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Research Article

CNT Reinforced Silver Nanocomposites: Mechanical and Electrical Studies

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Nanoindentation hardness and elastic modulus of the silver/MWCNT (multiwalled carbon nanotubes) composites, fabricated by modified wet mixing technique, are studied in the present work. CNT reinforced silver nanocomposites, fabricated by introducing 4.5 volume percentages of CNT in the silver matrix, have increased elastic modulus and approximately 50% higher hardness than pure nanosilver. It is also observed from the results that the electrical conductivity of the fabricated materials was decreased by increasing the CNTs volume %.

1. Introduction

Metallic nanoparticles due to their size dependent properties have attracted the attention of researchers during last decade. Noble metals such as silver are particularly interesting due to their unique properties. Silver nanoparticles exhibit excellent antibacterial, electrical, and thermal properties [1, 2]. However pure silver is soft which restricts its use as a contact material in electrical circuits. Carbon nanotubes with Young's modulus as high as 1TPA and hardness as high as 150 GPa are considered as ideal reinforcements to improve the mechanical properties of metals [3, 4]. It is believed that use of CNT as filler for silver matrix would produce a composite with excellent mechanical, electrical, and thermal properties.

However, reinforcement of CNTs into metal matrix remains a challenge due to their entangled structure. The CNTs are held together by weak, noncovalent interactions. These interactions are π-π attractive bonding, electrostatic, and van der Waal forces. Because of these interactions, CNTs have tendencies to agglomerate. In wet mixing method, ultrasonic cavitation succeeds in overcoming these challenges [5]. Bakshi et al. have summarized state of the art in the field [6]. Most of the research work in this regard has been reported with copper and aluminium matrices and very few reports are available on CNT reinforced Ag nanocomposites [7, 8].

Keeping above points in view, we herein report the fabrication of MWCNT/silver nanocomposites through wet mixing technique and a study on their nanoindentation hardness and elastic modulus as well as electrical conductivity. The effect of CNT reinforcement on electrical conductivity and mechanical properties is compared to their counterpart pure silver fabricated under same conditions.

2. Materials and Methods

2.1. Fabrication of Ag/MWCNT Nanocomposite Powder. Multiwalled CNTs (purity >95%, diameter 20–30 nm, and length 15–30 μm) and silver nanoparticles of diameter 80–100 nm with purity greater than 98% were purchased from Nanoshel, USA. All the chemicals employed in this synthesis were of analytical grade and used without further purification.

Sample of Ag/MWCNT nanocomposite with 0, 1.5, 3.0, and 4.5 volume percentages was prepared using wet mixing method [9]. The weighed amount of functionalized MWCNT was soaked in 100 mL ethanol and sonicated for two hours. To the CNT solution, nanosilver powder was added with simultaneous mechanical stirring and sonication for another

Table 1

Composition	Theoretical density (gm./cm^3)	Measured density (gm./cm^3)	Relative density (%)	Relative porosity (%)
Ag	10.48	10.18	97.13	2.87
MWCNT (1.5 vol.%)/Ag	10.35	9.83	94.97	5.03
MWCNT (3.0 vol.%)/Ag	10.22	9.61	94.03	5.97
MWCNT (4.5 vol.%)/Ag	10.02	9.39	93.71	6.29

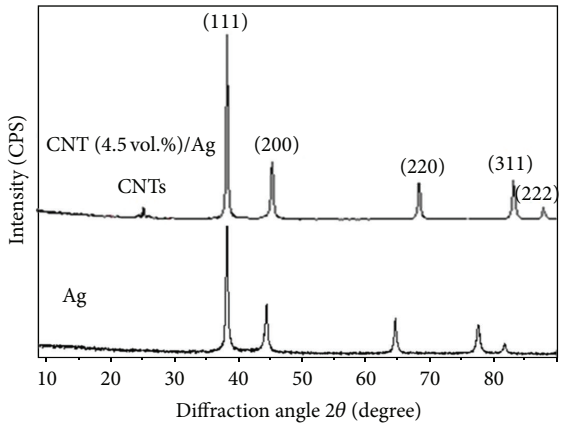

Figure 1: XRD spectra of CNT (4.5 vol.%)/Ag and Ag nanocomposite.

