

Facile Preparation of Nanosilver-decorated MWNTs Using Silver Carbamate Complex and Their Polymer Composites

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We successfully decorated multi-wall carbon nanotubes (MWNTs) with silver by reacting Ag-NPs with thiol-functionalized MWNT-SH. Ag alkylcarbamate complex was used as an Ag precursor. Uniform Ag-NPs (5-10 nm) were effectively prepared by microwaving within 60 s using 1-amino-4-methylpiperazine (AMP), which acts as a reaction medium, reducing agent, and stabilizer. The MWNTs were functionalized with 2-aminoethanethiol. Exploiting the chemical affinity between thiol and Ag-NPs, Ag-MWNT nanohybrids were obtained by spontaneous chemical adsorption of MWNT-SH to Ag through Ag-S bonds. The Ag-S-MWNTs were characterized by TGA, XRD, and TEM to confirm that Ag-NPs were uniformly decorated onto the MWNTs. The Ag-S-MWNTs were then employed as conducting filler in epoxy resin to fabricate electrically conducting polymer composites. The electrical properties of the composites were measured and compared with that containing MWNT-SH. The electrical conductivity of composites containing 0.4 wt % Ag-S-MWNT was four orders of magnitude higher than those containing same content of MWNT-SH, confirming Ag-S-MWNT as an effective conducting filler.

Key Words : Ag-NPs, 1-Amino-4-methylpiperazine, Silver alkylcarbamate, Microwave, Ag-MWNTs/epoxy composites

Introduction

Chemical approaches using a series of reductants and stabilizers have been extensively developed to enable the production of silver nanoparticles (Ag-NPs) on a large scale under simple and mild conditions¹⁻⁷ including use of silver alkylcarbamate precursor.⁸⁻¹⁷ However, each of these methods has its own advantages and limitations. From a practical viewpoint, the development of simpler, inexpensive, widely-applicable and environmentally-benign procedures is still an active area of research. One of the most promising methods for the reduction of silver alkylcarbamate complex to metallic silver is thermal reduction. However, these reactions are usually conducted under conventional refluxing conditions, a process that requires several hours of time. Thermal reduction by microwaving is a green, highly selective and efficient method for the rapid reduction of silver alkylcarbamate to silver metal without reducing agent.¹⁸

Many studies have been devoted to the fabrication of metal NP-decorated CNTs for unique electrical, magnetic, and optical properties.^{19,20} Among them, silver-decorated CNTs (Ag-CNTs) have gained extensive attention due to their potential applications as catalysts, optical limiters, advanced materials, *etc.*²¹⁻²³ To prepare well-defined Ag-CNTs, several different methods, including thermal decomposition reaction,^{21,24} vapor deposition,²⁵ surface chemical reduction,²⁶ and gamma-irradiation,²⁷ have been proposed. However, there are two major drawbacks associated with these methods: one is the weak interaction between Ag-NPs and the surface of the CNTs.^{28,29} In most cases, Ag-NPs are

formed inside the tubes due to capillary effect,^{30,31} leading to poor synergic effect of the Ag-CNTs nanohybrids. The other is agglomeration of Ag-NPs, causing difficulties in uniform decoration of the surface of the CNTs. To accomplish the effective production of Ag-CNTs, an easy and low-cost route is desired.

Epoxy resin-based CNT composites have been extensively investigated in view of their potential applicability to the electronics, aerospace, and automotive industries.³² It has been shown that by adding less than 1.0 wt % of CNTs to epoxy,³³ the electrical conductivity of the composite can be improved from around 10^{-13} to 10^{-4} S/cm. The measured electrical conductivities of CNT/epoxy composites typically range from 10^{-5} to 10^{-3} S/cm above the percolation threshold.³³ While further increase in CNT content above the percolation threshold can marginally enhance the electrical conductivity of composites, the solution viscosity becomes too high to produce void-free composites when the CNT content is higher than 1.0 wt %. This limits the use of CNT/polymer composites to applications where high CNT contents are necessary. Therefore, processing techniques for improving the electrical conductivity of composites below or near the percolation threshold are crucial to the production of highly conducting composites. Simulation results have indicated that the contact resistance of CNTs in composites plays a dominant role in contrast to the dominant role of the intrinsic resistance of CNTs.^{34,35} It is expected that the electrical conductivity of composites can be significantly improved if the contact resistance of CNT junctions in a polymer matrix can be reduced.

