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Review

# The Electrophoretic Deposition of Inorganic Nanoscaled Materials

—A Review-

無機ナノスケール材料の電気泳動堆積(総説)

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Electrophoretic deposition (EPD) is gaining increasing interest as a processing technique for production of novel inorganic nanostructured and nanoscale materials, including the use of nanoparticles, nanotubes, nanorods and related nanomaterials. Recent advances in the electrophoretic deposition of a great variety of ceramic and metallic nanoparticles, carbon nanotubes and other inorganic nanoscaled materials are discussed in this review. The purpose of the paper is to demonstrate the utility of an applied electric field to manipulate and control the deposition of electrically charged nanoscaled particles and other nanostructures on solid surfaces from liquid suspensions. A wide range of applications has been reviewed, demonstrating the high versatility and suitability of the EPD technique as a convenient nanotechnology processing tool. Nano-enamels and structural coatings, electrodes and films for fuel cells, capacitors, sensors and other microelectronic devices, fibre-reinforced and graded ceramic composites, nanostructured films and coatings for electronic, biomedical, optical, catalytic and electrochemical applications are some of the examples discussed. The combination of sol-gel methods and EPD for production of a variety of nanomaterials is also reviewed.

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## 1. Introduction

**E**LECTROPHORETIC deposition (EPD), a traditional processing method in the ceramic industry,<sup>1)</sup> is gaining increasing interest both in academia and in the industrial sector for production of new materials.<sup>2)-7)</sup> Consequently, a wide range of novel applications of EPD in the processing of advanced monolithic materials, composites and coatings is emerging. The interest in the EPD technique is based not only on its high versatility to be used with different materials and combinations of materials but also because EPD is a costeffective method usually requiring simple equipment. With EPD particulate deposits can be made in seconds on suitable surfaces of planar or more complex geometry. Moreover EPD has a high potential for scaling up to large product volumes and sizes, as well as to a variety of product shapes and 3D complex structures.<sup>2)-7)</sup>

EPD is achieved via the motion of charged particles dispersed in a suitable liquid towards an electrode under an applied electric field. Deposit formation on the electrode occurs via particle coagulation. Electrophoretic motion of charged particles during EPD results in the accumulation of particles and formation of a homogeneous and rigid deposit at the relevant electrodes.

The potential of the EPD technique for the realization of unique microstructures and novel (and complex) materials combinations in a variety of shapes and dimensions is being increasingly appreciated by materials scientists and technologists. This growing interest in EPD both in the academic and industrial communities has prompted the organization of

Corresponding Author: A. R. Boccaccini Tel: +44 207 594 6731, Fax: +44 207 594 6757 E-mail: a.boccaccini@imperial.ac.uk two international conferences in the last three years, which focused entirely on the application of EPD in materials processing.<sup>7)</sup> EPD has been recognized as the most versatile technique for particulate processing in terms of the wide range of dimensions it can be applied to, for example in terms of the thickness of deposits it can produce, as compared to other powder processing routes, and due to its applicability to nanoparticles and nanopowder assembly,<sup>8)</sup> as schematically shown in **Fig. 1**.

The synthesis and characterization of nanoscale materials and nano-structures are current areas of active research and development worldwide.<sup>9)</sup> The main focus of basic research



Fig. 1. Schema showing various particulate processing methods, dimensional ranges of application with current technologies and area covered by this review (modified after Van Tassel<sup>8)</sup>).

on nanostructured materials is, on one hand, to gain understanding of their intriguing physical and chemical properties (nanoscience), and, on the other hand, to utilize these novel nanomaterials in advanced (nano) technologies and in particular strategic applications. EPD, with its high versatility and ease of use, is revealing itself as one of the processing techniques of choice in the increasingly popular, strategic R & D field of nanomaterials. Nanoparticles and other nanoscaled materials are being used as starting elements for the synthesis of a variety of advanced materials, for example engineering and functional monolithic (nano)ceramics, structural and functional coatings, thick and thin films, bioactive materials, ceramic matrix composites (CMCs), as well as laminated and functionally graded materials of high microstructural homogeneity. No previous review article is available covering the particular application of EPD in the area of nanomaterials, in particular inorganic nanomaterials, as intended here.

Thus the present review covers recent significant developments in the field of EPD of nanoparticles, nanotubes, nanorods and related nanoscale structures. The pace of publications related to this topic has increased dramatically in recent years. During this period key advances have been made towards understanding basic mechanisms of EPD of nanostructures, expanding traditional applications of EPD (mainly in the field of ceramic processing) and exploring new application areas and new materials combinations. For completeness, a short section (Section 2) is included covering basic aspects of the EPD technique referring to recent published work in the area of fundamental understanding of the mechanism of EPD. For more complete reviews about the basic principles of EPD and its applications in general areas of materials science and technology Refs. 1)-8, 10) are recommended.

## 2. Fundamentals of electrophoretic deposition

The phenomenon of electrophoresis has been known since the beginning of the 19th century and it has found application in the past 40 years mainly in traditional ceramic technology.<sup>1)-3)</sup> As recently noted by van Tassel,<sup>8)</sup> over the last seventy years there have been more than a thousand articles and patents related to EPD.

EPD is essentially a two-step process. In the first step electrostatically charged particles suspended in a liquid migrate towards an electrode under the effect of an electric field (electrophoresis). In the second step, the particles deposit on the electrode forming a relatively dense, rigid and homogeneous compact or film. A post-EPD processing step is usually required, which include a suitable heat-treatment (firing or sintering) in order to further densify the deposits and to eliminate porosity.

Successful EPD requires the development of stable suspensions composed of electrostatically charged particles suspended in a suitable solvent where specific mechanisms are active keeping the particles from flocculating or agglomerating. The incorporation of surface charge on particles in suspensions is achieved by one or more of the following mechanisms: dissolution of ions from the particle, selective adsorption of ions from the solvent and adsorption of molecules from the solvent followed by preferential desorption of one of the dissociated ions.<sup>2),3),8)</sup>

In general, EPD can be applied to any solid that is available in the form of a fine powder (<30 microns) or a colloidal suspension. Indeed, examples of EPD of any material class can be found, including metals, polymers, carbides, oxides, nitrides and glasses.<sup>1)-7)</sup>

The basic mechanisms of EPD have been extensively consi-

dered in the literature mainly in the framework of the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory and particle double layer distortion on application of dc electric fields.<sup>2)</sup> There are however multiple theories put forward to explain particle interactions and kinetics of deposition, $^{2),3)}$ and further theoretical and modelling work is being carried out to elucidate the mechanisms of deposition and the role of electrochemical effects considering complex interactions between solvent, particles and electric field.<sup>8),10)-12)</sup> Moreover, numerical simulation has been used for the first time recently to model the buildup of a deposit of charged particles on an electrode during EPD.<sup>13),14)</sup> These studies are both of fundamental and practical interest as they provide insight into local variations of particle interaction processes during deposition, which can be used for optimization of EPD techniques. In particular related to the EPD of nanoparticles, a fundamental study on the formation of deposits during EPD has been provided by Sarkar et al..<sup>15)</sup> They observed the deposition of silica particles on silicon wafers as a function of deposition time, and compared the nucleation and growth of the silica particle layer with that of atomic film growth via molecular-beam epitaxy. A striking similarity was found between the two growth processes. This indicates possible new directions for further research as the equivalence between the two mechanisms provides insight into the growth kinetics of electrophoretically deposited films, in particular from nanoscale particles, and it can be used for optimization of the deposit microstructures.

