EFFECT OF SENSITIZING AND ACTIVATING PRETREATMENT ON THE ELECTROLESS PLATED MWCNTS

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1 Introduction

In 1991, Iijima from Japan found a kind of carbon molecules made up by tubular coaxial nanotubes, which were named carbon nanotubes (CNTs) and were widely concerned up to now [1-4]. Because of the almost perfect bonding structure blocking the intervention of impurities and defects, CNTs exhibit excellent mechanical and electrical properties [5-11]. Considering the relative weak magnetic properties of multi-walled carbon nanotubes (MWCNTs), it has been widely reported that a metal particle-contained coating layer was deposited on the surface of CNTs via the electroless plating method in order to further improve their electromagnetic properties [12-16]. Before electroless plating process, Pd active centers which are the activator for metal deposition must be firstly deposited on MWCNTs. Hence, a sensitizing and activating pretreatment process is quite necessary for the electroless plating [17-21]. It was revealed in our previous study that the successful electroless plating modification of MWCNTs is highly dependent on the activators, i.e. the sensitizing and activating pre-treatment of MWCNTs, for the metal deposition on the MWCNT surfaces. However, the sensitizing and activating pretreatment process has always been ignored to date. Here in this study, we used $SnCl_2$ as sensitizer and Pd as active centers of deposited metal particles. The effect of the sensitizing and activating pretreatment on the properties of the electroless plated MWCNTs was detailedly discussed by characterizing the morphologies and the compositions of the surface-coating layer on the MWCNTs.

2 Experimental

2.1 Materials and Sample Preparation

The MWCNTs with 10-30nm in diameter and 5-15μm in length were provided by Shenzhen Nanotechnologies Co.

The MWCNTs were firstly sensitized in $SnCl_2$ solution by bath-type -sonication at 45℃ for 30min. These sensitized MWCNTs were then activated in 0.006mol/L $PdCl_2$ solution dispersed with ultrasonic at 45℃ for 30min and dried at 110℃ before electroless plating. Ultrasonic agitation in sensitizing and activating process was used for dispersing MWCNTs in the solution and producing continuous coatings on the surface of MWCNTs.

The electroless plating of Co-Fe alloy was performed in an alkaline solution, the pH value of which was 9, controlled by the addition of ammonia solution, containing 0.099mol/L cobalt sulfate, 0.011mol/L iron sulfate, 0.31mol/L NaH_2PO_2 as reducing agent and 0.32mol/L $Na_3C_6H_5O_7$ as complexing agent. The process was optimized at 60℃ and then cobalt-iron alloy deposited MWCNTs were washed with distilled water and dried at 110℃.

2.2 Characterization

The morphologies were characterized by field-emission scanning electron microscope (FESEM) (S530, Oxford, U.K.). The composition of the surface-coating layer was obtained by energy dispersive spectroscopy (EDS) (LEO 1530, LEO, Germany).

The results did not contain the percentage of carbon, because the backing material includes carbon element. When characterizing the percentage of carbon, it was impossible to distinguish backing material from MWCNTs, leading to inaccurate results and wrong conclusions. Therefore the values of other elements were relative, not absolute.

3 Results and Discussion

Sensitizing and activating processes are the pretreatment procedure of electroless plating. The reaction mechanism of sensitizing process is to adsorb reductive Sn^{2+} on the surface of MWCNTs. And during the activation process, Pd^{2+} is reduced to Pd by Sn^{2+} deposited on the surface of MWCNTs, as shown in the following reaction formula:

$$Pd^{2+}+Sn^{2+}\rightarrow Pd+Sn^{4+} \quad (1)$$

The schematic diagram of sensitizing and activating processes of MWCNTs is shown in Fig. 1.

After the pretreatment procedure, the reduced Pd particles attach to the surface of MWCNTs firmly as active centers, which can facilitate Co-Fe metal deposition due to its strong catalytic activity during the electroless plating. Therefore, the content and distribution of Sn^{2+} exert obvious influences on the content and distribution of Pd particles reduced in the activating process, and furthermore can finally affect Co-Fe coating layers on the surface of MWCNTs.

In a word, the content of $SnCl_2$ $2H_2O$ in sensitizing process would finally influence the results of electroless plating.

The technological parameters of electroless plating procedure were optimized according to our former experiments. The influences of $SnCl_2$ H_2O in different content, as is shown in Table 1, on the depositing effect of Co-Fe alloy on the surface of MWCNTs is analyzed in this work. And the EDS result for atomic percentages of different elements on the surface of MWCNTs after electroless plating is shown in Table 2.

