ISSN: 2277-9655
Impact Factor: 4.116
CODEN: IJESS7

IJESRT

INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

SYNTHESIS OF AG/CNTS NANOCOMPOSITES AND THEIR ELECTRICAL PROPERTY

Jun Natsuki*, Toshiaki Natsuki, Yoshio Hashimoto

* Institute of Carbon Science and Technology, Shinshu University, 4-17-1 Wakasato, Nagano-shi, Nagano 380-8553, Japan

Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda-shi, Nagano 386-8567, Japan

Faculty of Engineering, Shinshu University, Wakasato, 4-17-1 Wakasato, Nagano-shi, Nagano 380-8553, Japan

DOI: 10.5281/zenodo.155090

ABSTRACT

We have developed a simple approach to synthesize silver nano-particles (AgNPs)/carbon nanotubes (CNTs) hybrid composites. First, AgNPs is fabricated by using chemical reducing agents. The resulting AgNPs by this procedure process are easily separated from the reaction mixture because of without using any organic solvent and external dispersing agent. Uniform sizes of AgNPs with less than 20 nm are easily obtained. Furthermore, the AgNPs are grafted onto the surface of carbon nanotubes (CNTs) to prepare hybrid nanocomposites. The Ag/CNT hybrid nanomaterials are firmed by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Their application can be used as conductive films due to good electrical property of CNTs with large aspect ratio.

KEYWORDS: Silver nanoparticles, Carbon nanotubes, Conductive films.

INTRODUCTION

Metallic nanoparticles have been used widely in various fields including catalysis and photonics. Among various metals, silver nanoparticles (AgNPs) have attracted a lot of attention in recent years because their optical and chemical properties are different from those of the bulk materials (Lewis 1993; Thomas 1988). Hence, these products find wide application in various fields including catalysis, photonics, electronics, and antibacterial applications. Nanometer-sized silver particles have shown dramatically changed optical, biological and electrical properties since their size shift varies from micro to nano dimension. The size and shape dependence properties are of interest for industrial application of electronics, catalysis, and photonics. In particular, the AgNPs can be used in the electronics industry for printed electronic circuits and transparent conductive films due to advantages such as high electrical conductivity (Lee and Chou 2005; Tsuruga and Abe 2008; Natsuki et al. 2015a; Zun et al. 2007). Currently, many methods and approaches have been reported for the synthesis of AgNPs by using chemical, physical, photochemical and biological routes (Natsuki et al. 2013; Natsuki et al. 2015b; Gurav et al. 1994; Vilchis-Nestor et al. 2008; Chen et al. 2012). Each method has advantages and disadvantages with common problems being costs, scalability, particle sizes and size distribution and so on. Physical and photochemical methods to prepare metal nanoparticles are usually need the very high temperature and vacuum conditions, and expensive equipments (Iravani et al. 2014; Kholoud et al. 2010; Toisawa et al. 2010). Chemical reduction methods to synthesis AgNPs are used extensively because they can be implemented under simple and mild conditions and can be used to prepare nanoparticles on a large scale. It is well known that AgNPs can be produced as a result of chemical reaction at low cost and in high yield.

Carbon nanotubes (CNTs) have attracted considerable attention because of their excellent mechanical, chemical and electric properties (Treacy et al. 1996; Popov 2004). Recently, metal nanoparticles such as AgNPs composites hybridized with CNTs have potential to be developed as transparent and conductive thin films that complement indiumtin oxide (ITO). The AgNPs decoration has a beneficial effect on the electrical conductivity of CNTs

ISSN: 2277-9655
Impact Factor: 4.116
CODEN: IJESS7

because the inherent electrical conductivity of AgNPs is superior to the CNTs without silver. The combination of AgNPs with CNTs can integrate the properties of these two components to form AgNPs/CNTs hybrid nanocomposites for use as transparent conductive materials. Some studies reported that CNTs could be used as *potential materials* for transparent conductive films (Jung et al. 2013, Lee et al. 2011; Corio et al. 2004). The conductive films reinforced with CNTs exhibited flexibility and strength properties than that of ITO films because CNTs had the advantage of being flexible and excellent mechanical properties.

