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Research Article

Structural Properties of Cu-MWCNT Composite

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Abstract

Copper/copper oxide/carbon nanotube (Cu/CuO/CNT) composite thin films were prepared by like electrophoretic deposition (EPD) method. The corbon nanotubes collacted on the Cu copper substrates were characterized by SEM (Scanning Electron Microscopy), XPS (X-Ray Photoelectron Spectroscopy) and FTIR (Fourier Transform Infrared Spectroscopy). Carbon nanotubes are functionalized to collect carbon nanotubes on copper substrate using the EPD method. It was observed in FTIR measurements that functionalized carbon nanatubes were negatively (OH^-) loaded. It is shown by SEM images that cabron nanatubes are collected on copper substrate. Cu, O and C elements were observed in the XPS measurements, it was observed that the O ratio was quite high and there was CuO formation.

Keywords: MWCNT, CNT-Cu composite, CNT coatings on metal

Cu-MWCNT Kompozitlerinin Yapısal Özellikleri

Öz

Bakır/bakır oksit/karbon nanotüp (Cu/CuO/CNT) kompozit ince filmler, elektroforetik biriktirme (EPD) yöntemine benzer şekilde hazırlanmıştır. Nanotüp filmler SEM (Taramalı Elektron Mikroskopu), XPS (X-Ray fotoelektron Spektroskopisi) ve FTIR (Fourier Dönüşümlü Kızılötesi Spektroskopisi) ile karakterize edilmiştir. EPD yöntemi ile bakır alttaş üzerine karbon nanotüpleri toplamak için karbon nanotüpler fonksiyonel hale getirilmiştir. Fonksiyonel hale getirilen karbon nanotüplerin negatif (OH^-) olarak yüklendiği FTIR sonuçlarında gözlenmiştir. Kabron nanotüplerin EPD yöntemi ile bakır alttaş üzerine toplandığı SEM görüntüleri ile gösterilmiştir. XPS ölçümlerinde Cu, O ve C elementleri gözlenmiş, oksijen oranın oldukça fazla olduğu ve CuO oluşumu gözlenmiştir.

Anahtar Kelimeler: MWCNT, CNT-Cu kompozit, metal üzerinde CNT

1. Introduction

Industrially produced MWCNTs have lower values due to they are produced under the form of tangles or agglomerates in which each nanotube grows randomly in all three spatial directions with structural defects and in presence of impurities (mainly the catalyst). In industrial applications we need materials with higher thermal and electrical conductivity. The MWCNTs can be metallized to create the desired material. This process is carried out by joining the metal and metal oxide nanoparticles into MWCNTs. Cu, Fe, Ni, Zn, Cu_2O, ZnO, SnO_2 have been used to make the MWCNTs metallized, these metals were planted, grafted or stacked to the

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structure or to the structure surface (Akbaba et al., 2018; Kumar et al., 2018; Lassègue et al., 2017). Electrodeless deposition, sonochemical deposition, liquid impregnation, deposition under supercritic fluid, chemical vapor deposition (CVD), chemical solution route, sol-gel, chemical precipitation, diffusion, solvo-thermal, wet chemistry, thermal decomposition reaction and gamma-irradiation techniques are used to metallize the MWCNTs (Kumar et al., 2018; Lassègue et al., 2017).