# 3. EPD of ceramic nanoparticles

The electrophoretic deposition of ceramic nanoparticles (particle size <100 nm) is regarded as a special colloidal processing method and it 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.<sup>2),3),5)</sup> Relevant studies focusing on different systems, where the utility of EPD of nanoparticles has been demonstrated, are reviewed in this section. We have followed a general rule of considering only those studies dealing with particles of dimensions <100 nm, unless otherwise stated.

## Monolithic ceramics and films

EPD represents an advanced colloidal processing technique to produce highly homogeneous ceramic materials. Extensive research on the processing of monolithic structural ceramics as free standing objects by EPD of nanoparticles has been published and reviewed in previous papers.<sup>2),3),5),6),16)</sup> In most studies the use of nanoparticles was mainly considered with the purpose to achieve a fine microstructure of the final ceramic products and to lower the sintering temperature. In a recent paper Tabellion and Clasen<sup>6)</sup> have reviewed previous work on the fabrication of large components, free standing objects, hollow bodies and objects of complex 3D shape using EPD of silica nanoparticles (commercially available fumed silica) in aqueous suspensions. Examples of components fabricated from silica nanoparticles (Aerosil, Degussa, Frankfurt, Germany) in aqueous suspension, shaped by EPD and subsequently sintered under optimized conditions, are shown in Fig. 2.<sup>6)</sup> 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 as a shaping method for fabricating homogeneous glassy phase free mullite ceramics and composites.<sup>16),17)</sup>

A great variety of functional ceramic films are being produced by electrophoretic deposition of nanoparticles. For

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Fig. 2. Examples of ceramic objects fabricated by electrophoretic deposition of silica nanoparticles from aqueous suspensions and subsequent heat-treatment: (a) opaque, and (b) transparent components.<sup>6</sup> (Micrographs courtesy Prof. R. Clasen, published with permission).

example nano-structured BaTiO<sub>3</sub> and Eu-doped BaTiO<sub>3</sub> thin films have been recently reported, which were produced by EPD of nanoparticles from acetylacetone based suspensions.<sup>18),19)</sup> Films of <1  $\mu$ m thickness of uniform microstructure and very smooth surface finish were obtained. In related research on ferroelectric films, (Ba, Sr)TiO<sub>3</sub> films with thickness between 1 to 20  $\mu$ m have been fabricated recently by electrophoretic deposition using (Ba, Sr)TiO<sub>3</sub> nanopowders synthesized by different routes, such as conventional solid phase synthesis, sol-gel and co-precipitation processes.<sup>20)</sup> Further work on the potential of EPD of nanopowders for production of ferroelectric (BaTiO<sub>3</sub>) multilayer structures has been presented by Randall.<sup>21)</sup>

EPD has been also used by several authors to form a great variety of dense, nanostructured functional films from water-based and non-aqueous suspensions of nanocrystalline particles, including ZnO,<sup>22)-25)</sup>  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,<sup>26)-28)</sup> zirconia,<sup>29)</sup> pyrite (FeS<sub>2</sub>),<sup>30)</sup> lead zirconate titanate (PZT),<sup>31),32)</sup> diamond,<sup>33)</sup> yttria<sup>34)</sup> and zeolites.<sup>35)-37)</sup> Nanocrystalline and submicrometric (~150 nm) zirconia particles are also popular starting materials for preparation of films by EPD for applications as varied as solid oxide fuel cell electrolytes<sup>38)</sup> or interlayers for joining ceramic parts.<sup>39)</sup>

Another material very frequently investigated for electrophoretic production of thin and thick films is nanocrystalline TiO<sub>2</sub>. In 1994, Matthews et al.<sup>40)</sup> produced porous titania thin films on electronically conducting glass for photovoltaic cells from commercially available TiO<sub>2</sub> nanoparticles (Degussa P-25, Frankfurt, Germany). Constant-current electrophoretic deposition from a dispersion of titanium dioxide in 2-methoxyethanol followed by air-drying and annealing was employed. A 30 cm<sup>2</sup> prototype photovoltaic cell was con-



Fig. 3. Microstructure of  $TiO_2$  coatings on a metallic (stainless steel) fibre mesh at (a) low and (b) high magnifications, obtained by EPD of titania nanoparticles from acetylacetone suspensions.<sup>44)</sup> The images show the high degree of particle packing achieved leading to a homogeneous film microstructure (Reprinted from Ref. 44) with permission from Elsevier).

structed with electrophoretically deposited TiO<sub>2</sub>, and tested. More recently, the same commercially available TiO<sub>2</sub> nanopowders have been used to produce porous nanostructured films by EPD on a variety of substrates including metallic plates,<sup>41)</sup> SiC and carbon fibres<sup>42),43)</sup> and metallic fibres and meshes.<sup>44)</sup> In all cases suspensions of TiO<sub>2</sub> nanoparticles in acetylacetone with addition of iodine were used. EPD was carried out under constant voltage conditions at voltages in the range 10-20 V for 2-10 min. Figure 3 shows the microstructure of a TiO<sub>2</sub> coating produced by EPD of nanocrystalline titania particles on a metallic (stainless steel) fibre mesh at low and high magnifications. The images show the high degree of particle packing achieved leading to a homogeneous film microstructure. Films of up to  $20\,\mu\text{m}$  in thickness were produced.  $^{\rm 43), 44)}$  The porous  $\rm TiO_2$  nanostructured coatings are considered of interest for photocatalytic applications as the main component of the starting material is of crystalline modification anatase. After sintering at 800°C for 2 h considerable densification of the TiO<sub>2</sub> was achieved.<sup>42),44)</sup> Titania is a very biocompatible material, thus dense titania coatings on stainless steel fibre meshes should enhance the application possibilities of these fibrous structures as porous substrates in orthopaedic surgery, due to improved corrosion resistance provided by the dense oxide coating. In their established research activities in the area of EPD under strong magnetic fields (10 T), Uchikoshi et al. have also investigated the formation of oriented titania deposits from nanocrystalline titania particles.<sup>45)</sup> It was found that by changing the angle between the directions of the magnetic and electric fields during EPD, the orientation of the crystals in the deposit could be controlled.

