RESEARCH PAPER

Nanostructured carbon nanotube/TiO$_2$ composite coatings using electrophoretic deposition (EPD)

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Abstract Electrophoretic deposition (EPD) has been used to combine multi-walled carbon nanotubes of diameter in the range 20–30 nm and commercially available TiO$_2$ nanoparticles (23 nm particle size) in composite films. Laminate coatings with up to four layers were produced by sequential EPD, while composite coatings were obtained by electrophoretic co-deposition of carbon nanotubes and TiO$_2$ nanoparticles, respectively. Scanning electron microscopy was used to characterize the resultant microstructures. The mechanism of EPD of carbon nanotube/TiO$_2$ nanoparticle composites is discussed.

Keywords Carbon nanotubes · TiO$_2$ nanoparticles · Electrophoretic deposition · Nanocomposites · Coatings

Introduction

New fields of research based on carbon nanotubes (CNTs) and CNT containing materials are the focus

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of considerable efforts worldwide (Kaneto et al. 1999). The high potential of CNTs for applications in functional and biomedical devices is based on their nanomorphology and outstanding mechanical and electrical properties (Kaneto et al. 1999; Berber et al. 2000; Krishnan et al. 1998; Deheer et al. 1995).

Titanium dioxide (TiO$_2$) is a common biocompatible ceramic used for coatings of metal implants to achieve anti-bacterial effect or corrosion resistance, as well as high biocompatibility (Kokubo et al. 2003; Cui et al. 2005). Photocatalysis is another field where TiO$_2$ is used, the crystalline phase anatase being a very effective photocatalyst (Hashimoto et al. 2005; Jitianu et al. 2004).

The combination of CNTs and TiO$_2$ nanoparticles can lead to interesting novel composite materials and devices with relevant properties for a variety of functional and biomedical applications. It has been reported, for example, that the combination of CNTs with TiO$_2$ can enhance the photocatalytic activity of TiO$_2$ (Jitianu et al. 2004). CNTs are excellent carrier substrates for TiO$_2$ nanoparticles, due to their high structural integrity and the high surface area they provide due to the possibility of building a mesoporous structure. A recombination of the e$^-$/h$^+$ pairs produced by irradiation of the TiO$_2$ is less likely, as the 1-D structure of the CNTs leads to high conductivity and so to a high percolation of the electrons. This explains why CNTs may increase the quantum yield of the photocatalytic process. Yu et al. (2005) reported that functionalized CNTs on one hand

increase the band gap leading to less recombination between the e^-/h^+ pairs and on the other hand increase the number of OH⁻ radicals due to the large number of hydroxyl groups available.

Multilayer coatings of CNTs and TiO$_2$ nanoparticles might find also applications in biomedical implant coatings and tissue engineering scaffolds. CNTs have been reported to be biocompatible (Zanello et al. 2006) and they support the proliferation of osteoblast cells. Other studies have demonstrated that porous structures containing CNTs can be used as scaffolds for tissue engineering (Corre-Duarte et al. 2004; Aoki et al. 2006).

Several processing methods for the production of ceramic nanocomposites and laminates are available. From the commercial and practical point of view, electrophoretic deposition (EPD) offers several advantages. EPD is a cost-effective and process efficient technique for fabrication of free-standing objects and coatings from particulate materials, which is applicable to complex component shapes and large dimensions (Boccaccini et al. 2006). EPD can be seen as two combined processes: first the migration of charged particles dispersed in a liquid medium (electrophoresis) under an applied electric field and secondly the coagulation process of the particles at the electrode (Van der Biest et al. 1999). In order to obtain a homogenous deposition it is essential that the suspension used is a well-dispersed and stable system. The development of EPD as a processing method for manipulating CNTs (Thomas et al. 2005; Du et al. 2002) and TiO$_2$ nanoparticles (Kaya et al. 2005; Boccaccini et al. 2004) has started in recent years. There has been, however, no previous research done in the field of co-deposition of CNTs and TiO$_2$ nanoparticles or on producing multilayer coatings consisting of CNTs and TiO$_2$ nanoparticles by EPD.