Here, we report a new preparation method of Ag-NPs (5–10 nm) in AMP as a weak reducing agent and a solvating and stabilizing agent of NPs. A silver cabamate complex was used as an Ag-precursor. Upon microwaving for 10–60 s, uniform Ag-NPs with sizes of 5–10 nm were rapidly synthesized. A simple approach is proposed to decorate MWNTs with Ag-NPs based on the adsorption of Ag-NPs with thiol-functionalized MWNTs, with the goal of enhancing the electrical conductivity of MWNTs and thus reducing the contact resistance of MWNT junctions in a polymer matrix. The Ag-S-MWNTs were incorporated into an epoxy resin as conducting fillers to prepare electrically conducting composites. The CNT dispersion state in epoxy, the electrical properties of the composites containing Ag-S-MWNTs, were investigated and compared with those containing functionalized MWNT-SH.

Experimental

Reagents and Analyses. 1-Amino-4-methylpiperazine (AMP), dicyclohexylcarbodiimide (DCC), and 2-aminoethanethiol were obtained from commercial sources (Sigma-Aldrich Chem. Co.) and used without further purification. An isopropyl alcohol solution of Ag-complex (silver 2-ethylhexylammonium carbamate (Ag-EHCB) 2-ethylhexyl amine complex, 10 wt %) was purchased from InkTec Co., Ltd., Korea (Figure 1). Carboxyl functional MWNTs (8–15 nm diameter and 10–50 mm length) were purchased from Nanostructured & Amorphous Materials Inc. Size and morphology of the as-prepared Ag-NPs were observed using a Philips TECNAI-FE12 transmission electron microscope (TEM, 120 kV). Briefly, the particles were dispersed in methanol, after which a drop of the solution was placed on a carbon-coated copper grid and allowed to air-dry. The X-ray diffraction (XRD) patterns were recorded using a Rigaku Rotaflex Rad-B diffractometer (Rigaku Corp., Japan) with Cu target Cu K α radiation, a tube voltage of 40 KV, and 60 mA in the range of 5–90°.

Preparation of Ag Nanocolloid in AMP by Microwave Reduction. Ag-EHCB complex solution (3.5 g) dissolved in AMP was prepared and stirred at 25 °C for 5 min. The solution was then reduced by microwave irradiation for 10, 20, 30, and 60 s. After reduction of Ag-complex had com-

pleted, the solution immediately changed to red brown or blue brown in color. The progress of the reaction was monitored periodically by UV-vis spectroscopy. Ag-NPs were collected by centrifugation and characterized by TEM and XRD. The bulk electrical conductivity of composites was measured at room temperature using a programmable curve tracer (Sony Tektronix 370A).

Preparation of Thiol-Functionalized MWNTs. In a typical procedure, carboxyl-functionalized MWNTs were spread in ethanol at a concentration of 0.3 mg/mL and sonicated for 10 min. An excess of DCC ethanolic solution (0.5 mg/mL) was added, and the relative solution was stirred for a few minutes. Finally, a 5 mM solution of 2-aminoethanethiol was added, and the solution was stirred again for 24 h at room temperature. The amount of 2-aminoethanethiol was selected to be double the estimated carboxylic group concentration. The obtained thiol-functionalized MWNTs tended to precipitate slowly after the reaction. The precipitate obtained 24 h after the reaction was separated from the solution by filtration, washed to remove unreacted molecules and by-products, and then dispersed in ethanol by sonication for 30 min.