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EPD of nanoparticles to produce superconducting films and other superconducting structures is a research area of increasing interest. In a recent study, Kawachi et al.<sup>46)</sup> fabricated YBa<sub>2</sub>Cu<sub>4</sub>O<sub>8</sub> films on silver substrates from nanosized starting materials. Calcinated YBa<sub>2</sub>Cu<sub>4</sub>O<sub>8</sub> clusters were ground and sonicated in an iodine and acetone bath. The electrophoretically deposited films were sintered at 780°C for 100 h. X-ray diffraction (XRD) patterns of the films confirmed YBa<sub>2</sub>Cu<sub>4</sub>O<sub>8</sub> single phase. Moreover grain aligned YBCO thin films were produced by the same group<sup>47)</sup> using EPD in a magnetic field. The solvent was an electrolyte consisting of acetone and iodine. A DC voltage between 40 and 200 V was applied between the anode (Pt) and the cathode (Ag) in the colloid, and a magnetic field of up to 5 T was applied to the bath using a superconducting magnet. When a magnetic field was applied in direction perpendicular to the elecrophoretic direction, X-ray diffraction patterns showed a c-axis alignment of the  $YBa_2CU_3O_{7-x}$  films. Another interesting application of EPD in the field of superconducting materials has been reported by Yoon et al..48) They prepared high-T-c superconducting membranes by means of EPD of nanosized superconducting particles into alumina supports. In related recent research, Jang et al.<sup>49)</sup> prepared superconducting  $Bi_2Sr_2CaCu_2O_{8+\nu}$  nanosheets in acetone suspension and used EPD to produce superconducting films on Ag substrates. Films of thickness  $< 3 \,\mu m$  were produced. The authors also reported the fabrication of microfibres of  $100 \,\mu\text{m}$  diameter by the same EPD technique.

The combination of electrodeposition and EPD is being applied by several researchers, notably by Zhitomirsky et al.<sup>50)-52</sup> to produce a variety of nanostructured thin and thick ceramic and composite films.

For example, in the method proposed recently for fabrication of cobalt oxide nanoscale films,<sup>50)</sup> electrophoretic deposition of poly(diallyldimethylammonium chloride) (PDDA) macromolecules or polyethylenimine (PEI)-Co<sup>2+</sup> complexes has been combined with cathodic electrosynthesis of cobalt hydroxide. By varying the concentration of the polyelectrolytes in solutions, the deposition time and the current density, the amount of deposited material and its composition can be varied. Heat treatment of the deposits resulted in decomposition of the hydroxide precursor and burning out of polymer to form cobalt oxide films. This method should enable the formation of thick nanostructured oxide films of different compositions. For example zirconia films of high homogeneity have been produced recently by the same technique.<sup>52)</sup> Zhitomirsky et al.<sup>51)</sup> have reviewed previous work on the production of nanostructured ceramic and hybrid materials via electrodeposition, and the combination of EPD and other conventional electrochemical methods has been highlighted as a special branch of nanotechnology. Certainly more research efforts in this interesting area of electrochemistry based methods for production of nanostructured functional and structural films is expected, where EPD plays a fundamental role.

## Structural, functional and bioactive coatings

R & D activities related to the production of ceramic coatings by EPD of nanoparticles are in continuous expansion both in industry and academia. The EPD method provides a very convenient alternative to other techniques such as thermal and plasma spraying, slurry-dipping, sputtering and CVD.<sup>10</sup> Coatings for electronic, biomedical, optical, catalytic and electrochemical applications as well as structural ceramic coatings for environmental, erosion or oxidation protection are being produced by EPD of nanoparticles.<sup>3),5),10),53)</sup> Among the remarkable properties of ceramic nanopowders their high sintering activity is of great interest, which should lead to relatively low sintering temperatures tolerable also for metal substrates of relatively low melting point. A good example of protective inorganic coatings obtained from EPD of nanoparticles, termed nano-enamels, was presented by Nguyen et al..<sup>54)</sup> They worked with multicomponent oxide particles of selected sizes in the range 12-145 nm, synthesized from alkoxides. The particles were composed of silica, boron oxide, sodium oxide and phosphorous pentoxide. The additives were directly doped into the silica matrix by hydrolysis and polycondensation reactions and EPD was carried out in mixtures of water and ethanol as solvent. Using constant voltage conditions (4-20 V), deposition times of 1-10 min and addition of polydiethoxysiloxane as binder, crack-free coatings of up to  $30 \,\mu m$ thickness were produced after sintering at 400°C.<sup>54)</sup>

The deposition of ceramic nanoparticles by EPD has been proposed also to produce protective coatings on carbon, silicon carbide and metallic  ${\rm fibres}^{42)-44)}$  as well as on carboncarbon,<sup>55)</sup> SiC/SiC<sup>44)</sup> and C/C-SiC composites.<sup>56)</sup> Titania coatings fabricated by EPD of commercial TiO<sub>2</sub> nanoparticles mentioned above (P25, Degussa, Germany) on SiC and carbon fibres were shown to provide protection up to 1000°C in oxidising atmosphere.<sup>42),43)</sup> In case of carbon/carbon composites, silica, alumina and silica-alumina (mullite composition) suspensions were used and the nanoscaled coatings produced were shown to provide oxidation protection at 600°C.<sup>55)</sup> In similar research, hydrothermally derived yttrium disilicate  $(Y_2Si_2O_7)$  nanopowder (12 nm average size) was dispersed in water at pH 9.7 and electrophoretically deposited on SiC/SiC composite plates at constant voltage of 8 V for 1.5 min.<sup>44)</sup> The vttrium disilicate deposits were sintered at 1050°C to yield homogeneous coatings of 90  $\mu$ m thickness.

Metal-ceramic protective coatings on stainless steel plates have been produced by combining EPD and galvanic deposition.<sup>57)</sup> A ZrO<sub>2</sub>-Ni composite coating with interpenetrating microstructure was produced. For EPD of the ceramic component, a suspension consisting of zirconia nanoparticles (average size 40 nm), ethanol and addition of 4-hydroxybenzoic acid was used.<sup>57)</sup> The zirconia deposits were partially sintered to create an open porous structure (porosity = 40-50%), which was subsequently filled with Ni by galvanic deposition. The combination of EPD of ceramic nanoparticles and subsequent galvanic deposition to produce metal-ceramic coatings is expected to be an area of increasing research efforts due to the advantages it offers in terms of microstructural control and better adhesion of the composite coating to the substrate, in comparison with other techniques.

A great variety of functional coatings are being produced by EPD of nanoparticles. For example, adherent, uniform and porous TiO<sub>2</sub> films for photocatalytic applications have been obtained by a novel process involving the simultaneous cathodic electrodeposition of Ti(iv) peroxo complex and EPD of nanocrystalline TiO<sub>2</sub> particles (Type P25, Degussa AG, Germany) on Al cathodes.<sup>58)</sup> The authors suggested that the electrodeposit formed from the soluble Ti(iv) peroxo complex acts as a matrix that captures the nanocrystalline titania particles deposited by EPD. Interestingly, under the experimental conditions tested, the peroxo ligand decomposes, probably being cathodically reduced, and the matrix is thus transformed into amorphous TiO<sub>2</sub>.<sup>58)</sup> In more recent work, titania photoelectrodes for use in flexible dye-sensitised solar cells have been produced by EPD from wide band gap nanocrystalline TiO<sub>2</sub> without the use of a surfactant or any post-thermal treatments.<sup>59)</sup> Moreover, porous and dense nanostructure

 $TiO_2$  coatings have been developed by EPD of nanoparticles on metallic fibres and meshes, as mentioned above.  $^{44),60)}$ 

