Fabrication of Copper/Multiwalled Carbon Nanotube Composites Containing Different Sized Nanotubes by Electroless Deposition

Susumu Arai* and Takuma Osaki

Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University Nagano-shi, Nagano 380-8553, Japan

Cu/multiwalled carbon nanotube (MWCNT) composites containing two different sized MWCNTs were fabricated using an electroless deposition technique in aqueous solution. In order to disperse the MWCNTs in the solution, an anionic dispersant of sodium dodecyl sulfate (SDS) and a polymeric dispersant of hydroxylpropyl cellulose (HPC) were used. The dispersibility of the MWCNTs in solution was evaluated by measuring the particle size distribution. The zeta potential for the MWCNTs was also evaluated to examine the dispersibility. Uniform Cu/MWCNT composites containing the two different sized MWCNTs were fabricated through the electroless copper deposition process from a solution containing copper ions, a complexing agent, a reducing agent, and two dispersants, SDS and HPC, in addition to the two different sized MWCNTs.

The dispersibility of MWCNTs in the copper matrix has often been a problem. Electrodeposition, an electrochemical method, has been investigated for fabricating Cu/CNT composites. This method has several advantages. For instance, Cu/CNT composites can be formed at ambient temperature and atmospheric pressure. Different from the electrochemical method, a chemical method called electroless deposition enables the formation of metal layers on both conductive and non-conductive objects. Our group has previously reported the frictional properties of Cu/multiwalled carbon nanotube (MWCNT) composites fabricated using the electroless deposition method. With regard to the thermal properties of metal/CNT composites, Al/CNT composites containing different sized CNTs fabricated using a metallurgical method showed excellent high thermal conductivity. Therefore, Cu/CNT composites containing different sized CNTs are expected to be potential candidates for materials with high thermal conductivity and other functional materials.

To realize the formation of uniform Cu/MWCNT composites containing different sized MWCNTs by electroless deposition, the dispersion of the MWCNTs in solution is important. Since MWCNTs are hydrophobic, the introduction of hydrophilic groups, such as the hydroxyl group or carboxyl group, on the surface of the MWCNTs and/or the addition of dispersants of MWCNTs are needed to disperse the CNTs in aqueous solutions. To graft hydrophilic groups on the surface of CNTs, acid treatment,24 high pressure torsion,25,26 microwave sintering,27 and the rolling method.28 However, the dispersibility of CNTs in the copper matrix has often been a problem.

In the present study, the fabrication of Cu/MWCNT composites containing different sized MWCNTs using an electroless deposition technique was explored. The dispersibility of MWCNTs in electroless copper deposition solutions containing large amounts of ions was investigated and the formation of Cu/MWCNT composites incorporating different sized MWCNTs homogeneously was demonstrated.

Experimental

CuSO₄ · 5H₂O, H₂SO₄, glyoxylic acid, ethylenediamine-N,N',N'-tetraacetic acid disodium salt (EDTA·2Na), PdCl₂, SnCl₂ · 2H₂O, HCl, Sodium dodecyl sulfate (SDS), and hydroxypropylcellulose (HPC, viscosity: 2.0–2.9 mPa·s) were obtained from Wako Pure Chemical Industries, Ltd. Two different sized commercially available MWCNTs were used. Larger MWCNTs (MWCNT-L) were obtained from Showa Denko K. K. (commercial name: VGCF) and smaller MWCNTs (MWCNT-S) were obtained from Bayer MaterialScience (commercial name: Bay tube C70P). The microstructure of the MWCNT-L and MWCNT-S was analyzed using a field emission scanning electron microscope (FE-SEM, SU-8000, Hitachi Co., Ltd.) and a scanning transmission electron microscope (STEM, HD-2300A, Hitachi Co., Ltd.). SEM and STEM experiments were conducted at an acceleration voltage of 5 kV and 200 kV, respectively. The MWCNT-L has a stick shape and the MWCNT-S has a curved shape (Figures 1a and 1d). The diameters of MWCNT-L and MWCNT-S are 100–150 nm and 15–20 nm, respectively (Figures 1a, 1b, 1d and 1e). Both MWCNTs undoubtedly have multiwalled structures (Figures 1c and 1f). The lengths of the MWCNT-L and MWCNT-S could not be determined with certainty from the SEM and TEM characterizations, but the catalog values are ca. 10 μm and 10–15 μm, respectively. Pure copper plates (B-60-P05, Yamamoto-Ms Co., Ltd.) were used as substrates. Pure water from a
water purifier (RFP343RA, Advantec MFS, Inc.) was used in all the experiments.