When nanoparticles are added onto MWCNTs, the structure and morphology of MWCNTs varies considerably. MWCNTs decorated with nanoparticles are used extensively in areas such as quantum memory elements, broad-band optical limiters, catalysts, electrodes, semiconducting devices, antimicrobial agent, field electron emitters, gas and bio sensors (Shao et al., 2011). There are many studies on metal and metal oxide addition into the structure of MWCNTs (Dhall & Jaggi, 2016; Prakash et al., 2017; Shao et al., 2011; Staudinger et al., 2017). On the other hand, MWCNTs have been added into other structures to produce the material with the desired properties for some industrial applications. MWCNTs have been grown on Cu-Fe nano-catalyst substrate. As a result of the process, catalytic recovery was observed, particularly for the Cu-Fe bilayer structure (Akbaba et al., 2018). Reinforced copper metal matrix composites (MMCs) was supported with MWCNTs and the wear behavior of this supported material has been investigated. It was observed that stationary dispersion of MWCNTs into the matrix material improved the hardness value and the wear resistance of this new composite is higher (Faneca et al., 2018). Low content MWCNTs-doped electrically conductive polymer films were prepared by multilayer spray coating technology. The application areas of these films are electrodes or charge transport layers in sensor systems. These composite materials exhibited low surface and sound resistance these characters offered different and efficient application options. Because of their lightness and high mobility, the MWCNTs were able to percolate to an electrical conductive network structure in a polymer matrix (Singh et al., 2015). To improve conductivity, MWCNTs are embedded in biodegradable poly-DL-lactide (PLA) nanofibers by using the electrospinning process. With adding MWCNTs, morphological degradation, mass loss, the reduction of polymer molecular weight and the pH value degradation in media were determined. This created composite material offer suitable application area for bone tissue engineering. With the same approach, poly (ε-caprolactone) (PCL) via graphene oxide (GO) biodegradable nanosheets were reinforced with MWCNTs to adjust the electrical, thermal and mechanical properties of nanosheets (Kim et al., 2013; Pizzutto et al., 2011). In other study Polyurethane/MWCNT nanodielectric thin films were made by using solution grown method. Strong interactions and extremely large interfacial area of MWCNTs allowed for the preparation of such a composite polymer matrix. It was observed that with adding MWCNTs the electrical and thermal conductivity, the tensile modulus, temperature stability of the structure improved excellently (Das et al., 2016).

It is understood from the above that the nanocomposite materials needed by the industry are formed by adding different metal and metal oxides into MWCNTs or by adding MWCNTs to various metal and metal oxide containing composites. In this study, a similar method with electrophoretic deposition (EPD) method is presented in Figure 1.

2. Materials and Method

The new accumulation method has been developed within in this study to collect MWCNTs on copper. With this method, the MWCNTs, which were functionalized, were affected by the electric field and the voltage applied to the electrode was ensured the MWCNTs to accumulate on the surface. When the potential difference is applied, the CNTs in the solution must be loaded in order to advance the carbon nanotubes onto the substrate. In order to achieve this load, the functional groups must be connected to the carbon nanotubes and this function is carried out by treating MWCNTs with acids. For this reason, functional MWCNT (f-MWCNTs) is the first stage.

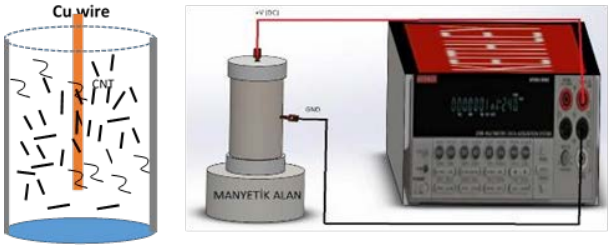


Figure 1. Schematic representation of carbon nanotube deposition technique on copper.

The FTIR graph in Figure 2. shows typical C=O and O-H bonds due to the COOH group occurring after acid application in f-MWCNT. The peak seen at 1051 cm^{-1} and 3600 cm^{-1} belongs to the O-H bond, which is the last addition in COOH. The peak at 1585 cm^{-1} is the peaks of the voltage vibration of the MWCNTs -C=C- bonds (Kumar et al., 2018). The peaks seen at 1051 cm^{-1} and 1211 cm^{-1} show the C-O bonds in various chemical environments (Akbaba et al., 2018). It is important to connect the COOH group to the CNT to provide the ideal dispersion of water or f-MWCNTs in liquid solutions up to pH 7 (Faneca et al., 2018). As can be seen from the Figure 2. (a), FTIR analysis of f-MWCNTs revealed 6 peaks which were not visible in pure carbon nanotubes. These newly emerging peaks are peaks of carboxyl and amine groups.