There has been also considerable research on the electrophoretic deposition of bioactive ceramic nanoparticles on metallic substrates for biomedical applications, e.g. implants, in particular hydroxyapatite (HA) nanoparticles.  $^{61)-63)}$  The interest in EPD stems from the high purity and stoichiometry of HA coatings deposited from HA nanoparticles. One of the first efforts in this area was by Zhitomirsky and Gal-Or.<sup>61)</sup> who prepared nanoscale HA powders which were then immersed in isopropyl alcohol for EPD. For successful EPD of HA nanoparticles on Ti<sub>6</sub>Al<sub>4</sub>V substrates, voltages in the range 10 to 200 V and deposition times of 10 s to 5 min were used, whilst the distance between electrodes in the EPD cell was 15 mm. In that early work, Zhitomirsky et al. $^{61}$ analysed the different EPD behaviour of HA particles of micrometre and nanometre size ranges. They noted that the influence of the electric field on EPD behaviour strongly depends on the absolute particle size and particle size distribution in suspension. Similar nanoscaled HA particles were used by the same authors to synthesise HA microfibres.<sup>64)</sup> More recently, Wei et al.<sup>63)</sup> deposited nano-precipitates of HA on metal substrates by the following methods: i) the acid base method, which produced plate-like nanoparticles with 2.5:1 aspect ratio, but led to severely cracked coatings; ii) the calcium acetate method, which produced needle-like nanoparticles with a 10:1 aspect ratio, and slightly cracked coatings; and iii) the metathesis method, which produced rounded nanoparticles with a 2:1 aspect ratio and high-quality crack-free coatings.<sup>63)</sup> The authors suggested that the less equiaxed the nanoparticles, the more cracked are the coatings obtained by EPD. Electrophoretically deposited coatings made of nanocrystalline hydroxyapatite have been also produced on etched titanium surfaces.<sup>65)</sup> In related research composite coatings of nano-HA and a bioactive glass have been produced by a co-EPD method.<sup>62)</sup> The co-deposited glass played an important role in increasing the bonding strength between coating layer and substrate. It has been recognised that the fabrication of nanostructured HA coatings on Ti and Ti alloys presents some difficulties related to the drying and sintering shrinkage of the coatings and chemical reactions between the HA and substrates during high temperature heat-treatment.<sup>66)</sup> To remediate this problem, a novel electrochemical strategy based on co-deposition of HA nanoparticles and natural polymer (chitosan) macromolecules has been developed recently.<sup>66),67)</sup> This approach offers the advantage of room temperature fabrication of a nanostructured bioactive coating which provides corrosion protection for Ti and Ti alloy substrates. Electrodeposition was performed from diphasic HA and chitosan suspensions in a mixed ethanol-water solvent (17% water), containing up to 4 g/l of HA. The deposition of HA nanoparticles occurred by EPD while deposition of chitosan molecules occurred by electrochemical deposition. The process was carried out at constant voltage between 8 and 12 V and the distance between electrodes was 15 mm.<sup>66),67)</sup> Coating thickness varied linearly with deposition time. Deposition times of 10 min led to deposit thickness of up to  $\sim$  30  $\mu$ m. The concentration of HA in the deposits could be varied up to values of  $\sim$ 80 mass%. Figure 4 shows typical microstructures of HA-chitosan composite coatings obtained on Ti gauze substrate by this novel technique.<sup>66)</sup> Recently, the same co-deposition method has been adapted to produce nanostructured HA/chitosan composite coatings on stainless steel plates and wires.<sup>67)</sup> It is likely that this novel method will be expanded to include other polymers of high biomedical interest such as



Fig. 4. SEM micrographs of chitosan-HA composite deposits obtained from a 4 g/l HA suspension in a mixed ethanol-water solvent (17% water) containing 0.5 g/l chitosan on a Ti gauze substrate at (a) low and (b) high magnification. EPD parameters: Voltage: 12 V, deposition time: 20 min<sup>66</sup> (Micrographs courtesy Prof. I. Zhitomirsky, published with permission).

biodegradable polylactides. The use of a polymer with inherent binding properties and excellent film forming ability enables the production of adherent and dense coatings. Thus the method offers the potential for fabrication of advanced nanocomposite coatings on biomedical implants.

Results in the literature thus suggest that electrophoretic deposition method can be one of the best and most cost-effective alternatives for relatively thin and homogeneous nano-structured HA-based coating on metallic biomedical devices, including implants. Nanostructured surfaces of implants are thought to be more efficient for attachment of osteoblast cells and for bonding to living tissue<sup>68)</sup> and thus EPD of nanoscaled coatings represent a significant design tool towards improved implants.

Ceramic matrix composites (CMCs)

EPD is being used for the production of fibre reinforced ceramic and glass matrix composites with a variety of ceramic matrices and fibres.<sup>69)</sup> The use of ceramic nanoparticles to fabricate CMCs by EPD was introduced by researchers at the University of Birmingham, England, in the early 90s.<sup>70),71)</sup> The technique is particularly attractive for production of CMCs of complex fibre architecture as reinforcement, e.g. 2-D fibre fabrics, where it is difficult to achieve adequate infiltration of ceramic particles into the inter-fibre spaces.<sup>71</sup>) The main advantages of EPD of nanoparticles over a conventional slurry-dipping route are: reduced processing times and improved control over green body microstructure as ceramic nanoparticles are made to efficiently infiltrate the fibre performs used as reinforcement. Aqueous or non aqueous suspensions of ceramic nanoparticles are usually considered for forming the matrix, and both conductive (e.g SiC Nicalon<sup>®</sup>, carbon) and non conductive (e.g. alumina or mullite) fibres have been used as reinforcement.<sup>17),69)-74)</sup> Recent research on this subject has been reviewed elsewhere.<sup>75)</sup> It has been reported that in the special case of non-conductive fibres (e.g. alumina or mullite fibres), the fibre weave is placed in front of the deposition electrode and the ceramic deposit forms on the electrode growing around and through the fibre mat.<sup>69)</sup> A schema of a typical EPD cell, commonly used for the infiltration of single nonconductive fibre mats with ceramic nanoparticles, is shown in Fig. 5.<sup>76)</sup> Deposition in vertical and opposite direction to the gravitational force is usually carried out to separate effects of EPD and sedimentation. As in all EPD based processing routes, a suitable suspension for EPD should contain ceramic (nano) particles with high surface charge well dispersed in a liquid solvent.