The base composition of electroless copper deposition solution was 0.06 M CuSO₄·5H₂O + 0.03 M glyoxylic acid monohydrate (CHOCOOH·H₂O) + 0.1 M EDTA·2Na. The pH value was adjusted to 12.1 using KOH. The glyoxylic acid and the EDTA were the reducing agent and complexing agent of Cu²⁺, respectively. To disperse MWCNTs in the electroless copper deposition solution, dispersants (SDS, HPC and SDS+HPC) were added to the base electroless copper deposition solution, and the MWCNTs were continuously added. To disperse MWCNTs efficiently, the solution with MWCNTs was ultrasonicated for 5 min using a homogenizer (Ultrasonic Homogenizer US-300T, Nissei Co.). The dispersibility of MWCNTs in the electroless copper deposition solutions was evaluated using a laser diffraction particle analyzer (SALD-7000, Shimadzu Co.) at room temperature. The measurements were carried out using the copper deposition solutions without the reducing agent (glyoxylic acid) to avoid the copper deposition reaction during the measurement. The zeta potentials for MWCNTs in solution were evaluated using an electrophoresis zeta potential analyzer (Model 502, Nihon Rufuto, Co. Ltd.). Since the copper electrodeposition solutions are aqueous solutions, the zeta potentials were calculated using the Smoluchowski equation:

\[ \mu = \frac{\varepsilon_0 \varepsilon_r \zeta}{\eta} \]

where \( \mu \) is electrophoretic mobility, \( \varepsilon_0 \) is relative dielectric constant of water, \( \varepsilon_r \) is dielectric constant of vacuum, \( \zeta \) is zeta potential, and \( \eta \) is the viscosity of the solution. The zeta potential was determined by measuring electrophoretic mobility of MWCNTs. Since the copper deposition solutions have high conductivity and the measurement of the electrophoretic mobility of MWCNTs was difficult, the solutions were diluted approximately 100 times with pure water to reduce the conductivity of the solutions. The measurement was conducted 20 times and the average value was calculated as the measurement value.

In order to start the electroless copper deposition reaction, the copper substrates were pre-treated. The substrates were first degreased by soaking in a commercially available alkaline solution at 60°C for 5 min (C-4000, C. Uyemura & Co. Ltd.). After soaking in 10% H₂SO₄, the copper substrates were immersed in a 4.4 × 10⁻² M SnCl₂·2H₂O + 0.12 M HCl solution at 35°C for 5 min to cause adsorption of Sn²⁺ ions (sensitization). The substrates were then immersed in a 5.6 × 10⁻⁴ M PdCl₂ + 0.12 M HCl solution at 35°C for 5 min to form palladium catalytic nuclei on their surfaces (activation). After the pre-treatment, the substrate was immersed in the electroless copper deposition solution with the MWCNTs and dispersants. A 1 L borosilicate glass beaker was used as the reaction vessel and 500 mL volume of the solution was used. Copper deposition was carried out at 60°C for 120 min with magnetic stirring.

The fabricated Cu/MWCNT composites were observed using the FE-SEM. The mean thickness of the copper deposit was calculated from its weight and the weight of the incorporated MWCNTs was ignored. The phase structure of the Cu/MWCNT composites was evaluated by X-ray diffraction (XRD) using Cu Kα₁ radiation with the thin film diffraction mode (SmartLab, Rigaku Co.); the incident angle was 1°.

