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Review

Electrophoretic deposition of carbon nanotube–ceramic nanocomposites

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Abstract

The purpose of this paper is to present an up-to-date comprehensive overview of current research progress in the development of carbon nanotube (CNT)–ceramic nanocomposites by electrophoretic deposition (EPD). Micron-sized and nanoscale ceramic particles have been combined with CNTs, both multiwalled and single-walled, using EPD for a variety of functional, structural and biomedical applications. Systems reviewed include SiO_2/CNT, TiO_2/CNT, MnO_2/CNT, Fe_3O_4/CNT, hydroxyapatite (HA)/CNT and bioactive glass/CNT. EPD has been shown to be a very convenient method to manipulate and arrange CNTs from well dispersed suspensions onto conductive substrates. CNT–ceramic composite layers of thickness in the range <1–50 μm have been produced. Sequential EPD of layered nanocomposites as well as electrophoretic co-deposition from diphasic suspensions have been investigated. A critical step for the success of EPD is the prior functionalization of CNTs, usually by their treatment in acid solutions, in order to create functional groups on CNT surfaces so that they can be dispersed uniformly in solvents, for example water or organic media. The preparation and characterisation of stable CNT and CNT/ceramic particle suspensions as well as relevant EPD mechanisms are discussed. Key processing stages, including functionalization of CNTs, tailoring zeta potential of CNTs and ceramic particles in suspension as well as specific EPD parameters, such as deposition voltage and time, are discussed in terms of their influence on the quality of the developed CNT/ceramic nanocomposites. The analysis of the literature confirms that EPD is the technique of choice for the development of complex CNT–ceramic nanocomposite layers and coatings of high structural homogeneity and reproducible properties. Potential and realised applications of the resulting CNT–ceramic composite coatings are highlighted, including fuel cell and supercapacitor electrodes, field emission devices, bioelectrodes, photocatalytic films, sensors as well as a wide range of functional, structural and bioactive coatings.

Keywords: Films; Suspensions; Nanocomposites; Nanotubes; Electrophoretic deposition

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1. Introduction

Electrophoretic deposition (EPD) is a well-known colloidal ceramic processing method[1] which is gaining increasing interest as a simple and versatile technique for the production of coatings and films from nanoparticles and carbon nanotubes.[2] The technique allows the fabrication of coatings, thin and thick films, the shaping of bulk ceramic objects and the infiltration of porous substrates with ceramic particles.[1–3] Comprehensive reviews on the application of EPD in ceramic technology are available.[3–5] EPD is achieved via the motion of charged particles, dispersed in a suitable solvent or aqueous solution, towards an electrode under an applied electric field. Electrophoretic motion of charged particles during EPD results in the accumulation of particles and the formation of a homogeneous and rigid deposit on the relevant electrode. The success of EPD is based on its high versatility which facilitates its use with different materials and combinations of materials. In addition, EPD is a rapid, cost-effective method which requires simple equipment enabling material layers (thin and thick films) to be made in only seconds or minutes. Moreover EPD has a high potential for scaling up to large product volumes and sizes, as well as to a variety of component shapes and complex structures.[4,5] EPD is also considered one of the processing methods of widest application potential in the field of nanomaterials.[2]

Nanoparticles and other nanoscaled materials such as carbon nanotubes (CNTs) are starting materials for the synthesis of a variety of advanced (nano)structures, including structural and functional coatings, thick and thin films, bioactive materials as well as laminated and functionally graded materials of high microstructural homogeneity. CNTs attract enormous attention due to their extraordinary properties caused by their unique structure, aspect ratio and size.[6,7] The exploitation of these features in a variety of applications, from microelectronics and field emission devices to structural composites and biomedical materials, constitutes a wide and expanding research field.[8,9] In fact many of the remarkable properties of CNTs are now well established[10–12] and current major efforts are devoted to the exploitation of these properties in specific applications.[12,13] In this context, one of the challenges is to tackle the problem of manipulating CNTs, individually or collectively, to produce the particular CNT arrangement needed in each application. Moreover, if the interest is to combine CNTs with other materials to form composites, it is essential to develop processing methods that enable homogeneous dispersion of the CNTs in the appropriate matrices. In particular for the combination with inorganic matrices to form CNT–ceramic or CNT–glass composites, the intrinsic difficult processability of CNTs due to their tendency to agglomerate makes extremely complicated their integration and dispersion into ceramic or glass matrices, this being still a demanding challenge for technologists, as reviewed elsewhere.[14]

EPD has been shown to be a very convenient technique for manipulating individual CNTs in liquid suspensions with the aim to produce ordered CNT arrays. A comprehensive overview of the field of EPD of CNTs has been published,[15] where the preparation and characterisation of stable CNT suspensions and the mechanism of EPD of CNTs were discussed. Recent research has investigated the EPD of CNTs for a variety of specific applications such as field emission devices, supercapacitors and photocatalytic coatings, which confirm the excellent capability of EPD to manipulate, arrange and orientate multiwalled and single-walled CNTs.[16–18] In this context, the high aspect ratio and surface charge of functionalized CNTs used for EPD make them also suitable scaffolds or hosts for other nanoparticles via adsorption or nucleation at the acidic sites. For example, metallic and ceramic nanoparticles[19–21] have been homogeneously deposited on the surface of oxidized CNTs; including catalytic[22] and rare earth particles.[23] Moreover, stable diphasic suspensions of CNTs and nanoparticles have been shown to be suitable precursors for production of advanced CNT-based ceramic composites.[24–26]

The increasing volume of research dealing with the application of EPD to produce carbon nanotube–ceramic composites, as discussed at a recent international conference,[27] has motivated the preparation of this review paper. This paper is thus the first review covering comprehensively research work carried out worldwide in the field of EPD of carbon nanotube–ceramic (and carbon nanotube–glass) composites highlighting the different systems developed in the short time since the first results in the field (on SiO_2–CNT composites) were published.[28] The experimental characteristics of relevance, such as functionalization of CNTs, design of suspensions for EPD (both single and diphasic suspensions) as well as the specific EPD parameters, such as deposition time, electric field and electrode materials, are discussed for different systems investigated, addressing also the effects of processing conditions on the final quality of CNT–ceramic nanocomposites. The paper highlights also potential applications of the resulting CNT–ceramic nanomaterials produced by EPD.

2. CNT and ceramic particle suspensions for EPD

A complete analysis of the preparation and characterisation of CNT suspensions for use in EPD has been presented in a previous review paper.[15] For completeness this section includes a brief discussion of the key aspects involved in the development of stable CNT suspensions, in particular in relation to the dispersion of CNTs in suitable solvents that must be combined with ceramic nanoparticle suspensions for EPD of CNT–ceramic composites.

It is well known that as-produced CNTs are intrinsically inert, often aggregated or entangled, and may contain impurities (such as amorphous carbon or catalytic metal particles).[29] A post-synthesis treatment is usually required to purify and disperse the CNTs in a suitable solvent. Typically, thermal oxidation is used followed by an acid reflux treatment in concentrated HCl, and finally a thermal annealing treatment is included to purify the raw material. In addition, surfactants can be used to disperse the CNTs using sonication.[30] Alternatively, a mixture of concentrated nitric and sulphuric acids can simultaneously purify, shorten and functionalize CNTs.[31,32] This treatment leads to chemical interaction at defective sites in CNTs which results in the formation of fragmented CNTs decorated with carboxylic acid and other oxygen-containing groups. These acidic groups

Table 1
Examples of suspensions used for EPD of CNTs.

CNT type	Suspension characteristics	Ref.
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	32
SWNTs	10 mg of SWNTs with 100 mg of tetraoctylammonium bromide (TOAB) or Nafion in 25 ml of tetrahydrofuran (THF)	34
MWNTs	Ethanol with EPI-Rez resin and EPI-CURE curing agent (aliphatic amine)	35
MWNTs	Mixtures of acetone and ethanol in different volume ratios	36
MWNTs	0.125 mg/ml (CNT/isopropyl alcohol) and small amount of bezalkonium chloride	37
SWNTs	Isopropyl alcohol with $NiCl_2$	38
MWNTs	Isopropyl alcohol solution containing $Mg(NO_3)_2$; ethyl cellulose was also added to improve dispersion	39
SWNTs	Ethyl alcohol with $MgCl_2$	40
SWNTs	Tetraoctylammonium broamide (TOAB) in tetrahydrofuran (THF).	41, 42
SWNTs	Methanol or dimethylformamide (DMF) with <1 wt% concentrated sodium hydroxide	43
MWNTs	Isopropyl alcohol (IPA)	44
MWNTs	2 g of CNTs mixed with 500 ml n-pentanol with a small amount of anhydrous $Mg(NO_3)_2$	45
SWNTs	SWNTs in *n*,*n*-dimethylformamide (DMF)	46
SWNTs	CNTs in 0.1% sodium dodecyl sulfate (SDS) water solution	47
MWNTs	Initial purification using nitric acid. 0.3 g of purified CNTs and 0.6 g of sodium dodecyl sulfate (SDS) in 1.41 l of water	48

electrostatically stabilise the CNTs in water, or other polar liquids, by developing a negative surface charge, leading to a significant increase in the stability of the suspension, making it suitable for EPD.[33] As reviewed elsewhere,[15] several types of solvents have been used to prepare CNT suspensions for EPD, including distilled water, acetone and ethanol mixtures and other organic solvents such as isopropyl alcohol, n-pentanol, ethyl alcohol, tetrahydrofuran (THF) and dimethlyformamide (DMF). A selection of organic media developed for dispersion of multiwalled and single-walled CNTs for EPD, with potential application also for dispersion of ceramic nanoparticles, is presented in Table 1.