In this study, we try to prepare AgNPs/CNTs hybrid nanocomposites. First, AgNPs were prepared using chemical reducing agents, and then the AgNPs were decorated onto double-walled carbon nanotubes (DWCNTs) and their characteristics were evaluated using various analytical techniques. AgNPs/CNTs hybrid nanocomposites can be used as highly conductive and strength films due to good electrical property of AgNPs and CNTs with large aspect ratio.

EXPERIMENTAL

Materials

Silver nitrate ($AgNO_3$), trisodium 2-hydroxypropane-1,2,3-tricarboxylate hydrate (Na_3Ct), and 2-dimethylaminoethanol (DMAE) were obtained from Wako Pure Chemical Industries Ltd., Japan. Polyvinylpyrrolidone (PVP, molecular weight ~10,000) was obtained from Tokyo Chemical Industry Co. Ltd., Japan. Multi-walled CNTs (d = 20-30 nm) were Wako Pure Chemical Industries Ltd., Japan. 2,5-dihydroxybenzoic acid (DHB) were obtained from Wako Pure Chemical Industries Ltd.

Synthesis of colloidal AgNPs

The colloidal AgNPs were synthesized by the method reported in my precious work (Natsuki et al. 2015b). PVP (1.0 g) was dissolved in deionized water (20 ml) by stirring for 10 min at room temperature. $AgNO_3$ (2.94 mmol) was added and the solution was stirred for 10 min to allow the $AgNO_3$ to dissolve. An aqueous solution of Na_3Ct (2.94 mmol) in deionized water (20 ml) was added dropwise using a micro-pump. After all of the Na_3Ct solution had been added, an aqueous solution of DMAE (0.294 mmol) in deionized water was added to the reaction mixture. The mixture was then stirred at room temperature for one hour. The color of the solution gradually changed from white to pale brown. The AgNPs were separated from the solution by centrifugation (5000 rpm), washed twice with deionized water (20 ml), and then redispersed in ethanol (10 ml).

Functionalized of CNTs

Oxidizing CNTs with sulfuric acid or nitric acid is a well known chemical treatment for nanotubes. The CNTs were functionalized by the chemical oxidation in concentrated sulfuric acid and nitric acid, generating –COOH groups on the tube surface (Reddy et al. 2007; Lee et al. 2011). In order to generate -COOH groups, the CNTs were treated with concentrated nitric acid in order. CNTs (0.15g) were boiled at 120°C in HNO_3 (70 ml) for 10 h. Then the mixture was centrifuged (5000 rpm) for 1 min., and washed with deionized water several time to remove residual HNO_3, then the CNTs were redispersed in deionized water (1 L) and kept for 24 h, until the PH of the suspension became neutral, and CNTs were separated and dried at 60 °C for 24 h to obtained power of modified CNTs. The resulting powder of CNTs was used for further use in this study.

Combination of silver nanoparticles to the surface of carbon nanotube

At first solution ***1*** was prepared as follow: Silver nanoparticles in ethanol (5 mL, obtained in 2.2) were sonicated for 10 min and then reacted with cysteamine hydrochloride (0.23 g) in ethanol (95 mL) at 80 °C for 6 h in an oil bath, after cooled to room temperature to give solution ***1.*** Second, solution ***2*** was prepared as follow: Functionalized CNTs (0.05 g) were sonicated in ethanol (100 mL) for 1 h. DHB (0.08 g) was added to the suspension, which was then sonicated for 30 min to give solution ***2.*** Finally, the solution ***1*** and solution ***2*** were mixed and stirred at room temperature for 24 h. The AgNPs/CNTs nanocomposites were obtained after centrifuged, washed with pure water, and then dried overnight at 60 °C. Other AgNPs/CNTs nanocomposites were prepared by the same reaction procedure described above by varying the amounts of colloidal AgNPs, that were 1.7 ml, 5.0 ml, 8.3 ml.