Results and Discussion

Figure 2 shows the effects of the dispersants on the dispersibility of MWCNT-L and MWCNT-S in the electroless copper deposition solution. The amount of MWCNTs was 2 g dm⁻³ in all the solutions. For the laser diffraction particle size analysis, the particle shape was assumed to be spherical. Since the MWCNTs have a stick or fibrous shape and not a spherical shape, the particle diameters in the figures do not show the diameters of the MWCNTs. However, these charts clearly present the degree of dispersion of the MWCNTs. For the dispersibility of MWCNT-L, the particle size became smaller with increasing SDS concentration (Figure 2a). In contrast, the particle size distributions for MWCNT-L were almost the same for different concentrations of HPC and they were also shifted toward smaller particle diameters than those with SDS (Fig. 2b). The particle size distributions of MWCNT-L with the

![Figure 2. Dispersibility of MWCNTs: Distributions of particle size for (a), (b), (c) MWCNT-L and (d), (e), (f) for MWCNT-S, with SDS, HPC and SDS+HPC, respectively.](https://www.journals.aps.org/jes)
Figure 3. Zeta potentials for MWCNTs: (a) Effects of concentrations of dispersants on zeta potentials for both MWCNTs. (b) Effects of SDS/HPC molar ratio on zeta potentials for both MWCNTs.

The fabrication of Cu/MWCNT composites was conducted with selected dispersant conditions considering the dispersibility of the MWCNTs. Copper deposition occurs by the following redox reaction:

$$\text{Cu}^{2+} + 2\text{CHOOCOOH} + 4\text{OH}^- \rightleftharpoons \text{Cu}^0 + 2\text{C}_2\text{O}_4^{2-} + 2\text{H}_2\text{O} + \text{H}_2$$

[2]
Figure 5. Surface SEM images of deposits fabricated from electroless copper deposition solutions containing MWCNT-L with various types of surfactants: (a) 10 g dm$^{-3}$ SDS, (b) 2 g dm$^{-3}$ HPC, (c) 1 g dm$^{-3}$ SDS + 1 g dm$^{-3}$ HPC, (d) 1.4 g dm$^{-3}$ SDS + 0.6 g dm$^{-3}$ HPC.

This overall reaction, which consists of reduction of copper ions and oxidation of glyoxylic acid, proceeds catalytically on the surface of the deposited copper. During this reaction, MWCNTs adsorb on the deposited copper and are incorporated in the copper matrix, resulting in Cu/MWCNT composites. The surface morphologies of deposits fabricated from the electroless copper deposition solutions with MWCNT-L and MWCNT-S are shown in Figures 5 and 6, respectively. The MWCNT concentration in the electroless copper deposition solutions was 2 g dm$^{-3}$ in all cases.

For the case of SDS (Figure 5a), aggregates of MWCNT-L are seen on/in the copper matrix. This corresponds to the dispersibility of MWCNT-L in the solution (Figure 2a). Despite the good dispersibility of MWCNT-L with HPC (Figure 2b), no MWCNT-L was seen on/in the deposited copper (Figure 5b). Since the copper deposition is a catalytic reaction, as described above, the adsorption of a large amount of HPC on the deposited copper surface might suppress the catalytic reaction, resulting in reduced copper deposition and consequently no co-deposition of MWCNTs. Actually, the thickness of the

Figure 6. Surface SEM images of deposits fabricated from electroless copper deposition solutions containing MWCNT-S with various types of surfactants: (a) 10 g dm$^{-3}$ SDS, (b) 2 g dm$^{-3}$ HPC, (c) 1 g dm$^{-3}$ SDS + 1 g dm$^{-3}$ HPC, (d) 1.4 g dm$^{-3}$ SDS + 0.6 g dm$^{-3}$ HPC.
Table I. Thickness of copper deposits fabricated under various conditions.

| Condition                                      | Thickness (μm) |
|------------------------------------------------|----------------|
| MWCNT-L 2 g dm⁻³ + SDS 10 g dm⁻³                | 8.6            |
| MWCNT-L 2 g dm⁻³ + HPC 2 g dm⁻³                | 0.59           |
| MWCNT-L 2 g dm⁻³ + SDS 1 g dm⁻³ + HPC 1 g dm⁻³ | 5.7            |
| MWCNT-L 2 g dm⁻³ + SDS 1.4 g dm⁻³ + HPC 0.6 g dm⁻³ | 7.0           |
| MWCNT-S 2 g dm⁻³ + SDS 10 g dm⁻³                | *              |
| MWCNT-S 2 g dm⁻³ + HPC 2 g dm⁻³                | 0.58           |
| MWCNT-S 2 g dm⁻³ + SDS 1 g dm⁻³ + HPC 1 g dm⁻³ | 4.5            |
| MWCNT-S 2 g dm⁻³ + SDS 1.4 g dm⁻³ + HPC 0.6 g dm⁻³ | 5.4           |
| MWCNT-L 1 g dm⁻³ + MWCNT-S 1 g dm⁻³ + SDS 10 g dm⁻³ | *             |
| MWCNT-L 1 g dm⁻³ + MWCNT-S 1 g dm⁻³ + HPC 2 g dm⁻³ | 0.47          |
| MWCNT-L 1 g dm⁻³ + MWCNT-S 1 g dm⁻³ + SDS 1 g dm⁻³ + HPC 1 g dm⁻³ | 3.2           |
| MWCNT-L 1 g dm⁻³ + MWCNT-S 1 g dm⁻³ + SDS 1.4 g dm⁻³ + HPC 0.6 g dm⁻³ | 5.3           |

