Effect of Activation Site Density on Copper Encapsulation of MWCNTs by Electroless Deposition

IOP Conf. Series: Materials Science and Engineering **438** (2018) 012003 doi:10.1088/1757-899X/438/1/012003

Effect of Activation Site Density on Copper Encapsulation of MWCNTs by Electroless Deposition

Dr. Md. Muktadir Billah[1] and Dr. Quanfang Chen[2]

[1,2]MEMS and Nanomaterials Lab, University of Central Florida, Orlando, FL 32816, USA
E-mail: [1]mdmuktadirbillah@knights.ucf.edu
Abstract. Importance of the activation site density on final encapsulation of multi-walled carbon nanotubes (MWCNTs) with copper was investigated in this study. MWCNTs, sensitized with tin and activated with silver, were used as precursors to prepare copper-decorated nanotubes. The effect of activation bath pH was found to be critical to control the density of silver-activation sites and to produce uniform encapsulation of carbon nanotubes (CNTs) with copper in the subsequent electroless deposition method. The morphology of the copper decorated nanotubes was studied using Field Emission Gun Scanning Electron Microscope (FEG SEM) and Energy Dispersive Spectroscopy (EDS).

1. Introduction

Since its discovery by Iijima [Iijima, S., 1991], multi-walled carbon nanotubes (MWCNTs) have been attracted by the researchers and academicians worldwide because of their extraordinary combination of superlative mechanical properties, excellent thermal conductivity (3000 W/m-K) with superior thermal stability and high electric conductivity [Endo et. al., 2002; Berber et. al., 2000; Salvetat et. al., 1999]. The intrinsically strong in-plane atomic bonding of carbon nanotubes (CNTs) offer high young's modulus (1.0–1.8 TPa), high tensile strength (30–200 GPa) and high elongation at break (10–30%) [Lau and Hui, 2000; Wong et. al., 1977; Salvetat-Delmotte and Rubio, 2002; Poncharal et. al, 1999; Qian et. al, 2002]. However, there is still challenge to exploit CNTs especially in metal matrix composites because of issues stemmed from the weak CNT-metal interface. Interest in metallization of CNTs has been growing over the years to overcome these issues. Such metallization, which offers excellent potential for CNTs for their reinforcement in the metal matrix, can be achieved by controlled electroless deposition [Chand, 2000; Li et. al., 1999; Arai and Endo, 2003; Arai and Endo, 2004]. For interconnecting materials, metal coated CNTs are the potential reinforcing agent. Among all the coating metals, copper got immense interest among the researchers for ages [Peng and Chen, 2012; Arai and Fujii, 2011; Wang et. al., 2014].

Numerous studies have been accompanied for uniform encapsulation of CNTs with metals. As reported widely, uniform and smooth metal coating is determined by the activation site density and their distribution [Qunqing Li et. al., 1997; Serp et. al., 2003; M. A. Fraga, 2002]. Extensive studies have been reported on the effect of activation site density to decorate CNTs with Nickel. However, for copper reported studies are still limited. After replacing Pb, silver has been used as catalytic seed for electroless copper plating in two-step activation process for long [Uzunlar et. al., 2013; Billah and Chen, 2015; Wei and Roper, 2014]. This study focused on the effect of activation site density of silver on copper encapsulation of CNTs. Since, silver

reduction rate is controlled by the pH of the electroless solution; here authors studied silver activation of CNTs as a function of pH value of the silver nitrate solution to optimize pH for uniform copper coating on CNTs.

2. Experimental procedure

The multi-walled carbon nanotubes of diameter 30-50 nm and axial dimension 10-20 μm were procured from Cheap Tubes Inc. The purified nanotubes had purity greater than 95%. For the initial surface treatment as received nanotubes were ultra-sonicated for 2 hours at 60^{o}C in an aqueous solution of HNO_3 (70%). The nanotubes were then rinsed with de-ionized (DI) water until pH 7 was reached. Then 50 mg CNTs were ultrasonically dispersed in 50 ml 0.1 M $SnCl_2$/0.1 M HCl for 30 minutes for the pre-activation (surface catalysts) [Y. Wang et. al. 2006]. After the pre-activation the Sn^{2+}- sensitized CNTs were separated and washed with DI water thoroughly. The activation of the sensitized CNTs were accomplished by stirring 50 mg sensitized CNTs for 2 hours in 50 ml aqueous solution of $AgNO_3$ (9 g/L) and NH_3 solution. The pH of the activation solution was varied over a range of 7-12 with NH_3 solution to study the effect of pH on silver deposition. The activated CNTs were then washed with DI water again and filtered off. Ultra-sonication was employed periodically to prevent agglomeration.

