Characterization of carbon nanotube decorated silver nanoparticles

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Abstract. Silver nanoparticles (Ag NPs) prepared using the exploding wire process has been decorated with carbon nanotubes (MWCNTs, SWCNTs). Well dispersion of silver NPs is achieved by a simple chemistry process on the surface of CNTs. The structure, optical and morphology of silver nanoparticles decorated with carbon nanotubes were characterized by x-ray diffraction, Atomic force microscopy, and field emission scanning electron microscopy. The illustrated outcome that the UV-Visible absorption and electrical conductivity properties effectively improved for CNT/Ag NPs. The absorption spectrum of silver nanoparticles shows absorption at ultraviolet wavelength zone and there is low peak between (300-900nm) while the absorption of CNT/silver nanoparticles (Ag NPs) increased significantly from UV to near IR region. Field emission scanning electron microscopy analysis shows that silver nanoparticles are decorated on carbon nanotubes without any impurities, with average particle size about (50-80nm) for Ag-NPs, 44nm for MWCNTs/Ag-NPs and 30 nm for SWCNTs/Ag NPs. It was observed that Ag NPs enhanced the electrical conductivity of CNTs from (2.36 ×10⁻¹ (1/Ω.cm)) to (1.03×10⁴ (1/Ω.cm)) for SWCNTs/Ag NPs and (8.83×10⁴ (1/Ω.cm)). It is observed that Ag NPs adding enhanced the electrical properties of CNTs. The results show that Ag-coated CNTs have important optoelectronic applications such as solar cell and photodetector.

Keywords: CNTs, Ag NPs, exploding wire method, optical Structure properties.

1. Introduction

Carbon nanotubes (CNT) have attracted significant research interest and they are widely used because of their excellent chemical, physical and electrical properties. Multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) are considered ideal materials for different applications. [1, 2]. Metal nanoparticles (NPs) have gained a lot of interest in the fields of electronic, chemistry, and biology because, the high surface to volume ratio together with the size effect gives nanoparticles discriminative different properties (chemical, optical, electronic and magnetic) from those of bulk material[3, 4]. To synthesize metal nanoparticles, there are different techniques used such as a laser beam [5], electron beam, mechanical milling [6], electrical exploding wire [7], chemical vapor deposition [8] and electro-chemical method [9]. Decorating CNTs with metal nanoparticles provides new opportunities for researchers who have important applications in various fields, and is expected to exhibit different properties from individual CNTs [2]. Among the
different metal nanoparticles, Ag NP has been proven to have excellent property, making it suitable for different applications. CNT/Ag NPs has attracted great attention due to its importance in photodetectors [10, 1], gas sensor [11, 12], biosensor [13], etc.

Electrical explosion of wire method (EEW) is one of the vapor phase methods in which particles are produced by evaporating a thin metal wire by passing high current through it [14]. The phenomenon of electric explosion of wires (EEW) reduces to the following “When a high density (10⁴–10⁶ A/mm²) current pulse, which is usually produced by the discharge of a capacitor bank, passes through a wire, the density of the energy in the wire may considerably exceed the binding energy because of a high rate of the energy injection and an expansion lag of the heated material. As a result, the material boils up in a burst, a bright light flashes, and a mixture of superheated vapor and boiling droplets of the exploding wire material and a shockwave scatter to the ambient atmosphere”. In the other words the phenomena of (EEW) have been widely dependent on plasma physicists for generation and confinement of plasmas [15]. The properties of EEW synthesized nanoparticles depend on several parameters, including wire shape, such as wire (length and diameter) and material size, electrical circuit characteristics, and environmental media. There have been many experiments made to decorate CNTs with metal nanoparticles (Ag, Au) such as by Waleed K. Mahmood et al [16], and Ngo X. Dinh et al [17].

In the current work, we provide a simple system for the production of Ag NPs depended on the explosion of silver wire in distilled water, following this decoration of CNTs surface by Ag nanoparticles. The structural, morphological, and electrical properties of CNT-silver nanoparticles are studied using different characterization techniques.