*Accurate thickness could not be measured. The deposits were easily peeled from substrates.

copper film was smaller than those of copper films fabricated from solutions with other types of surfactants (Table I). In contrast, uniform Cu/MWCNT-L composites were fabricated from the solutions with SDS+HPC (Figures 5c and 5d). These results are consistent with the good dispersibility of MWCNT-L in the solutions (Figure 2c). In contrast, dense aggregates of MWCNT-S are seen on/in the copper matrix (Figure 6a). This is consistent with the lower dispersibility of MWCNT-S in the solution (Figure 2d). Similar to the case of MWCNT-L, in spite of good dispersibility of MWCNT-S with HPC (Figure 2e), no MWCNT-S was seen on/in the deposited copper (Figure 6b). The reason for this may be the same as in the case of MWCNT-L with HPC (Table I). In contrast, uniform Cu/MWCNT-S composites were fabricated from solution with SDS+HPC. In particular, the dispersibility of MWCNT-S with SDS:HPC=7:3 is higher than that with SDS:HPC=1:1. These results are also consistent with the dispersibility of MWCNT-S in the solutions (Figure 2f).

Figure 7 shows the surface morphologies of Cu/MWCNT composites fabricated using electroless copper deposition solutions containing both MWCNT-L and MWCNT-S with different ratios of SDS and HPC. The concentration of MWCNT-L and MWCNT-S was 1 g dm⁻³ and the total amount of surfactants was 2 g dm⁻³. In the case of SDS:HPC = 1:1, both MWCNTs were incorporated, however, the dispersibility of MWCNT-S was rather low. In contrast, in the case of SDS:HPC=7:3, both MWCNTs were incorporated uniformly. These results are consistent with the dispersibilities of both MWCNTs in the solutions (Figure 2c and 2f) and the appearance of Cu/MWCNT-L (Figures 5c and 5d) and Cu/MWCNT-S (Figures 6c and 6d).

Figure 8 shows XRD patterns for Cu/MWCNT composite films. Figures 8a, 8b and 8c show the XRD patterns for Cu/MWCNT-L (Figure 5c), Cu/MWCNT-S (Figure 6c), and Cu/MWCNT-L+MWCNT-S (Figure 7c), respectively. All of the diffraction peaks could be assigned to face-centered-cubic copper. In electroless copper deposition, cuprous oxide (Cu₂O) is often formed in the copper deposit, and it degrades the properties of the copper film. However, no Cu₂O was formed in the Cu/MWCNT composites in the present study. No diffraction peaks due to the MWCNTs can be seen owing to their weak intensity.

Thus, the proposed method is useful for fabricating uniform Cu/MWCNT composites incorporating different sized MWCNTs homogeneously. Furthermore, this method can be applied not only to

Figure 7. Surface SEM images of Cu/MWCNT composites containing different sized MWCNTs fabricated using copper deposition solutions with different SDS:HPC ratios: (a) SDS:HPC=1:1, (b) high magnification image of (a), (c) SDS:HPC=7:3, and (d) high magnification image of (c).
MWCNTs such as MWCNTs and single-walled carbon nanotubes. Cation of uniform Cu/CNT composites containing multiple types of MWCNTs homogeneously. The deposited copper, resulting in Cu/MWCNT composites containing both large-sized and small-sized MWCNTs into the electroless copper deposition solution. An anionic surfactant (SDS) and a polymeric surfactant (HPC) are dispersed homogeneously in the solution and they act as a redox reaction occurs catalytically on the deposited copper. During the copper deposition process, the adsorbed MWCNTs are incorporated independently in the deposited copper, resulting in Cu/MWCNT composites containing different sized MWCNTs homogeneously. This unique approach has the potential to be applied to the fabrication of uniform Cu/CNT composites containing multiple types of CNTs such as MWCNTs and single-walled carbon nanotubes.