Finally the activated CNTs were transferred to the copper electroless bath for decorating with copper. The composition of the electroless copper bath was 0.03 M $CuSO_4 \cdot 5H_2O$, 0.25M $EDTANa_2$, $CHOCOOH \cdot H_2O$ and 10 ppm 2, 2'-Bipyridine ($(C_5H_4N)_2$). $CuSO_4 \cdot 5H_2O$ was used as copper ion source, $EDTANa_2$ as complexing agent, $CHOCOOH \cdot H_2O$ as reducing agent and 2, 2'-Bipyridine ($(C_5H_4N)_2$) as stabilizer [Mallory and Hajdu, 1990; Caturla, 1995]. CNTs were added to the electroless bath at 60^{o}C and temperature was held constant during the deposition period. The electroless bath was placed into an ultrasonic cell bath where the frequency was fixed at 42 kHz and power at 100 W. The deposition was carried out in short time for 2 minutes after bubbles came out. The pH of the solution was adjusted at 12.2 with NaOH. Finally the copper decorated CNTs were rinsed with DI water, filtered off and dried in vacuum. The Sn-sensitized, Ag-activated and copper coated nanotubes were investigated with FESEM and EDS.

3. Results and discussion

The as received MWCNTs were first oxidized using HNO_3 (70%) since the oxidation allows better dispersion of the CNTs in the electrolytes [Peng et. al. 2007]. Also because of the oxidation metal nano particles form strong covalent bond with CNTs. Covalent bonds are much stronger than the weak van der Waals bond that is formed in absence of oxidation [Zhong and Lukes, 2006]. The sensitized CNTs were observed under FEG SEM (Fig. 1a) and the EDS spectrum confirmed the presence of Sn (Fig. 1b). The sensitization temperature was selected at higher than room temperature to produce highly tin-rich catalyst sites. It is evident that either heating of the catalytic solution or increasing pH of the solution promotes crystallization of tin-rich catalytic sites during the sensitization process [Froment et. al., 1995].

Silver was deposited on the sensitized CNTs by electroless deposition method using silver nitrate solution. The pH of the solution was varied from 7-12. All the CNTs were then studied under FEG SEM and presence of silver was confirmed with the EDS spectra. In Fig. 2 wt. percentage of the deposited silver is plotted against pH value of silver nitrate solution. The weight percentage of deposited silver was used as a measure of the plating rate. It is evident here that silver was deposited over a wide range of pH value with quite different rate. Silver deposition was apparent for pH value 7. For further increase of pH of the solution, deposition rate was gradually accelerated exhibiting a maxima in the deposition rate at pH value 10. Later deposition rate was drastically decreased for higher pH values.

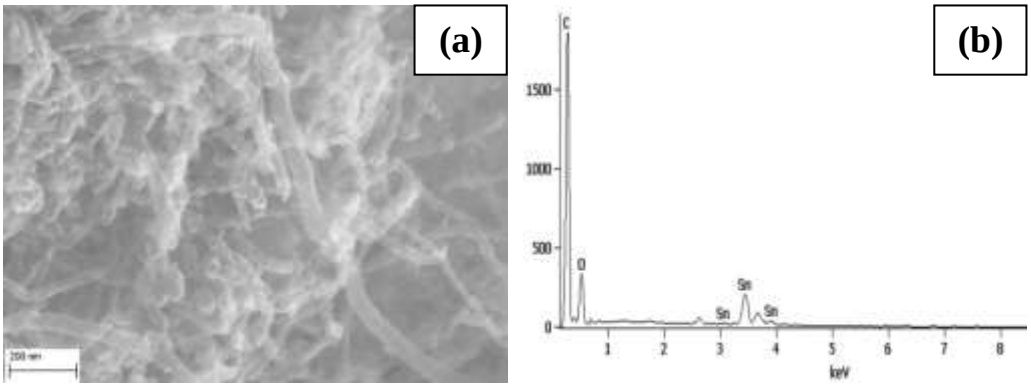

Figure 1. SEM image (a) and EDS (b) of sensitized MWCNTs..