Recently, alumina-alumina (all-oxide) CMCs of very high

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Fig. 5. Schema of a typical EPD cell commonly used for the infiltration of single non-conductive fibre mats with ceramic nanoparticles.<sup>76</sup> Deposition in vertical and opposite direction to the gravitational force is usually carried out to separate effects of EPD and sedimentation.

oxidation resistance have been developed by EPD utilizing nano-Al<sub>2</sub>O<sub>3</sub> particles in ethanol suspension with addition of 4-hydroxybenzoic acid (4-HBS).<sup>76)</sup> In this particular system it was shown that success of the infiltration of fibre mats by EPD relies on both the nanoparticles in suspension and the fibres having the same polarity. Under these conditions, when the particles approach the fibre mat, repulsion forces appear between the charged particles and fibres of same polarity. The magnitude of these forces depends on the relative distance between particles and fibres. Due to the applied external electrical field, each charged particle is attracted to the fibre mat, which is fixed to the electrode. However the particles are repelled before they can reach the fibre surfaces (coagulation point) due to the charges on the fibres. It was hypothesised<sup>76</sup>) that under the effect of the repulsive forces due to the surrounding fibres, the particles follow the path with the fewest possible obstacles until reaching the next interstice between adjacent fibres. Thus, when the particles reach the electrode or the surface of previously deposited particles, they have no further possibility to move and so the electrophoretic ceramic deposit grows with a high particle packing density. The typical microstructure (fracture surface) of a Nextel<sup>®</sup>-type (alumina) fibre mat infiltrated by alumina nanoparticles by EPD is shown in Fig. 6a. It is observed that a high level and homogeneous infiltration of nanoparticles has been achieved by EPD in a very compact packing density. This good quality infiltration leads to a highly dense and homogeneous ceramic matrix upon sintering, as Fig. 6b shows.  $^{76)}$  It has been also discussed that in the case where fibre and particle have opposite surface charge, it can be expected that coagulation occurs on the first layer of fibres encountered by the travelling particle. Consequently the formation of a deposit on the outer fibre layer will block or at least make more difficult the movement of the particles towards the interior of the fibre mat, resulting in poor infiltration and low quality microstructure of the green body.

### Porous and functionally graded materials

There has been considerable interest in using EPD to impregnate porous structures with ceramic nanoparticles. In an early effort, Gal-Or et al.<sup>77)</sup> have used EPD for impregnation of silica nanoparticles into porous graphite. It was shown that ceramic particles are completely induced into porous graphite, and, under optimal EPD conditions, the whole cross section of the specimens was penetrated. The amount of infiltrated material was found to increase with the ratio of dielectric





Fig. 6. SEM micrographs showing (a) typical microstructure (fracture surface) of a Nextel<sup>®</sup>-type (alumina) fibre mat infiltrated by alumina nanoparticles by EPD, and (b) high level and homogeneous infiltration of nanoparticles achieved by EPD, which leads to a highly dense and homogeneous ceramic matrix upon sintering.

constant to viscosity of the solvent, as predicted by the Smoluchowski equation,<sup>77)</sup> as well as with particle concentration and field intensity. However, it was found that due to simultaneous build-up of an overlying deposit, the penetration as a function of deposition time usually reaches a plateau prior to the filling of the whole pore volume. This effect can be used conveniently to fabricate functionally graded materials (FGMs) by impregnation of specially designed open porous ceramic or metallic bodies with nanoscaled particles. EPD has been shown to be a very convenient technique for homogeneously incorporate functional ceramic nanoparticles into porous bodies for FGM fabrication.<sup>78)</sup> Continuously graded structures can be obtained in contrast to most of other common processing techniques, e.g. powder technology, and the gradient and depth of impregnation can be adjusted reproducibly up to several centimetres by adjusting the EPD process parameters. Oetzel et al.<sup>78)</sup> have shown the impregnation of silica green bodies with gradient in density and pore size distribution with ceramic nanoparticles such as nanoscaled silica, alumina and zirconia. Aqueous suspensions were used in all cases, which is the solvent favored by the group of Clasen et al. for EPD of ceramic nanoparticles.<sup>6)</sup>

Structural FGMs have been also produced by EPD using smart combinations of nanoparticles in suspensions as starting materials. For example, Kaya<sup>79)</sup> fabricated Al<sub>2</sub>O<sub>3</sub>-Y-TZP/Al<sub>2</sub>O<sub>3</sub> functionally graded composites of tubular shape, incorporating a tough central layer with graded composition (Al<sub>2</sub>O<sub>3</sub>-Y-TZP) and a hard outer surface layer of pure nanostructured alumina.

## Electrophoretic sol-gel deposition

A particular improvement of the EPD technique for the formation of thin and thick inorganic films of high structural

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homogeneity is the so-called electrophoretic sol-gel deposition. This method was firstly investigated in the late 1980s by Clark et al.<sup>80)</sup> for alumina coatings on aluminium alloy substrates. The technique was developed later by Kishida et al. for preparation of silica<sup>81)</sup> and titania<sup>82)</sup> thick films. Early work was also carried out on sol-gel EPD of aluminoborosilicate sols for optical applications.<sup>83</sup> The principle of this method is the combination of the sol-gel technique for nanoparticle preparation and EPD for the in-situ deposition of the particles. Both protective and functional films can be produced by sol-gel deposition and a few examples are reviewed next. Katagiri et al.<sup>84)</sup> have prepared transparent thick films on glass substrates coated with indium tin oxide using phenyltriethoxysilane-derived particles. Using these particles provides a significant advantage for low temperature densification of the films  $(400^{\circ}C)$ , in comparison for example with pure silica films. Castro et al.<sup>85)</sup> have employed the technique for obtaining crack-free, glass-like silica protective coatings on metals. Another related application of EPD and sol-gel techniques was demonstrated by Laubersheimer et al.,<sup>86)</sup> who produced piezoceramic microcomponents from liquid metal-organic lead-zirconate titanate (PZT) precursors. In their modified sol-gel route, EPD is performed using current densities of 2 mAcm<sup>-2</sup> and field strength of 10-40 V cm<sup>-1</sup>. The sol particles are electrophoretically deposited on a microstructured mold covered by a gold layer while gelation occurs simultaneously. A similar procedure using sol-gel EPD on a suitable mold was developed to fabricate barium titanate with patterned microstructure.87) A partially hydrolysed highly concentrated solution of barium and titanium alkoxides was used. Other examples of functional coatings prepared by sol-gel EPD are zirconia, lead-zirconate-titanate<sup>88)</sup> and antimonic acid thin films<sup>89)</sup> deposited on stainless steel or Pt-coated glass substrates.

Another application of sol-gel EPD has been presented by Damjanovic et al.,<sup>56)</sup> who fabricated protective mullite coatings on C/C-SiC composites through hydrolysis and condensation of tetraethoxysilane (TEOS) and aluminium-tri-secbutylate. Sol-gel processing combined with EPD has also been developed for production of SiC whisker reinforced zirconia composites of high microstructural homogeneity.<sup>90)</sup> In a recent investigation devoted to production of biphasic SiO<sub>2</sub>-ZrO<sub>2</sub> coatings on stainless steel by sol-gel EPD, Castro et al.<sup>91)</sup> prepared sols via acid catalysis using a commercial colloidal suspension of zirconia and two silica alkoxides; tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES). Suspensions with 10, 15 and 25 mol% of ZrO<sub>2</sub> were prepared. The results showed that the amount of water incorporated in the colloidal suspension is the factor that limits the maximum ZrO<sub>2</sub> content. The parameters associated with the EPD process (current density, electric field, potential and deposition time) were seen to affect the quality of the deposits, as expected. The combination of sol-gel processing and nanoparticle EPD has been also demonstrated by Castro et al.<sup>92)</sup> for production of thick silica coatings. It was shown that incorporation of nanoparticles in the initial sol led to substantial increase in the coating thickness  $(5 \,\mu m)$ . Sol-gel electrophoretic deposition has been used also to infiltrate porous substrates with nanoparticles, for example SiO<sub>2</sub> and TiO<sub>2</sub> nanoparticles into arrays of nanopores in anodized aluminum  $(Al_2O_3/Al)$  substrates.<sup>93),94)</sup> Matsuda and Tatsumisago<sup>95)</sup> have recently reviewed the electrophoretic sol-gel deposition method in its application to a variety of materials, including silica, titania and polysilsesquioxane thick films and coatings.

