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Preparation and preliminary property study of carbon nanotubes films by electrophoretic deposition

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Abstract

Thin films of carbon nanotubes were prepared by electrophoretic deposition (EPD) method. The nanotubes films were characterized by SEM and were found that the microstructure of the films was greatly affected by the composition of solvent used in EPD processing. The electrical surface resistance of the EPD films was relatively large, which possibly resulted from the hydrogen adsorption at the nanotubes walls during deposition process.

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1. Introduction

Because of their novel structure and remarkable properties, carbon nanotubes have attracted tremendous attention since the discovery by Iijima [1] in 1991, and a great deal of efforts have been devoted to understanding and characterizing their properties and developing the applications [2–8].

However, due to the extreme difficulties of manipulating carbon nanotubes, most experimental measurements have been made indirectly or do not represent the condition that would be experienced in practical materials; thus, it is extremely difficult to get tangible experimental evidence and reliable data to validate the predictions that suggest the extraordinary properties of carbon nanotubes. As a result, we are still largely in a primary stage to probe and investigate

the material properties, and have proceeded even more slowly for practical applications. On the other hand, it is unclear whether or not the properties of carbon nanotubes could be fully exploited in a macroscopic composite. So it is essential to fabricate macroscale assembly of carbon nanotubes to conduct all the conventional tests at nano-structured samples of manageable dimensions to examine the material properties, which in turn will lay a solid foundation to facilitate further studies of related issues. The uses of carbon nanotube-based materials for the development of electromechanical actuators [9], supercapacitors [10–13], batteries [14] and electrochemical sensors [15–20] are just some of the attempts.

Up to now, there is still no viable method reported to prepare such macroscale assembly and the most widely used method is to simply evaporate or filter carbon nanotubes suspension [9,21] to get a so-called nanotube sheet or nanotube “paper”. Among other problems, the process is very time-consuming, tedious and virtually lacks quality control.

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On other hand, the electrophoretic deposition (EPD) [22] method may be chosen as an alternative in which charged particles dispersed in a stable suspension are driven by a DC electric field to move towards an oppositely charged electrode and build up a densely and uniformly packed/bonded layer. EPD has the advantages of short formation time, simple deposition apparatus and suitability for mass production as in electric coating industry. Most importantly, there is little restriction in the shape of the substrates formed. All these make EPD promising in better preparation of nano-structured macro-devices.

In this communication, we report such a study of using EPD method to produce carbon nanotube sheet.

2. Experimental

Multi-walled carbon nanotubes with a diameter range of 70 to 140 nm [23], prepared with chemical vapor deposited technique, were used. Mixtures of acetone and ethanol with different volume ratios were used as the suspension solvent, and the carbon nanotubes were dispersed into the solvent, after ultrasonicated for 30 min, to form a stable suspension. Two electrodes were kept parallel at 50 mm apart in the suspension; a constant deposition voltage of 45 V was used for EPD. The deposition current was measured using a Hewlett-Packard Multimeter.

3. Results and discussion

3.1. Effects of solvent on the microstructure of the films

It was found that the compositions (the volume ratio of acetone and ethanol) of the solvent itself greatly affect the microstructure of the nanotubes film. Shown in Fig. 1 are the SEM images of the deposited nanotubes films using different compositions of solvents. When pure acetone was used as the solvent, that is, the volume of ethanol is 0; the internal structure of the deposited film was porous, though the surface was relatively smooth. The typical pore size estimated from the SEM images is about 70 μm . It is highly possible that the pores in the sheets were caused by the evolution of hydrogen during the EPD

process. That is the hydrogen will evolve during EPD process, according to the following reaction between iodine and the solvent [22].



The protons generated were adsorbed by the suspended nanotubes, making them positively charged. Application of a DC field forced the positively charged nanotubes to move towards and deposit onto the cathode, evolving the hydrogen at the same time. It is conceivable that certain amount of hydrogen may not escape from the solution fast enough so as to cause the porous structure of the film.

Alternatively, pure ethanol was used as the suspension medium to prepare the EPD film; unfortunately, the multimeter detected no current during the EPD process, indicating that deposition did not occur at all. One possible reason may be that the 'CH₃-' in ethanol is much more stable than that in acetone and the reaction between iodine and ethanol could not take place, at least under our experiment conditions.

To compromise, mixtures of acetone and ethanol with volume ratio of 2:1, 1:1 and 1:2 were used as the solvents in the EPD experiment, respectively. The results confirm that the volume ratio of the solvent has a significant effect on the microstructure of the film. When the volume ratio is 2:1, the pore size in the film did not change too much from the case of pure acetone; it is still in the same range (65–70 μm , estimated from SEM). When the volume ratio is 1, the pores in the film reduce to only about 1 μm or smaller. The reason for the pore size reduction is still not very clear, but one possibility is that the density of hydrogen evolved during EPD process decrease with the decreasing of hydrogen ion, when more ethanol was added. However, when the mixture of acetone and ethanol with a volume ratio of 1:2 was used, the deposition rate was very slow compared with those of previous cases, and when the film formed was taken out from the suspension, the film separated from the cathode due to the poor adhesion.