Preparation of MWNTs and Ag-NPs Hybrid. Ag-complex solution (3.5 g) was dissolved in AMP and stirred at 25 °C for 5 min. The reduction reaction was carried out by microwave irradiation for 10, 20, 30, and 60 s. After the reaction, thiol-functionalized MWNTs (0.01 to 0.04 g) were introduced to the Ag nanocolloidal solution for the collection of as-prepared Ag-NPs. Ag-S-MWNTs were collected by centrifugation and characterized by TEM and XRD.

Preparation of Ag-S-MWNT/Epoxy Composites. The composites were prepared from diglycidyl ether of bisphenol A (DGEBA, YD-128S, Kukdo Chem. Co. LTD.) using a curing agent, *m*-phenylenediamine (*m*-PDA, Sigma-Aldrich). MWNTs were dispersed in 2-propanol before adding the DGEBA, after which the mixture was sonicated for 30 min at 45 °C. The mixture was then degassed at 80 °C for 1 h to eliminate the entrapped air and the remaining 2-propanol. Then, *m*-PDA hardener (14.5 wt %) was added to the mixture. After mixing, the compound was molded into a flat plate and cured at 80 °C for 2 h, followed by post-cure at 150 °C for 2 h. Composites containing 0.40 wt % of functionalized MWNT-SH and Ag-S-MWNTs were prepared.

Results and Discussion

The reduction of Ag-complex to Ag(0) was carried out using microwave radiation for the preparation of the Ag-NPs colloidal solution. Upon microwaving, the AMP solution changed from colorless, to dark green, and then to brown during the reaction time from 10 to 60 s. As shown in the UV-vis spectra of Figure 2, when the microwaving time was extended to 10, 20, 30, and 60 s, the specific absorption at 397 nm after 10 s slightly shifted to 398 nm, and the intensity increased to the level before the reaction. These findings indicate that formation of Ag-NPs occurred, which could be confirmed in the photos in Figure 3.

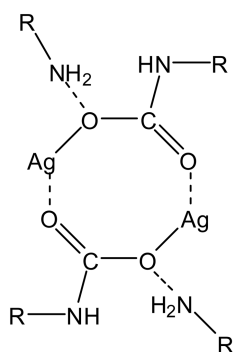


Figure 1. Structure of silver alkylcarbamate complex.

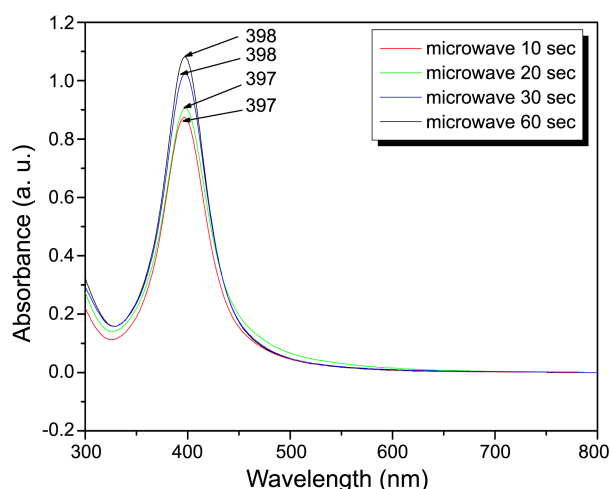


Figure 2. UV-vis absorption spectra of silver colloidal solutions obtained from Ag-complex using irradiation of microwave for 10, 20, 30 and 60 s.

