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# Kinetic Investigation of Carbon Nanotube Deposition by DC Electrophoretic Technique

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## ABSTRACT

In this paper, kinetics of DC electrophoretic deposition (EPD) of carbon nanotubes (CNTs) are investigated. Suspension of carbon nanotubes in pure ethanol with addition of magnesium nitrate was used as deposition media. The effect of main EPD parameters such as deposition time, applied voltage and the CNTs concentration on deposit yield were investigated. The variation of current density vs. time and the effect of magnetic stirring were also examined. The results are in good agreement with Hamaker's law and the deposit yield increases with increasing of applied voltage and CNTs concentration but there is a deviation from linear trend in longer deposition times. Stirring could compensate some of this deviation but increases the current density fluctuations. Prog. Color Colorants Coat. 4(2011), 51-58. © Institute for Color Science and Technology.

### 1. Introduction

Nanoparticles can be manipulated or sorted via several techniques such as magnetic sorting, filtration, centrifugation and electric field-based approaches [1]. Electrophoretic deposition (EPD) is one of electric field-based techniques for moving, deposition or separation of nanomaterials. This method, first was discovered by F.F. Ruess [2], high DC voltages are applied to stable suspensions of charged particles. EPD is commonly employed in processing of ceramics, coatings and composite materials. This technique is a high-level efficient process for production of films or coatings from colloidal suspensions [3]. Zhitomirsky considered two electrodeposition (ELD) and electrophoretic deposition (EPD). ELD produces colloidal particles in cathodic reactions

D is commonly on EPD kinetics of ceramic particles, especially for carbon nanotubes [11,12].

an applied electric field [4].

In our previous works [13-16], the kinetic behavior of  $SnO_2$  nanoparticles, Si powder and CNTs in AC electric fields were investigated. The obtained results showed that the deposit yield increased with the increasing of time and voltage but decreased with increasing the electric field frequency. In this paper, we examined the

for subsequent deposition while EPD is achieved via

motion of charged particles towards an electrode under

BaTiO<sub>3</sub> [6], hydroxyapatite [7], lead zirconate titanate

(PZT) [8], yttria stabilized zirconia (YSZ) [9], carbon

nanotubes (CNTs) [3,10], etc. have been deposited using

EPD technique. However little works have been reported

A number of materials such as  $Al_2O_3$  and  $ZrO_2$  [5],

effect of EPD parameters such as deposition time, applied voltage and solid concentration on deposit yield of carbon nanotubes which has a different nature from that of ceramic powders. Most of all, the effect of an external force such as centrifugal force caused by stirring during deposition process, on EPD kinetics has not been studied yet. Consequently, the variation of current density with time and the effect of stirring on deposition rate are also investigated.

#### 2. Experimental

suspensions of 0.01 and 0.03 wt% (0.075 and 0.25 mg/mL, respectively) multi-walled carbon nanotubes (MW CNTs) (Plasma Chem GmbH) in pure ethanol were prepared (Merck, art#100983) using ultrasonic agitation for 10 min. The CNTs (purity>95%) were 1-10 micrometer in length and 5-20 nm in diameter. The SEM image of the as-received CNT powder is shown in Figure 1. In order to create more surface charge on the CNTs, 0.3 and 0.9 Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (Merck) added to the MWCNTs ethanol suspensions, respectively. Mg(NO<sub>3</sub>)<sub>2</sub>. 6H<sub>2</sub>O creates positive surface charge, therefore the positively charged particles deposit on the cathode or negative electrode.

Two aluminum flat plates were used as depositing and counter electrodes with a distance of 3 cm. The length, width and thickness of each electrode were 50 mm, 17.5 mm and 0.8 mm, respectively. The setup used for the deposition process consisted of a DC power supply and two multimeters for measuring voltage and electric current (Figure 2). After deposition, the coatings were dried at 50 °C for 1 hr. A 0.0001 balance was used to measure the deposit weight.







Figure 2: Electrophoretic setup.

The deposition time ( in some sections the deposition time are increased) and the distance between the electrodes for all the experiments were 1 min and 3cm, respectively.