As mentioned previously, dispersing CNTs homogeneously in a suitable solvent is an essential step for their controlled manipulation using EPD. The aim is to avoid agglomeration and entanglement of CNTs to produce dense, locally ordered CNT films.[32] In this context, the stability of CNT suspensions, determined by measurement their ζ-potential values, has been considered mainly in aqueous and ethanol-based suspensions.[15] As-produced CNTs have usually a small, positive ζ-potential in the acidic region with an isoelectric point in the pH range 5–8.[49] After oxidation, the presence of surface acid groups decreases the isoelectric point to values often pH <2. The adhesion of CNTs to substrates, the suspension stability and the deposition rate during EPD can be improved by including charger salts in the suspension.[30,37,38,40] It is also evident that the direction of CNT movement during EPD is determined by the surface charge: oxidized nanotubes are typically negatively charged and they migrate to the positive electrode.[49] The analysis of the literature, as reviewed elsewhere,[15] also reveals that CNT films produced by EPD exhibit isotropic appearance with a degree of two-dimensional orientation parallel to the electrode surface (approaching a random planar distribution of CNTs), as shown in Fig. 1. The final morphology of the EPD CNT layers is generated during drying of the deposit. Since electric fields can align individual CNTs, it is possible to obtain arrays of CNTs perpendicularly orientated to the electrode surface.[46]

Once a porous CNT coating or film (such as the one shown in Fig. 1) has been obtained, EPD can be employed to deposit ceramic or metallic nanoparticles onto the ceramic film with the aim of infiltrating the porous CNT structure, or to fabricate layered composite structures (Fig. 2a). Alternatively, composite CNT/nanoparticle coatings can be obtained by electrophoretic co-deposition from stable suspensions containing CNTs and one or more other components. The various components may be separately dispersed, coming together only during EPD or may be preassembled to form more complex building blocks in suspension (Fig. 2b). In this last case, if ceramic (or metallic) nanoparticles are used, these can be made to uniformly coat individual CNTs by tailoring their zeta-potential, promoting heterocoagulation and self-assembly of the different species in suspension. Alternatively, if large (micron-sized) particles are used, the CNTs can wrap individual ceramic particles forming charged CNT-coated particulates in suspension, which will migrate to the relevant electrode upon application of the electric field to form the composite deposit. Schematic diagrams show-

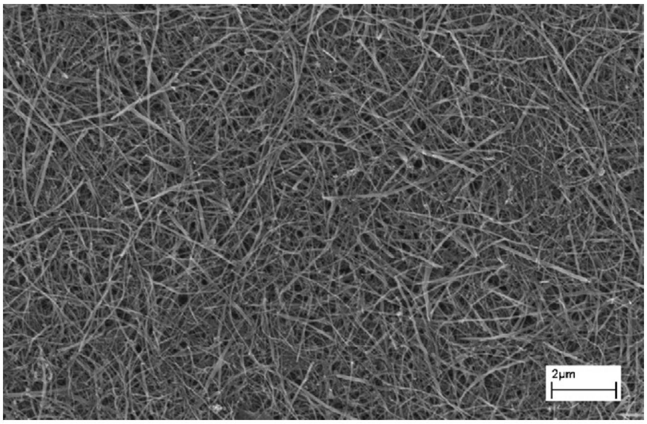

Fig. 1. SEM image showing the top surface of a CNT film produced in the authors' laboratory by EPD from aqueous suspension (electric field: 20 V/cm, deposition time: 5 min), showing two dimensional orientation of CNTs parallel to the electrode surface.

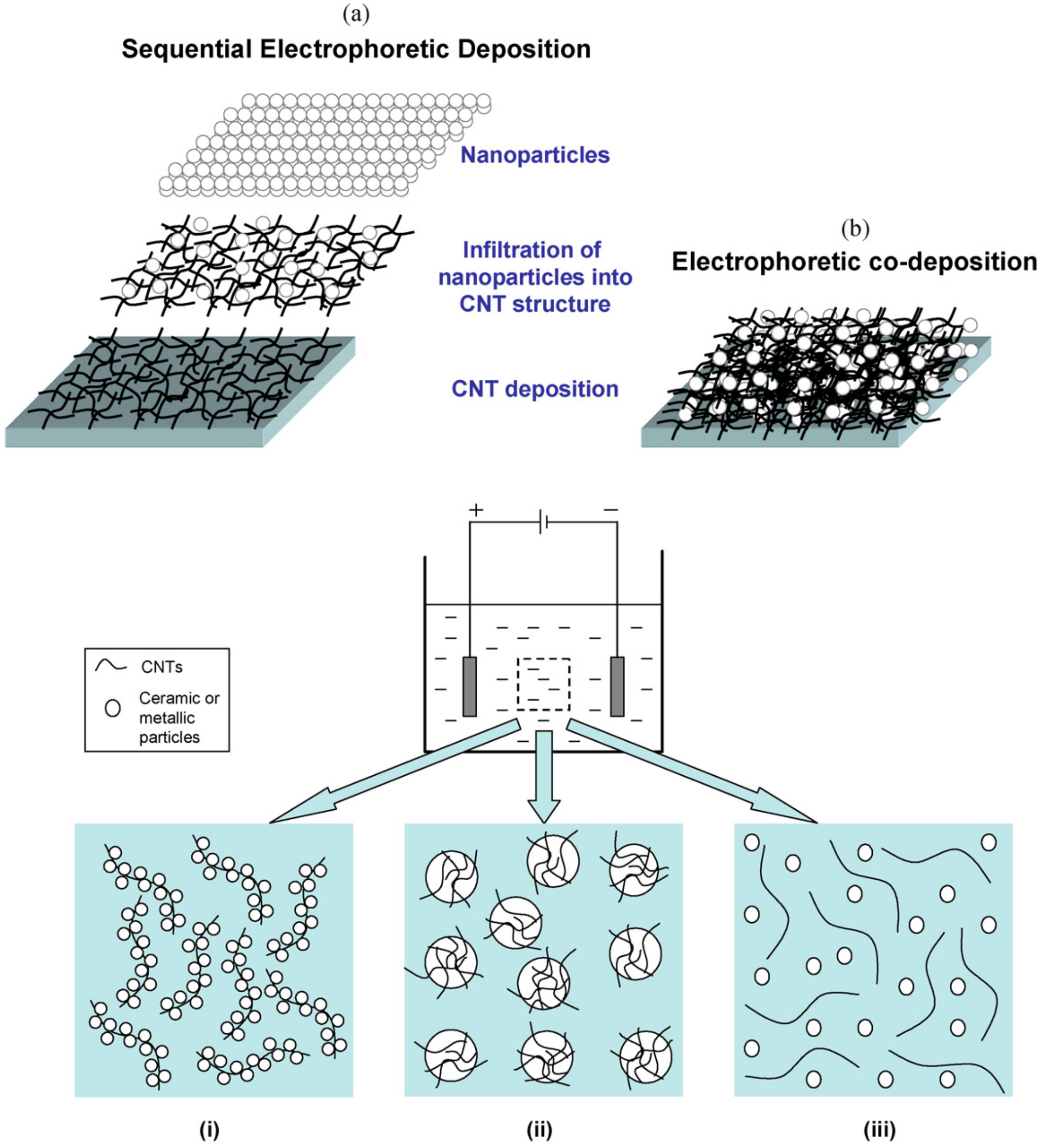

Fig. 2. Different strategies to fabricate CNT/ceramic nanocomposites by EPD: (a) schematic diagrams showing sequential deposition of CNTs and nanoparticles to form layered heterostructures and electrophoretic co-deposition; (b) schematic diagram showing different alternatives to produce CNT/particulate composites by electrophoretic co-deposition: (i) self-assembly of nanoparticles coating individual CNTs, (ii) heterocoagulation of CNTs onto individual (larger) particles, and (iii) simultaneous deposition of CNTs and ceramic (or metallic) particles exhibiting the same charge polarity in suspension.

ing the mentioned processing strategies are shown in Fig. 2a and b and specific examples of these different approaches to fabricate a variety of CNT–ceramic nanocomposites by EPD are discussed in the following sections.