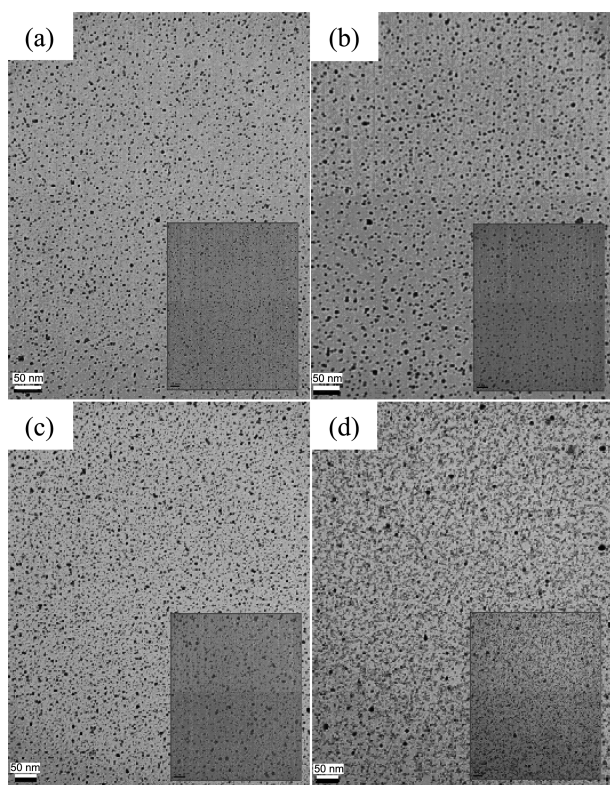


Figure 3. TEM images of Ag-NPs obtained from the Ag-complex by microwaving for (a) 10 sec, (b) 20 sec, (c) 30 sec, (d) 60 sec (inset images are other Ag-NPs prepared under same condition).

TEM studies on Ag-NPs were conducted to evaluate the shape and size of the particles exposed to microwave irradiation in silver alkylcarbamate complex solution after 10, 20, 30, and 60 s. As shown in Figure 3(a), Ag-NPs with small size (5–10 nm) were obtained from the silver colloidal suspension prepared by microwave irradiation for 10 s, whereas the small amount of Ag-NPs with 10–15 nm size were produced by microwaving for 60 s as shown in Figure 3(d). Most of the Ag-NPs colloids were well-dispersed and

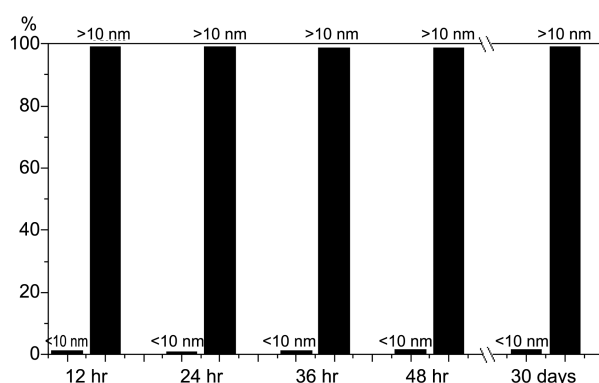


Figure 4. Stability of Ag-NPs colloidal solution prepared by irradiation of microwave (determined by calculation based on several TEM images).

showed polygon-shaped morphology as shown in Figure 3. Reduction of silver carbamate complex in AMP by microwave irradiation produced Ag-NPs with relatively uniform distribution compared with other previously reported methods. However, growth of the Ag-NPs was found to depend on the microwaving time, and the size of Ag-NPs was within 15 nm. The particle size distribution became slightly broad with an increase in microwaving time, that is, the colloidal system maintained monodispersion with increased microwaving time.

In this study, AMP was used as a silver colloidal solution, a reducing agent of Ag(I) carbamate to Ag(0), and a stabilizer of NPs. Therefore, we easily prepared a size-controlled Ag-NP colloidal solution within 60 s without any contamination of by-products based on its versatile role in synthesizing the Ag-NPs. Figure 4 shows the long-term stability of Ag colloidal solution. The dispersed Ag-NPs maintained the same size for 30 days.

To create binding sites for the Ag-NPs, the carboxyl-terminated MWNTs were thiol-functionalized by reacting with aminoethanethiol with the aid of a dicyclohexylcarbodiimide (DCC) condensation agent as reported by Liu.³⁶ 2-Aminoethanol-functionalized MWNTs showed a shoulder at 2590 cm^{-1} , indicative of amide-bond formation. A shoulder at 1630 cm^{-1} remains, indicating that not all carbonyl groups are derivatized in its FT-IR spectra. The thiol-functionalized MWNT-SH has the ability to adsorb and collect the Ag-NPs in the stable colloidal solution by forming S-Ag linkages. Thus, we developed a facile synthetic method for producing the silver-CNT nanohybrids by reaction of Ag-NPs solution with thiol-functionalized MWNTs.