Characterization

UV–Visible spectra of AgNPs were obtained with a Hitachi U-4100 UV–Vis spectrophotometer as suspensions in an optical cell. Transmission electron microscopy (TEM) images of the AgNPs, modified CNTs, and Ag/CNT hybrid nanomaterials were obtained using a TEM (JEM-2100, JOEL, Japan) with an accelerating voltage of 200 kV. Energy-dispersive spectroscopy (EDS) analysis was carried out by a Hitachi S-5000 scanning electron

ISSN: 2277-9655
Impact Factor: 4.116
CODEN: IJESS7

microscope (SEM) equipped with an EDS instrument using a dried powder sample of AgNPs. X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD) was performed with a standard Mg Kα (1256.6 eV) X-ray source operating at 10 mA and 15 kV to characterize the elemental composition and chemical states of the samples.

RESULTS AND DISCUSSION

Figure 1 shows the results of EDS analysis for the synthesized AgNPs. The intense peak around 3 keV confirms that the presence of silver particles and they are highly pure. No impurities are observed besides small amounts of carbon and oxygen, which indicates that the used reagents have not remained.

TEM images of the AgNPs are shown in Fig. 2. It is observed that the diameter of the CNTs is less than 10 nm. The enlarged view (Fig. 2b) of AgNPs indicates high crystalline nature of the resulting AgNPs. The lattice spacing is 0.236 nm that matches well to the distance of (1 1 1) plane for the face-centered cubic (FCC) crystal structure.

TEM images of the CNTs are shown in Fig.3. The image (a) shows the CNTs without functionalized, and the image (b) show CNTs functionalized with acid. It is clear that the diameter of the CNTs is about 40 nm. Furthermore, some defects on their walls after modified (Fig. 3b) by acid treatment are observed compared with that before acid modification (Fig. 3a), which is very important for AgNPs to be grafted onto the CNTs surfaces.

Figure 4 shows TEM images of AgNPs/CNTs nanocomposites, Figure 4a-c shows that different amount of AgNPs are grafted onto the CNTs surfaces, respectively. When only a small amount of AgNPs is used, there is no incomplete covering of the AgNPs on the surface of CNTs. A weight ratio of AgNPs/CNTs of 0.08/5.0 ml seems to be the optimum to cover the surface of CNTs. It can be found from Fig. 4c that agglomeration of AgNps on the surface of CNTs occurs when excess AgNPs are added. This indicates that there is no enough -COOH group on the surface of CNTs that reacted with AgNPs. It can be observed from Fig. 4b that the AgNps have circular morphology and they homogeneously and strongly are adhered to the surfaces of the CNTs without agglomeration. The diameters of the AgNPs grafted onto the surface of the CNTs are also less than 10 nm. The volume resistivity of the AgNPs is about 2.9×10^{-5} Ωcm, which is close to that of metallic silver with order 10^{-6}.

XPS evaluation was carried out to determine the elemental composition and functional groups. Figure 5 shows XPS survey spectra of the pristine CNTs and modified CNTs. both pristine and modified CNTs exhibit a strong carbon (C 1s) peak at 284 eV and oxygen (O 1s) peak at 532 eV. The modified carbon nanotube (CNT) clearly shows an O 1s peak with higher intensity than that of the pristine CNT. The atomic percentage ratios for the pristine CNTs are 98.68% for C 1s and 1.32% for O 1s, while those of the modified CNTs are 92.42% for C 1s and 7.58% for O 1s. The higher intensity of the O 1s peak confirms that many oxygen functional groups (carboxyl and hydroxyl) are introduced onto the surface of the CNTs modified by acid treatment. Furthermore, XPS survey spectrum of AgNPs/CNT nanocomposites is shown in Fig. 6. In addition to the peaks of CNTs, Ag 3d peaks from Ag 3d5/2 and Ag 3d3/2 appear at 368 and 374 eV, respectively. Ag 3p peaks from Ag 3p3/2 and Ag 3p1/2 are observed at 573 and 604 eV, respectively. The presence of Ag 3d and Ag 3p peaks proves the formation of AgNPs on the CNTs surface.

