydrophilic CNTs and ITO surface [40,64]; the second is the presence of the charger salt, $MgCl_2$, since Mg^{2+} ions form hydroxides at the surface of the negative electrodes that assist the interfacial bonding [64]. Girishkumar et al. [41] introduced APS coating on OTE surface to obtain more uniform electrophoretically deposited films of CNTs. As mentioned above, Thomas et al. [31] successfully obtained CNT films, up to 10 μm thick, strongly adhered to stainless steel electrodes. This result was achieved without any special treatment of the electrode, but the strong adhesion may again relate to the formation of surface hydroxides, which can hydrogen bond to the oxidised nanotubes.

Kamat et al. [44] extensively investigated the assembly of solubilised SWCNTs into linear bundles at high dc field (>100 V) and their deposition on OTE at relatively low dc voltage (∼50 V). Purified SWCNTs were solubilised by mixing with tetraoctylammonium bromide (TOAB) in tetrahydrofuran (THF). SWCNTs films of varying thickness were obtained by adjusting the deposition time. At high dc voltage of > 100 V, the CNTs did not deposit, but became aligned perpendicularly to the two electrodes (parallel to the field). EPD was achieved on OTEs held 5 mm apart in a dc field of 100 V/cm [43].

The influence of electrode separation was investigated by Kurnosov et al. [36]. Their interest was the use of EPD CNT films for field emission applications; they found that the uniformity of field emission depended significantly on the electrode separation. The best uniformity was obtained at the lower end of the separations tested (0.3–1.8 cm). The authors observed that for larger electrode separations, the emission sites were concentrated at the edges of the electrodes due to non-uniformity of the electric field.

MWNTs can be synthesised by a range of methods, loosely divided into high temperature (eg arc discharge) and intermediate temperature chemical vapour deposition (CVD) processes; high temperature processes produce more crystalline but less pure material in small quantities, CVD produces commercial amounts of relatively pure but defective material. MWCNTs synthesised by the arc

Table 2
Overview of EPD parameters used in previous research on EPD of carbon nanotubes

Electrode properties	EPD parameters			Reference
	Constant voltage	Deposition time	Distance between electrodes	
Stainless steel ($1 \times 1 \times 0.2$ cm^3)	5–50 V	0.5–10 min	20 mm	[31]
Aminopropoxysilane (APS) pretreated Optically Transparent Electrodes (OTEs)	500 V & 50 V	1 min & 2 min	∼6 mm	[38]
Carbon Fibre paper Electrodes (CFE) ($2.25 \times 2.25 \times 0.6$ cm^3)	∼40 V	–	∼5 mm	[42]
Aluminium electrodes	45 V	–	50 mm	[34]
Metal electrodes	45 V	–	50 mm	[33]
Titanium (1×1 cm^2) electrodes	–	–	–	[35]
Cathode: Glass plate (1 cm × 0.5 cm) with ITO coating Anode: Glass plate (1 cm × 0.5 cm) with aluminium coating	100–200 V	–	18, 11, 3 & 1 mm	[36]
Silicon wafer (cathode) and stainless steel mesh as an anode	30–600 V	–	20 mm	[25]
Stainless steel mesh (cathode) and a gated triode structure formed on a glass substrate (anode)	30–200 V	–	–	[46]
Indium tin oxide (ITO) coated glass	–	–	–	[40]
Conducting glass electrodes, optically transparent electrode (OTE)	100 V	–	5 mm	[43]
Conducting glass electrodes, optically transparent electrode (OTE)	<100 V & >100 V	2–3 min	5 mm	[44]
Polyimide film coated with titanium (cathode) and stainless steel (anode)	100 V	1–2 min	–	[37]
Stainless steel	20 V	–	10 mm	[26]
Patterned metal substrates	10–50 V	–	–	[32]
Patterned dielectric substrate with 1 μm thick polysilane film coating	2000 V/cm	A few min	–	[38]
Nickel and stainless steel substrates or metal-plated glass plate	200–300 V	2 min	20 mm	[65]
Nickel substrates (10×10 mm^2) etched with 20% HNO_3 for 10 min	20 V	5 min	–	[45]

discharge method have been reported to show weaker attachment to the substrate than those synthesised by CVD [35].

A summary of the electrophoretic deposition parameters used in the literature, including electrode materials, deposition time, deposition voltage and electrode separation, is presented in Table 2.