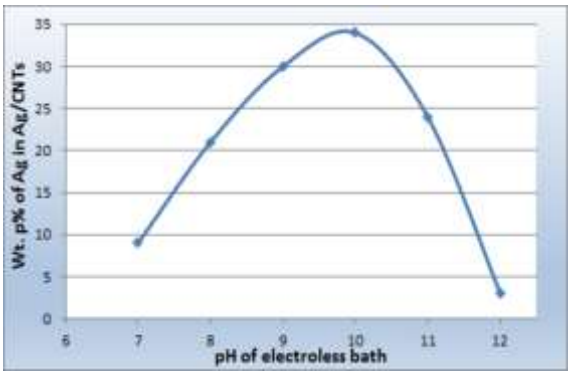

Figure 2. Rate of silver deposition as a function of pH.

SEM shows the plating morphology of the Ag/CNTs in Fig. 3. Though the presence of silver was identified with EDS for pH value 7-8, CNTs were not coated uniformly with silver (Fig. 3a & b). Fig. 3c shows that CNTs are completely encapsulated with silver. A large magnification is shown in Fig. 4 with the EDS spectrum. The Ag/CNTs composite was fibrous without agglomeration as ultra-sonication was employed periodically during silver deposition. But for higher pH values coated CNTs showed agglomerating tendency due to excessive silver deposition with large silver crystals identified on CNT surfaces (Fig. 3d & e). For pH 12 silver deposition was of trace amount (Fig. 3f).

Fig. 5 shows the Cu encapsulated MWCNTs. Cu was deposited on CNTs activated with silver as particles at pH 8 (Fig. 5a) and as the CNTs were fully covered with silver at pH 9 (Fig. 5b). It appeared that as the CNTs were entirely coated with silver, excessive normal growth rate of copper caused large copper crystals and some copper particles were detached from CNT surfaces. However, CNTs were better coated with copper as silver was present as high density activation sites rather than complete encapsulating the CNTs. High density activation sites allowed significant lateral growth of the subsequent coating material to get uniform coating without excessive crystal growth [Qunqing Li et. al., 1997, Jagannatham M. et. al., 2015].