Conclusions For the fabrication of Cu/MWCNT composites containing different sized MWCNTs, an electroless copper deposition technique was applied. An anionic surfactant (SDS) and a polymeric surfactant (HPC), as well as a combination of the two, were used to disperse the large-sized and small-sized MWCNTs into the electroless copper deposition solution. Both MWCNTs were well dispersed into the solution using the combination of SDS and HPC. Cu/MWCNT composites containing different sized MWCNTs independently and homogeneously could be obtained from electroless copper deposition solutions, in which the different sized MWCNTs were dispersed homogeneously.

Acknowledgment This work was supported by a Grant-in-Aid for Scientific Research (B) (No. 26289270) from the Japan Society for the Promotion of Science (JSPS).

References
1. S. Berber, Y. K. Kwon, and D. Tomanek, Phys. Rev. Lett., 84, 4613 (2000).
2. B. Q. Wei, R. Vajtai, and P. M. Ajayan, Appl. Phys. Lett., 79, 1172 (2001).
3. M. F. Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly, and R. S. Ruoff, Science, 287, 637 (2000).
4. J. P. Lu, Phys. Rev. Lett., 79, 1297 (1997).
5. S. R. Baskhi, D. Lahiri, and A. Agarwal, Int. Mater. Rev., 55, 41 (2010).
6. K. Chu, H. Guo, C. Jia, F. Yin, X. Zhang, X. Liang, and H. Chen, Nanoscale Res. Lett., 5, 868 (2010).
7. S. Cho, K. Kikuchi, T. Miyazaki, K. Takagi, A. Kawasaki, and T. Tsukada, Scr. Mater., 63, 375 (2010).
8. S. Cho, K. Kikuchi, and A. Kawasaki, Acta Mater., 60, 726 (2012).
9. E. Khalighi, M. Torikachvili, M. A. Meyers, and E. A. Olevsky, Mater. Lett., 79, 256 (2012).
10. C. Guidi, R. L. Pavlenko, V. Turyg, A. Weibelt, P. Puch, C. Estournes, A. Peigney, W. Bacsica, and C. Laurent, Carbon, 58, 185 (2013).
11. S. M. Uddin, T. Mahmud, C. Wolf, C. Gnan, I. Kolaric, A. Volkmer, H. Holler, W. Wienecke, S. Roth, and H. J. Fehl, Compos. Sci. Technol., 70, 2253 (2010).
12. C. B. Lin, Z. C. Chang, Y. H. Tung, and Y. Y. Ko, Wear, 270, 382 (2011).
13. A. K. Shukla, N. Nayan, S. V. V. N. Murty, and S. C. Sharma, Mater. Sci. Eng. A, 560, 365 (2013).
14. M. R. Akbarpour, E. Salahi, F. A. Hesari, A. Simchi, and H. S. Kim, Mater. Sci. Eng. A, 528, 4690 (2011).
15. P. Jeni, E. Y. Yoon, J. Gubicza, H. S. Kim, J. L. Labar, and T. Ungar, Mater. Sci. Eng. A, 528, 4690 (2011).
16. P. Jeni, J. Gubicza, E. Y. Yoon, H. S. Kim, and J. L. Labar, Compos. Part A, 51, 71 (2013).
17. K. Rajkumar and S. Aravidin, Wear, 270, 613 (2011).
18. S. J. Yoo, S. H. Han, and W. J. Kim, Carbon, 41, 687 (2013).
19. S. Arai and M. Endo, Electrochem. Solid-State Lett., 7, C25 (2004).
20. S. Arai, T. Saito, and M. Endo, J. Electrochem. Soc., 157, D147 (2010).
21. S. Arai and A. Kato, J. Electrochem. Soc., 160, D380 (2013).
22. S. Arai and T. Kanazawa, ECS J. Solid State Sci. Technol., 3, P201 (2014).