3.2. Preliminary study of the electrical property of the film

The electrical property of the film was measured preliminarily. The electrical surface resistance of the

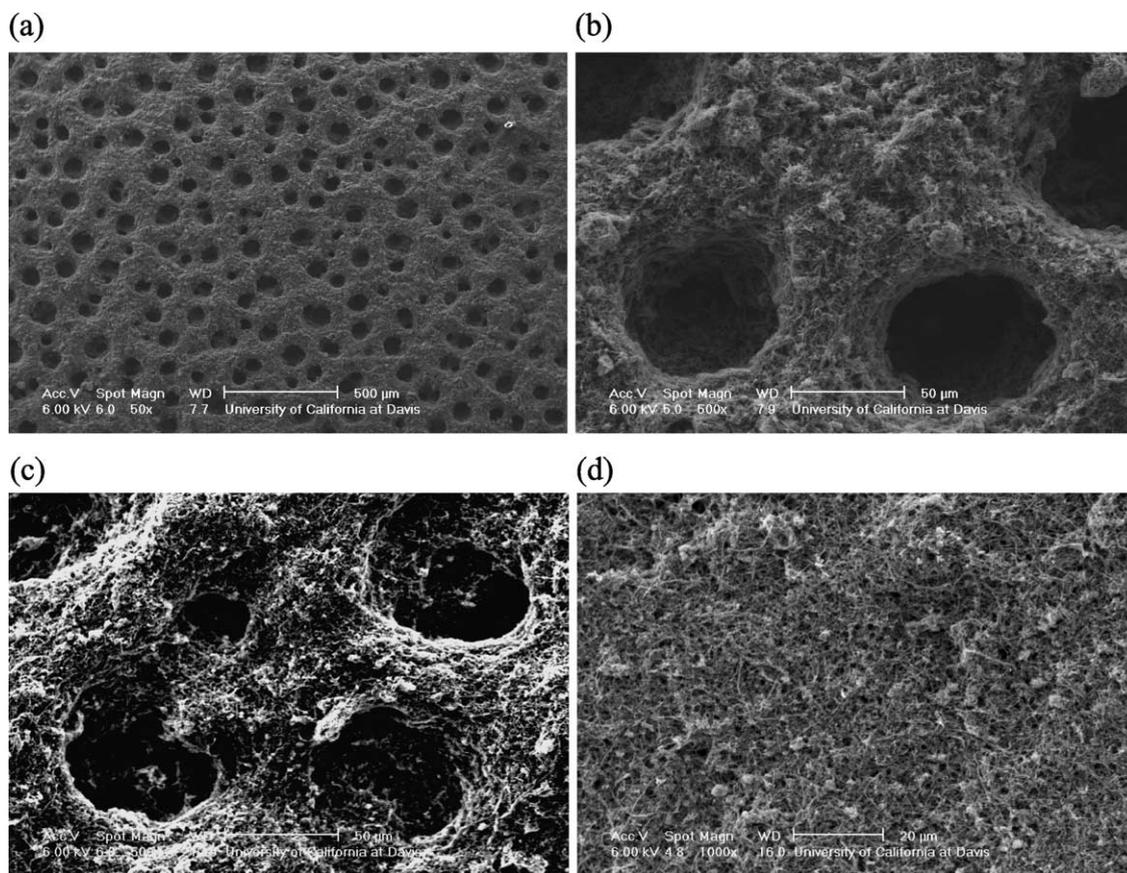


Fig. 1. SEM images of EPD film prepared using different suspension media. (a) Pure acetone, low magnification; (b) pure acetone, higher magnification; (c) volume ratio 1:2; (d) volume ratio 1:1.

EPD film prepared using mixture of acetone and ethanol with volume ratio of 1 was shown to be in the range of kilo ohms (10-mm separation between the contacts), while the resistance of a nano-structured film made with filtering method from the same source was found to be about 50–60 Ω .

Basically, the electrical property of carbon nanotubes is determined by the density of states (DOS). Depending on the chiral angle of the atomic lattice and the diameter of the tubes, the electronic structure of a carbon nanotube changes from conductive to semi conducting [24–27]. In addition, adsorption of function groups by carbon nanotubes would cause a rehybridization from sp^2 to sp^3 of the carbon atoms on the nanotube attached to the chemisorbed species [28], thus results a reduction of the π -conjugation of

the nanotubes, which reduces the $p\pi$ -derived DOS, and increases the resistance of nanotubes resistance.

In our experiments, it is unlikely that the helicity of the tubes has changed much during the EPD process, since the carbon nanotubes are well graphitized. So we hypothesize that the main reason for the high resistance of EPD film was the transformation of sp^2 to sp^3 caused by the presence of function group on or inside the carbon nanotubes, though we cannot completely rule out other factors.