#### 3. Results and discussion

#### 3.1. Effect of voltage

The relation between the deposit weight, W, and the electric field intensity, E, can be described by conventional Hamaker equation [2] as follows:

$$\mathbf{w} = \int_{t_1}^{t_2} \mu. \mathbf{E}. \mathbf{A}. \mathbf{C}. \mathbf{dt}$$
(1)

where  $\mu$  is electrophoretic mobility, E is field strength , A is the surface area of the electrode, C is the particle mass concentration in suspension and t is time.

The deposit yield (deposit weight per surface area) was measured at different voltage (150, 300, 450, 600, 750 and 900 V). Deposit weight for voltages less than 150 V was so low to get the accurate measurement. The Y-V curves in Figure 3 show that the deposit yield increases linearly with increasing the applied voltage which is in agreement with equation 1. Figure 3 indicates that the deposit yield increases rapidly by increasing the CNT concentration from 0.01 to 0.03 wt%, therefore the deposit yield at constant voltage (900 V) increases from 5  $\mu$ g/mm<sup>2</sup> for 0.01 wt% to 9.7  $\mu$ g/mm<sup>2</sup> for 0.03 wt%. The linear increase of deposit yield vs. applied voltage was also observed for 0.01 wt% TiO<sub>2</sub> particles (Figure 4) as a ceramic powder confirming the accuracy of the above experiments.



Figure 3: Y-V curves for 1 min EPD from 0.01 and 0.03 wt% CNT suspensions.



Figure 4: Y-V curve for 1 min EPD from 0.01 wt% TiO<sub>2</sub> suspensions.

Macrographs of the CNT thick films are shown in Figures 5(a-c), which indicate the difference between the aluminum electrode before (Figure 5(a)) and after EPD process at different applied voltage 150V (Figure 5(b)) and 750 V (Figure 5(c)). It can be seen that more CNTs

are deposited at higher voltages, consequently the underlying aluminum surface is covered entirely with CNTs. These qualitative observations are in good agreement with quantitative measurements (Y-V curves shown in Figure 4).



**Figure 5:** The surface of electrode before (a) and after(b) EPD process of CNTs deposition at applied voltage 150V (b), 750 V (c), TiO<sub>2</sub> thick film obtained a 600 V (d), SEM images of CNT (e) and TiO<sub>2</sub> (f) thick films.

For comparison, the  $TiO_2$  thick film obtained at constant deposition voltage of 600 V is also shown in Figure 5(d). The SEM images of the corresponding CNT and  $TiO_2$  films are also illustrated in Figures 5(e) and 5(f), respectively. Figure 5(e) shows the random deposition of CNTs which results in a porous thick layer but the  $TiO_2$  thick film consisted of agglomerated particles and short microckracks.

#### 3.2. Effect of time

The variation of deposit yield (Y) versus time (t) for two different deposition voltages of 150V and 450 V (with and without stirrer) is shown in Figure 6. It shows that at deposition voltage of 150 V, the deposit yield increases linearly with increasing time to 7 min. But at higher voltages (450 V), it is clearly evident that the deposition rate is linear during the initial time (until 4 min) of deposition. However, the deposition rate decreases at very long deposition times.



Figure 6: Y-t curves obtained at (a) 150 V, (b) 450 V with no stirring and (c) 450 V under stirring condition.



Figure 7: 0.03 wt% CNT suspensions (a) before and (b) after 10 min EPD at 450 V under stirring.

Three possible reasons can be accounted for this phenomenon: (1) the reduction of CNTs concentration caused by settling of some CNTs agglomerates, (2) the reduction of CNTs concentration after 4 min caused by EPD deposition, and (3) the increase of deposit resistance. In order to investigate the first and the second possibilities, we repeated the EPD process at constant deposition voltage (450 V) under stirring conditions. The resulted Y-t curve at voltage (450 V) under stirring conditions (Figure 6) shows that due to the prevention of CNTs settlement, the stirring of the suspension not only prevent of reduction in deposit yield, but also able to increases it slightly after 10 min. However it is evident from the Figure 6 that the rate of deposition decreases with increasing time under stirring condition, due to the interaction of centrifugal force with electrophoretic force. Therefore the settling contribution to weight reduction can be prohibited by stirring the suspension during EPD process.