3. SiO_2/CNT composites

EPD of ceramic nanoparticles (particle size <100 nm) is being used to produce monolithic ceramic materials, ceramic coatings and films, functionally graded materials, as well as laminate and ceramic matrix composites of high microstructural homogeneity.[2] The most common approach is the production of an electrostatically stabilised dispersion, which requires the preparation of a solvent medium in which the particles acquire high zeta-potential, while keeping the ionic conductivity of the suspensions low. Tabellion and Clasen[50] have reviewed previous work on the fabrication of large components, free standing objects, hollow bodies and objects of complex 3D shape by EPD of silica nanoparticles (e.g. commercially available fumed silica) in aqueous suspensions. Investigations have been carried out also on diphasic suspensions, for example silica-alumina colloidal suspensions of mullite composition, where the objective was to use EPD for fabricating homogeneous mullite ceramics and composites.[51] The combination of silica nanoparticles with multiwalled CNTs by EPD was investigated by Chicatun et al.,[52] who prepared

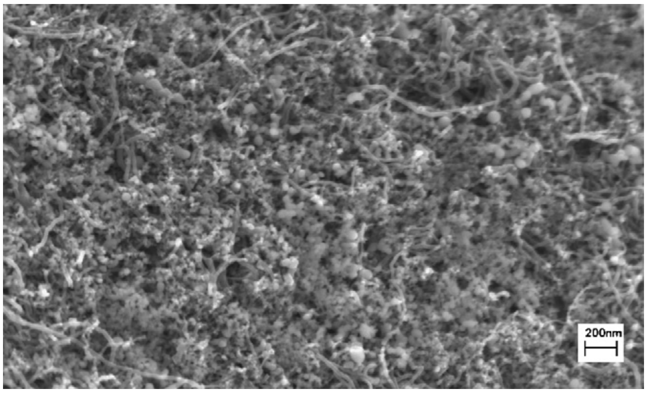

Fig. 3. SEM image of a SiO_2/CNT composite layer fabricated by electrophoretic co-deposition of CNTs and SiO_2 nanoparticles according to the procedure developed by Chicatun et al.[52]

SiO_2/CNT composite films on metallic substrates for applications as porous nanostructured coatings in the biomedical field and in thermal management devices. Commercially available multiwalled CNTs were used without any post-synthesis treatment and distilled water was the solvent. Aqueous dispersions of hydrophilic fumed silica (AERODISP W 1824, Degussa, Germany) were considered as source of SiO_2. A range of surfactants was investigated in their suitability to produce stable CNT suspensions, including: octylphenolpoly (ethylenglycolether) × (Triton X-100), polyacrylic acid (PAA), cetyltrimethyl ammonium bromide (C16TMAB), sodium dodecyl sulfate (SDS) and polyvinyl butyral (PVB). Iodine (99.999%) was used as a charge promoter, following previous experience on the use of iodine as charger in ceramic suspensions.[53] To prepare optimal CNT suspensions in distilled water, the surface properties of CNTs were modified with Triton X-100 and iodine. The suspension for electrophoretic co-deposition of CNTs and SiO_2 nanoparticles was prepared by mixing the aqueous CNT suspension with different volume ratios of the fumed silica dispersion. EPD experiments involved constant deposition time (in the range 1–5 min) and different applied voltages in the range 20–55 V. The parameters were varied depending on the concentration of silica in suspension. A typical microstructure of the materials produced by electrophoretic co-deposition is presented in Fig. 3. Layered CNT/SiO_2 porous composites were obtained by sequential EPD experiments alternating the deposition of CNTs and SiO_2 nanoparticles.[52] After deposition, the CNT film was dried at room temperature for 24 h and the EPD coated electrode was used to deposit the layer of silica nanoparticles. In order to reduce the amount and size of cracks in the films, different drying methods were investigated, including dipping the samples in liquid paraffin for 8 h at 90 °C. SEM results show that the CNTs were efficiently mixed with SiO_2 nanoparticles to form a network structure.[52] Possible applications of CNT/SiO_2 films are as porous coatings in the biomedical field, thermal management devices, biomedical sensors and other functional applications.[54] Applications where field emission properties are required should be also mentioned for these nanocomposites. For this application, novel Ag/SiO_2/CNT composite films have been produced by pulsed voltage electrophoretic co-deposition.[55] Multiwalled CNTs were suspended in a mixture of isopropyl alcohol and ethanol containing SiO_2 and Ag particles of average particle size 1.55 and 0.9 μm, respectively. CNTs, Ag and SiO_2 powder in the weight percentage ratio of 20:30:50 were dispersed in a isopropyl alcohol and ethanol mixed solution in the volume ratio of 3:1. Two types of surfactants, polyethyleneimine and Disperbyk-184 (BYK Chemie, Germany), were added to the suspension as dispersants and surface charger for the CNTs and the suspended particles, respectively. In order to increase the electrolyte concentration, 5×10^{-4} mol of $Mg(NO_3)26H_2O$ was added to the powder suspension. It was found that SiO_2 and Ag particles enhanced the bonding between CNTs and ITO glass (used as substrate) and the conductivity of the films, respectively. A pulsed voltage method, instead of conventional constant electric field, was used, as pulsed plating can yield coatings with improved surface appearance and properties (smoothness and refined grins). The pulsed plating parameters, controlled by applying 35 V for 1 s and −0.1 V for 1 ms, were found to be the optimum parameters for depositing films that exhibited microstructures and possessed field emission properties.[55] Fig. 4 shows cross-sectional SEM micrographs of a CNT/Ag/SiO_2 composite film prepared by constant voltage and pulsed voltage conditions, showing also the results of EDS analysis. Carbon nanotubes deposited by the pulsed voltage tended to align uniaxially in the direction of the applied electric field. The paper of Wang and Huang[55] thus is the first study to show the electrophoretic co-deposition of CNTs and two other particulate species to produce complex CNT containing metal–ceramic nanocomposites. The results confirm the versatility of the EPD technique and future applications of EPD to consider other combinations of ceramic and metallic particles with CNTs are expected following these successful results.

4. CNT/TiO_2 composites

A great variety of functional ceramic films are being produced by electrophoretic deposition of TiO_2 nanoparticles following the first work published by Matthews et al.,[56] who produced porous titania thin films on electronically conducting glass for photovoltaic cells. TiO_2 nanoparticles are being used to produce porous nanostructured films by EPD on a variety of substrates including metallic plates,[57,58] SiC and carbon fibers[53] and metallic meshes.[59] In most cases a standard suspension of TiO_2 nanoparticles in acetylacetone with addition of iodine was used and EPD has been carried out under constant voltage conditions (10–20 V) for deposition times <10 min, leading to high degree of particle packing in homogeneous film microstructures of up to 20 μm in thickness.[59,60] Porous TiO_2 nanostructured coatings are considered of interest for photocatalytic applications and the main component of the starting material is usually anatase.[61] Titania is also a biocompatible material, thus titania coatings on stainless steel or titanium alloys can find applications in orthopaedic implants. It has been therefore a natural or obvious development to explore the fabrication of CNT–TiO_2 composites by EPD considering the benefit of combining these two materials, which include enhancement the photocatalytic effectiveness of TiO_2[61,62] and improvement of TiO_2 mechani-