From Table 2, it should be noticed that the element compositions are similar, regardless of the content of $SnCl_2$ $2H_2O$. The sum percentages of element Co and element Fe are all above 93%, while the percentages of other elements are much lower than that. Consequently, it can be concluded that most of the sensitized Pd molecules on MWCNTs were coated by Co-Fe alloy during the electroless plating, which leads to very low percentages of other elements content. In addition, it can be demonstrated that the optimized technological parameters of electroless plating procedure would effectively promote the deposition of the coating layers of Co-Fe.

The EDS result shows that there are no significant differences of major elements (such as Fe, Co, Pd and Sn) under different content of $SnCl_2$ $2H_2O$. And

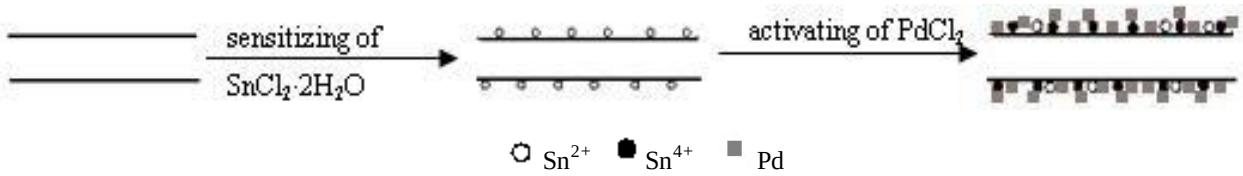

Fig.1. Sensitizing and activating processes of the carbon nanotubes

Table.1. Different content of $SnCl_2$ $2H_2O$ in sensitization solution

Components	$SnCl_2$ $2H_2O$/mol/L						
content	0.44	0.39	0.33	0.28	0.22	0.17	0.11

Table.2. EDS result of electroless plated MWCNTs

Content of $SnCl_2$ $2H_2O$ mol/L	Atomic%				
	P	Fe	Co	Pd	Sn
0.44	4.5	5.8	87.2	1.7	0.8
0.39	2.3	3.9	91.3	2.0	0.5
0.33	1.8	3.4	93.1	0.9	0.8
0.28	1.5	4.4	93.4	0.4	0.3
0.22	1.6	2.8	95.0	0.5	0.1
0.17	1.6	5.3	92.4	0.7	0
0.11	0	1.5	96.1	2.1	0.4

this result suggests that good quality Co-Fe-plated MWCNTs can be obtained during all the electroless Co-Fe plating processes with different content of $SnCl_2$ $2H_2O$ in the pretreatment procedure. Therefore, it is very significative to characterize the morphologies of Co-Fe-plated MWCNTs by FESEM.

Fig.2~Fig.8 show the morphologies of Co-Fe-plated MWCNTs when using different content of $SnCl_2$ $2H_2O$.

As shown in Fig. 2(a), the surface of MWCNTs is coated with a compact metal layer when the content $SnCl_2$ $2H_2O$ is 0.44mol/L; and there are also a great number of free metal bulks among the adjacent nanotubes. Furthermore, the nanotubes are bonded to each other by those free metal bulks, which leads to poor dispersibility of MWCNTs and generates certain negative effects on electromagnetic properties of the Co-Fe-plated WMCNTs ulteriorly.

The most possible reason for the free metal bulks generating is that the content of Sn^{2+} is excessive relative to Pd^{2+}, and the content of Sn^{2+} absorbed on the surface of MWCNTs in sensitizing process correspondingly increases. Meanwhile, MWCNTs have a tendency for agglomerating due to their high length-diameter ratio. As a result, there is a great quantity of Sn^{2+} dissociating among the carbon nanotubes in the pretreatment solution as well as deposited on the surface of MWCNTs. And it makes large amount of Pd active centers while activating process, some of which can't attach to the surface of MWCNTs and exist in dissociative condition within the solution. Hence, in the electroless plating process, a great number of reduced metal atoms attach to dissociative Pd particles, which results in large numbers of free metal bulks, while other metal atoms are deposited on the surface of MWCNTs.

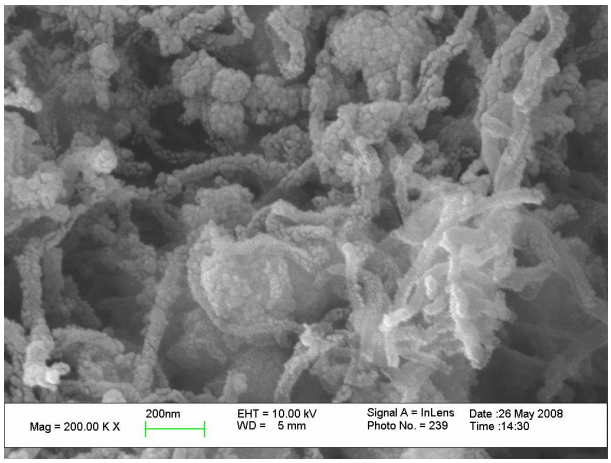

Fig.2. FESEM morphology of MWCNTs deposited with Co-Fe when using 0.44mol/L $SnCl_2$ $2H_2O$.