2. Experimental Techniques

2.1 Synthesis of Ag-NPs by EEW

This work provides easy and effective devices for the processing of large numbers of metal nanoparticles for the wire explosion. In a reaction vessel of 500ml, the electro explosion of the wires (EEW) is accomplished to remain the two electrodes and the medium of the explosion. The wire goes and strikes the silver plate without bending in its way as Fig.1 shown, Teflon beaker was used to fix the two electrodes. The metal plate is passes through two groves on the surface of one block, while the wire was passes through a glass tube connected to the other block which placed opposite to the previous one. Both electrodes were joined to the two terminals of the 36V DC batteries by thick copper wires. The metal plates are fixed on the base of Teflon beaker filled with 30 ml of distilled water and just touching the first electrode through precise mechanical movement for 15 to hit, and then nominated by filtration paper. The silver nanoparticles will be stuck in the solution.
Fig. (1) A schematic diagram for Ag nanoparticles prepared by (EEW) set up.

The circuit remains disconnected until the wire mechanically touches the board. Due to the high current density through the wire, the wire explosion process occurs in a short period of time. This in turn opens the circuit for another explosion process. Silver wires of purity 99.99%, diameters of 1 mm length and plates (dimension: 2 cm², 0.3 mm; Purity: 99.99%) used in the explosion process.

2.2 Decoration of Ag NPs on Carbon Nanotubes (SWCNT & MWCNT)

The carbon nanotubes used in this work are multi-walled carbon nanotubes (MWCNTs) and single wall carbon nanotubes (SWCNTs) supplied by Nanostructured & Amorphous Materials, Inc. The diameter of the MWCNTs range from 10-30 nm, length 1-2 µm and of 95% purity, and for SWCNTs range from 1-2 nm, length ~30 µm and of 90% purity. In the next step, the decoration of Ag-NP on CNT (SWCNT and MWCNT) was carried out. After forming silver nanoparticles, 10 ml of Ag-NPs was added with 0.05 g of SWCNT and MWCNT stirred for 12 h and followed by 1 hour sonication.

3. Result and Discussion

3.1 UV-Visible spectroscopy

The UV-Visible absorption spectrum of the pure Ag NPs, SWCNT/Ag, and MWCNT/Ag prepared in water media are measured using Shimadzu UV-1800 spectrophotometer, all spectra are measured in a quartz cell at room temperature. The scanning range of CNT/Ag NPs absorption was (190-1000) nm using distilled water as a reference sample. Fig. 2 shows the UV-Visible absorption spectra as a function of wavelength.
The UV-Vis spectrum observed that the Ag nanoparticles has fine structure absorption band in UV-Visible wavelength region of (~290 nm to 440 nm). The presence of narrow resonance absorption peaks is attributable to the excitation of surface plasmon vibrations in the silver nanoparticles; Surface Plasmon Resonance (SPR) band for Ag-NPs extended in the 450-510 nm range [18] with a peak position around 470 nm. A flat area was found in the phase at 300-400 nm region, which indicates there is no absorption in this region or absorption is weak in this region.

According to Fig. 3 MWCNT/Ag and SWCNT/Ag NPs absorb light in the range of UV, Visible and NIR (300-1000 nm) but the (SPR) peak smaller than Ag-NPs because Proximity-induced charge transfer between (SWCNTs & MWCNTs) and silver could deplete the number of electrons available for surface Plasmon generation in the silver nanoparticles [18, 19].

FTIR studies have been performed in the range 400 cm\(^{-1}\) to 4000 cm\(^{-1}\) for the identification of the functional group of the Ag NPs, MWCNTs/Ag NPs and SWCNTs/Ag NPs deposited on quartz
substrates. Fig. 4a, b and c show the FTIR spectrum for pure Ag NP, MWCNTs/Ag and SWCNTs/Ag NPs.

To determine possible interactions between the surface of silver nanoparticles and CNTs (SWCNT & MWCNT) molecules, the FTIR spectra of Ag nanoparticles were reported. By comparing the FTIR spectra of both silver nanoparticles and CNTs, it was found that in the FTIR spectrum of SWCNTs/Ag and MWCNTs/Ag, several peaks obtained by pure Ag-NPs were repeated with changes in location as well as in transmission band intensity. However, for the spectrum of the pure Ag-NPs, the
transmission band at (2968, 1720) cm\(^{-1}\) which can be assigned to the C-H symmetric stretching vibration is slightly shifted to (2926, 1752) cm\(^{-1}\), proving the interaction between the (SWCNTs and MWCNTs) molecules and Ag nanoparticles, and the broad peak appeared in the range of (3446, 3461 and 3500 cm\(^{-1}\)) are attributed to O-H stretching vibration are in accordance with literature values \[17, 20\], the C=C bonding of aromatic rings of carbon skeleton structure were found at 1624 cm\(^{-1}\).