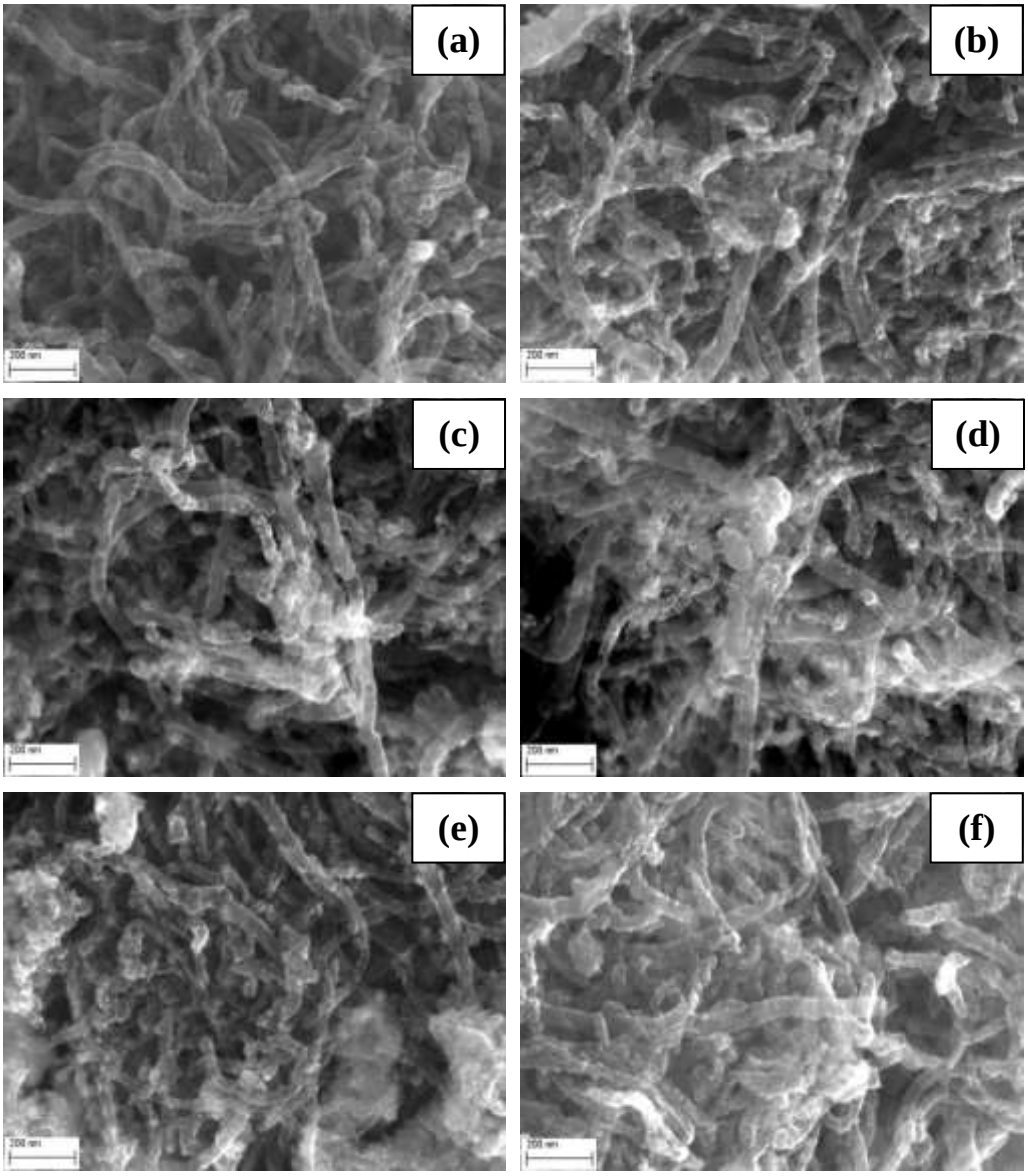

Figure 3. Ag/MWCNTs for different pH value of silver nitrate solution, pH=7 (a), pH=8 (b), pH=9 (c), pH=10 (d), pH=11 (e), pH=12 (f).

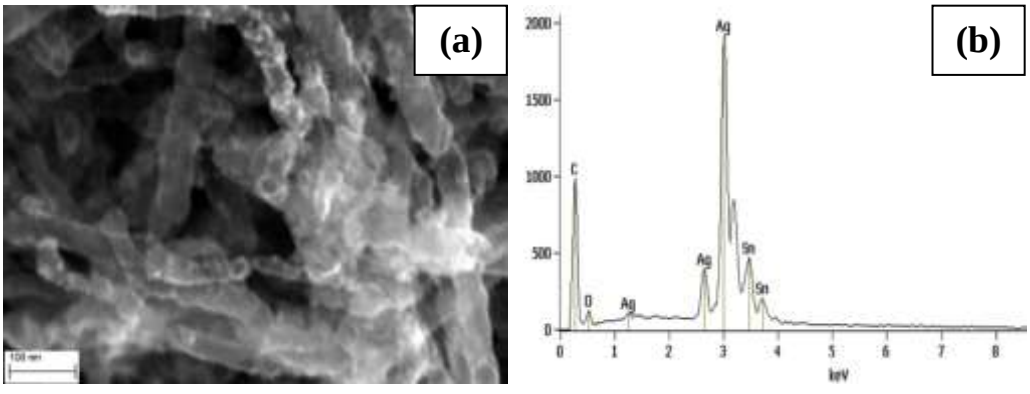

Figure 4. Ag encapsulated MWCNTs (a) and EDS spectrum (b).