## EPD of metallic nanoparticles and metallic phase nanostructures

There is comparably less research work published in the specialized literature devoted to the electrophoretic deposition of metallic nanoparticles in comparison to ceramic nanoparticles. Most research is being carried out regarding the EPD of colloidal metallic particles, including Au, Ag, Pt, Pd, as well as semiconductor nanoparticles such as CdSe, for functional applications, representative references of this research field are Refs. 96)-109). The deposition of metallic nanoparticles on suitable substrates is seen as a powerful tool for the development of advanced materials with new electronic, magnetic, optic, thermal and photocatalytic properties.<sup>96)</sup> Moreover ordered arrays of such metallic (and semiconductor) nanoparticles in 2D or 3D configurations should exhibit novel properties not attainable in individual particles. Potential areas of application of such 2D and 3D arrays of metallic nanoparticles are in Raman scattering films, selective solar absorbers, photovoltaic cells, optical grating, antireflective surface coatings, photoluminiscent devices, diodes, sensors, nanostructured electrodes, on chip electrical connectors, as well as data storage and microelectronic devices. Combination of electric and magnetic fields to deposit magnetic nanoparticles, e.g. Co, has also been investigated and the technique has been called "magnetophoretic deposition."<sup>110</sup> Moreover electrophoretic deposition has been proposed for the fabrication of semiconductor-metal composite nanostructures. For example, noble metal particles of Au, Pt and Ir were deposited on nanostructured TiO<sub>2</sub> films by EPD for investigation of the role of metal nanoparticles on the photocatalytic activity of titania films.<sup>111)</sup>

A more detailed description of each of the applications suggested for metallic nanoparticle assemblies and the comprehensive discussion on how EPD is being conveniently used as a powerful and versatile tool for manufacturing of devices from metallic nanoparticles deserve a dedicated treatment. Such an analysis is therefore beyond the scope of this general review paper.

Other applications of EPD of metallic nanoparticles have been suggested by Clasen et al..<sup>112),113)</sup> They have recently used EPD to incorporate functional nanosized metallic particles into nanoporous glass bodies. The main advantage of the EPD technique here is that it involves lower temperatures than traditional glass melting, and thus components with relatively low thermal capability can be incorporated into glass hosts, as for example CdS/Se nanoparticles. Thus EPD represents a very useful technique for the doping of glasses with nanoparticles. The optical properties of the glasses depend on the size of the incorporated nanoparticles, which form a secondary phase. This alternative EPD based method opens new perspectives for replacing toxic cadmium compounds, which are at present the only dopants for preparing intensively colored red glass.<sup>113)</sup> A related study was conducted by Subramanian et al.,111) who deposited noble metal particles of Au, Pt and Ir on nanostructured titania films using EPD.

In the field of electronic devices, EPD of silver nanoparticles has been investigated<sup>114)</sup> as a process to form electrode layers for electroceramic applications. Silver powder with spherical morphologies with diameters of 10 nm were dispersed in non-aqueous suspensions and deposited with excellent control of both surface roughness and particle packing. These deposits were sintered into dense homogeneous films. In a more recent publication,<sup>115)</sup> the same group has demonstrated the integration of electrophoretic deposition into electronic device manufacture; in particular in the production of multilayer structures by incorporation of patterned depositions by either overcasting the patterned deposition with a particulate slip to form a multicomponent tape, or direct lamination of the patterned deposition to a low temperature co-fired ceramic tape. It was shown that electrically conducting layers can be formed by EPD of metallic nanoparticles (or submicrometric particles) at an average thickness of only two times the diameter of the starting powder.<sup>115</sup>

Electrophoretic deposition has been also suggested to contribute to the electrochemical process of producing novel reactive oxide (e.g. oxides of Y, Ce, Zr, Hf and La) dispersed intermetallic (e.g. Ni<sub>3</sub>Al) coatings.<sup>116)</sup> The method is based on a combination of conventional electrodeposition and sedimentation and the initial deposit of oxide (nano) particles from the plating bath is thought to be an electrophoretic step, where the particles adsorb ions like Ni<sup>2+</sup> or solvent molecules. The method has been only applied very recently  $^{116)}\ to\ produce\ a$ variety of novel oxidation resistant intermetallic-based coatings, and due to the industrial relevance of this application area, the method is bound to attract R & D interest and efforts in the future. Although the development of EPD techniques in this novel area (metal phase containing nanomaterials and nanostructures) is in the initial stage, results so far are encouraging and indicate great potential for future R & D efforts.

### 5. EPD of carbon nanotubes

Although carbon nanotubes (CNTs) were first observed almost thirty years ago,<sup>117)</sup> Iijima's report in 1991<sup>118)</sup> triggered enormous world-wide interest in these archetypical nanomaterials; over three thousand publications on CNTs appeared in the year 2004 alone. Single-walled carbon nanotubes (SWCNTs) consist of one layer of the hexagonal graphite lattice curved 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. CNTs are often capped at their ends by one 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. As diameter increases, at some point the perfect cylindrical structure is lost and the structure becomes more similar to a vapour-grown carbon fibre.

Many of the remarkable properties of CNTs are now well established,<sup>119)-122)</sup> and their exploitation in a wide range of applications forms a major part of current R & D efforts.<sup>123)</sup> 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 disperse the CNTs homogeneously in the appropriate polymer, ceramic or metallic matrix. This section reviews current research on the application of the EPD technique for the manipulation of CNTs, and highlights potential applications of the resulting structures.

5.1 Preparation and characterization 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). Usually a post-synthesis treatment is 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,



Fig. 7.  $\zeta$ -potential of as-produced SWCNTs, SWCNTs purified by acid treatment, and associated carbonaceous impurities (modified after Ref. 131)).

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.  $^{124)}$ 

Alternatively, a mixture of concentrated nitric and sulphuric acids can simultaneously purify, shorten and functionalise the CNTs.<sup>125),126)</sup> 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 stabilize the CNTs in water, or other polar liquids, by developing a negative surface charge. In addition they can be useful sites for further chemical modification. Titrations indicate that typical concentrations of surface groups are in the range of  $\sim 10^{21}$  sites per gram of CNT.<sup>126)</sup>

The stability of CNT suspensions, determined by zeta potential measurements, has been studied mainly in aqueous and ethanol-based suspensions.<sup>127)-130)</sup> As-produced CNTs have a positive  $\zeta$  potential in the acid 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,  $\zeta$  potential measurements on SWCNTs suggest that carbonaceous impurities on CNTs can be isolated from the SWCNTs due to their greater  $\zeta$  potential at low pH values (see Fig. 7).<sup>131</sup>

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 CNTs, starting with dried material typically produces a poor dispersion, or at least a low yield of well-suspended material. Using oxidised nanotube suspensions without drying improves dispersion quality but again the yield is uncertain. 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 suspensions.<sup>129),132)</sup> 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<sup>130),133)-138)</sup> have been homogeneously decorated on the surface of oxidized CNTs;

these particles can be catalytic,<sup>139)-141)</sup> or can contain rare earth metals.<sup>128),142)</sup> Stable suspensions of these "composite" CNTs are interesting precursors for production of advanced CNT-based nanostructured coatings by EPD. These composite coatings are attractive nanostructures for a variety of structural, functional and biomedical applications, and some recent examples are given below (Section 5.3).