Figure 5(a) shows the Ag colloidal solution in a vial. The colloid solution was well-dispersed and stable after standing for 30 days without any precipitation. Upon introducing the thiol-functionalized MWNTs into the Ag-NP colloidal solution with a size of 5–10 nm, the MWNTs adsorbed all of the Ag-NPs instantaneously within 5 min to form Ag-S-MWNT composites. Finally, the resulting solution faded, and the created Ag-S-MWNTs were precipitated as shown in Figure 5(b).

The precipitated Ag-S-MWNTs were analyzed by a

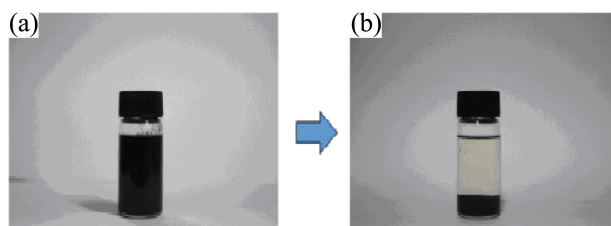


Figure 5. Images of Ag-NPs colloidal solution (a) before and (b) after treatment of MWNT-SH.

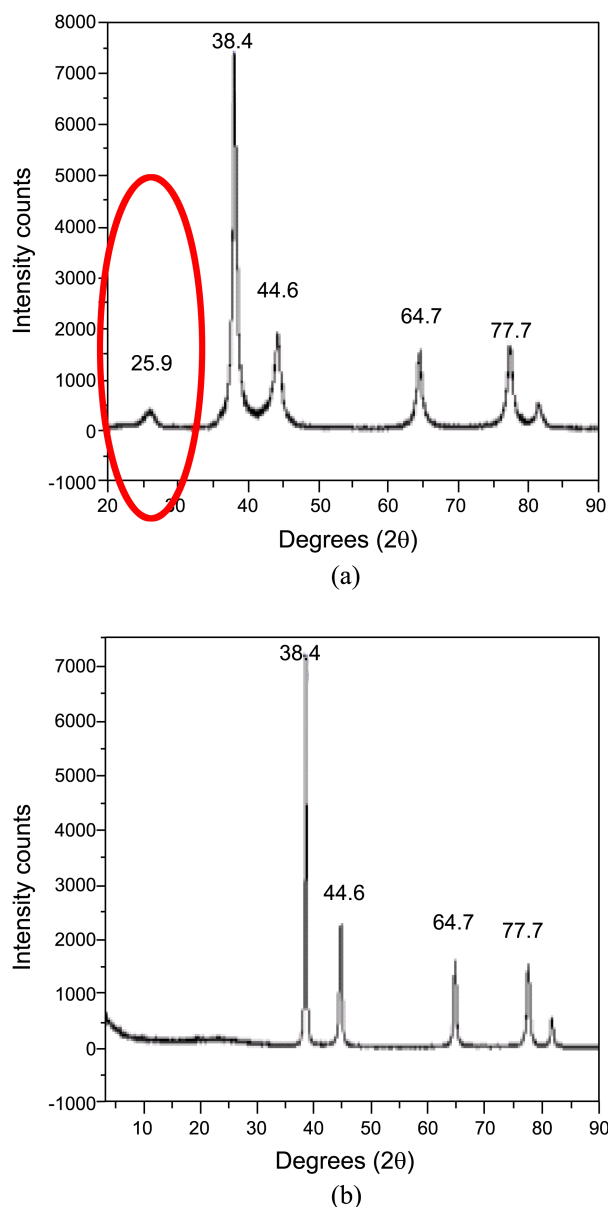


Figure 6. Powder XRD patterns of (a) Ag-S-CNTs prepared from Ag-NPs and MWNT-SH and (b) Ag(0) NPs prepared from Ag-complex.