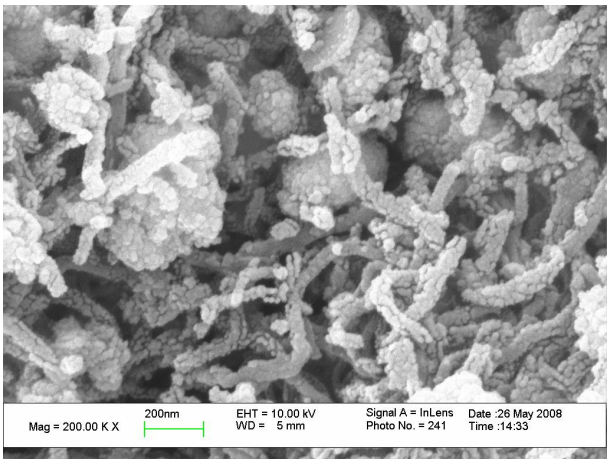

Fig.3. FESEM morphology of MWCNTs deposited with Co-Fe when using 0.39mol/L $SnCl_2$ $2H_2O$.

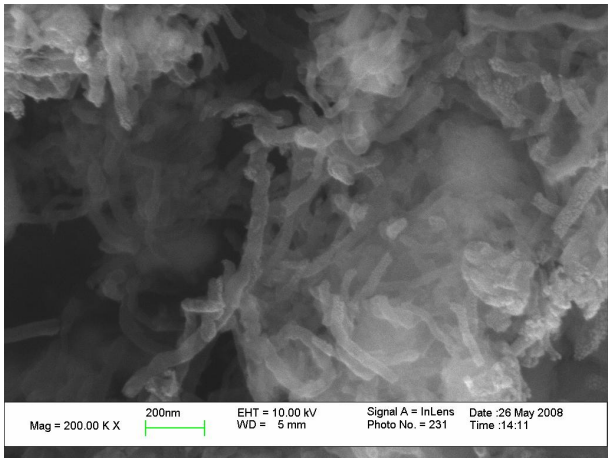

Fig.4. FESEM morphology of MWCNTs deposited with Co-Fe when using 0.33mol/L $SnCl_2$ $2H_2O$.

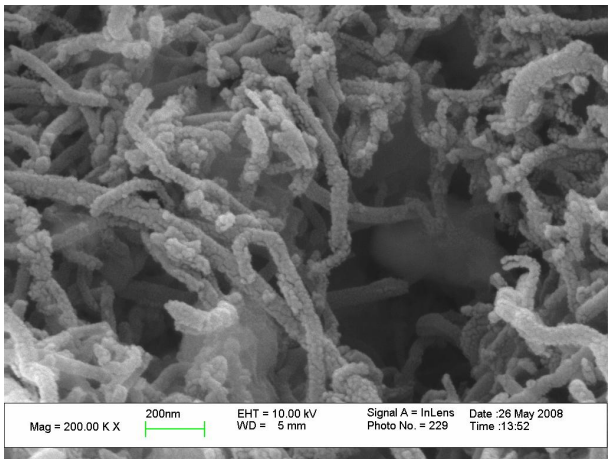

Fig.5. FESEM morphology of MWCNTs deposited with Co-Fe when using 0.28mol/L $SnCl_2$ $2H_2O$.

Fig.3~Fig.5 show the similar morphologies of Co-Fe-plated MWCNTs as Fig.2, which can be explained by the same theory that excessive Sn^{2+} has

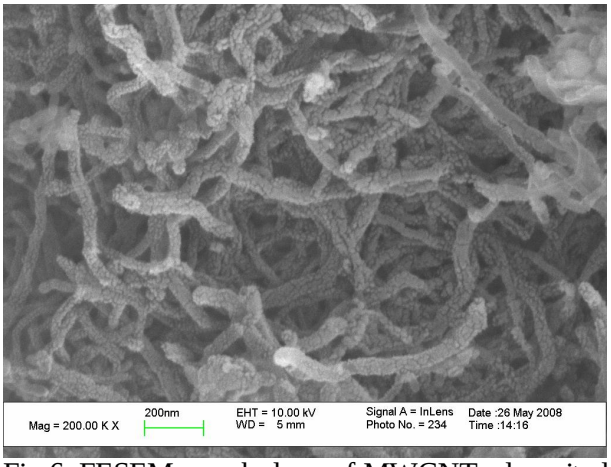

Fig.6. FESEM morphology of MWCNTs deposited with Co-Fe when using 0.22mol/L $SnCl_2$ $2H_2O$.