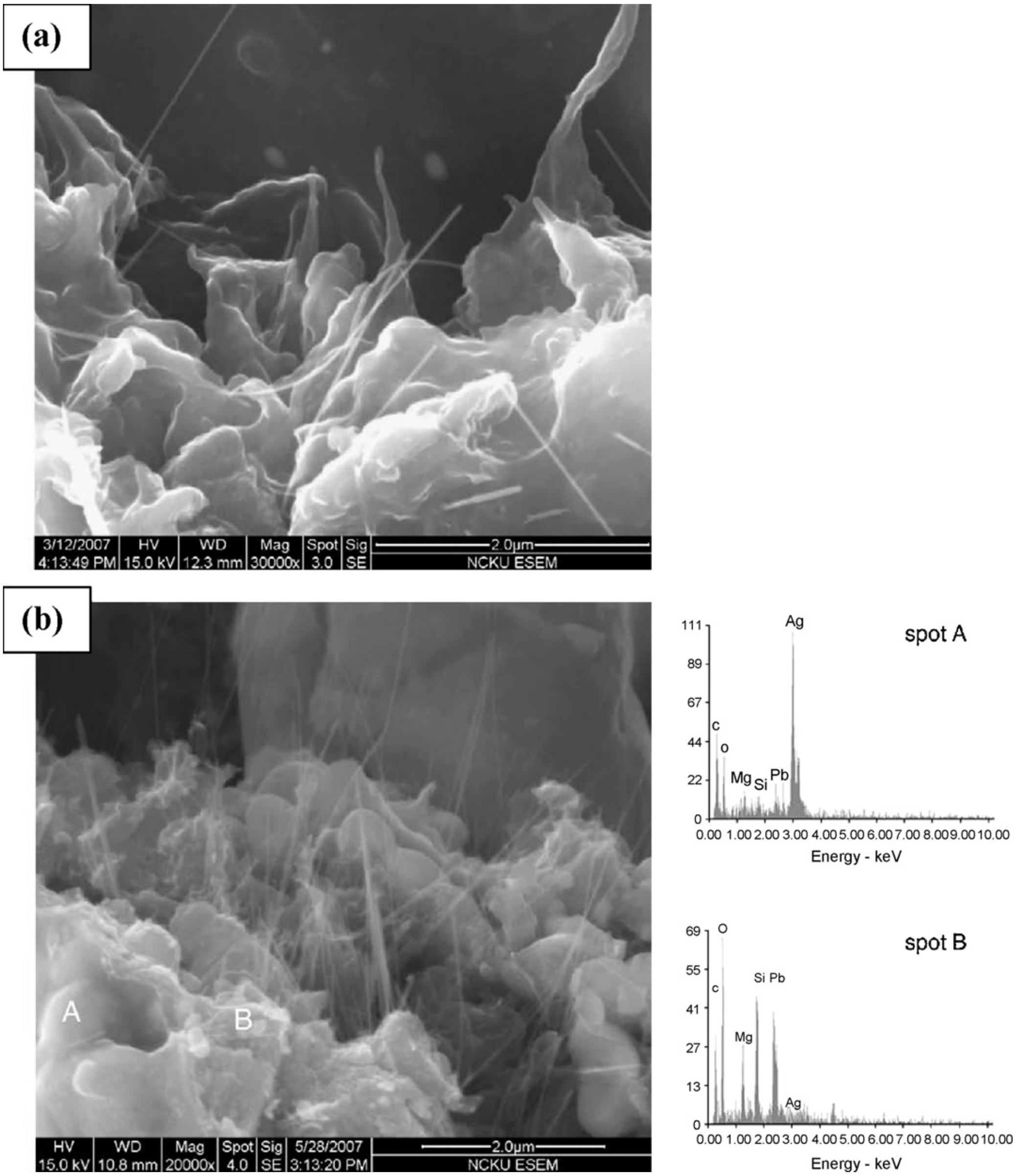

Fig. 4. Cross-sectional SEM micrographs of CNT/Ag/SiO_2 composite films prepared by EPD using (a) constant voltage and (b) pulsed voltage conditions, showing also the results of EDS analysis (spots A and B in (b)).[55] (Images published with permission of Elsevier.)

cal properties.[63] Homogeneous and thick deposits of CNTs have been coated and infiltrated with TiO_2 nanoparticles by EPD using commercial TiO_2 nanoparticles (P25, Degussa, Frankfurt, Germany) with mean diameter of 23 nm. The coating and infiltration of porous CNT assemblies with TiO_2 nanoparticles represent useful steps towards homogeneous incorporation of CNTs in structural and functional titania matrices. Pre-coating CNTs before deposition should eliminate agglomeration and improve the properties of composites.

The first research work in this particular system was carried out using multiwalled CNTs, grown by chemical vapour deposition (CVD), and commercial TiO_2 nanopowder.[64] Acid oxidation was used to produce well dispersed aqueous CNT suspensions: 0.8 g of CNTs were refluxed in 60 ml of mixed (1:3) concentrated nitric and sulphuric acids at 130 °C for 30 min, following by washing in water to pH 7. The suspension was then centrifuged, to remove remaining agglomerates, at 3000 rpm for 30 min. The suspension was further diluted for use in EPD. For co-deposition of CNTs and TiO_2 nanoparticles on stainless steel substrate, Kaya and co-workers[64] prepared suspensions by mixing 3.5 g of TiO_2 nanopowder with 31.5 g of CNT aqueous solution (of 0.6 mg/ml CNTs concentration). pH values were adjusted by adding either sodium hydroxide (NaOH) or hydrochloric acid (HCl). A field strength of 20 V/cm and deposition time of 4 min were used and the pH of the suspension was fixed at pH 5. Although the co-deposition mechanism was not investigated in detail in that study,[64] the evidence suggested that co-deposition has occurred due to the opposite signs of the surface charges (zeta potential values) of CNTs and TiO_2 nanoparticles at the working pH. Electrostatic attraction between CNTs and TiO_2 particles leads to the creation of composite particles in suspension (see Fig. 2a), consisting of TiO_2 nanoparticles

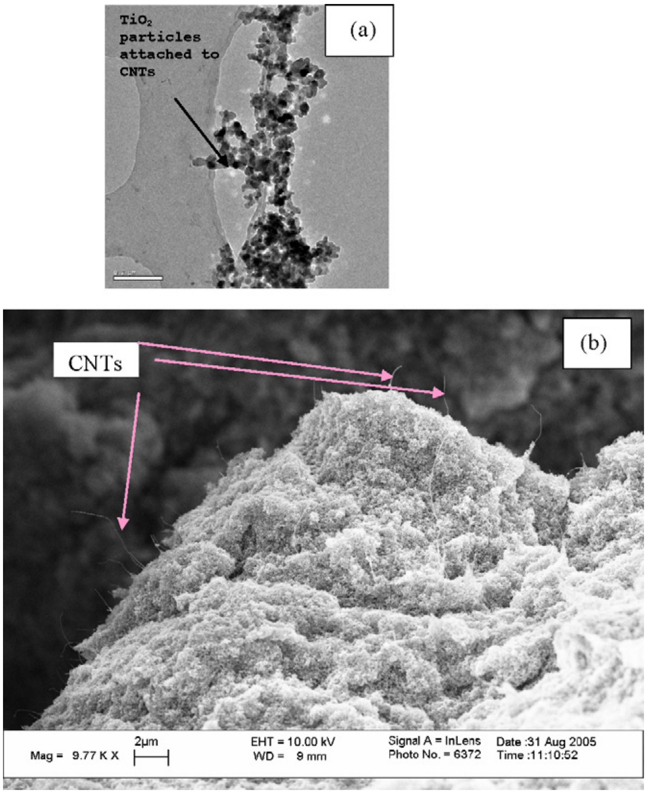

Fig. 5. (a) TEM image of a carbon nanotube coated by TiO_2 nanoparticles in aqueous suspension at pH 5. (b) FEG-SEM image of a TiO_2/CNT composite obtained by electrophoretic co-deposition on a planar stainless steel substrate. The coating was intentionally ruptured to reveal the fracture surface, CNTs are observed emerging from the surface (marked by arrows).[64] (Images published with permission of Springer.)

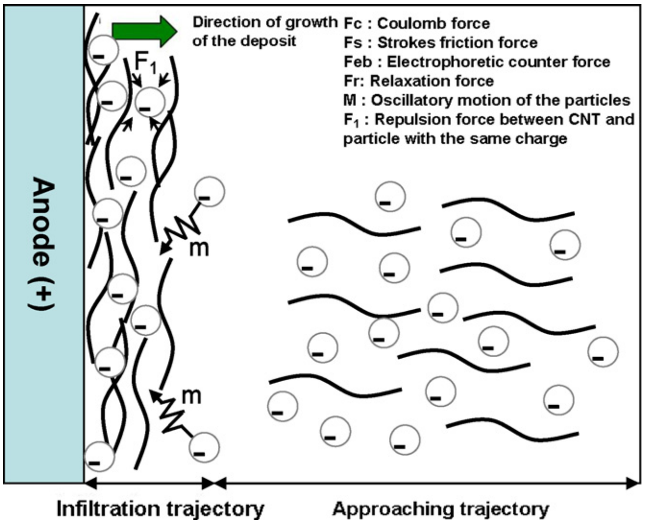

Fig. 6. Schematic representation of the electrophoretic co-deposition of negatively charged CNTs and titania nanoparticles in suspension.[66]

homogenously attached onto the surface of individual CNTs, as seen in Fig. 5a.[64] Under the applied electric field, these net negatively charged "composite TiO_2/CNT" elements should migrate to and deposit on the working electrode (the anode in this case). The process of EPD at constant voltage conditions was optimised to achieve homogeneous and well adhered deposits of varying thicknesses on the metallic substrates.[64] A fracture surface of a TiO_2/CNT deposit fabricated in this way is seen in Fig. 5b.[64] The image reveals the presence of CNTs protruding from the fracture surface. This type of porous CNT/titania nanostructures is potentially useful for nanoelectronic devices and photocatalytic substrates[65] but, after sintering, they could lead also to dense CNT reinforced TiO_2 structural coatings.