As mentioned above, beyond the fabrication of uniform, planar, CNT-based coatings and films, EPD can be applied to deposit CNTs onto complicated structures, including microwires, porous substrates and fibrous bodies or textile structures. The fabrication of more complex patterns of CNT deposits by EPD can be realised by using masks or by designing combinations of conductive and non-conductive surfaces. Thick CNT films, such as those shown in Fig. 4, displaying an ordered 3-D structure and relatively high packing density, also exhibit some degree of flexibility [31]. Owing to their coherent microstructure and the fact that no binder is required, they are interesting candidate materials for supercapacitor electrodes and other functional applications.

The results presented in the literature demonstrate that manipulation of CNTs by EPD is a very attractive approach, likely to be a focus of upcoming research efforts in the near future. As discussed below, EPD is a potentially powerful method to produce CNT-based devices, particularly because there are few alternatives for depositing (and aligning) CNTs on the required range of (metallic) surfaces. Similarly, EPD of CNTs can be seen as a very effective process to create CNT membranes and nanofilters which are more commonly made by slow and tedious filtration of CNT suspensions [65].

4. Nanoscaled CNT/particulate composite films by EPD

Once a porous CNT coating or film has been obtained, EPD can be employed to deposit ceramic or metallic nanoparticles with the aim of infiltrating the CNT structure, or producing a layered structure. Alternatively, composite CNT/nanoparticulate coatings can be obtained by co-electrophoretic deposition from stable suspensions containing two or more components. The various components may be separately dispersed, coming together only during EPD or may be preassembled to form a more complex building block. These opportunities have yet to be investigated systematically, but some indicative promising results have been obtained, as summarised in this section.

Homogeneous and thick deposits of CNTs, which have been coated and infiltrated with TiO_2 nanoparticles, were recently obtained by co-electrophoretic deposition in our laboratory. Commercial TiO_2 (P25, Degussa, Frankfurt, Germany), with mean diameter 23 nm, was introduced into porous CNTs films containing voids up to 100 nm in diameter; the CNTs were prepared as reported previously [31]. Co-EPD was carried out at a constant electric field of 20 V/cm. Fig. 5a shows a SEM image of infiltrated TiO_2 nanoparticles bonded to individual CNTs obtained by EPD [66]. Due to the complementary surface charge of CNTs (negatively charged) and TiO_2 nanoparticles (positively charged) the two components attract each other in aqueous suspensions at the pH selected. These forces result in the deposit of TiO_2 nanoparticles on the surface of individual CNT, as shown in the TEM images (Fig. 5b). Under an applied DC voltage, the TiO_2-coated CNTs migrated to the anode leading to a porous CNT/TiO_2 deposit, as shown in Fig. 5a and discussed in detail elsewhere [66]. Similarly, CNT/SiO_2 nanoparticle composite films have been obtained by EPD from aqueous suspensions, as discussed elsewhere [67]. The stock silica suspension used, Aerodisp W1824 (Degussa, Frankfurt, Germany), had a pH of 5. The solid loading of the suspension was 24 mass% and SiO_2 particles had mean diameter of 50 nm. Fig. 6 shows that the deposit is a 3-D network of interwoven CNTs coated and infiltrated by the SiO_2 nanoparticles. This type of porous CNT/titania and CNT/silica nanostructures may be useful for