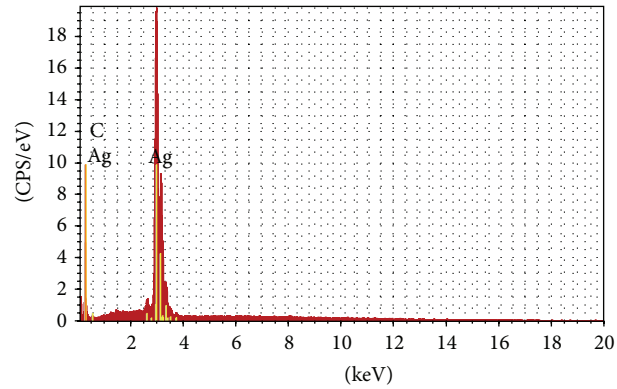

Figure 2: EDS characteristic profile of CNT (4.5 vol.%)/Ag nanocomposite powder.

two hours. The mixture solution was then dried at 50°C on a hot plate to obtain CNT/Ag nanocomposite powder.

2.2. Consolidation of Ag/CNT Nanocomposite Powder. The CNT/Ag nanocomposite samples were then compacted into pallets of size 13 mm × 2 mm at a pressure of 320 MPa using uniaxial molding press. All the CNT/Ag pallets were then sintered in a horizontal tube furnace with attached programmable temperature controller for 12 h under nitrogen atmosphere. The heating rate was maintained at a rate of 5 K min^{-1} to obtain a sintering temperature of 800°C.

2.3. Density Measurements and Its Comparison with Theoretical Values. Densities of various samples were measured and compared with theoretical values. Archimedes principle was used to calculate experimental densities of the samples. Deionized water was used as the immersion fluid during the experiment. Theoretical densities were calculated assuming materials are fully dense and there is no interfacial action. Theoretical densities were calculated using ROM (rules of mixture) method which states that

$$\rho_{\text{th}} = V_r \rho_r + (1 - V_r)\, \rho_m, \tag{1}$$

where ρ_{th}, ρ_r, and ρ_m are densities of composite, reinforcement, and matrix, respectively. V_r is the volume fraction of the reinforcement in the sample.

Numerical values of densities used for silver, multiwall CNTs, and single-wall CNTs were taken as 10.48 g/cm^3, 1.8 g/cm^3, and 1.3 g/cm^3, respectively.

Analysis of the data shown in the table clearly demonstrates that the densities of the sintered sample are more than the Ag/CNT powder. This increase in densities is attributed to pore shrinkage and grain growth of samples.

A comparison of theoretical densities and observed densities is given in Table 1.

2.4. Measurement of Hardness, Electrical Conductivity, and Characterization. X-ray diffraction patterns of the powdered samples were recorded on a PANalytical 3050/60 X'Pert-PRO using CuKα radiation. Morphology and microstructure of the nanopowder were studied using scanning electron microscope (SEM) FEI Quanta FEG 450 operated at 15 KV. CETR-Apex nanoindenter (Bruker) with Berkovich diamond tip with a radius of 100 nm was used for nanoindentation testing. The indenting system, kept on a vibration resistant table, had a load and displacement resolution of 1 μN and 0.1 nm, respectively. Standard loading scheme of 5 s upload, 5 s dwell, and 5 s unloading was used for the study. For the measurement of electrical conductivity, four-probe apparatus using Keithley 2400 source meter and nanovoltmeter was used.