23. K. Sasaki, A. Kuroda, K. Katagiri, N. Takahashi, A. Nagai, Y. Ito, and A. Kakitani, Proceedings of the 33rd Japan Symposium on Thermophysical Properties, Osaka, Japan, Oct 3-5, 2012.
24. K. Esumi, M. Ishigami, A. Nakajima, K. Sawada, and H. Honda, Carbon, 33, 279 (1995).
25. L. Jiang and L. Gao, Carbon, 41, 2923 (2003).
26. Q. Chen, L. Dai, M. Gao, S. Huang, and A. Mauv., J. Phys. Chem. B, 105, 618 (2001).
27. B. Vignolo, A. Penicau, C. Coulon, C. Sauder, R. Pailler, C. Journet, P. Bernier, and P. Poulin, Science, 290, 1331 (2000).
28. M. J. O’Connell, S. M. Bachilo, C. B. Huffman, V. C. Moor, M. S. Strano, E. H. Haroz, K. L. Rialon, P. J. Boul, W. H. Noon, C. Kittrell, J. Ma, R. H. Hauge, R. B. Weisman, and R. E. Smalley, Science, 297, 593 (2002).
29. C. Richard, F. Balavoine, P. Schultz, T. W. Ebbesen, and C. Mioskowski, Science, 300, 775 (2003).
30. M. F. Islam, E. Rojas, D. M. Bergey, A. T. Johnson, and A. G. Yodh, Nano Lett., 3, 269 (2003).
31. V. C. Moore, M. S. Strano, E. H. Haroz, R. H. Hauge, R. E. Smalley, J. Schmidt, and Y. Talmon, Nano Lett., 3, 1379 (2003).
32. L. Jiang, L. Gao, and J. Sun, J. Colloid Interface Sci., 260, 89 (2003).
33. K. Yurekli, C. A. Mitchell, and R. Krishnamoorti, J. Am. Chem. Soc., 126, 9902 (2004).
34. T. Hertel, A. Hagen, V. Talalayev, K. Arnold, F. Henrich, M. Kappes, S. Rosenthal, J. McBride, H. Ulbricht, and E. Flahaut, Nano Lett., 5, 511 (2005).
35. J. Steinmetz, M. Glerup, M. Pailler, P. Berrier, and M. Holzinger, Carbon, 43, 2397 (2005).
36. Y. Tan and D. E. Resasco, J. Phys. Chem. B, 109, 14454 (2005).
37. N. Grosio, P. van der Schoot, J. Meulidijk, and C. E. Koning, Langmuir, 23, 3646 (2007).
38. Z. Sun, V. Nicolosi, D. Rickard, S. D. Bergin, D. Ahnere, and J. N. Coleman, J. Phys. Chem. C, 112, 10692 (2008).
39. A. J. Blanc, C. E. Lenehan, and J. S. Quinton, J. Phys. Chem. B, 114, 9805 (2010).
40. W. H. Duan, Q. Wang, and F. Collins, Chem. Sci., 2, 1407 (2011).
41. J. N. Barisci, M. Tahan, G. W. Wallace, S. T. Badea Vaugien, M. Maugay, and P. Poulin, Adv. Funct. Mater., 14, 133 (2004).
42. T. Takahashi, C. R. Lucelescu, K. T. Uchida Ishii, and H. Yajima, Chem. Lett., 34, 1516 (2005).
43. Y. Yan, J. Cui, P. Potschke, and B. Voit, Carbon, 48, 2063 (2010).
44. B. Suarez, B. M. Simonet, S. Cardenas, and M. Valcarcel, J. Chromatogr. A, 1128, 282 (2006).
45. K. C. Park, M. Fujishige, K. Takeuchi, S. Arai, S. Morimoto, and M. Endo, J. Phys. Chem. Solids, 69, 2481 (2008).
46. E. J. W. Verwey and J. Th. G. Overbeek, Theory of the Stability of Lopohidic Colloids, Elsevier, Amsterdam-New York (1948).
47. S. Shimabashyahi, T. Uno, and M. Nakagaki, Colloid Surf. A, 123–124, 283 (1997).
48. H. Homma and T. Kobayashi, J. Electrochem. Soc., 141, 730 (1994).
49. J. Shu, B. P. A. Grandjean, and S. Kaligaum, Ind. Eng. Chem. Res., 36, 1632 (1997).