Figure 7 shows the field-emission SEM (FE-SEM) image of CNT coatings on polyester terephthalate **(**PET) film. The surface resistance values of PET substrates are obtained to be 93, 26 and 9.6 kΩ/sq for different CNT coating concentration of 0.75, 1.5 and 3 ml, respectively. The CNT coating substrates can be suitable for electrostatic discharge materials.

CONCLUSIONS

In summary, we develop a simple strategy for synthesizing Ag/CNTs hybrid nanocomposites. First, AgNPs is fabricated by using chemical reducing agents, and then the AgNPs were grafted onto the surface of CNTs to fabricate Ag/CNT hybrid nanomaterials. TEM, and XPS analyses revealed the morphology, structure, and elemental composition of the AgNPs and Ag/CNTs hybrid nanocomposites. The AgNPs are less than 10 nm in diameter and show no agglomeration when adhered to the surface of CNTs. The CNT coating substrates exhibits a good surface electrical property that is suitable for electrostatic discharge materials.

ACKNOWLEDGEMENT

This work was supported by JSPS KAKENHI Grant Number JP26420698.

ISSN: 2277-9655
Impact Factor: 4.116
CODEN: IJESS7

REFERENCES

[1] Chen, SF, Zhang H (2012) "Aggregation kinetics of nanosilver in different water condition", Adv. Nat. Sci.: Nanosci. Nanotechnol., Vol.3, pp.035006-1-7.
[2] Corio P, Santos AP, Santos PS, Temperini MLA, Brar VW, Pimenta MA, Dresselhaus MS (2004) "Characterization of single wall carbon nanotubes filled with silver and with chromium compounds", *Chem. Phys. Lett.*, 2004. Vol.383, pp.475-480.
[3] Gurav AS, Kodas TT, Wang LM, Kauppinen EI, Joutsensaari J (1994) "Generation of nanometer-size fullerene particles via vapor condensation", *Chem. Phys. Lett.*, vol.218, pp.304-308.
[4] Iravani S, Korbekandi H, Mirmohammadi SV, Zolfaghari B (2014) "Synthesis of silver nanoparticles: chemical, physical and biological methods", *Res. Pharm. Sci.* Vol.9, pp.385-406.
[5] Jung H, Yu JS, Lee HP, Kim JM, Park JY, Kim D (2013) "A scalable fabrication of highly transparent and conductive thin films using fluorosurfactant-assisted single-walled carbon nanotube dispersions", *Carbon*, Vol.52, pp.259-266.
[6] Kholoud MM, Nour AE, Eftaiha A, Warthan AA, Ammar RAA (2010) "Synthesis and applications of silver nanoparticles", 2010, *Arab. J. Chem.*, Vol.3, pp.135-140.
[7] Lee H, Chou KS (2005) "Inkjet printing of nanosized silver colloids", *Nanotechnology*, 2005. Vol.16, pp.2436-2411.