powder X-ray diffractometer. The XRD pattern of the Ag-NPs showed peaks at 25.9, 38.4, 44.6, 64.7, and 77.7°, confirming the presence of Ag(0) and MWNTs in the sample as shown in Figure 6(a) and (b). The diffraction peaks at 2θ of 38.00°, 44.4°, 64.5°, and 77.5° were readily indexed to

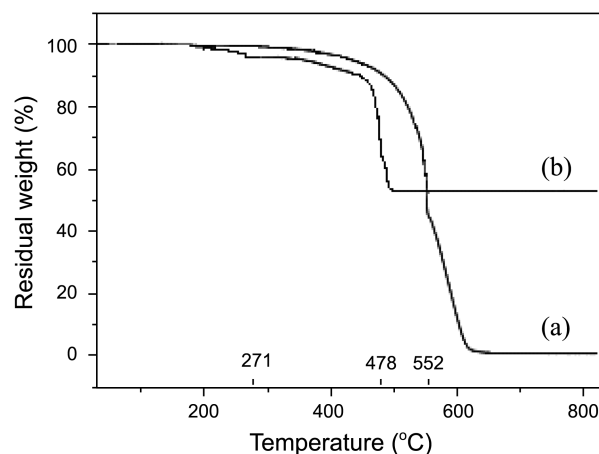


Figure 7. TGA data of (a) thiol-functionalized MWNT-SH and (b) Ag-S-MWNT.

(111), (200), (220), and (310) reflections of silver metal crystals on both hybrid structures, respectively, representing the face-centered cubic (fcc) phase of silver. Specifically, the peak at 25.9° with prominent peak counts showed the presence of MWNTs, which was the same as in the JCPDS cards.

TGA analysis also showed the existence of Ag-NPs and organic stabilizer. The primary decomposition temperature and weight loss of Ag-S-MWNTs were very significant, about 271 °C and 5% of the organic part, respectively, whereas the weight loss of MWNT-SH upon heating from 25 to 612 °C was about 97% as shown in Figure 7. The differences in decomposition temperature of MWNT bodies for the two samples may be attributed to the different catalytic abilities of naked and Ag-NPs with respect to thermally degradable MWNTs. The attached silver contents, estimated from the residual weight of the functionalized samples at 800 °C, were 53% for Ag-S-MWNTs, which is much higher than that of other methods.³⁷

Figure 8 shows the TEM images of the resulting Ag-S-MWNTs prepared from the reaction of Ag-NPs with the thiol-functionalized MWNT-SH. When 0.01 g of thiol-functionalized MWNT-SH was introduced into the Ag colloidal solution and sonicated for 30 s, not all of the Ag-NPs reacted

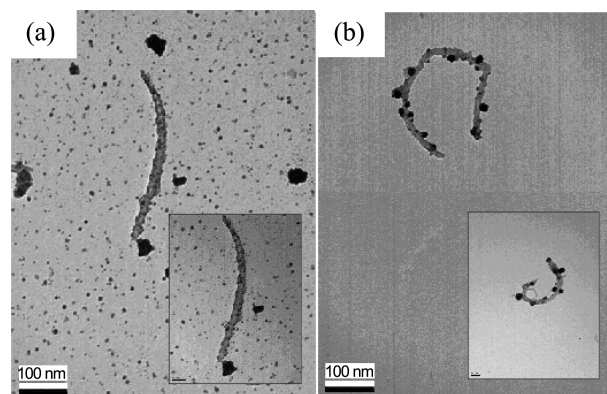


Figure 8. TEM images of a Ag-S-MWNT obtained from the reaction of Ag-NPs with (a) 0.01 g and 0.02 g of MWNT-SH.