Experimental

The optimization of suspension parameters for obtaining a stable and well-dispersed CNT suspension was carried out in a separate investigation (Chicatún et al. 2007). Multiwalled CNTs in dried powder form (Yorkpoint New Energy Sci. & Tech. Department Co. Ltd., Guangzhon, China) were used. Figure 1 shows a TEM image of the as-received
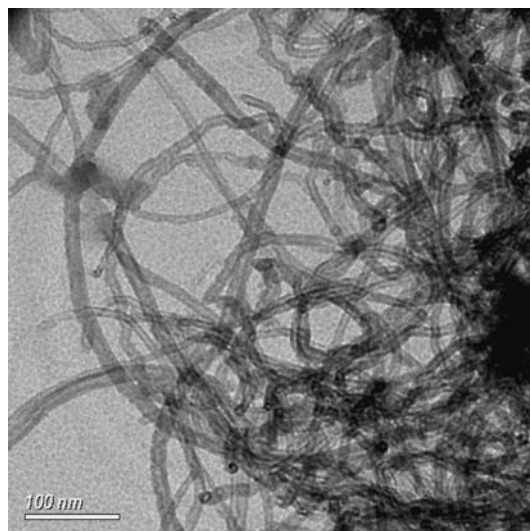

Fig. 1 TEM micrograph of the as-received CNTs showing presence of multiwalled CNTs and a considerable degree of entanglement

CNTs, showing the presence of entangled multiwalled CNTs of diameter 20–30 nm. The suspension used for EPD was prepared using 100 ml distilled water, 0.6 g CNTs, 0.15 ml Triton X-100 and 6 ml iodine (99.999%, Aldrich). The mixture was ultrasonicated for at least 4 h and then centrifuged at 3,000 rpm at 20°C for 15 min, in order to eliminate possible CNT agglomerates. The recipe for the suspension of TiO$_2$ nanoparticles in acetylacetone was taken from our previous studies (Boccaccini et al. 2004). The TiO$_2$ nanopowder used was grade P25 (Degussa AG, Germany) which has a mean particle diameter of 23 nm. The theoretical densities of CNTs and TiO$_2$ used in this investigation were 1.65 g/cm^3 (Shaffer et al. 1998) and 3.96 g/cm^3 (Fredel and Boccaccini 1996), respectively

For electrophoretic co-deposition, suspensions containing various volume ratios of CNT to TiO$_2$ were prepared and ultrasonically mixed for at least 4 h. The following CNT:TiO$_2$ volume ratios were investigated 1:4, 1:3, 1:2 1:1, 1:0.25 and 1:0.1. The electrodes were stainless steel (316L) foils with the following dimensions: $10 \times 10 \times 0.2$ mm^3. The stainless steel substrates were cleaned with acetone and distilled water in an ultrasonic bath before the deposition process. The deposition time for all experiments was set at 4 min and all EPD experiments were carried out at constant voltage conditions.

The optimized electric field strength used for the single deposition of CNTs and TiO$_2$ nanoparticles was 55 and 2.5 V/cm, respectively. The optimized electric field strength for the co-deposition varied between 20 and 55 V/cm. All samples were dried in horizontal position in air at room temperature. For the laminate coatings the deposited layers were dried for at least 20 h before deposition of the next layer.

The cross-sections of the deposits were observed by scanning electron microscopy (SEM) using a LEO Gemini Field Emission Gun-Scanning Electron Microscope (FEG-SEM, Carl Zeiss, Hertfordshire, UK). The coatings produced by co-deposition were further characterized by thermogravimetric analysis (TGA) (Perkin Elmer Pyris 1) in order to investigate the relative content of the deposited materials. The following TGA programme was used: heating rate of 10°C/min up to 1,000°C with an oxygen gas flow of 20 ml/min.

Results

EPD of CNTs and TiO$_2$ layers

As mentioned previously, the optimal electric field strength to obtain successful CNT films was 55 V/cm. It was observed that increasing deposition time yielded a linear increase in thickness of the CNT films. A SEM image of the as-produced, randomly oriented homogeneous CNT films can be seen in Fig. 2. It was found that higher voltages produced more homogenous CNT films exhibiting uniform thickness. However, electric field strength above 55 V/cm resulted in excessive gas evolution at the depositing electrode (anode) leading to heterogeneous CNT film formation. On the other hand, CNT films produced from electric fields lower than 10 V/cm were non-uniform and they tended to detach from the electrode when the samples were removed from the suspension.