3. Results and Discussion

3.1. Microstructural Characterization. The microstructure of fabricated Ag/CNT nanocomposite was analyzed by X-ray diffraction (XRD), electron diffraction spectroscopy, and electron microscopy. XRD patterns of Ag/CNT (4.5 vol.%) and pure nanosilver powder have been compared in Figure 1. The diffraction peaks at 38.9°, 45.1°, 65.1°, and 78.2° correspond to (111), (200), (220), and (311) reflections of FCC phase of silver. Crystalline nature of the sample is indicated in the pattern. A slight hump in the curve from base line between 2θ values of 20°–30° indicates the presence of CNTs in the sample. It is evident from diffraction pattern that peaks corresponding to (220), (311), and (311) shift toward higher diffraction angles on CNT reinforcement. This shift is

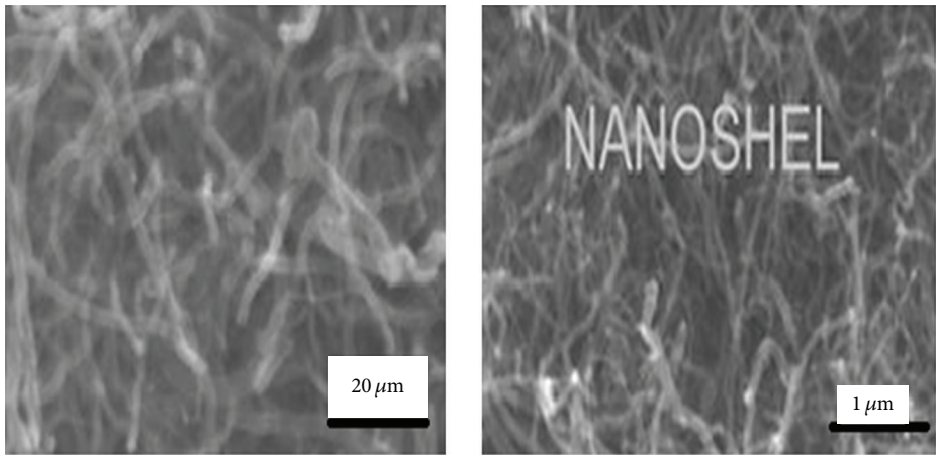

Figure 3: SEM images of carbon nanotubes.

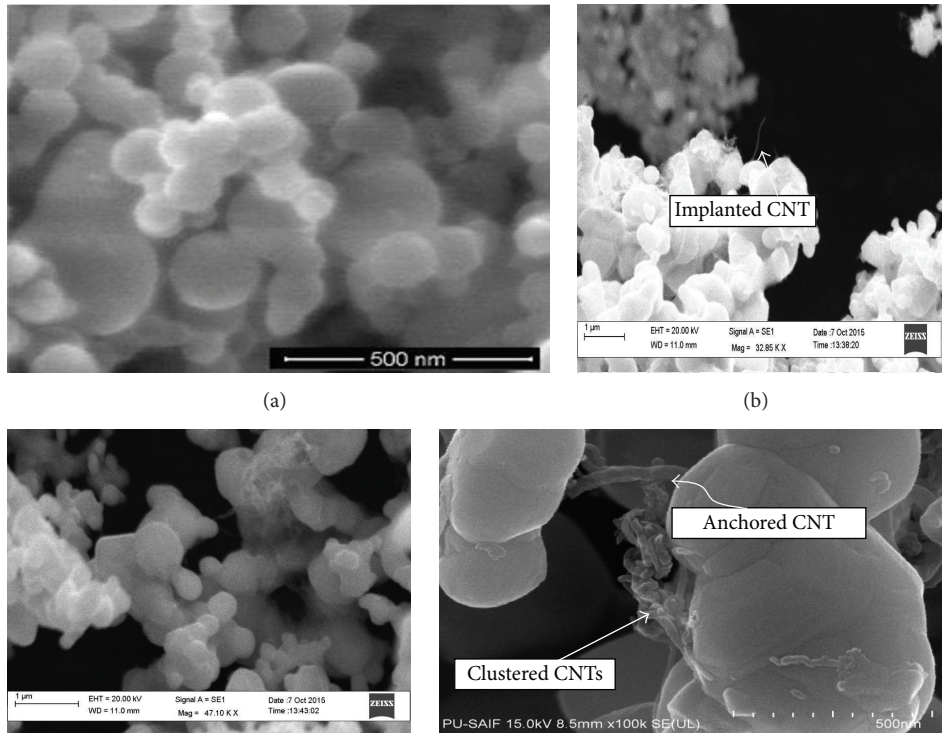

Figure 4: SEM images of CNT/Ag nanocomposite: (a) 0 vol.% CNT, (b) 1.5 vol.% CNT, (c) 3.0 vol.% CNT, and (d) 4.5 vol.% CNT.