### 3.3 X-Ray Diffraction Study

The X-Ray diffraction used to study crystalline structure of the Ag nanoparticles, SWCNTs/Ag and MWCNTs/Ag. This technique used (XRD -6000 labs, supplied by SHIMADZU, X-ray source are Cu Kα). The X-ray is used to determine the dimensional parameters for crystals and for the size estimation. For this purpose the following equation, known as the Scherrer equation is used [16]:

\[
D = \frac{k\lambda}{\beta\cos\theta} \quad (1)
\]

Where \(k\) is the shape factor, the dimensionless shape factor has typical value 0.9. \(D\) is the particle size. \(\lambda\) is the wavelength for X-ray source (X-ray source is Cu Kα with \(\lambda=1.5406\)Å). \(\beta\) is the full width at half maximum (FWHM) in rad. \(\theta\) is the diffraction angle. The XRD patterns of silver nanoparticles, silver-MWCNTs, and silver-SWCNTs samples were displayed in Figure 5a, b and c.
Fig. 5. XRD patterns of (a) pure Ag Nanoparticles thin film, (b) MWCNTs/Ag NPs thin film and (c) SWCNT/Ag NPs thin film.

In Figure 5a, It can be shown that the pristine Ag-NPs sample exhibits a high (111) peak at 38.1°, (200) peak at 44.3°, (220) peak at 64.6° and (311) at 77.5° crystalline planes of metallic Ag indicate the Face-center Cubic (F.C.C) (JCPDS No. 04-0783). After the decoration of silver nanoparticles on CNTs, The Ag-MWCNTs XRD pattern reveals two obvious diffraction peaks. at 2 theta 26.2° which correspond to (002) for MWCNT and 44° match with both MWCNT (100) and Ag-NPs (200)[21] as shown in figure (5b). SWCNTs/Ag NPs composites, the diffraction pattern appeared at 2 theta of 26.2° for SWCNTs correspond to (002) and 44.1° for Ag-NPs correspond to (200)[16] as shown in figure (5c). These results compared with the standard JCPDS line given in table (3.1) with estimated the crystal size via the Scherrer formula Eq. (1).

Table 1. Crystal size of Ag-NPs, SWCNTs/Ag NPs and MWCNTs/Ag NPs as estimated via Scherrer formula.

| Sample                | 2Theta (degree) | cos θ  | β  (degree) | Avg. crystal size (D) nm | (hkl)  |
|-----------------------|-----------------|-------|-------------|--------------------------|--------|
| Ag-NPs               | 38.1            | 0.94  | 0.19        | 0.58                     | (111)  |
|                       | 44.3            | 0.926 | 0.24        |                          | (200)  |
|                       | 64.5            | 0.84  | 0.29        |                          | (220)  |
|                       | 77.5            | 0.77  | 0.48        |                          | (311)  |
| MWCNTs/Ag NPs        | 26.2            | 0.97  | 1.2         | 0.88                     | (002) CNTs |
|                       | 44              | 0.927 | 0.09        |                          | (200) CNTs |
|                       |                 |       |             |                          | Ag NPs  |
| SWCNTs/Ag NPs        | 26.2            | 0.97  | 0.84        | 0.91                     | (100) CNTs |
|                       | 44.1            | 0.926 | 0.09        |                          | (200) Ag NPs |

3.4 Atomic Force Microscope (AFM)

The surface morphology and topography of the Ag NPs layer is shown in Fig. 6a, SWCNTs/Ag NPs layer in Fig. 6b and MWCNTs/Ag NPs in Figure 6c.

The prepared Ag NPs were analyzed using AFM. Picture shown in Fig. 6a is for the morphology of the Ag NPs, it seems that the Ag NPs had homogenous distribution with small cluster and the surface roughness was 9.807 nm, 11.7 nm height and average diameter 28.06 nm.
Fig. 6a. 3-D AFM image and distribution chart of pure Ag NPs thin film.

Fig. 6b displays the surface morphology and topography of the SWCNTs/Ag NPs layer observed from the micrograph of the AFM. It is noted that there was a normal distribution and homogeneous porous and 19.5 nm surface roughness, 19 nm height and average diameter was 58.14 nm.