A relevant paper investigating the fabrication of TiO_2/CNT composite layers by EPD was published by Cho et al.[66] Both the sequential deposition of alternating layers of CNTs and TiO_2 nanoparticles and the co-deposition of TiO_2/CNT composites were investigated.

The mechanisms involved in electrophoretic co-deposition of equally charged particles has been explained by considering the different trajectories of nanoparticles in suspension, as shown in Fig. 6,[66] which follows from an earlier investigation on Al_2O_3 suspensions.[67] The first region, the "approaching trajectory", occurs at a given distance from the working electrode, where both CNTs and titania particles move towards the deposition electrode only under the influence of the externally applied electric field. The second region, the "infiltration trajectory", occurs close to the deposition electrode where the charge of the deposited CNT films influences the motion of the incoming charged particles. When CNTs and TiO_2 particles possess the same charge, repulsive forces act between them, as schematically shown in Fig. 6. However, the particles are repelled before they can reach the CNT surfaces due to the charges on the CNTs. It can be assumed that under the effect of the repulsive forces, due to the surrounding CNTs, the particles will follow the path with the fewest possible obstacles until reaching the next interstice between adjacent CNTs. This mechanism of infiltration could be equally applied to the sequential EPD process (Fig. 2a), where the titania nanoparticles initially infiltrate the porous CNT layer and then build up a deposit to form a second layer. Using sequential EPD, four-layer TiO_2/CNT laminate composite coatings were produced by Cho et al.[66] The adhesion of the films to the metallic substrate was qualitatively investigated by using adhesive tape. It was found after removal of the tape that the CNTs layer (the first layer deposited) remained adhered to the substrate with minimal disruption of the CNT structure indicating qualitatively good interfacial adhesion. The reasons for this relative high adhesion may be related to the formation of metal hydroxides at the electrode surface during EPD.[5,49] These hydroxides could then hydrogen bond to the surfaces of the CNTs. Investigation of the composite coatings indicated that the CNT layer can act to reinforce the ceramic coating by providing a crack deflection and delamination path, however quantitative results were not reported.[66] More recently, Jarernborn et al.[63] have investigated the effect of multiwalled CNTs of commercial origin in reducing microcrack formation in EPD films deposited on F-SnO_2 conducting substrates. The authors used suspensions of TiO_2 nanoparticles (Degussa) in acetylacetone with addition of iodine. The development of film thickness with applied voltage was investigated, indicating that with increasing voltage between 5 and 20 V, the thickness increased from 2 to ~8 µm.[63] The presence of CNTs was confirmed to reduce the problem

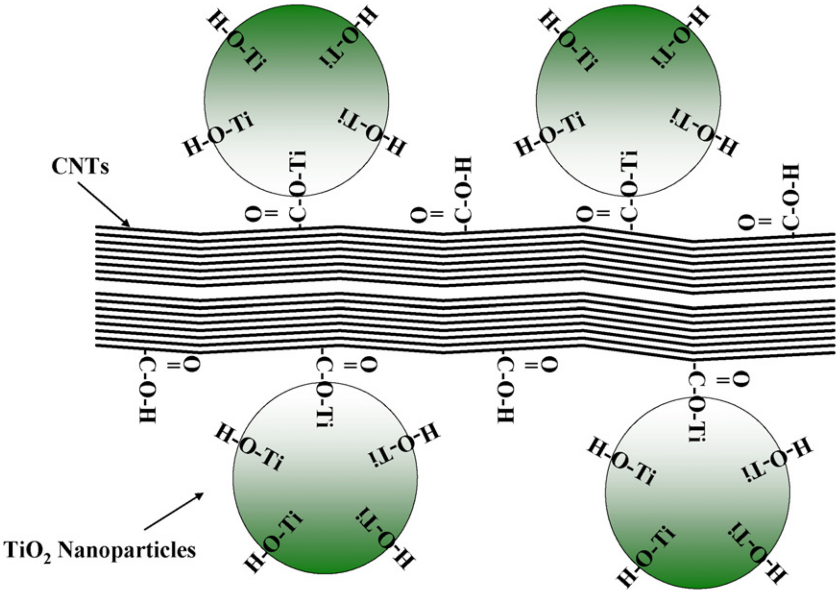

Fig. 7. Schematic diagram showing the suggested interaction of hydroxyl and carboxyl groups on the surfaces of functionalized CNTs and TiO_2 nanoparticles leading to strong bonding.[63]

of microcracking in TiO_2 films by bonding to TiO_2 nanoparticles through the interaction of hydroxyl and carboxyl groups, as schematically explained in Fig. 7.[63]

5. Manganese dioxide/CNT composites

In a recent investigation, an EPD technique has been developed for the fabrication of composite films containing manganese dioxide nanofibers and multiwalled CNTs for application in electrochemical supercapacitors (ES).[68] Manganese dioxide nanofibers were prepared by a chemical precipitation technique. As-prepared, large aspect ratio nanofibers with length in the range 0.1–1 μm and diameter of 2–4 nm showed low crystallinity and contained adsorbed water. Commercially available multiwalled CNTs (Arkema) with average diameter ~15 nm and length ~0.5 μm were used. EPD of manganese dioxide and CNTs was performed from aqueous suspensions containing 0–5 g/l manganese dioxide, 0.1–0.5 g/l sodium alginate and 0–0.5 g/l CNTs. Sodium alginate polyelectrolyte was used as a dispersant, charging additive and binder for EPD of both manganese dioxide nanofibers and CNTs. Nanostructured films were deposited on conductive substrates (stainless steel foils and graphite) and exhibited a fibrous, crack free and porous microstructure with pore size in the range 10–100 nm. It was suggested that the porous structure of manganese dioxide deposits is beneficial for ionic conductivity, whereas CNTs can provide improved electronic conductivity.[68] The films were relatively uniform with thickness varying between 1 and 20 μm by controlling the deposition voltage in the range 10–50 V and the deposition time in the range 1–10 min. The distance between the substrates and platinum counter electrodes was 15 mm. Fig. 8 shows SEM images of the surface and cross-section of MnO_2/CNT composites at different magnifications, prepared under different EPD conditions.[68] Cyclic voltammetry (CV) data for films tested in 0.1 MNa_2SO_4 solutions showed ideal capacitive behaviour and higher specific capacitance (SC) in the voltage window of 0–1.0 V, in comparison to standard calomel electrode (SCE). Composite films containing manganese dioxide and CNTs showed higher SC compared to the pure manganese dioxide films without CNTs. Moreover, SC was seen to decrease with increasing scan rate and increasing film thickness. The composite films prepared by EPD can be used as electrode materials for electrochemical supercapacitors.[69]

6. Fe_3O_4/CNT composites

The research field of functional CNT nanocomposites, which investigates the integration of CNTs and functional nanoparticles into single material structures for a range of device architectures, has received much attention for their potential applications in next-generation luminescent, magnetic, and energy-storage devices.[70–72] This area comprises three major research themes: functionalization of CNTs surfaces with nanoparticles[73]; co-deposition of CNTs and nanoparticles into thin films and alternating, multilayered deposition of CNTs and nanoparticles.[74] These heterostructures are integral to several existing and proposed magnetic, optical and energy-storage devices.[75–77] The fabrication of functional layered CNT–nanoparticle composites relies on the ability to deposit homogeneous layers of CNTs and nanoparticles on top of one another. Of the developed film fabrication methods for nanomaterials, EPD has been demonstrated to be one of the most attractive techniques for the deposition of highly ordered carbon nanotube and nanoparticle films.[2,15] As mentioned above, EPD provides substantial control over the film thickness and the deposition rate, and offers a degree of site-selectivity. Despite these advantages, integration of functional magnetic particles and CNTs in layered structures by EPD has not been extensively investigated so far. In the first paper published in this field,[74] alternating layer, iron oxide (Fe_3O_4)