attributed to strains developed at CNT-Ag interface during ultrasonication of CNT/Ag composite powders. Average crystallite size of nano-Ag was calculated to be 17 nm using Scherer formula [10].

The composition of Ag/CNT nanocomposites was analyzed using electron dispersive spectroscopy (EDS). EDS characteristics profile (Figure 2) confirms the presence of Ag and carbon in the material. The peaks at 3.0, 3.2, and 3.4 Kev correspond to binding energies of Ag while peaks situated at binding energies of 0.25 Kev correspond to carbon.

Morphology of the fabricated Ag/CNT nanocomposite is shown in Figure 4. SEM images of the carbon nanotubes are shown in Figure 3. It is evident from the figure that CNTs are curled and twisted with each other to form big CNT bundles. This agglomeration of CNTs is due to strong van der Waal attraction between the tubes.

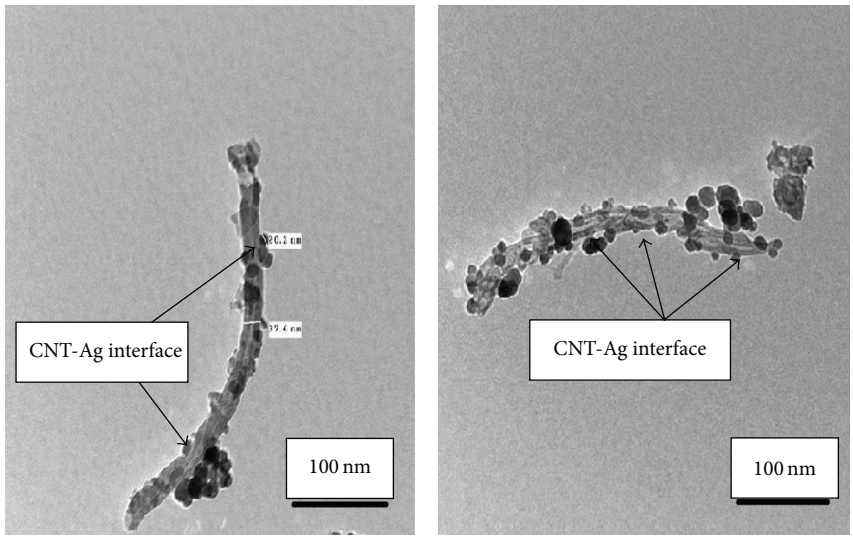

Figure 5: TEM images of CNT/Ag nanocomposite.

Figure 4 demonstrates that CNTs are homogenously dispersed into silver matrix. Innovative wet mixing method has managed to avoid the agglomeration of CNTs to a great extent. However some CNT clusters are visible in CNT (4.5 vol.%)/Ag composite.

Morphology of CNT/Ag composite was further analyzed using transmission electron microscopy (TEM). Close contact between CNT and silver particles is clearly visible in the micrographs. TEM micrographs reveal that a CNT-Ag interface has been created which is critical in gradation of mechanical properties in the nanocomposite. Grain size has also been determined using TEM analysis and is quite close to crystallite size calculated from XRD using Scherer formula.

Structural integrity of functionalized CNTs, sonicated CNTs, and CNT/Ag nanocomposite was analyzed using Raman Spectroscopy. A typical Raman spectrum has two characteristic peaks corresponding to D-band (disorder) at 1341.76 cm^{-1} and G-band (Graphite) at 1570.73 cm^{-1} (Figure 6). It can be seen from spectra that D to G band intensity ratio is 0.76 for functionalized CNTs and it is 0.79. Ratio further increases for CNT/Ag composite with increase in CNT content. This increase implies that more defects are created on CNT surface during fabrication process. G line shifts to higher wave number due to strains experienced by CNTs during ultrasonication.