Fig. 6b. 3-D AFM image and distribution chart of SWCNTs/Ag NPs thin film.

The AFM of the MWCNTs/Ag NPs is shown in Fig. 6c the surface morphology of the MWCNTs/Ag NPs film had a good a uniform surface with regular distribution of the MWCNTs/Ag nanoparticles with the surface roughness was 39.5 nm, 22 nm height and average diameter 112.5 nm.

Fig. 6c. 3-D AFM image and distribution chart of MWCNTs/Ag NPs thin film.

3.5 Field Emission Scanning Electron Microscope (FESEM)

Scanning Electron Microscope images give the nanoparticles distribution, nanoparticles size, show shape and the structure of nanocrystal, mode FESEM from MIRA3 TESCAN, where high-resolution images of the surface of a sample is acquired. From Fig. 7a the FESEM shows spherical clustered and luminous spots (indicated by circles and in inset image) that correspond to silver nanoparticles, the average particle size of Ag NPs were ranging about (50-80nm).

These nanotubes were subsequently decorated with silver nanoparticles, Fig. 7 b, c show the FESEM of decoration Ag NPs on MWCNTs SWCNTs. The light spots on the CNT surfaces are the
silver nanoparticles. The image shows that the nanoparticles on the surface of the CNTs are fairly homogeneously distributed and the density of the attached nanocrystals is high.

Metal nanoparticles are easy to agglomerate, so that NPs are conjugated with CNTs to overcome these problems related to the stabilization, separation and recovery of NPs and prevent their aggregation [2].

Fig. 7a. FESEM images of pure Ag NPs with different magnification (500 nm &10 µm).

Fig. 7b. FESEM images of MWCNTs/Ag NPs with different magnification (200 nm & 1 µm).
3.6 Hall Effect Measurement

The Hall Effect was used to study the electrical properties of CNTs and Ag NPs (charge concentration, conductivity, carrier mobility, Hall coefficient and resistivity). Table 2 shows the Hall measurements parameter for CNTs and Ag NPs.

| Parameter                  | Ag NPs       | SWCNTs/Ag NPs | MWCNTs/Ag NPs |
|----------------------------|--------------|---------------|---------------|
| Charge Concentration (1/cm³)| 1.08*10¹³    | 1.99*10²²     | 1.80*10²²     |
| Conductivity (1/Ω.cm)      | 2.36*10⁻¹    | 1.03*10⁴      | 8.83*10⁴      |
| Mobility (Cm²/Vs)          | 1.36*10⁶     | 3.22          | 3.07*10⁴      |
| Hall coefficient (cm⁻³.C⁻¹)| -5.78*10⁵    | 3.14*10⁻⁴     | 3.4810⁴       |
| Resistivity (Ω.cm)         | 4.23         | 9.708*10⁻⁵    | 1.132*10⁻⁵    |
| Type                       | N-type       | P-type        | P-type        |

The table shows that electric conductivity CNTs/Ag NPs become much higher than Ag NPs and the concentration of carriers increase when CNTs decorated with Ag NPs. Also it can be seen that CNT decorated with Ag NPs converts from n-type to p-type when Ag NPs add to CNTs, which results in a shift in the Fermi energy from the valence band to mid-gap. The electrical transport of CNT/Ag NPs is improved when the CNTs decorated with Ag NPs.

4. Conclusions

The decoration of MWCNTs and SWCNTs with silver nanoparticles synthesized through exploding wire method was studied. Due to the simplicity of this synthesis, low-cost fabrication of large quantities of long-lived silver nanoparticles, the exploding wire method can be suggested to prepare the silver nanoparticles. It was found that the nanoparticles were spatially well dispersed on the carbon nanotubes. Integration of carbon nanotubes with AgNPs significantly improved CNTs optical absorption. CNT / Ag NPs absorb light in the range of 300-1000 nm better than CNTs alone, which demonstrates the special effects of noble metal on optical absorption of CNTs. The FTIR spectra proving the interaction between the (SWCNTs and MWCNTs) molecules and Ag nanoparticles. The FESEM image shows that the nanoparticles on the surface of the CNTs are fairly homogeneously distributed. It is suggested that decoration the CNT surface with AgNPs could change its characteristics of the materials from n-type to p-type. The experimental results have shown that the CNT/Ag NPs can become important building blocks for nanoscale photodetector applications.

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