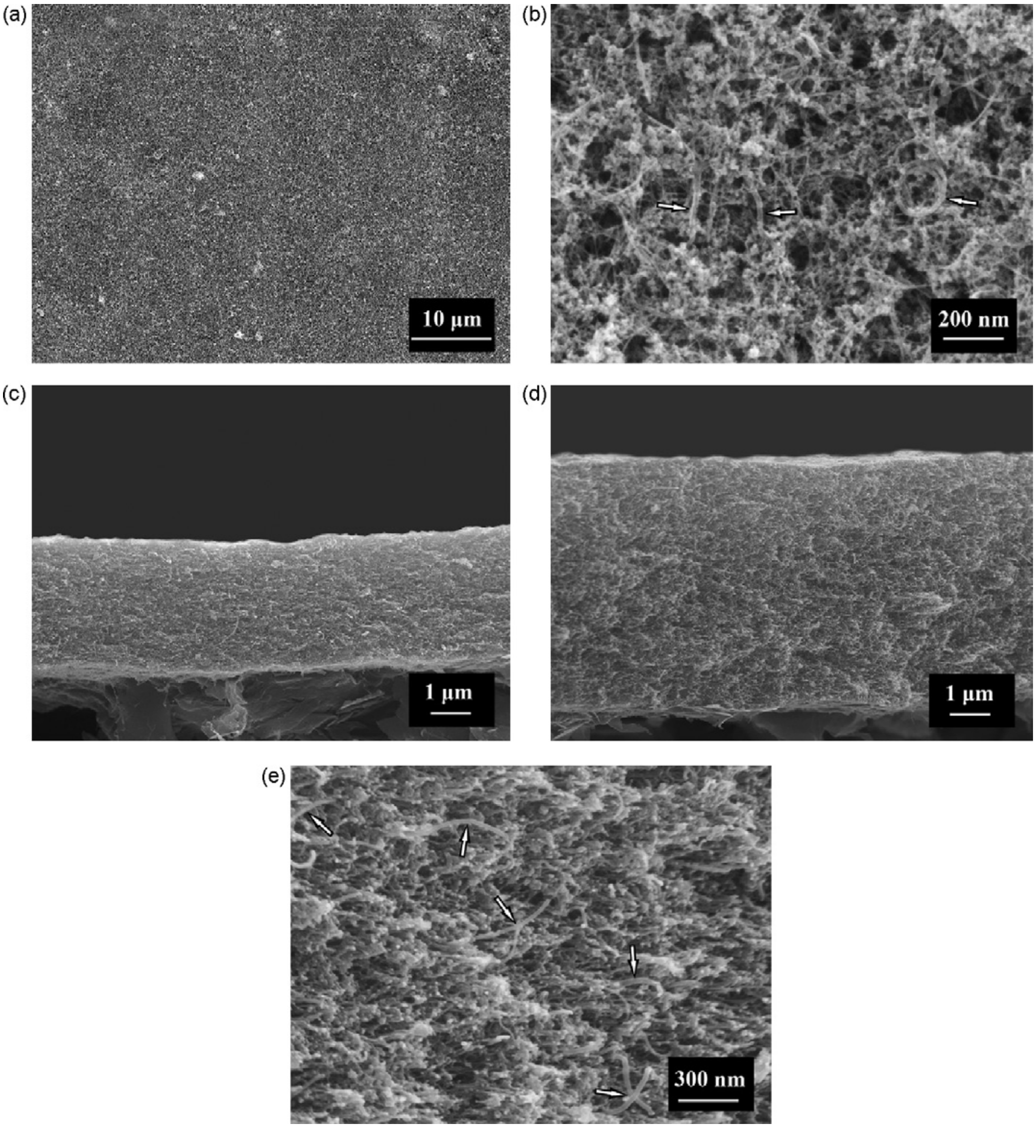

Fig. 8. SEM images of MnO_2/CNT composite deposits obtained by electrophoretic co-deposition (deposition voltage 15 V) from a sodium alginate solution[68]: (a and b) surface of the deposits on a stainless steel substrate at different magnifications, (c and d) cross-sections of the deposits of different thickness on graphite substrates and (e) high magnification image of a cross-section (arrows show carbon nanotubes). (Images published with permission of Elsevier.)

nanocrystal/multiwalled CNT composite films were fabricated by EPD on stainless steel and gold substrates. Low field-high current and high field-low current EPD conditions were integrated to produce the composite films. The low field-high current EPD approach produced porous mats from aqueous CNT suspensions, while the high field-low current EPD approach produced tightly packed nanoparticle films from a dispersion of Fe_3O_4 nanoparticles in hexane. The surface coverage and homogeneity of the iron oxide films improved with repeated deposition on the same CNT layer. Large electric fields applied

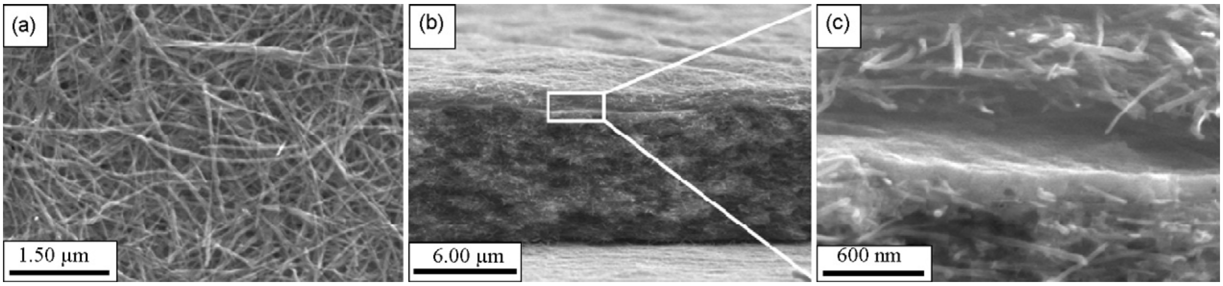

Fig. 9. (a) SEM image showing the top CNT layer of a CNT mat-Fe_3O_4 film-CNT mat composite. (b) Cross-sectional SEM image of the composite. (c) Magnified SEM image of the Fe_3O_4 film between the two CNT mats, according to Ref. 74. (Images published with permission of IOP Publishing Ltd.)

during EPD of Fe_3O_4 and strong van der Waals interactions among the nanoparticles led to tightly packed Fe_3O_4 films on the MWCNT porous layer to create CNT/Fe_3O_4 composite films. The assembly of CNT layers on top of the CNT–iron oxide film was carried out confirming the feasibility of producing multilayered CNT–Fe_3O_4 heterostructures suitable for a range of applications. The SEM image in Fig. 9 shows the cross-section of a Fe_3O_4 nanoparticle/CNT heterostructure obtained by EPD.[74] The thicknesses of the first CNT layer, the Fe_3O_4 film, and the second CNT layer are approximately 6 μm, 150 nm and 1 μm, respectively. The high magnification cross-sectional SEM image (Fig. 9) shows the sharp interfaces between the three layers confirming the suitability of EPD to produce these highly ordered nanostructures. Recently, this work has been expanded to include the fabrication by EPD of Eu_2O_3/CNT heterostructures for optical and energy-storage device applications.[78]

7. CNT containing bioactive materials

7.1. Research background

The development of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, (HA) and bioactive glass coatings by EPD is an area of increasing interest.[79–82] Zhitomirsky[82] was the first to use EPD for producing HA coatings on a variety of substrates and Roether et al.[83] applied for the first time EPD to coat polymer foams with Bioglass® particles. The remarkable high mechanical strength and nanoscaled morphology of CNTs make them attractive for biomedical applications, particularly for developing nanofibrous bioactive surfaces in combination with hydroxyapatite or bioactive glasses.[84–87] CNT layers have been shown to provide an optimal surface nanotopography for the adhesion of cells and their growth.[88,89] Combined with hydroxyapatite and bioactive glasses, CNTs also promote the formation of bone-like nanostructured calcium phosphate crystals (biomineralisation) when the coatings are in contact with biological fluids.[86] Additionally, the ultra-light but strong CNTs represent optimal reinforcing elements for bioactive glass or hydroxyapatite matrices, whereby CNTs can enhance also the function of biomedical coatings, for example for improved tracking of cells, sensing of microenvironments and delivering of transfection agents besides providing nanostructured surfaces for optimal integration with the host bone tissue.[89] CNTs can also be incorporated into coatings to impart novel properties such as electrical conductivity, which may aid in directing cell growth and bone tissue regeneration by facilitating the physioelectrical signal transfer.[88–90] The combination of CNTs with hydroxyapatite and bioactive glass particles to form novel nanostructured inorganic bioactive coatings by using EPD is discussed in the following sections. EPD methods developed recently[91,92] for the synthesis of functionalized single-walled CNTs/polymer composites, which enable also the co-deposition of HA particles, will not be discussed in this review, as they fall in the group of polymer composite films, which are beyond the scope of the present paper.