3.2. Analysis of Mechanical Properties. Nanoindentation technique has been used to measure hardness and elastic modulus of the nanocomposites for load-displacement measurements. The experiment was performed under constant displacement mode. The average of 5 × 5 indents made in separate portions of the specimen was taken as an observation. This was done to reduce the effect of heterogeneous nature of the specimen. Mechanical properties, namely, hardness and modulus of elasticity of Ag/CNT nanocomposite, were analyzed against multiwall CNT's concentration. The variation of hardness and modulus of elasticity with CNT volume percentage is shown in Figures 7 and 8, respectively.

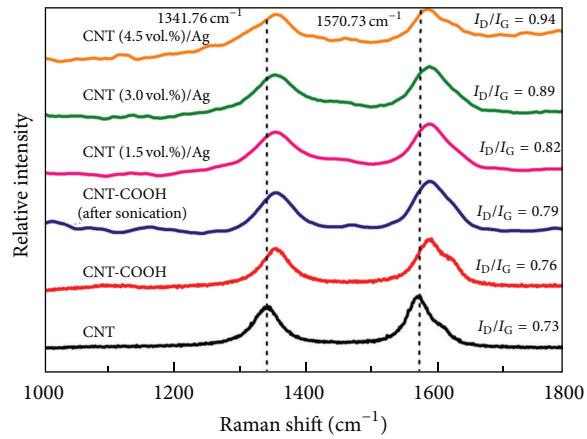

Figure 6: Raman spectra of CNT, CNT-COOH, and CNT/Ag nanocomposite.

Figures 7 and 8 clearly demonstrate that both the parameters increase with increase of CNT content in the silver matrix. The hardness increased sharply with increasing CNT content. In CNT/Ag nanocomposite containing 4.5 vol.% CNTs, the hardness of nanocomposite was 1.5 GPa which is 50% more than pure nanosilver. The elastic modulus of Ag/CNT nanocomposite also increases with increase of CNT volume content in silver matrix. Improvement in hardness is in agreement with earlier reported work of Daoush and coworkers [8]. Authors reported 100% increase in hardness of CNT/Ag nanocomposite fabricated by chemical reduction of metallic salt followed by spark plasma sintering on introduction of 10 vol.% CNTs.

Mechanical properties of a composite are influenced by combined effect of residual porosity, uniform distribution of CNTs, creation of a CNT-matrix interface, and volume of CNTs in the matrix [11]. It is evident from Table 1 that porosity of the material increases with increase in CNT content. However, this increase is very small which restricts

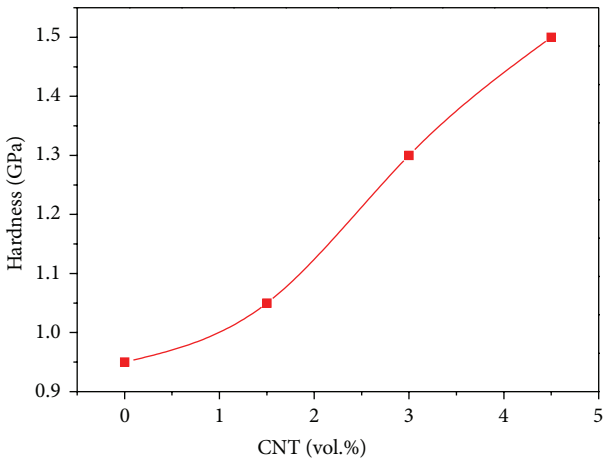

Figure 7: Variation of hardness of CNT/Ag nanocomposite with CNT volume content.