The adhesion of the CNT films to the substrate was qualitatively investigated by using adhesive tape as reported by Thomas et al (2005). In samples produced using the optimal EPD conditions, it was found after removal of the tape that the CNTs remained adhered to the substrates with minimal disruption of the CNT films. The result indicates good interfacial adhesion strength between the CNTs

and the stainless steel substrate. The reasons for this qualitatively high adhesion using the current EPD technique may be related to the formation of metal hydroxides at the electrode surface during EPD (Van der Biest et al. 1999; Thomas et al. 2005). These hydroxides could then hydrogen bond to the surfaces of the CNTs.

Laminate composites by sequential EPD

Two and four layer CNT–TiO$_2$ laminates were produced and their cross-sections were analysed. As the cross-sections for SEM examination were obtained by bending the substrate, the applied stress could induce delamination and cracking of the deposits. Therefore qualitative conclusions about the adhesion and structural behaviour can be drawn from observation of fracture surfaces. For example, the fracture surface of the two layer laminate showed that the upper layer, which consisted of TiO$_2$ nanoparticles, delaminated but the CNT layer stayed adherent on the stainless steel substrate. This indicates that the bending stress induced was high enough for the delamination of the TiO$_2$ layer and for crack development within that layer. On the other hand, a higher stress would be required for the delamination of the CNT layer.

SEM images of the four layer cross-section (Fig. 3) showed debonding of the first CNT layer from the stainless steel substrate. The bending stress induced seemed to increase due to the presence of the second CNT layer. However, higher stresses could be reached without debonding in the CNT–TiO$_2$ nanoparticle interface region. As observed in Fig. 3, the CNT layer seems to be acting as a crack inhibiting barrier. Figure 4 shows the interface region between the third CNT layer and the adjacent TiO$_2$ nanoparticle layers. The thickness of the CNT layers is about 1μm and that of the titania layers about 16 μm. Indeed, the effect of the CNT layer as possible reinforcement element in the sintered laminate composite remains to be investigated.

Composite coating by electrophoretic co-deposition

Suspensions for the co-deposition of CNTs and TiO$_2$ nanoparticles were prepared containing different volume concentrations of CNTs and TiO$_2$ nanoparticles.
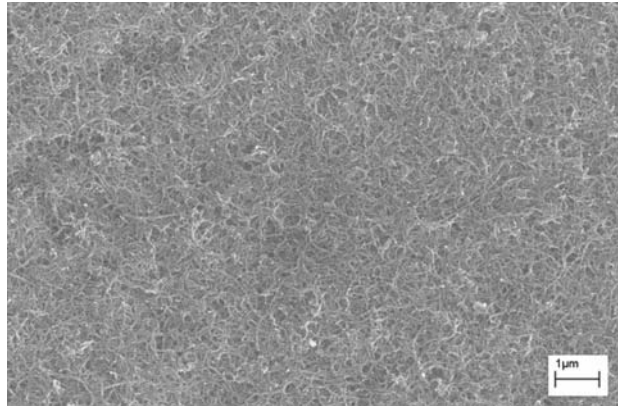
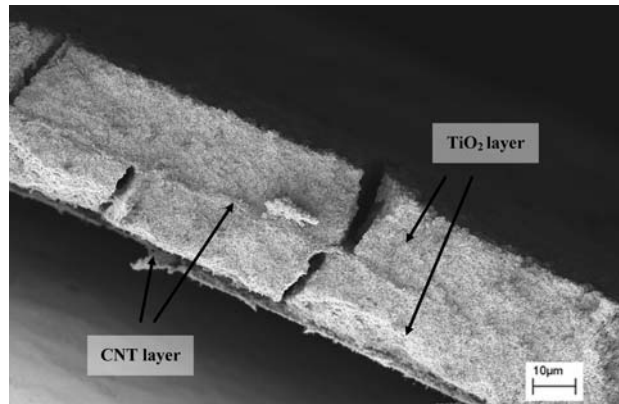**Fig. 2** SEM image showing the top surface of a CNT film deposited by EPD