Accumulation of CNTs on the copper surface and analysis of these structure are very important in various magnification parameters. Cu surfaces should be well controlled surfaces for good deposition. In this context, copper wires were firstly smoothed and cleaned. Nitric acid was used for copper cleaning. Nitric acid was more effective for the cleaning of copper and copper surfaces (Sengar et al., 2013; Viswanadham et al., 2016).

$$Cu\ (solid) + 4HNO_3\ (liquid) \rightarrow Cu\ (NO_3)2\ (liquid) + 2NO_2\ (gas) + 2H_2O$$

NO_2 gas bubbles, which are formed by etching of copper surface with nitric acid, remove impurities from the surface. If impurities on the copper surface are not removed, these impurities will adversely affect the accumulation of carbon nanotubes (Staudinger et al., 2017).

As can be seen from the Figure 3. although the surface is clean, it is very uneven. These surfaces have been found to be suitable since MWCNTs will contribute to their growth on the Cu surface.

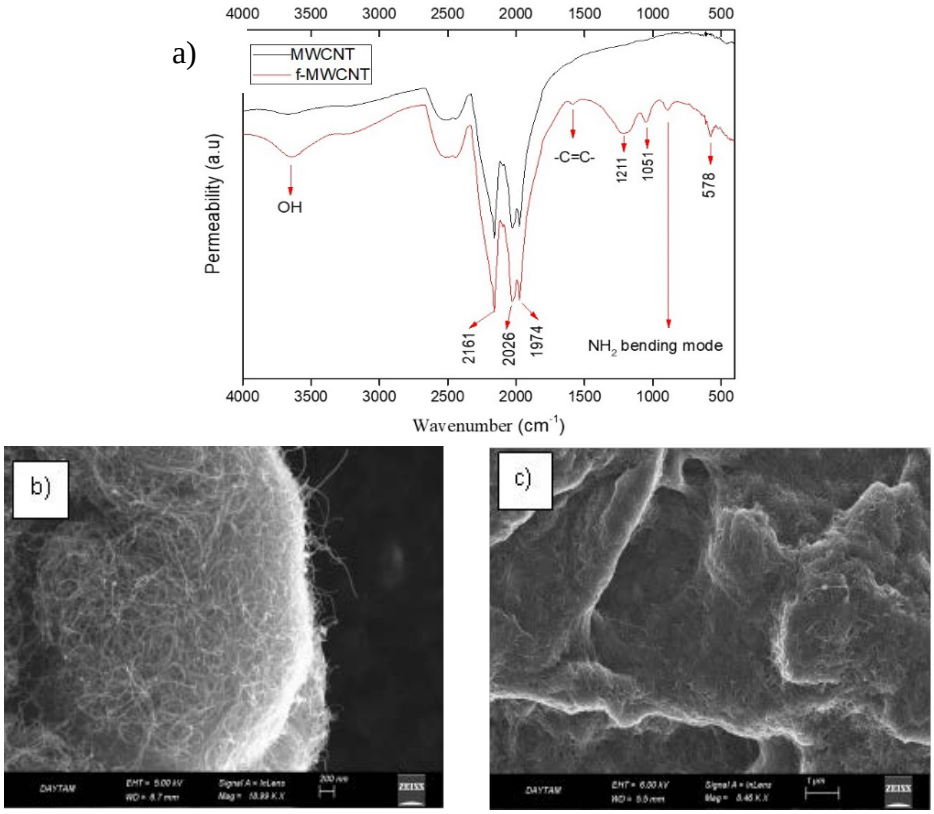
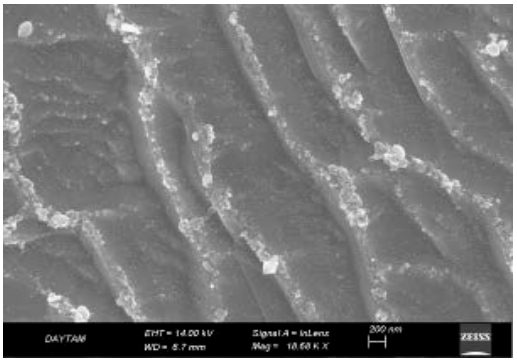