7.2. Hydroxyapatite/CNT composites

Synthetic hydroxyapatite (HA) is a biologically active calcium phosphate bioceramic commonly used to coat orthopaedic metallic implants or as bone replacement material.[93] Bioactive HA promotes bone growth along its surface but its mechanical properties are too low for many applications, such as load-bearing orthopaedic devices or robust coatings with adequate structural integrity. The combination of HA with CNTs is being investigated to exploit the extraordinary mechanical properties of CNTs to reinforce HA layers obtained by EPD.[64,84,87] In order to obtain an efficient mechanical reinforcement, the surface of CNTs must be functionalized not only to achieve a good dispersion of CNTs in the ceramic matrix (see Section 2), but also to induce an ideal interface between CNTs and HA, which will be ultimately responsible for an efficient load-transfer mechanism. The manufacturing and properties of CNTs-reinforced HA ceramic composites suitable for clinical bone graft procedures has been reported recently.[84,94] It has been shown for example[85] that CNT content affects the hardness and elastic modulus of HA/CNT composites, with an optimum CNT concentration of 0.1 wt% providing the maximum hardness of 3.46 GPa and elastic modulus of 69.5 GPa. However, research efforts devoted to processing CNTs-reinforced HA composite coatings by EPD have not been discussed in detail in the literature. Both plasma spraying[95] and laser surface alloying[87] have been applied to produce HA/CNT composite layers on Ti–6Al–4V alloys. These two techniques however are cost-intensive coating technologies and it is also difficult to control the coating parameters and thickness during processing. It is also known that both coating techniques present difficulties to control the phase content and distribution, which may result in the formation of the non-biocompatible CaO phase due to the high temperatures involved. Therefore, increasing research efforts are being devoted to develop HA/CNT coating layers by EPD.[64,96–98] In the first published report on this subject, CNT reinforced hydroxyapatite layers on Ti–6Al–4V biomedical alloy were obtained by EPD using sol–gel synthesised nano-sized (20–30 nm) HA particles mixed with multiwalled CNTs.[64] In subsequent research, homogeneous HA/CNT composite coating layers were obtained using different EPD processing parameters (applied voltage and deposition time).[96,97] In a recent work by Lin et al.,[98] HA nanoparticles and MWCNTs were dispersed in ethanol (with a concentration of 0.005 g/ml and a pH value of 5) and EPD was used to coat Ti alloys using an applied voltage of 30 V and a deposition time of 50 s, giving a deposit thickness of 10 μm. The resultant layer was sintered at 700 °C for 2 h under flowing argon. A bonding strength of 35.4 MPa was measured between the substrate and the HA/CNT composite layer, which was significantly high in comparison to the pure HA layer (20.6 MPa).[98] This results show an additional benefit of CNTs in enhancing the adhesion of the HA layer to the substrate. Recent research[99] has focused on the use of hydroxyapatite nanoparticles (20–30 nm) and high aspect ratio multiwalled CNTs (10–30 nm in diameter, up to 500 μm length and 40–300 m^2/g surface area) to form HA/CNT composites by EPD. The CNTs were first treated to attach carboxylic acid groups to their surfaces for carboxyla-

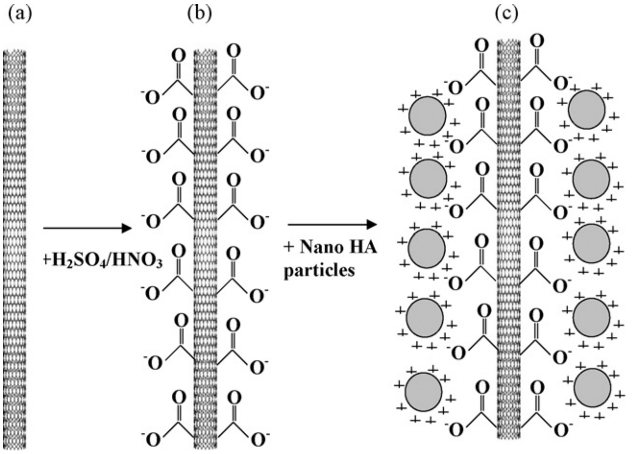

Fig. 10. Schematic representation of the process for anchoring HA nanoparticles (positively charged) onto functionalized CNTs (negatively charged): (a) as received CNT, (b) functionalized CNT and (c) attachment of nano-HA particles onto the modified CNT surface.

tion. A determined amount (0.5 g) of as-received MWCNTs was added to 500 ml of a mixture of 75% sulphuric (H_2SO_4) and 65% nitric acid (HNO_3) with a 3:1 (by volume) ratio. This mixture was ultrasonically sonicated for 6 h at 50 °C. Carboxylated CNTs were diluted in distilled water and then filtered. The presence of carboxylic groups induces a series of chemical reactions along the interface between CNTs and HA nanoparticles, enhancing the reinforcing efficiency of CNTs. Fig. 10 shows the schematic representation of the chemical functionalization of multiwalled CNTs using the mixture of H_2SO_4 and HNO_3. The surface charge of CNTs is expected to be negative (due to the presence of COOH groups) and therefore CNTs will attract positively charged particles via electrostatic attraction. HA powders were dispersed (5 wt%) in aqueous suspensions using Darvan C (as a dispersant) and the pH was adjusted to pH 4.[99] Surface modified CNTs were then added to the suspension containing dispersed HA particles and ultrasonically mixed for 3 h. Coating experiments on Ti6Al4V substrates were carried out using EPD under constant applied voltage of 20 V d.c. for a constant deposition time of 4 min. The coated samples were sintered at 600 °C for 2 h under flowing nitrogen.

Thus, in order to obtain homogeneous dispersion of CNTs in the HA matrix, the surface charge of HA nanoparticles and CNTs was adjusted to be of opposite sign (as explained above for TiO_2/CNT composites), so that they can attract each other and act as a single "composite particle" during EPD under the external electric field influence. Fig. 11a shows the fairly homogeneous microstructure of the HA/CNT deposit exhibiting no preferential agglomeration of HA particles or aggregation of CNTs, as desired. Moreover Fig. 11b shows the sintered structure of a EPD-formed HA/CNTs coating layer on Ti6Al4V alloy obtained by EPD (deposition time: 4 min, applied voltage: 20 V). The coating thickness of the sintered (600 °C, 2 h) material was ~25 μm (Fig. 11b) and no microcracks or inhomogenities were observed in the sintered layer.

As mentioned above, one of the main objectives of adding CNTs to HA is to increase the mechanical performance of the coating layer by inducing toughening mechanisms, such as crack deflection. The propagation of cracks induced by indentation technique on the monolithic HA and on a HA/CNT composite (2 wt% CNTs) was investigated,[96,97,99] indicating that no crack deflection occurs in the monolithic material but possible toughening mechanisms such as nanotube crack bridging and debonding appear to be active in the composite, as inferred from Fig. 12a and b, respectively. The authors[99] also investigated the effect of CNT addition on the bonding strength of the electrophoretic deposited layer on the alloy substrate. It was found that after sintering at 600 °C for 2 h under flowing nitrogen gas, the bonding strength for the coating containing 2 wt% CNTs was higher than for the 1 wt% composite (2.76 and 1.84 MPa, respectively), while the bonding strength for the HA coating (no CNT) was only 0.7 MPa, in agreement with the results of Lin et al.[98] No delamination or peeling of the coating layer was observed, which is ascribed to the presence of the CNTs network acting as a reinforcement of the sintered HA layer, as also observed in TiO_2/CNT composite layers.[63]

7.3. Bioactive glass/carbon nanotube composites

Bioactive silicate glasses, for example "45S5" Bioglass® of composition (in wt%): 45% SiO_2, 24.5% Na_2O, 24.5% CaO