Fig. 3 Cross-section SEM image of the four-layer CNT–TiO$_2$ laminate composite coating
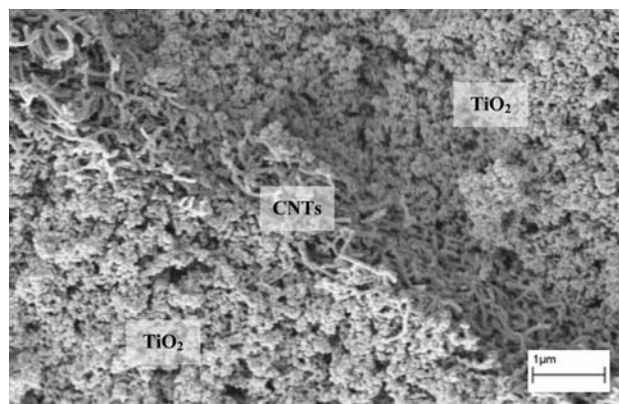

Fig. 4 Interface region between the third CNT layer and the TiO$_2$ nanoparticle layers in four-layer CNT–TiO$_2$ laminate composite coatings

A stable dispersion was achieved by sonication for at least 4 h. No sedimentation was observed within the first hour for low titania concentrations and within minutes for higher amounts of titania.

SEM observation of the deposited cross-sections reveals that the quality of the coatings varies strongly. The coatings for the volume ratios 1:4 (Fig. 5a), 1:3 and 1:1/10 (Fig. 5b) exhibit a homogenous distribution of CNTs and TiO_2 throughout the whole thickness with a high amount of porosity. The coatings for the concentration ratios (CNT:TiO_2) 1:2, 1:1 and 1:1/4 did not exhibit a good distribution of the nanoparticles. The coatings seemed to be very dense and have excessive surfactant incorporated, as the titania nanoparticles were almost not visible under SEM. This could be due to the stability problems of the suspension during the actual EPD process. TGA was performed to investigate if the coatings contained the same CNT–TiO_2 volume concentration ratio as the starting suspensions. The experimentally determined values were compared to the ideal ones, which were taken to be those of the fresh suspensions, a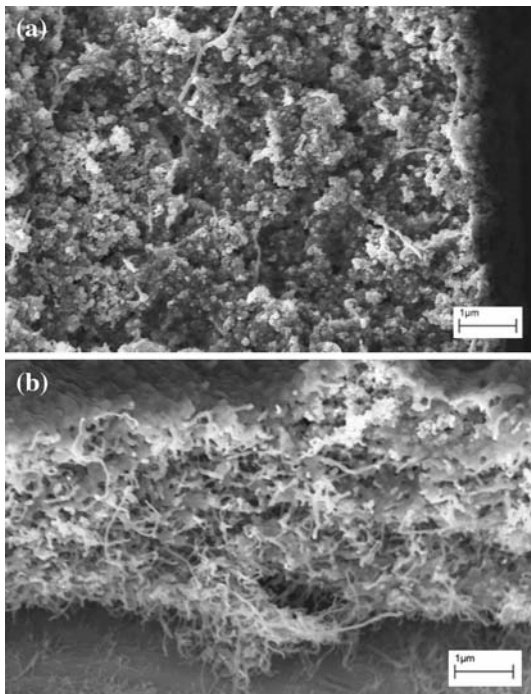s shown in Fig. 6. In all cases the experimental values were found to be higher than those of the starting suspensions, e.g. more titania nanoparticles than expected had been deposited. The increasing relative concentration of titania in the suspension is thought to be responsible for this behaviour, even if the value for the suspension with volume ratio 1:4 is in fairly good agreement with the expected ratio.

By further analysis of the SEM images (e.g. in Fig. 5) it was possible to observe that titania nanoparticles were individually infiltrated into the porous CNT films rather than adsorbed onto individual CNTs. The mechanisms involved in electrophoretic co-deposition can be explained with a schematic diagram as shown in Fig. 7 describing the motion of the nanoparticles in suspension. The first region, namely the ''approaching trajectory'' (Stoll et al. 2006), occurs in the suspension at a given distance away from the electrodes, 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'' (Stoll et al. 2006), occurs close to the deposition electrode where the charge of the deposited CNT films influences the motion of the charged particles. Knowing that both CNTs and particles possess the same charge, there are repulsive forces acting between particles and CNTs as schematically shown in Fig. 7. Due to the applied external electric field, each negatively charged particle is attracted to the previously deposited CNT film
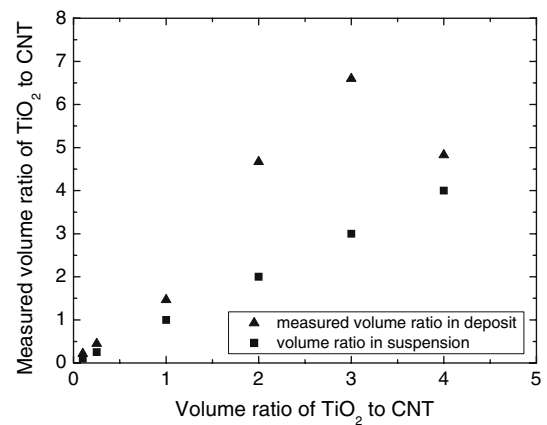