Figure. 2. a) FTIR spectrum of f-MWCNT and pure MWCNTs b) SEM image of pure MWCNTs c) SEM image of f-MWCNT.

Deposition of MWCNTs on Substrate

The system we have designed to deposit MWCNTs onto Cu electrodes is shown in Figure 1. The operation of the system is based on the fact that a voltage applied to the Cu electrode and the accumulating container. This voltage application causes functionalized MWCNTs to be deposited on the Cu electrode. First of all, the MWCNTs are placed in the solvent liquid solution in a conductive cylindrical container. A potential difference is applied between the outside of the cylindrical container and the submerged copper electrode which we want to accumulate on the MWCNTs. Since the MWCNTs are loaded with negative ions, negative pole is applied to the outer surface of the conductive container and positive pole is applied to the copper wire for magnification.



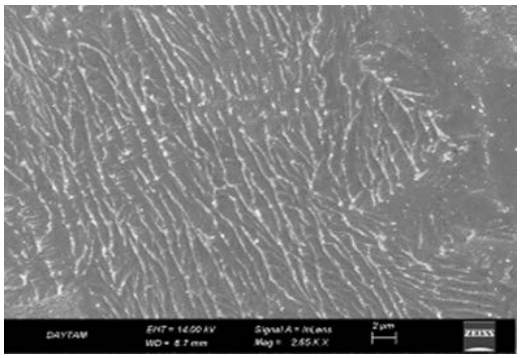


Figure. 3. SEM images of cleaned copper surfaces.

Thus, the Cu surface is activated for the functionalized MWCNTs. Experiments using different parameters were repeated while preparing the liquid MWCNTs solution. At these magnifications, 2 mg MWCNT was added to 100 mL of DI water and magnification was carried out by stirring with the magnetic stirrer. SEM images of some samples are shown in Figure 4.
As can be seen from Figure 4. the carbon nanotubes were sparsely distributed to the copper surface. In addition, the diameters of the growing carbon nanotubes were measured and determined to be approximately 23.5 nm by using *ImageJ* program. Thus, it has been observed that CNTs can be grown on the copper surface by using this technique.
X-ray photoelectron spectroscopy (XPS) analysis of copper/MWCNT structure was performed. In this method, electrons are removed from the material surface by sending X-rays and photoelectrons are formed. The energies of these photoelectrons are measured on the electron analyzer. In this way, information is obtained about which atoms and which orbit of photoelectrons are detached. Thus, elemental analysis can be carried out by this method because the energies of electrons that break from certain layers of the atom vary according to the element.

3. Results and Discussion

In Figure 5., the binding energies of the electrons that are removed from the 2p, 3s, 3p layers of the copper element are seen as peaks in the spectrum. There are also peaks corresponding to the specific binding energies of oxygen (O) and carbon (C). The following results can be obtained from the XPS spectrum;
1. On the surface of the investigated material (at a depth of about 10nm) there is no atom or molecule other than Cu, C, O and Cu_xO_y elements and molecules. Therefore, no impurity atoms were found.
2. The peaks at the sides of the Cu2p peak are peaks of copper oxide (Cu_xO_y). Copper oxide can be seen for three reasons; a. Copper may be oxidized in its natural environment. b. It may be oxidized from deionized water in solution. It may be bound to the copper surface from the carboxyl groups bound to the functionalized MWCNTs in the solution and formed the copper oxide structure.