Figure 7 shows the CNTs suspension before (Figure (7a)) and after (Figure (7b)) applying the deposition voltage (450V) for 10 min, which is evident that before

deposition process, the CNTs are uniformly dispersed in the ethanol. However, after 10 min deposition, the amount of CNTs in the suspension has decreased and the dark color of the suspension has disappeared. Consequently, the reduction of weight after a prolonged deposition time may be to some extent resulted from reduction in CNT concentration in the suspension caused by deposition. The same behavior is reported by Besra et al [2] who mentioned that for deposition of ceramic under constant voltage powders but varying concentration, the rate of deposition decreases asymptotically with deposition time. Therefore, in order to prevent this effect, the deposition should be carried out under constant concentration.

In the case of ceramic materials, in a constant deposition voltage, in which the potential difference between the electrodes is maintained constant, the electric field influencing electrophoresis decreases with deposition time because of the formation of an insulating layer of ceramic particles on the electrode surface. But during the initial period of EPD, there is generally a linear relationship between deposition mass and time [2]. In this work, the same behavior was observed for CNTs which are not considered as a ceramic material.

The current density (J) curves vs. deposition time (t) at different applied voltage 150 V (without stirring), 450 (with and without stirring) and 750 V (without stirring) are shown in Figure 8. The electric current was measured

every 20 seconds until a sufficient time was passed (7-10 min). It is obvious that in all experiments, the current density decreases with increasing deposition time even under stirring condition. In one hand, we know that carbon nanotubes can behave as metallic or semiconductor materials based on their chiral vector and that the band gap decreases with increase of nanotube diameter. In addition, the energy gap for MWCNTs whose diameters vary from 10 to 30 nm is about or less than 0.05 eV [17]. Hence, all the MWCNTs can be considered to be metallic at room temperature. In the other hand, the J-t curves show that by increasing the thickness of the CNT layer, the electric conductivity of the deposited film decreases. This phenomenon can be attributed to the higher resistivity of randomly oriented carbon nanotubes [18] as shown in SEM image of the deposited film (Figure 5(e)) and the presence of some semiconducting CNTs in the film. Consequently, the CNT thick film behaves as a low conductive layer.

Comparison between Figures 8(b) and 8(c) reveals that under the stirring condition, the fluctuation of the current density is much higher, although the range of the maximum current density minus minimum current density ( $\Delta J=J_{max}-J_{min}$ ) is approximately the same (about 0.3) for both cases. The corresponding values of  $\Delta J$  for 150 and 750 V are 0.1 () and 0.6, respectively. Therefore, it is apparent that the  $\Delta J$  increases proportional to the applied voltage.



Figure 8: J-t curves obtained at (a) 150 V (with no stirring), (b) 450 V(with no stirring), (c) 450 V (under stirring) and (d) 750 V(with no stirring).



### 4. Conclusions

Kinetics of EPD process for deposition of carbon nanotubes have been studied. The deposit yield increased by increasing applied voltage and CNT concentration in the suspension. This relationship was in good agreement with EPD theoretical relations considered for ceramic powders. The deposition yield curves vs. time showed that at low voltages, the deposition rate is entirely linear. However, at higher voltages, during the initial period of EPD, there is generally a linear relationship between deposition yield and time, on the other hand in longer times the deposition rate decreases due to the reduction of CNTs concentration (caused either by settling or EPD deposition). In addition, the stirring could affects the

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deposition rate and prevents it from further reduction in longer deposition times. It also has a slight influence on the current density fluctuations but the current range remained unchanged under stirring condition. As well as current density reduction due to the resistivity of the thickened film. Although multi-walled CNTs are mostly metallic at room temperature, the electrical conductivity of the film because of random orientation of carbon nanotubes and the presence of some semiconducting CNTs is low. In addition, the stirring affects the deposition rate and prevents it from further reduction at longer deposition times. It also has a slight influence on the current density fluctuations but the current range remained unchanged under stirring condition.

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