[8] Lee SH, Teng CC, Ma CCM, Wang I (2011) "Highly transparent and conductive thin films fabricated with nano-silver/double-walled carbon nanotube composite", *J. Colloid. Interface Sci.*, 2011. Vol.364, pp.1-9.
[9] Lewis LN, (1993) "Chemical catalysis by colloids and clusters", *Chem. Rev.*, 1993. Vol.93, pp.2693-2730.
[10] Natsuki J, Natsuki, T, Abe, T (2013) "Low molecular weight compounds as effective dispersing agents in the formation of colloidal silver nanoparticles", *J. Nanopart Res.*, 2013. Vol.15, pp.1483-1-8.
[11] Natsuki J, Natsuki T, Hashimoto Y (2015a) "A Simple Approach to Synthesize Silver Nanoparticles and Their Electrically Conductive Property", *Inter. J. Mater. Eng.*, Vol.5 pp.129-132.
[12] Natsuki J, Natsuki T, Hashimoto Y (2015b) "A review of silver nanoparticles: Synthesis methods, properties and applications", *Inter. J. Mater. Sci. Appl.*, 2015b. Vol.4, pp.325-332.
[13] Popov VN (2004) "Carbon nanotubes: properties and application", *Mater. Sci. Eng.: R: Reports*, 2004, Vol. 43, pp.61-102.
[14] Reddy ALM, Ramaprabhu S (2007) "Pt/SWNT-Pt/C Nanocomposite Electrocatalysts for Proton-Exchange Membrane Fuel Cells", *J. Phys. Chem. C*, 2007, Vol.111, pp.16138-16146.
[15] Thomas JM (1998) "Colloidal metals: past, present and future", *Pure Appl. Chem.*, 1988. Vol.60, pp.1517-1528.
[16] Toisawa K, Hayashi Y, Takizawa H (2010) "Synthesis of highly concentrated Ag nanoparticles in a heterogeneous solid-liquid system under ultrasonic irradiation", Materials Transactions, vol.51, pp.1764-1768, 2010.
[17] Tsuruga S, Abe T (2008) in *Proceedings of the Pan-Pacific Imaging Conference*, 2008. Tokyo, Japan. Preparation of electro-conditive inkjet inks through silver halide photographic emulsion 56-59.
[18] Treacy MMJ, Ebbesen TW, Gibson JM (1996) "Exceptionally high Young's modulus observed for individual carbon nanotubes", *Nature*, Vol.381, pp.678-680.
[19] Vilchis-Nestor, AR, Sanchez-Mendieta V, Camacho-Lopez MA, Gomez-Espinosa, RM, Camacho-Lopez, MA, Arenas-Alatorre JA (2008) "Solventless synthesis and optical properties of Au and Ag nanoparticles using Camellia sinensis extract", *Mater. Lett.* 2008, Vol.62, pp.3103-3105.
[20] Zun LY, Lu GH, Mao S, Chen JH (2007) "Ripening of silver nanoparticles on carbon nanotubes", *NANO: Brief reports and reviews*, 2007. Vol.2, pp.149-156.