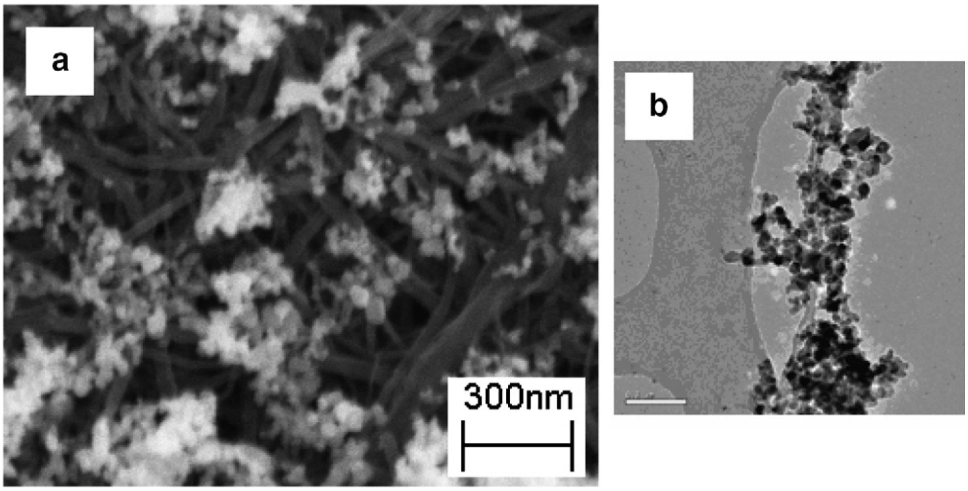

Fig. 5. (a) SEM image showing the surface of a CNT film which has been coated and infiltrated with TiO_2 nanoparticles, obtained by co-electrophoretic deposition [66], (b) TEM image of a carbon nanotube coated by TiO_2 nanoparticles in aqueous suspension at pH 5.

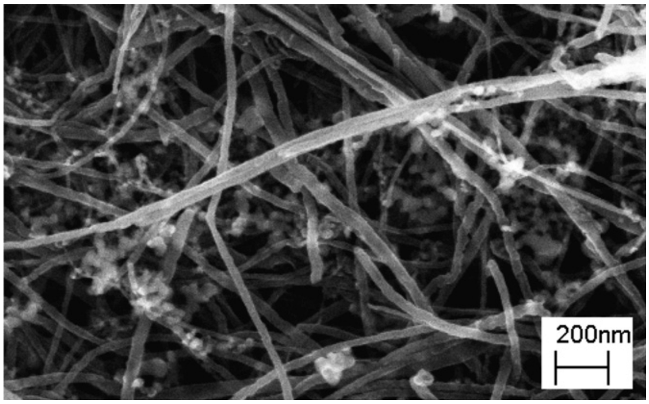

Fig. 6. SEM image of a CNT film, which has been coated and infiltrated with SiO_2 nanoparticles, obtained by co-electrophoretic deposition from aqueous suspensions [67].

nanoelectronic devices [68]. More straightforwardly, the coating and infiltration of porous CNT assemblies with nanoparticles can be seen as a useful step towards homogeneous incorporation of CNTs in hard, structural and functional matrices [68]. Pre-coating CNTs before deposition should eliminate agglomeration and improve the properties of eventual composites.

5. Applications of CNT films by EPD

CNT films produced by EPD are suitable for a wide range of applications; suggestions to date include field emission devices, biomedical scaffolds, catalyst supports, structural composites and coatings as well as large surface area electrodes for fuel cells, capacitors and gas sensors. So far, the development of CNT-based devices from CNT films produced by the EPD method has been focused mainly on the field emission properties. It is well known that CNTs are promising candidates for field emission devices, due to their high aspect ratio, small size, structural and chemical stability and thermal conductivity; these features are responsible for a low emission threshold and high emission current densities compared to other alternatives.

Jin et al. [46] made an aligned SWCNTs/polypyrrole composite film by EPD; they investigated the resulting field emission properties for this triode-type field emission array which showed an emission current of 35 μA at anode voltage of 1000 V and gate voltage of 60 V. Gao et al. [26] made a more simple measurement of the field emission properties of SWCNTs where the CNTs were electrophoretically deposited onto stainless steel substrates from SWCNTs/DMF or SWCNT/ethanol suspensions. The emission measurements made on these randomly orientated SWCNTs films exhibited an initial current density of 83 mA/cm^2 with a decay of 28% after 10 h.

According to theoretical predictions, SWCNTs can be either metallic or semi-conducting depending on the tube diameter and helicity [69]. MWCNTs, on the other hand, tend to be metallic due to their larger size [70], and thus they have a reliably high electrical conductivity. In addition, current growth methods for MWCNTs are simpler than those for SWCNTs. As mentioned above, the influence of CNT fabrication technique on field emission properties was studied by Bae et al. [35] utilising two types MWCNTs, synthesised by arc discharge and CVD methods. The study showed that the field emission properties of MWCNTs do not only depend on the electrical conductivity, but also on the structural quality such as walls and caps of MWCNTs. As demonstrated in Fig. 7, acid-treated CNTs were far less efficient emitters than other types of CNTs. It was suggested that acid treatment CNTs leads to opening of the capped ends [28] and a resulting local change in work function [71].