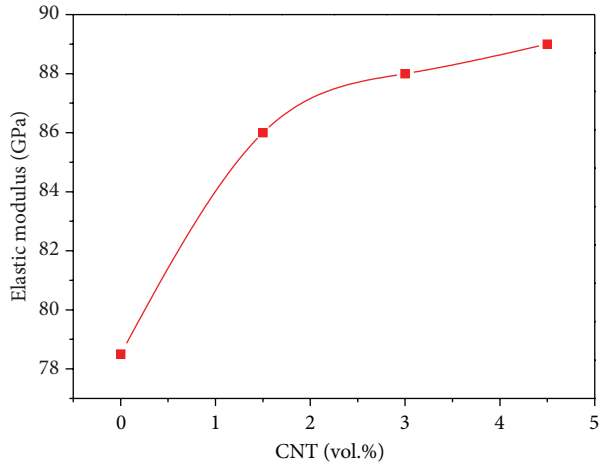

Figure 8: Variation of elastic modulus of CNT/Ag nanocomposite with CNT volume content.

its effect on the change in mechanical properties. Thus, the improvement in hardness and elastic modulus of the composite on incorporation of CNT in silver matrix may be attributed to higher stiffness and strength of the CNTs as compared to the metal matrix. Microstructural analysis discloses that CNTs are uniformly distributed into silver matrix which resulted in increased hardness and higher modulus of elasticity. TEM micrographs in Figure 5 indicate that wet mixing method succeeded in creating a strong interfacial adhesion between CNTs and metal matrix. This was crucial in transferring the applied load from the matrix to the CNTs. Homogenous distribution of CNTs inside the grain boundaries restricts matrix deformation leading to improved hardness and modulus of elasticity [12]. The trends of observed results are in complete agreement with reported work on Cu or Al [13, 14].

3.3. Analysis of Electrical Properties. The standard four-probe method was used to measure the electrical conductivity of the

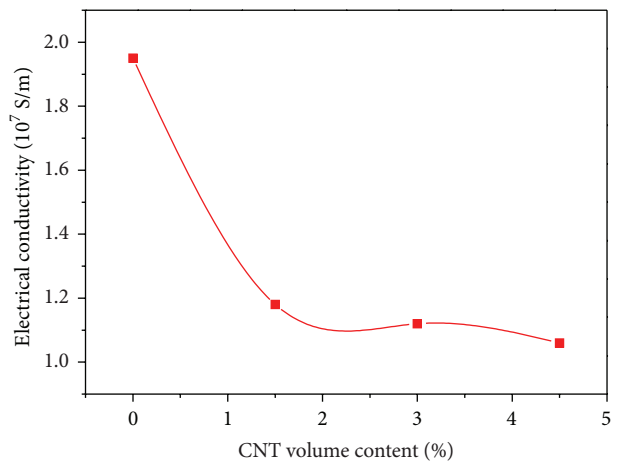

Figure 9: Variation of electrical conductivity of CNT/Ag nanocomposite.

samples. Electrical conductivity is found to decrease with the increase in CNT volume content as evident in Figure 9. In Raman spectrum, increase in I_D/I_G ratio is due to creation of more defects on CNT surface during fabrication process. A large number of defects on CNT surface will lead to more CNT-Ag interfaces. Degradation in electrical conductivity is attributed to electron scattering at these interfaces.

Residual porosity is another factor which influences electrical conductivity of material. It can be seen from Table 1 that porosity increases with increase in CNT content into silver matrix. Increased porosity also contributes to decrease in electrical conductivity.

Thus combined effect of residual porosity and electron scattering at CNT-metal interface along with CNT agglomeration at higher CNT content is responsible for degradation in electrical conductivity.

4. Conclusions

In the present study, wet mixing method has been successfully extended to fabricate CNT/Ag nanocomposites. CNTs are uniformly distributed inside silver matrix. Nanoindentation mechanical tests reveal that the nanostructure CNT/Ag composite possesses a combination of high hardness and elastic modulus compared with its counterpart developed under similar conditions. Superior mechanical properties of the CNTs were responsible for this improvement. Furthermore, electrical conductivity of the material decreases with CNT reinforcement due to CNT agglomeration and electron scattering at the interface.

Competing Interests

The authors declare that they have no competing interests.

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