FIGURE CAPTIONS

Figure 1 EDS spectrum of silver nanoparticles
Figure 2 TEM micrographs of silver nanoparticles
Figure 3 TEM micrographs of (a) CNTs; (b) functionalized CNTs.
Figure 4 TEM of micrographs of Ag/CNT nanocomposites: (a) AgNPs (1.7 ml) / CNT; (b) AgNPs (5.0 ml)/CNT; (c)AgNPs (8.3 ml)/CNT
Figure 5 XPS survey spectra of pristine CNTs, and functionalized CNTs.
Figure 6 XPS survey spectrum of AgNPs/CNTs.
Figure 7 FE-SEM images of AgNP coatings on polyester terephthalate **(**PET) film

ISSN: 2277-9655
Impact Factor: 4.116
CODEN: IJESS7

Figure 1 EDS spectrum of silver nanoparticles

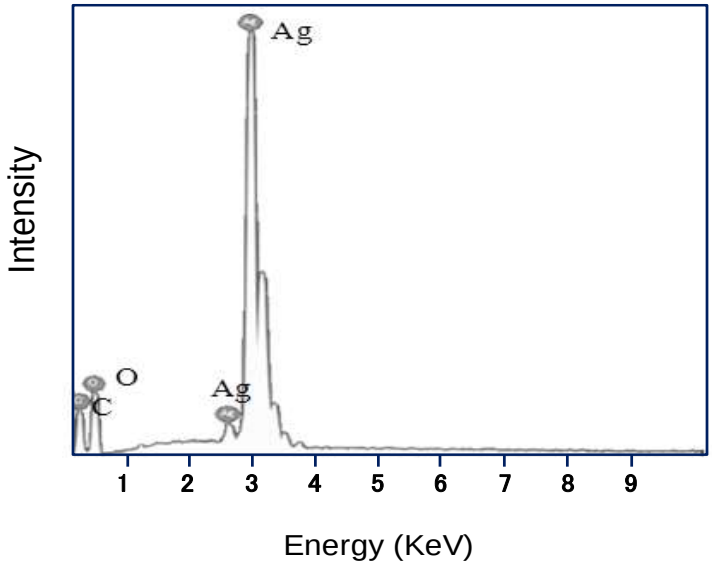
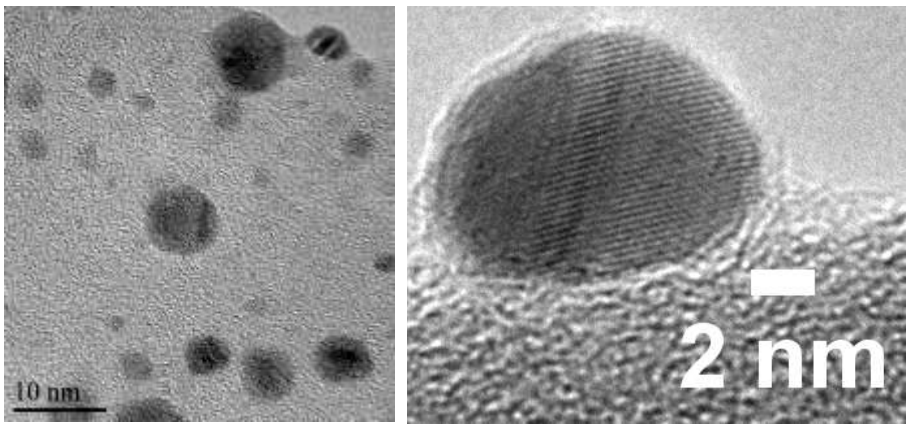
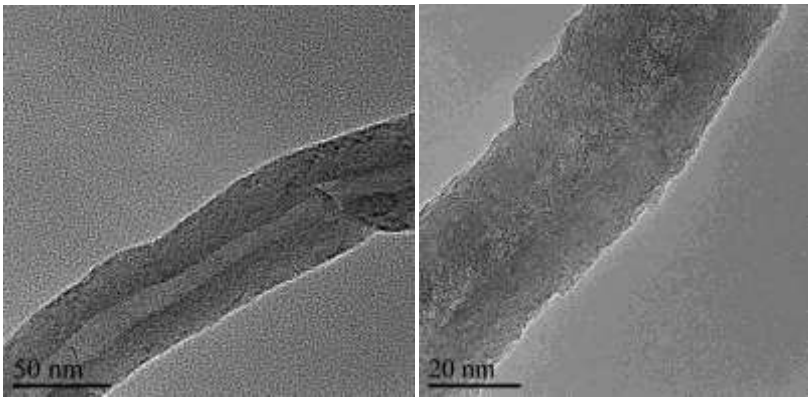


Figure 2 TEM micrographs of silver nanoparticles



(a) ***(b)***

Figure 3 TEM micrographs of (a) CNTs; (b) functionalized CNTs.



(a) ***(b)***

ISSN: 2277-9655
Impact Factor: 4.116
CODEN: IJESS7

Figure 4 TEM of micrographs of Ag/CNT nanocomposites: (a) AgNPs (1.7 ml) / CNT; (b) AgNPs (5.0 ml)/CNT; (c)AgNPs (8.3 ml)/CNT