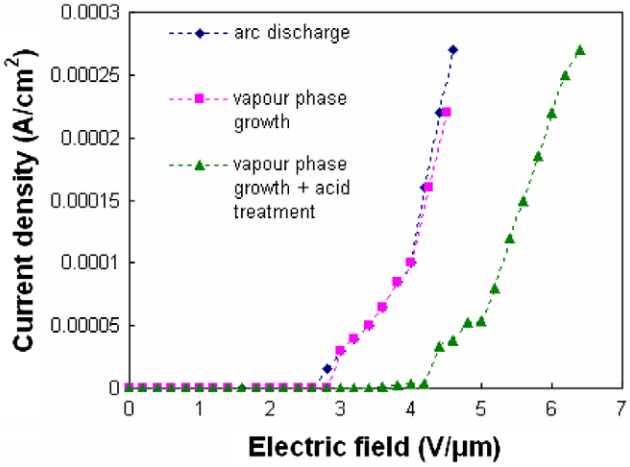

Fig. 7. I–V characteristics of electrophoretically deposited films consisting of MWCNTs obtained by different fabrication process (modified after [35]).

Patterned CNTs films, about 3 μm thick, were electrophotetically deposited on silicon substrates by Zhao et al. [25]. Their measurements of field emission properties showed improved current density (30 mA/cm^2) and applied electric field (8 V/μm) compared to MWCNT films grown in situ (shown in Fig. 8). These values reflect that

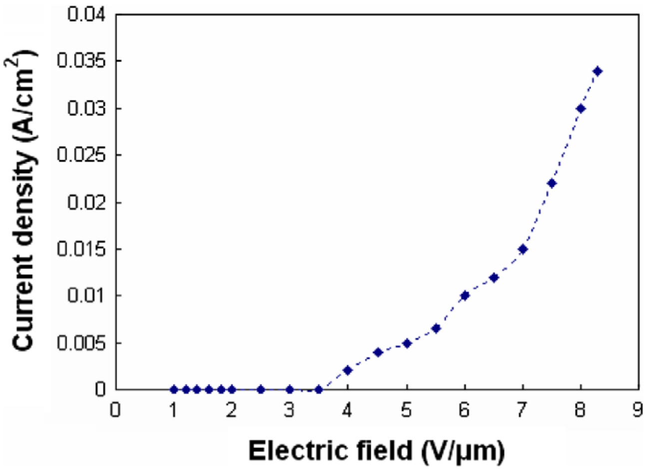

Fig. 8. I–V characteristics of electrophoretically deposited MWCNTs films (modified after [25]).

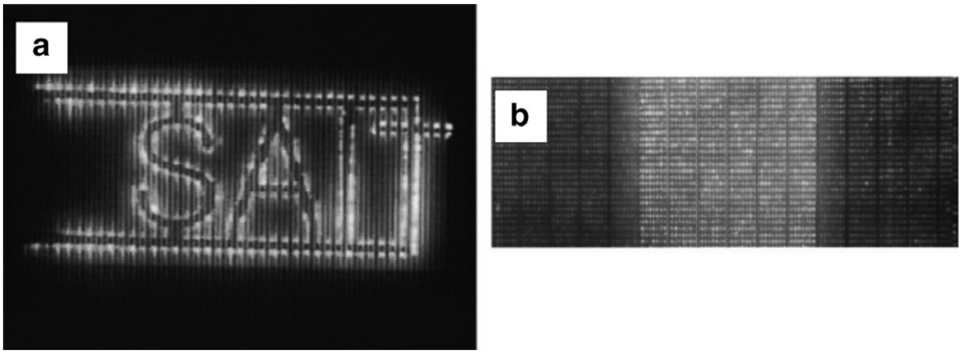

Fig. 9. (a) Emission image of the CNTs deposited by electrophoresis, (b) emission image of a triode-type CNT-FED at colour phosphor screen (reprinted with permission from [32], Copyright [2001], American Institute of Physics).

MWCNTs arrays exhibit, in general, excellent electron field emission properties.