The change of the helicity of the nanotubes during the EPD process was precluded by a simple experiment in which the EPD film was heat-treated at about 300 $^\circ\text{C}$ for 1 h followed by resistance measurement. It was found that the resistance was still in the same range of kilo ohms, indicating that the high resistance

was not caused by adsorption of function groups such as carboxylic acid, which can be easily removed at higher temperature [28].

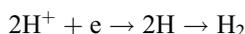
Yet, our UV–visible spectra study, which acts as a powerful probe to sidewall chemisorption [29], confirmed that the chemisorption did occur. Fig. 2 is the UV–visible spectra of various nanotubes samples.

It can be seen that the spectrum of nanotubes in the film with filtering method exhibited an absorption band at about 209, 231 and 276 nm, while the results from the EPD sample showed no peak at 231 nm, and

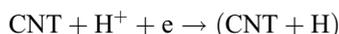
the remaining two peaks shifted to higher wavelengths. In addition, the shoulder of the latter peak is much broader. After the EPD film was heat-treated at 300 °C, this latter peak shifted back to 275 nm, and the second peak reappeared near 231 nm (227 nm in this case), but the first peak did not shift back to 208 nm as in the case of filtered film. This may be attributable to the disturbance in the lower wavelength range of UV spectra, or because there are still other kinds of species than carboxylic acid groups adsorbed on the wall of nanotubes. But at least one thing is clear; the high resistance of EPD sample was not caused by the adsorption of the function group like carboxylic acid.

Another possible cause is likely due to the adsorption of hydrogen, considering the capability of hydrogen storage of carbon nanotubes. Basically there are two methods to store hydrogens in carbon nanotubes; one is to store hydrogens via high pressure and the other is by electrochemical charge–discharge cycling method; both were investigated recently [30–36].

Note that there is electrochemical reaction on the cathode during EPD in our experiments:



So it is highly possible that the following reaction took place at the same time:



It was reported that the exterior walls are mostly favorable adsorption sites in multi-walled nanotubes [30]. The adsorption of hydrogen atoms at the exterior or interior of the inner and/or outer walls would enlarge the diameter of nanotubes, enhance the sp^3 rehybridization, and cause the increase of resistance of the samples.

4. Conclusion

In conclusion, we speculate that the hydrogen adsorption at the nanotubes wall might have caused the increase of the electric resistance of the EPD films made in this study. So it is necessary to find an EPD system in which there is no hydrogen evolution on the cathode, or an EPD system in which the

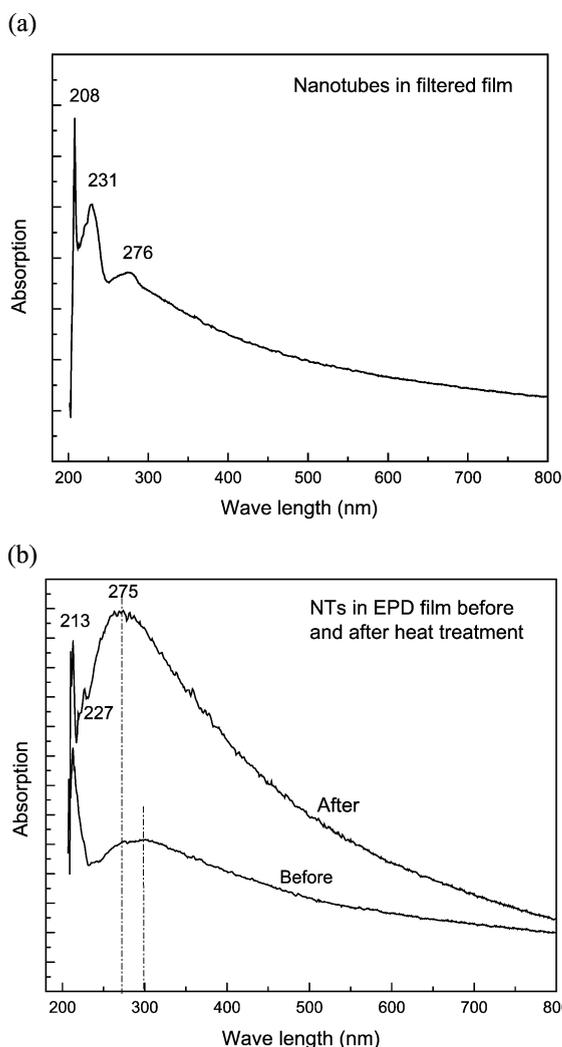


Fig. 2. UV–visible spectra of carbon nanotubes in (a) filtered film, (b) EPD film before and after heat treatment.

nanotubes are deposited on anode. On the other hand, this phenomenon may reveal some potential applications of nanotubes in some electrochemical studies, such as to form the electrode in rechargeable battery and actuators.

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