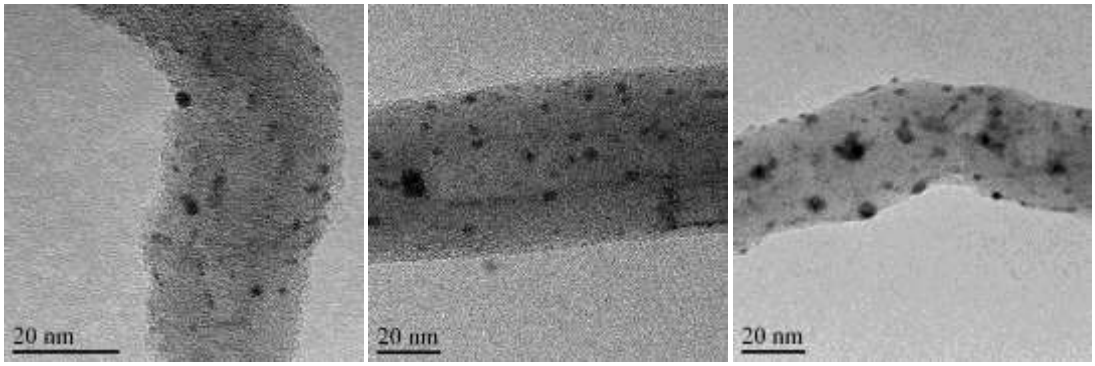


Figure 5 XPS survey spectra of pristine CNTs, and functionalized CNTs.

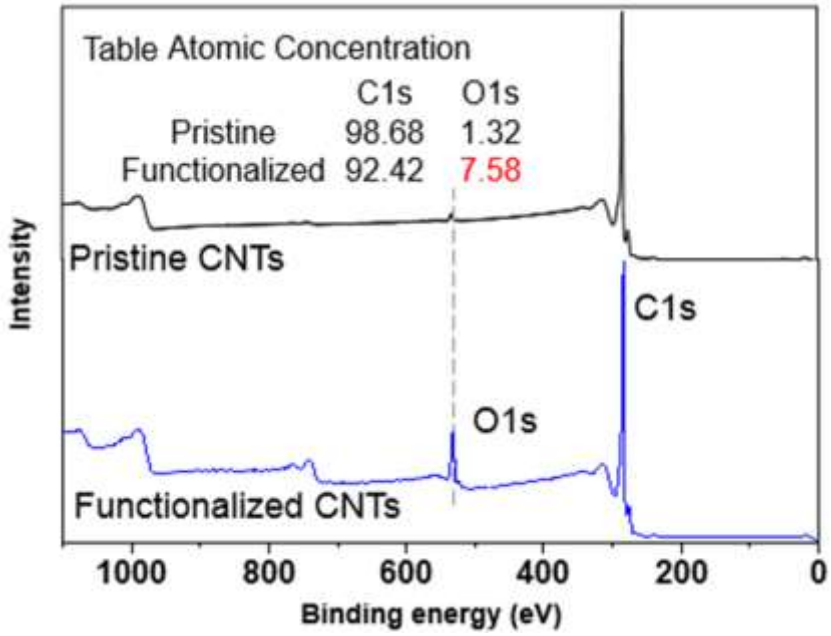
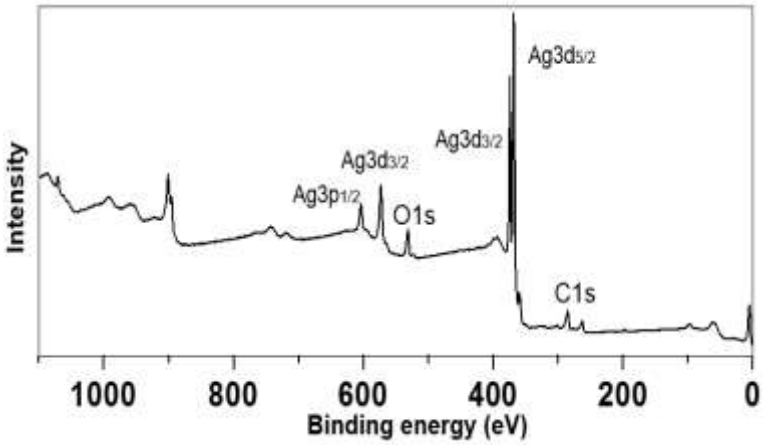


Figure 6 XPS survey spectrum of AgNPs/CNTs.



ISSN: 2277-9655
Impact Factor: 4.116
CODEN: IJESS7

Figure 7 FE-SEM images of AgNP coatings on polyester terephthalate **(**PET) film