Fig. 5 Images of the cross-section of the CNT–TiO_2 composite coatings by electrophoretic co-deposition with a volume ratio CNT:TiO_2 of (**a**) 1:4 and (**b**) 1:0.1

Fig. 6 Comparison between the deposited volume ratios of TiO_2 nanoparticles to CNT and the initial volume ratio in suspension
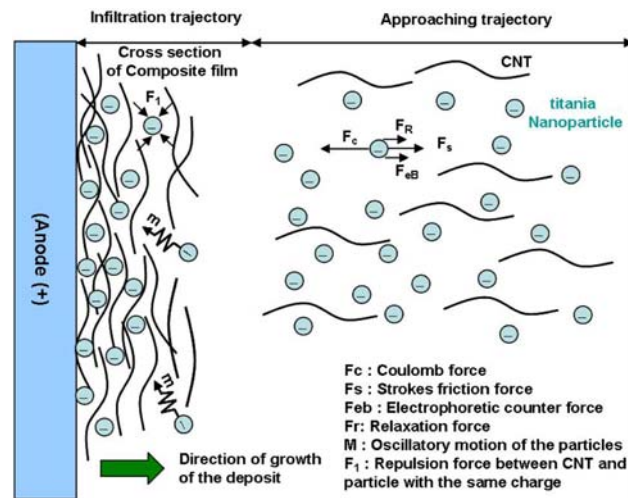
Fig. 7 Schematic illustration describing the motion of titania particles as they infiltrate negatively charged CNT films during EPD

because this is fixed (adhered) to the depositing electrode. However, the particles are repelled before they can reach the CNT surfaces due to the charges on the CNTs. It can be hypothesized 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. A similar mechanism has been proposed for the infiltration of aluminium fibre mats by Al_2O_3 particles (both positively charged) in a recent investigation (Stoll et al. 2006). 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 certain extent of porosity.

This mechanism of infiltration could be equally applied to the sequential EPD process described above, where the titania nanoparticles initially infiltrate the porous CNT layer and then build up to form a second layer. Schematic illustrations summarizing the two experimental approaches investigated in this work, e.g. sequential EPD and electrophoretic co-deposition, are shown in Fig. 8.

Conclusions

The objective of this work was to develop composites of multiwalled CNTs and TiO_2 nanoparticles by sequential EPD and electrophoretic co-deposition. The development of a novel stable aqueous suspension containing both components for EPD was presented and the electrophoretic co-deposition of CNTs and titania nanoparticles was demonstrated for the first time. It was shown that it is possible to produce CNT–TiO_2 laminate coatings using sequential EPD on stainless steel substrates. The adhesion
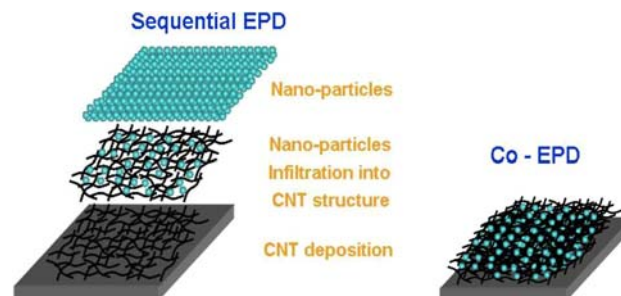

Fig. 8 Schematic illustrations of deposition mechanisms for sequential EPD and electrophoretic co-deposition

strength of the CNT layer to the stainless steel substrate was shown to be qualitatively higher than the strength of the interface between the CNT and TiO$_2$ layers, as demonstrated for the two-layer composite coating. Investigation of four-layer coatings indicated that in the non-sintered material the CNT layer may reinforce the ceramic coating by providing a crack deflection and delamination path. Further work should be done on sintered laminates and on the quantitative investigation of the mechanical properties of the coatings. Experiments evaluating the electrical conductivity and the photocatalytic properties of these coatings are of interest too.

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