Carbon nanotube field emission displays (CNT-FEDs) are promising for a range of situations including flat panel displays, cathode-ray tubes, and backlights for liquid crystal displays. CNT-FEDs have the potential to provide high quality moving images with low power consumption [72]. Choi et al. [32] showed that EPD is a useful technique to obtain an electron source with minimal out-gassing and to make triode-type carbon nanotube field emission displays. Acid-treated carbon nanotubes bundles with diameters of 10–30 nm were deposited selectively onto patterned metal cathode at DC 10–50 V. Numerical analyses of the field distribution around the patterned metal electrode showed that the field strength at the electrode edge is about three times higher than that in the middle due to strong field enhancement. The field variation is also obvious in the pattern of electron emission shown in Fig. 9(a) which show a much brighter signal at the edges of the electrodes. A brightness of 1000 cd/m^2 was achieved with uniform emission at 220 V on the gate and 900 V on the anode. As a step towards a practical display, an emission image of the CNT-based triode-type display panel on a red, green, and blue colour phosphor is shown in Fig. 9(b) [32]. The emission was reasonably stable, with less than 5% fluctuation over 12 h in a fully sealed unit.

Nakayama and Akita [38] fabricated field emission devices using electrophoresis to generate perpendicularly oriented CNTs; the structure and fabrication process are shown schematically in Fig. 10(a)–(c). Patterned electrodes are provided on a dielectric substrate, and coated with polysilane; UV degradation of the polymer introduces nanosize pores into which CNTs can fit [73]; during EPD the CNTs are aligned parallel to the field and are trapped in the polysilane film in the desired orientation. The process is attractive for practical applications when compared to the more usual method of generating aligned and patterned CNT arrays by CVD [74]; thermal CVD involves high processing temperatures so that glass or polymer substrates cannot be used. Although plasma-enhanced CVD can be used at lower temperatures, there are still difficulties in fabricating large area field emitter arrays.

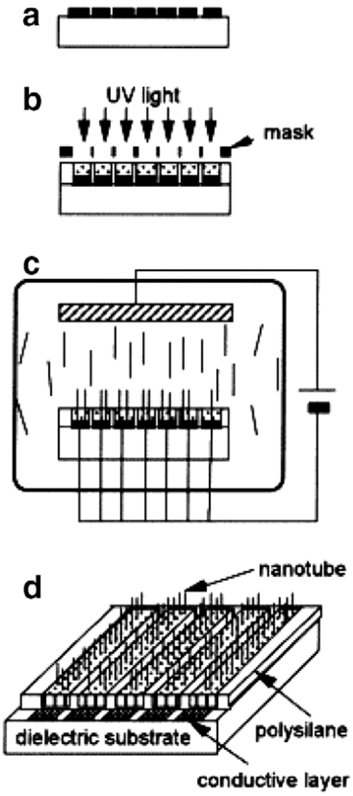

Fig. 10. Structure and fabrication process of the field emission device with array: (a) formation of patterned conductive layer, (b) polysilane film coating and exposure to UV light, (c) electrophoretic deposition of CNTs and (d) completed field emission device with vertically aligned CNTs. (Reprinted from Ref. [38] with permission from Elsevier.)

For field emission display (FED) and related devices, vertically aligned CNTs are preferred because they provide a low turn-on field and a uniform and stable electron emission [40]. The EPD method has the potential to produce highly efficient CNT-based FED devices due to its ability to fabricate large, vertically aligned, patterned nanotube arrays at low temperature [40,46,32,38]. However, according to the existing literature, the uniformity and stability of emission decreases after a number of I–V tests at high electrical field. This effect may be due to weak adhesion between CNTs and the electrodes, and this is a current subject of further investigation.

Large-scale (area and thickness around 10 cm^2 and 10 μm, respectively) and homogeneous MWCNT films were obtained by Yu et al. [39]. EPD was carried out for 2 min under DC voltage of 200–300 V between nickel (cathode) and stainless steel (anode), which were kept at a constant distance of 2 cm. They investigated the influence of a post-EPD Hydrogen Plasma Process (HPP) on the surface morphology, microstructure and electronic properties of the MWCNT film. The HPP caused a structural reconstruction of the CNTs, which improved the field emission properties. The initially smooth CNT surface was roughened by the formation of nanolumps. It was found that the turn-on emission threshold field was reduced from 4 V/μm to 1.1 V/μm after the HPP, and a high emission light spot density of about 10^5 A/cm^2 with a stable emission current was obtained.