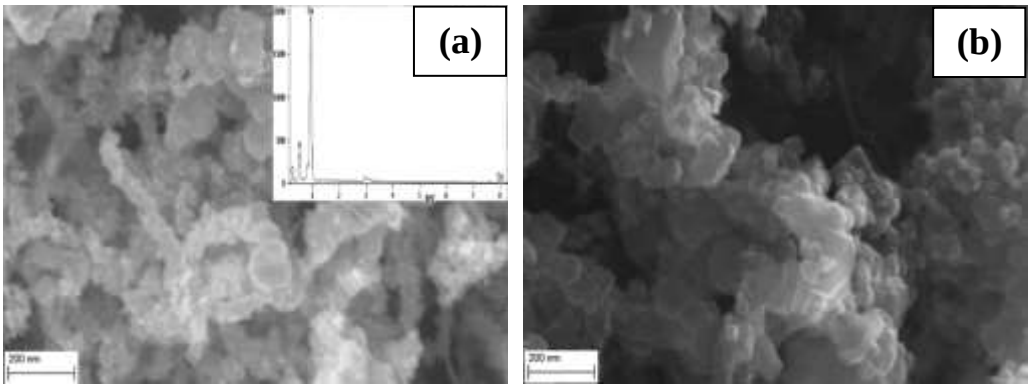

Figure 5. Cu/MWCNTs for Ag activation at pH=8 (a) and pH=9 (b).

4. Conclusion

In this study the deposition of silver and copper on MWCNTs were investigated using electroless deposition method. The acid treated CNTs were successfully coated with silver and copper. Silver was found to be deposited for a wide range of pH of silver nitrate solution. The pH was optimized for complete encapsulation of CNTs with silver. However for uniform copper deposition high density silver activation sites were found to be more effective than uniform silver coating on CNT surfaces.

5. Reference

[1] S. Arai and M. Endo, Electrochemical Common, 5 (2003) 797
[2] S. Arai, M. Endo, N. Kaneko, Carbon, 42 (2004) 641
[3] S. Berber, Y.K. Kwon and Tomanek D, Physics Rev Letter, 84 (2000) 4613
[4] M.M. Billah and Q. Chen, Journal of Electronic Materials, 45 (2016) 1
[5] F. Caturla, F. Molina, M. Sabia, F. Rodriguez-Reinoso and A. Esteban, Journal of Electrochemical Society, 142 (1995) 4084
[6] S. Chand, Journal of Material Science, 35 (2000) 1303
[7] M. Endo, Y.A. Kim, T. Fukai, T. Hayashi, K. Oshisa, M. Terrones, T. Yanagisawa, S. Higaki and M.S. Dresselhaus, Applied Physics Letter, 80 (2002) 1267
[8] M.A. Fraga, E. Jord˜ao, M.J. Mendes, M.M.A. Freitas, J.L. Faria, and J.L. Figueiredo, Journal of Catalysis, 209 (2002) 355
[9] M. Froment, E. Queau, J. R. Martin, and G. Stremsdoerfer, Journal of Electrochemical Society, 142 (1995) 3373
[10] Iijima, S. Nature, 56 (1991) 354
[11] M. Jagannatham, S. Sankaran, H. Prathap, Applied Surface Science, 324 (2015) 475
[12] K.T. Lau and D. Hui, Journal of Electronic Materials, 33 (2000) 263–77
[13] Y.B. Li, B.Q. Wei, C.L. Xu, J. Jiang and D.H. Wu, Journal of Materials Science, 34 (1999) 5281
[14] Y.T. Peng, Y.Z. Hu and H.Wang, Tribological Letter, 3 (2007) 247
[15] Y. Peng and Q. Chen, Journal of Electrochemical Society, 159 (2012) 72
[16] D. Qian, Appl. Mechanics, 55 (2002) 495
[17] L. Qunqingi, S. Fan, W. Han, C. Sun and W. Liang, Journal of Applied Physics, 36 (2011) 501
[18] J.P. Salvetat, J.M. Bonard, N.H. Thomson, A.J. Kulik, L. Forro, W. Benoit and L. Zuppiroli, Applied Physics A, 69 (1999) 255
[19] P. Serp, M. Corrias, and P. Kalck, Applied Catalysis A, 253 (2003) 337
[20] S. Arai and J. Fujii, Journal of Electrochemical Society, 158 (2011) 506
[21] E. Uzunlar, Z.Wilson and P.A. Kohl, Journal of Electrochemical Society, 160 (12) 3237
[22] F. Wang, S. Arai and M. Endo, Electrochemistry Communications, 6 (2004) 1042
[23] Y. Wang, X. Xu, Z. Tian, Y. Zong, H. Cheng, and C. Lin, Chemical European Journal,

(2006) 2542
[24] X. Wei and D.K. Roper, Journal of Electrochemical Society, 161 (2014) 235
[25] H. Zhong and J.R. Lukes, Physics Rev. B, 74 (2006)125