## 5.2 EPD of multiwalled and single-walled CNTs

Surprisingly, there are relatively few reports on the application of EPD to the production of organised coatings containing CNTs. The earliest investigations appear to be those of Du et al.,<sup>143)</sup> who explored the possibility of using EPD to deposit MWCNTs from ethanol/acetone suspensions on metallic substrates. They observed strong hydrogen evolution at the cathode, leading to a porous film of nanotubes with pore size ranging from 1 to 70  $\mu$ m. The same research group reported the fabrication CNT-reinforced polymer films by EPD.<sup>144)</sup> The CNTs were dispersed in and co-deposited from an ethanol solution containing both the resin and the curing agent 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 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.144) In principle, the method could be applied to a range of resin matrices and it merits further development for production of CNT/polymer composites.

Boccaccini et al.<sup>145)</sup> successfully deposited homogeneous MWCNT films onto stainless steel substrates using EPD from aqueous suspensions of acid-oxidised nanotubes, without employing additional surfactant, polymer, or stabilizing agent. No hydrogen evolution was observed during this deposition. This result contrasts with that of Du et al.<sup>143)</sup> and it may be attributed to the lower electric field strength used by Boccaccini et al.,<sup>145)</sup> 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 larger scatter of the yield and in poorer homogeneity of the CNT films.<sup>145),146)</sup> When EPD was carried out at the optimal parameters, very homogeneous CNTs deposits were obtained, as shown in Fig. 8(a) and (b);  $10 \,\mu m$  thick CNT coatings were produced in a single deposition step;<sup>145)</sup> several successive depositions on the same electrode yielded homogeneous thick films of up to 100  $\mu$ m thickness (Fig. 8(c)). It was also found<sup>146</sup> that the lifetime of the CNT suspensions, typically sufficient for up to 5 depositions before aggregation, could be extended by limiting the deposition time to less than 5 min.

EPD has been used only to a limited extent to deposit singlewall CNTs (SWCNTs). 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 additive (MgCl<sub>2</sub>).<sup>147)</sup> Other solvents investigated for SWCNT deposition include dimethyllformamide (DMF) and mixtures of distilled water and methanol.<sup>148)</sup> Films containing long SWCNT bundles were obtained. Some work has been also carried out on EPD of oxidized or surfactant-modified SWCNTs. Jin et al.<sup>149)</sup> co-deposited pyrrol and SWCNTs on ITO from an aqueous suspension, fabricating a 1  $\mu$ m thick



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Fig. 8. CNT porous films deposited by EPD: (a) surface of the CNT film showing homogeneous packing of CNTs, (b) fracture surface of a CNT film showing fibrous type fracture and (c) mounted and polished 100  $\mu$ m thick CNT film obtained after several successive EPD steps.<sup>145),146)</sup>

composite film where the CNTs where perpendicularly orientated to the substrate. Kamat et al.<sup>150)</sup> recently used EPD to deposit a thin film of SWCNTs modified with tetraoctylammonium bromide (TOAB) in tetrahydrofuran (THF) on optically transparent electrodes made of conductive glass. These 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 same group has reported on the fabrication of a membrane electrode assembly for hydrogen fuel cells by using EPD of SWCNTs support and Pt catalyst on carbon fibre electrodes.<sup>151)</sup> Both the electrophoretically deposited nanotubes and platinum retained their nanostructure morphology on the carbon fibre surface.

As mentioned above, beyond the fabrication of uniform, planar, CNT-based coatings, EPD can be applied to deposit CNTs onto complicated structures, including microwires, porous substrates and fibrous bodies or textiles.<sup>5)</sup> The fabrication of more complex patterns of CNT deposits 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. 8, displaying an ordered 3-D structure and relatively high packing density, also exhibit some degree of flexibility.<sup>148)</sup> Owing to the coherent structure and the fact that



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Fig. 9. CNT films, which have been coated and infiltrated with silica nanoparticles, obtained by co-electrophoretic deposition at (a) low and (b) high magnification.

no binder is required, they are interesting candidate materials for supercapacitor electrodes.

The results presented in the literature demonstrate that manipulation of CNTs by EPD is a very attractive technique, likely to be a focus of research efforts in the near future. EPD is a potentially powerful method to produce CNT-based devices, as discussed further below, particularly because few alternative techniques exist to deposit and align CNT on the required surfaces. Similarly, EPD of CNTs can be seen as a very effective process to create CNT membranes and nano-filters which are commonly made by slow and tedious filtration of CNT suspensions.<sup>152</sup>

5.3 Nanoscaled CNT/particulate composite films by EPD Once a porous CNT coating has been obtained, further EPD can be employed to deposit ceramic or metallic nanoparticles with the aim to infiltrating the film or decorating the surface. Alternatively, composite CNT/nanoparticulate coatings can be obtained by co-electrophoretic deposition from stable suspensions containing two components. Another option is the combination of EPD, for deposition of CNTs, with electrodeposition of a second metallic or ceramic phase. These opportunities have yet to be investigated systematically, but some indicative results have been obtained.

Figures 9(a) and (b) show deposits of CNT which have been coated and infiltrated with silica nanoparticles, obtained by co-electrophoretic deposition in recent experiments in our laboratory. EPD was carried out at a constant electric field of 2 V/cm for 2 min. The base silica suspension used, Aerodisp<sup>®</sup> W1824 (Degussa, Frankfurt, Germany), has a pH of 5. The mean diameter of SiO<sub>2</sub> particles was 50 nm and the solid loading in the suspension was 24 mass%. The images show that the deposit is a 3-D network of interwoven CNTs, which are coated and infiltrated by the silica nanoparticles. This type of porous CNT/silica microstructures may be useful for nanoelectronic devices.<sup>153)</sup> 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.<sup>153)</sup> Coating of CNTs should eliminate undesirable attractive interactions between CNTs, improving the properties of eventual composites.

## 5.4 Applications of CNT deposits by EPD

CNT films produced by EPD may be suitable for a wide range of applications; suggestions to date include field emission devices, biomedical scaffolds, catalyst supports, and large surface area electrodes for fuel cells, capacitors, and gas sensors. As mentioned above, Kamat et al.<sup>150)</sup> employed an electrophoretically deposited SWCNT layer as a support for platinum nanoparticles; the structure was subsequently shown both to oxidize methanol and to reduce oxygen in fuel cells more effectively than conventionally supported platinum nanoparticles. The platinum was deposited by electrodeposition from  $PtCl_6^{2-.150}$  In related research, membrane electrode assemblies for hydrogen fuel cells were fabricated by the same group by sequential EPD of SWCNTs and Pt particles.<sup>151)</sup>

CNTs are promising candidates for field emission devices, due to their high aspect ratio, small size, and structural stability; these features are responsible for a low emission threshold and high emission current densities compared to other alternatives. Jin et al.  $^{\rm 149)}$  made an aligned SWCNTs/polypyrrol 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  $\mu$ A at anode voltage of 1000 V and gate voltage of 60 V. Zhou et al.<sup>154)</sup> 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<sup>2</sup> with a decay of 28% after 10 h.