In another application sector, EPD is gaining increasing attention as a simple, low-cost technique for fabricating fuel cell electrode assemblies [42]. For fuel cell applications, EPD has the advantage that loading of the carbon support and catalyst elements can be controlled by simply varying the deposition time and voltage; EPD, therefore, constitutes a convenient method to produce membrane electrode assemblies (MEA) for fuel cells [42].

As mentioned above, Girishkumar et al. [41] employed an electrophoretically deposited SWCNT layer as a support for platinum nanoparticles; the structure was subsequently shown both to oxidise methanol and to reduce oxygen in fuel cells more effectively than conventionally supported platinum nanoparticles. Platinum was deposited by electrodeposition from $PtCl_6^{2-}$ [41]. In related research, MEAs for hydrogen fuel cells were fabricated by the same group by sequential EPD of SWCNTs and Pt particles [42]. The larger surface area of the nanotubes and the close contact between the carbon surface and the platinum catalyst should make the Pt/CNT/OTE system ideal for methanol oxidation.

It has been suggested that an aligned CNT film may offer much improved fuel cell performance over that of disordered CNTs due to a number of unique features [75]. First, the electronic conductivity of CNTs may be rather high along its axis, and, in principle, there can be perfect, lossless, electron movement within a single CNT, due to so-called ballistic transport [68]. Second, higher gas permeability is expected with oriented CNT films due to the open framework. Third, an aligned CNT film may also exhibit superhydrophobicity [75,76], which can greatly facilitate water removal within the electrode, therefore improving mass transport in proton-exchange membrane fuel cells (PEMFCs) or in direct methanol fuel cells (DMFCs).

It might be considered that pure CNT electrodes are not suitable for supercapacitor applications due to intermediate specific capacitances (between 4 and 146.6 F/g); however, very high power density systems have been fabricated from both SWNTs [77] and MWNTs [78]. Other candidates for supercapaitors are based on combinations of CNTs with pseudocapacitive components, such as transition metal oxides [79] or conducting polymers [47]. Lee et al. [45] recently examined the electrochemical performance of manganese oxide-carbon nanotube nanocomposite electrodes for potential use in supercapacitor applications. They employed the EPD method to deposit CNTs on nickel substrates, which were etched with nitric acid to increase the roughness of the surface. Then $MnO_x \cdot H_2O$ films were deposited on the Ni and CNTs/Ni substrates by an anodic technique to obtain MnO_x/Ni and MnO_x/CNTs/Ni electrodes; the average specific capacitances were 241 and 418 F/g, respectively. The results indicate that application of CNTs enhances energy storage capabilities, mainly by providing a low resistance, large surface area and mechanical stability. The BET surface measurements of the two electrodes showed that the MnO_x/CNTs/Ni electrode (20.2 m^2/g) had a larger surface area than that of MnO_x/Ni (6.0 m^2/g). Furthermore, MnO_x/CNTs/Ni electrodes preserved 79% of the original capacitance after 1000 cycles of cyclic voltammetry (CV) measurements. These results indicate that the CNT/transition metal oxide nanocomposite electrodes exhibit good capacitance and cyclability, and may be useful for supercapacitors.

Exploitation of CNTs in these and other applications will frequently rely on the attachment of functional groups or other nanostructures to the CNT surfaces. The combination of CNTs and nanocrystalline particles should have applications in field emission displays, nanoelectronic devices, biomedical scaffolds and drug delivery systems [80–82], antibacterial films and biosensors [81], photocatalytic nanostructures and in other functional composites [53–58]. For biomedical applications, the combination of CNTs with hydroxyapatite [81], Bioglass® [83] or collagen [82] is being explored. We anticipate that EPD and combinations of EPD and other colloidal processing methods will play a significant role in the development of such CNT/nanoparticle composite nanostructures. An interesting possibility is the combination of EPD with recent work on (di)electrophoretic separation of SWCNTs, which should allow the creation of structures with ordered regions of semi-conducting and metallic nanotubes [84].

6. Conclusions

The reviewed literature has revealed that EPD represents a very powerful tool for the ordered deposition of CNT and CNT-based nanostructures for a variety of applications. Given the great potential of EPD for manipulation of CNTs and their assembly into ordered deposits, films and coatings, it is likely that novel applications of EPD-based CNT structures will emerge. Further developments of the EPD process will allow the reliable fabrication of three dimensionally controlled nanostructures and nanocomposites either in the form of dense materials or with a required porosity; graded, aligned, and patterned features may also be incorporated as desired.

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