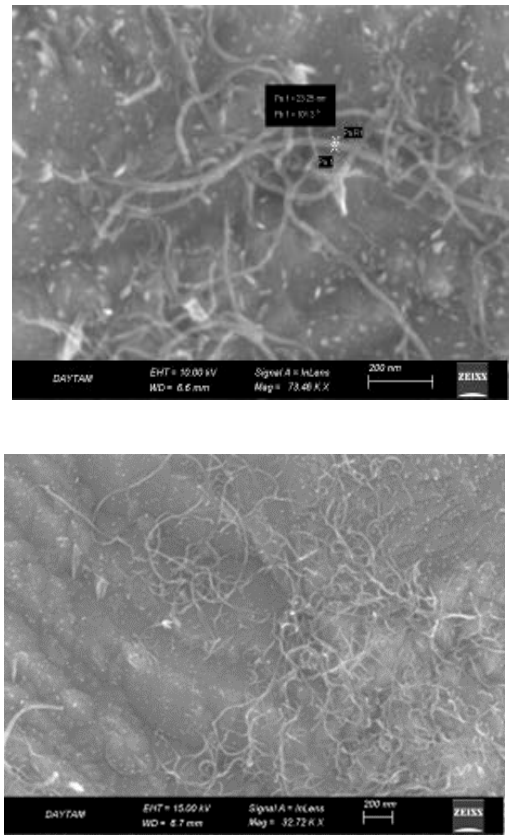


Figure 4. SEM images taken from different locations of MWCNTs grown on copper surface.

4. Conclusion

Production of CNT-Cu composite structures is very difficult since carbon does not dissolve more than 8ppm in copper. However, it is understood from the literature that CNT-Cu composite structures have an important potential in carrying electricity. Therefore, it is necessary to develop new methods to create a nanocarbon-copper composite. In this study, the attachment of CNTs to the copper surface was achieved by using a new method. The SEM and XPS results revealed that CNTs adhere to the copper surface with great success. In our opinion, the method proposed for the production of CNT-Cu composite structures will contribute to the literature in this area.

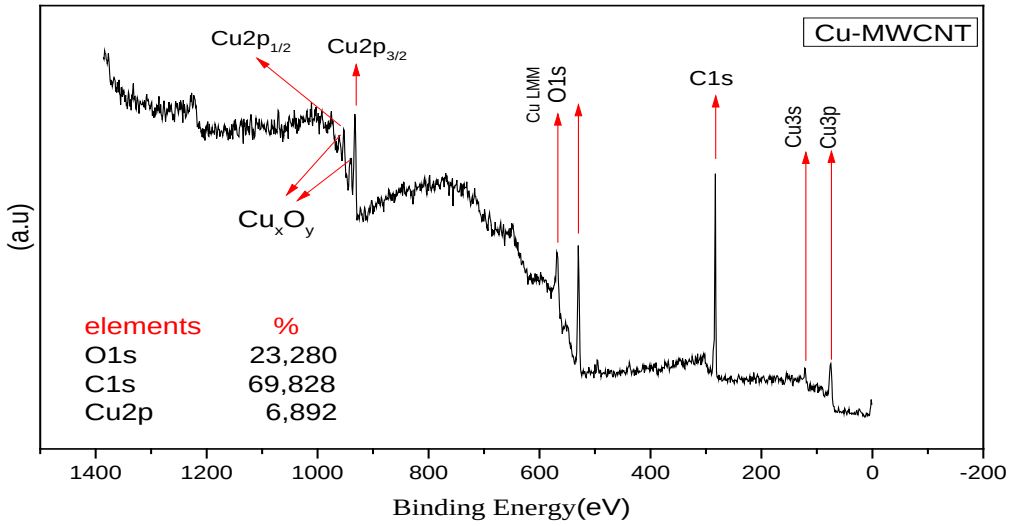


Figure. 5. XPS spectrum of Cu/MWCNTs structure.

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