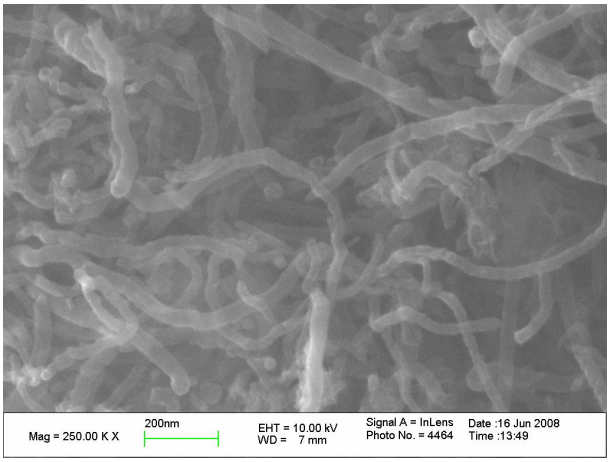

Fig.7. FESEM morphology of MWCNTs deposited with Co-Fe when using 0.17mol/L $SnCl_2$ $2H_2O$.

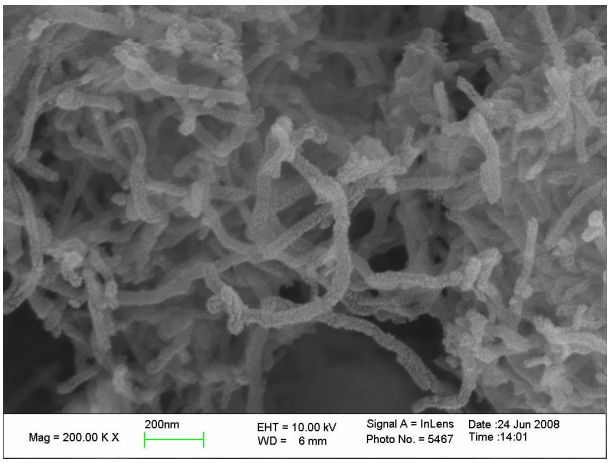

Fig.8. FESEM morphology of MWCNTs deposited with Co-Fe when using 0.11mol/L $SnCl_2$ $2H_2O$.

positive effects on producing free metal bulks among the adjacent nanotubes. What's more, it can be found from Fig.2~Fig.5 that the number of free metal bulks has a tendency to reduce as the content of $SnCl_2$ $2H_2O$ reducing from 0.44mol/L to 0.28 mol/L. And this suggests that reducing the content of $SnCl_2$ $2H_2O$ within a certain range can decrease the number of free metal bulks and improve the effect of the Co-Fe coating layers.

It could be found from the Fig.6 that there is a compact and well-distributed coating layer composed mainly by Co and Fe on the surface of MWCNTs. At the same time, there are few free metal bulks among the Co-Fe-plated MWCNTs. The results of FESEM reveal that when the concentration of $SnCl_2$ $2H_2O$ in pretreatment solution decreases to 0.22mol/L, the effect of electroless plating is much better.

Fig.7 and Fig.8 are FESEM morphologies of Co-Fe-plated MWCNTs when the content of $SnCl_2$ $2H_2O$ in sensitizing solution are 0.17mol/L and 0.11mol/L, respectively. As shown in Fig.7 and Fig.8, it can be seen that the surfaces of MWCNTs are very smooth, only with a few of metal atoms coating on the surfaces, and there are few free metal bulks among the MWCNTs. This is because that the Pd active centers are not sufficient engouh when using lower concentrations of $SnCl_2$ $2H_2O$ in pretreatment procedure, which generates fewer Co and Fe metal atoms, leading to the inhomogeneous Co-Fe coating effects on MWCNTs. Considering the content of carbon is not included in the test data, the EDS result shows that when the concentration of $SnCl_2$ $2H_2O$ are 0.17mol/L and 0.11mol/L, the sum percentages of metal Co-Fe on MWCNTs are almost the same as when using much more $SnCl_2$ $2H_2O$ in sensitizing process.

4 Conclusions

As the active centers, the content and status of Pd were directly related to the quality of the electroless plated MWCNTs. During the sensitizing and activating pretreatment process, the content and status of Pd active centers were highly affected by the volumetric ratio of $SnCl_2$ and $PdCl_2$. In this paper, the influences of the pretreatment, including the sensitizing and activating, on the surface-coated MWCNTS via electroless plating process were studied. And the results show that the optimal $SnCl_2/PdCl_2$ composition is 0.22mol/L of $SnCl_2$ when the concentration of $PdCl_2$ is determined as 0.006mol/L. Under the condition of other concentrations of $SnCl_2$, Co-Fe agglomerations

appear when the content is higher than 0.22mol/L and Co-Fe is insufficient on MWCNTs when lower.

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