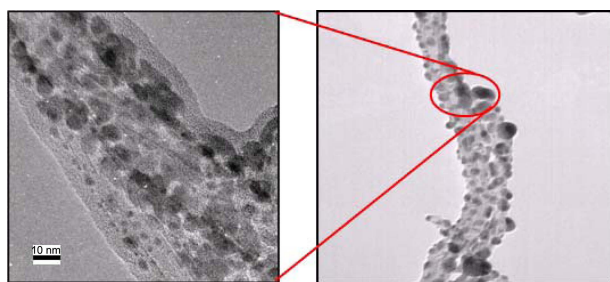


Figure 9. HR-TEM images of the Ag-NPs-decorated carbon nanotubes, Ag-S-MWNT.

with MWNT-SH as shown in Figure 8(a). As the concentration of MWNT-SH increased from 0.02 g in the Ag-NP solution, the MWNT-SH reacted with more of the Ag-NPs as shown in Figure 8(b). Figure 9 is a TEM image of the Ag-S-MWNT hybrids, on which Ag-NPs were distributed more densely and uniformly on the external surface of the MWNTs. The average diameter of the Ag-NPs on Ag-S-MWNTs hybrids was 5–15 nm, much smaller than the average size of the Ag-NPs deposited on MWNTs by other methods. These results suggest that functionalized MWNT-SH can be used to collect Ag-NPs in colloidal solution.

The morphologies of 0.40% MWNT/epoxy composites shed some light on the nanoscopic dispersion states of MWNTs. Small agglomerates were seen for the composites containing Ag-S-MWNTs, whereas these agglomerates were almost absent from the composites containing functionalized MWNT-SH.

It was expected that the Ag-NPs decoration would have a beneficial effect on the electrical conductivity of MWNTs since the inherent electrical conductivity of Ag is much higher than that of the MWNTs used in this study. The conductivity of the MWNTs increased significantly after silver decoration, showing effectiveness of silver in improving the conductivity of MWNTs. This observation has a practical implication in that the Ag-S-MWNTs are potentially useful as a conducting filler in polymer composites with unique properties, such as increased electrical conductivity, high aspect ratio, and reduced contact resistance in CNT junctions. Two composites containing MWNT-SH or Ag-S-MWNT presented a transition from the insulator to conductor. The incorporation of 0.40 wt % MWNT-SH increased the conductivity of the composite (from 2.29×10^{-13} to 0.91×10^{-3} S/cm) by about nine orders of magnitude.¹⁴ This observation was consistent with previous findings on CNT composites based on similar matrix materials.^{33,38–40} The composites containing Ag-S-MWNTs exhibited more pronounced enhancement of electrical conductivity than their counterparts containing MWNT-SH. For the same MWNT content of 0.40 wt %, a remarkable improvement in electrical conductivity of about 12 orders of magnitude was observed (from 2.29×10^{-13} to 0.97 S/cm), showing the advantage of Ag-S-MWNTs as an effective conducting filler to improve the conductivity of the composites.

Conclusion

In this study, we report a facile preparation method of Ag-NPs (5–10 nm) using microwave irradiation of AMP as a weak reducing agent and stabilizing agent. During microwaving of a silver carbamate complex in AMP for 10–60 s, uniform Ag-NPs with sizes from 5 to 15 nm were effectively synthesized. This method has potential as a tool for preparation of Ag-NPs to enable control of particle size at the nanometer scale as well as the uniformity of particle size. Further, Ag-S-MWNTs were also prepared by a simple method established for Ag-NPs decoration onto MWNTs after thiol-functionalization to create binding sites with Ag-NPs. Epoxy-based composites containing MWNT-SH with and without Ag-NPs were prepared. The electrical conductivity of the composites with Ag-S-MWNTs was significantly higher than those containing MWNT-SH with an Ag-S-MWNT content higher than 0.40 wt %, confirming the advantage of Ag-S-MWNTs as an effective conducting filler. Further evaluation of the other properties of Ag-S-MWNTs and the composites under end-use conditions is now in progress.

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