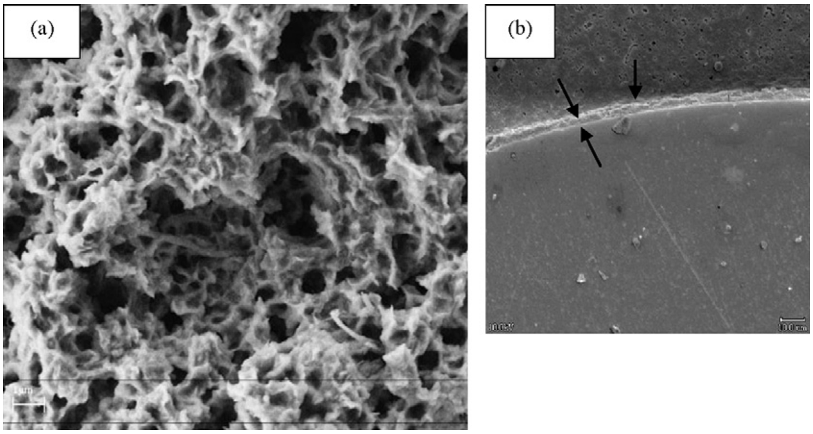

Fig. 11. FEG-SEM images of (a) HA/CNT deposit after EPD, and (b) cross-section of HA/CNT coated Ti6Al4V substrate after sintering (600 °C for 2 h) showing the macroscopic uniform structure of the coating.[99]

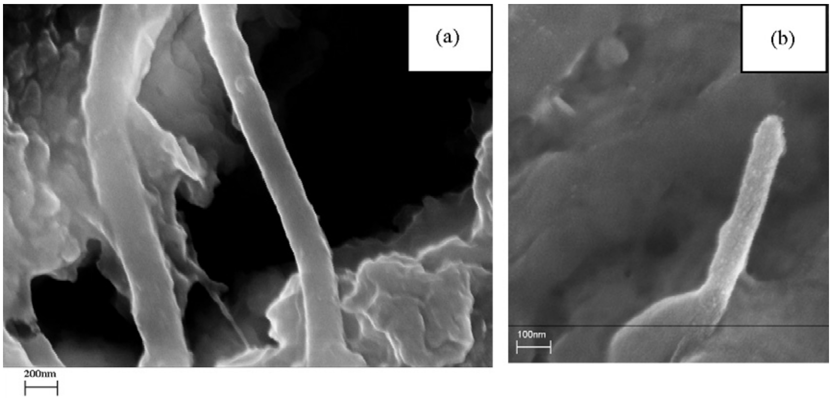

Fig. 12. FEG-SEM images of the fracture surfaces of a HA/CNT composite layer indicating nanotube crack bridging (a) and debonding (b), as possible toughening mechanisms in these composites.[99]

and 6% P_2O_5, were first developed in 1971[100] and they have been used in a range of biomedical applications such as non-load-bearing implants, bioactive coatings, bone cements and tissue engineering scaffolds[101–103] due to their excellent bioactivity and biocompatibility. In contact with body fluids, bioactive glasses form a biologically active hydroxycarbonate apatite (HCA) layer that is chemically and structurally equivalent to the mineral phase in bone.[101–103] This equivalence leads to strong interfacial bonding between implants and tissues. One approach to resolve the problem of the mechanical weakness and brittleness of bioactive glasses is to apply them as a coating on metallic substrates, e.g. Ti alloys or stainless steel.[81] These coatings improve both bioactivity and biocompatibility of implants as well as protect the metallic implants and orthopaedic devices from corrosion when in contact with body fluids. EPD has been used to deposit bioactive glass coatings on metallic substrates[81] and, more recently, the EPD technique was further developed for production of CNTs/Bioglass® layered composite films.[104] The bioactive glass powder used has a particle size between 1 and 15 μm, with at least 50% of the particles with diameter <3 μm. Multiwalled carbon nanotubes grown by a catalytic chemical vapour deposition (CCVD) method were used. The average outer diameter of the CNTs was ∼20 nm. After acid treatment of CNTs, a well dispersed aqueous CNT suspension with a concentration of 0.45 mg/ml was prepared. In the experiments of Cho et al.,[104] a sequential deposition method was applied to produce a coating of CNTs on bioactive glass layers. EPD was performed using electric field strengths in the ranges 10–40 V/cm and 2–10 V/cm for CNTs and Bioglass® suspensions, respectively, and different deposition times (1–4 min and 3–6 min for CNTs and Bioglass® suspensions, respectively). A similar technique has been used to deposit CNTs onto 3D Bioglass® scaffolds.[86] A SEM image showing the morphology of the deposited CNT layer is shown in Fig. 13, indicating that CNTs form a compact nanotopography on the Bioglass® surface.[86] There was minimal infiltration of CNTs into the microscopic pores of the glass structure and CNTs formed a surface nanoscaled fibrous pattern. Several applications of these novel nanocomposites are possible. For example, the porous network provided by the CNT-mesh on the Bioglass® surface represents a suitable bioactive nanofibrous surface to study cell attachment and growth. The incorporation of CNTs on the bioactive glass surface can provide also improved bioactive function for applications as coatings on orthopaedic implants for strong bonding with bone, similarly as discussed above for HA/CNT composites. In the field of biomimetic materials for tissue engineering, the CNT coated Bioglass® substrates produced by EPD (such as the one shown in Fig. 13) represent interesting scaffolds for the rapid growth of nano-hydroxyapatite crystals, when the composites are immersed in relevant biological fluids, such as simulated body fluid (SBF).[105] As shown in the literature,[86,105,106] the CNT mesh can be used to induce the ordered growth of a nano-HA surface layer to provide a nanostructured topography that resembles closely the surface of bone in its chemistry, crystallinity and morphology. The EPD of CNTs on bioactive glass scaffolds for bone tissue engineering has also been investigated.[86] It has been shown[104] that the presence of CNTs can enhance the bioactive behaviour of the Bioglass® surface since the CNT mesh is serving as a template for the ordered formation of nanostructured HA layers, which does not occur on uncoated Bioglass® surfaces. It should be pointed out that electrophoretic co-deposition from diphasic suspensions of bioactive glass particles and CNTs has not been investigated so far, remaining thus an important topic for

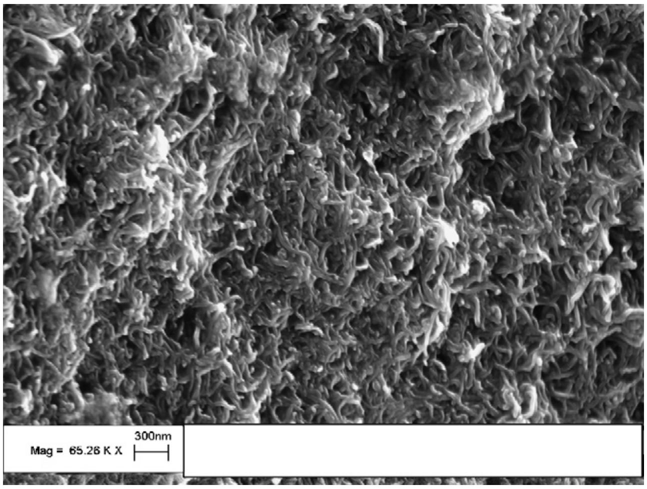

Fig. 13. SEM micrograph of a Bioglass® scaffold coated with CNTs by EPD following the process developed in a previous investigation.[86]

future research. Clearly, issues related to the biocompatibility of the CNT/Bioglass® composites in contact with host cells remain to be investigated, including possible cytotoxicity effects of CNTs.[89]

8. Conclusions

The reviewed literature has indicated that EPD is a powerful and versatile technique for the ordered deposition of CNTs and CNT–ceramic nanocomposites for a variety of applications. Successful examples involving combination of CNTs and SiO_2, TiO_2, MnO_2, Fe_3O_4, HA and bioactive glass, were discussed. EPD has great potential for manipulation of CNTs and for their assembly into ordered layers including thin films and coatings. Significant progress has been made in the design of suitable suspensions of well dispersed CNTs for use in EPD, both in aqueous and organic solvents. It is likely that novel applications of CNT structures will emerge as EPD continues to be explored to develop tailored CNT–ceramic systems, such as those discussed in this review. The combination of CNTs and nanocrystalline particles leads to functional heterostructures for applications in field emission displays, nanoelectronic devices, electrochemical supercapacitors, gas sensors, photocatalytic devices, biomedical scaffolds, drug delivery systems, antibacterial films, biosensors, and in other functional composites. For biomedical applications, the combination of CNTs with hydroxyapatite, bioactive glass or collagen is being explored, which is leading to advanced functional bioactive coatings. EPD (and combinations of EPD and other colloidal processing methods) will play a significant role in the development of such advanced CNT/nanoparticle composite nanostructures. EPD enables also the incorporation of other nanoparticles, including metallic nanoparticles, for the development of multiphase heterostructures. Further developments of the EPD process will allow the reliable fabrication of three dimensionally controlled nanostructures and nanocomposites containing CNTs, either in the form of dense materials or with a required pore structure; graded, aligned, and patterned features may also be incorporated as required.

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