Exploitation of CNTs in these and other applications will frequently rely on the attachment of functional groups or other nanostructures to their surfaces. The combination of CNTs and nanocrystalline particles should have applications in field emission displays, nanoelectronic devices, biomedical scaffolds and drug delivery systems,<sup>155)-157)</sup> antibacterial films and biosensors,<sup>156)</sup> photocatalytic nanostructures and in other functional composites.<sup>134)-139)</sup> For biomedical applications, the combination of CNTs with hydroxyapatite,<sup>155)</sup> Bioglass<sup>®158)</sup> or collagen<sup>157)</sup> is being explored. We anticipate that EPD and combinations of EPD and other colloidal processing methods will play a significant role in the achievement of such CNT/nanoparticle composite nanostructures.

Given the great potential of EPD for CNT manipulation, it is likely that novel applications of CNT deposits made by EPD will emerge. Further developments of the EPD process will allow the reliable fabrication of desired 3D structures with the particularly desired porosity, order and orientation. An interesting possibility is the combination of EPD with recent work on (di)electrophoretic separation of SWNTs, which should allow the creation of structures with ordered regions of semiconducting and metallic nanotubes.<sup>159</sup>

# 6. Fabrication of nanorods, nanowires, nanosheets and related structures

There is increased interest in the use of electrophoretic

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Fig. 10. An array of oxide nanorods fabricated by the template assisted electrophoretic deposition method.<sup>160</sup> (Micrograph courtesy of Prof. G. Z. Cao, University of Washington, USA).

deposition techniques for the fabrication of a variety of nanostructures, including nanorods, nanowires and ordered arrangements of these.

For example, significant research in this area is being carried out by the group of Cao et al.,<sup>160)-163)</sup> who use a combination of sol electrophoretic deposition and template-controlled growth to obtain oxide nanorod arrays. A variety of oxides have been considered, for example TiO<sub>2</sub>, SiO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>,  $V_2O_5$ , Sn-doped  $In_2O_3$  (ITO),<sup>160)-165)</sup> and a typical array of oxide nanorods is shown in Fig. 10. Nanorod growth occurs on a working electrode on aluminium sheets or conductive carbon tapes, with a Pt mesh used as the counter electrode. Template membranes were used for the growth of the nanorods, which were track-etched hydrophilic polycarbonate with pore diameters of 50-200 nm or anodic alumina membranes with pores of 200 nm and thickness of  $\sim$ 70  $\mu$ m. The sol is drawn into the pores of the membrane by capillary action and the Pt counter electrode is placed in the sol, parallel to the working electrode. A potential of 5 V is applied for up to 60 min. After retrieving from the EPD cell, the samples are dried and heat-treated at temperatures between 500 and 700°C in order to burn off the polycarbonate membrane and densify the nanorods. Alumina membranes are removed by dissolving in NaOH for 60 min. A similar method based on sol-gel EPD and template controlled growth in anodic alumina membrane has been used by Lin et al.<sup>166)</sup> for preparation of Fe<sub>2</sub>O<sub>3</sub> nanowire arrays.

The feature article by Cao<sup>160)</sup> explains in detail the method developed and the variety of nanorod assemblies fabricated by sol-gel EPD, which include also single crystal nanorods, and their potential applications in nanoelectronics.

EPD has been used also for the fabrication of ZnO nanowire arrays from colloidal suspensions.<sup>167),168)</sup> A templatemediated preparation for nanosized ZnO arrays was conducted by electrophoretic deposition in the nanochannels of anodic alumina membranes. It was found that both the morphology and the deposition rate of ZnO nanowire arrays were influenced by the pH of the suspension and the applied voltage. The deposition rate of nanowire arrays was high at the initial stage of EPD and then approached a saturation value, in agreement with common observations in EPD processes under constant voltage conditions.<sup>2)</sup> The deposition rate also increased with increasing zeta potential of the particles and the applied voltage for EPD of ZnO nanowires.<sup>167)</sup> The photoluminescence properties of ZnO arrays were largely determined by particle size and surface properties of the nanoparticles comprising the nanowire arrays. Another interesting application of the EPD technique combined with template processing is the synthesis of oriented HA nanorods.<sup>169)</sup>

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The analyzed literature reveals that a major advantage of EPD for the fabrication of nanorods and nanowires is the ability to grow large areas of uniformly sized and nearly unidirectionally aligned nanorods of various oxides, as mentioned above. The group of Cao et al.<sup>160)</sup> has shown also that sol electrophoretic deposition is an effective method for the formation of conformal coating of thin films of oxides on metal nanorods to produce metal-core oxide-shell composite nanowires.

In a recent investigation, Yui et al.<sup>170)</sup> developed an EPDbased method for the production of transparent photofunctional titania nanosheets on ITO electrodes. In this particular application EPD offers the advantage or relatively easy synthesis and handling of the nanolayers and the possibility of applying many layers in a single process. The films produced, constituted of titania nanosheets, are promising nanomaterials for the design of UV-visible light-sensitive energy conversion systems. The deposition of titania nanosheets was found to be significantly affected by the concentrations, viscosity, and pH values of the aqueous TiO<sub>2</sub> solutions. The deposited thin films were greatly improved by the addition of poly(vinyl alcohol) (PVA) into the solutions, which led to an increase in the deposition weight and optical transmittance and in improved adhesion to the substrate.

# 7. Conclusions

EPD is a very versatile and cost-effective material processing technique, offering control over microstructure, stoichiometry, microscopic and macroscopic dimensions and properties. The last 10 years have seen a significant increment of the applications areas where EPD is used with substantial technical advantages for manipulating nanoparticles, nanotubes, and other nanostructures, which can lead to commercial success and large-scale production. EPD, on its own, or integrated with other electrochemical strategies, is seen as a significant branch of nanotechnology and nanofabrication. While further developments of EPD applied to nanomaterials are likely to occur in the next few years, the authors foresee an important contribution of the technique to make reality several of the promises of nanotechnology. Specific areas where EPD of nanostructures is expected to increase are: fabrication of nanostructured and hybrid composite materials, functionally graded materials, laminated nanoceramics as well as nanostructured films and coatings and other nanostructures for functional applications, in the electric, dielectric, superconducting, semiconducting, optical, magnetic and biomedical fields. In the mentioned application areas, EPD has significant industrial relevance and commercial advantage over other fabrication routes, as it can be readily scaled up using inexpensive equipment. It is also recognized that further research efforts in the field of predictive analytical and numerical modeling of the EPD processes of nanomaterials are mandatory, in order to change the empirical, non-satisfactory time consuming trial-and-error approach which currently dominates the experimental work and technological developments in the area.

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