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# Ag-Doped Multiwalled Carbon Nanotube/Polymer Composite Electrodes

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Two types of carbon nanotube (CNT) based films were fabricated by adsorbing two different types of multiwalled carbon nanotubes (MWCNTs) on bacterial cellulose membrane templates. A bacterial cellulose membrane consists of ribbon-shaped nanofibrils that are arranged to form a porous 3D network. These characteristics lead to the uniform deposition of MWCNTs on the membrane structure and the final CNT based films with high surface areas. Two types of MWCNTs were used: (1) MWCNTs that had been purified by an acid treatment and (2) Ag-doped MWCNTs, which consisted of MWCNTs with Ag nanoparticles attached to their surfaces. The morphologies of the Ag-doped MWCNTs and CNT based films were examined using transmission electron microscopy. In addition, the electrical conductivity and electrochemical properties of the CNT based films were measured using a four-point probe and a cyclic voltammeter, respectively. The cyclic voltammetry data showed that the Ag particles attached to the MWCNT surfaces influenced the electrochemical properties of the CNT based films.

**Keywords:** Carbon Nanotubes, Silver Nanoparticle, Bacterial Cellulose.



## 1. INTRODUCTION

Carbon nanotubes (CNTs) are promising materials for electrochemical applications through their electronic and mechanical properties, and high surface area.[1] In addition, many researchers have produced CNT derivatives with more attractive features. Among these studies of CNT derivatives, particular attention has been focused on the preparation and properties of CNTs/metal nanohybrids. Novel metal nanoparticles have enormous potential on account of their specific size and shape dependent properties as well as their inherent electronic, optical, and catalytic properties.[2] Nanohybrids of CNTs and metal nanoparticles using Au, Pt, and Ag, show a synergetic effect by a combination of the two components with excellent properties. In particular, Ag-doped CNTs were examined for electroanalysis, catalysis, bactericides and sensors by attaching silver nanoparticles to the surface of the CNTs using a variety of methods and materials.[3,4]

CNTs fabricated as films are highly flexible, mechanically strong and easily processed. In addition, the high uniformity of the CNT distribution in a film can induce a conductive pathway, resulting in conducting CNT based films. Hence, CNT based films have been manufactured using several methods, including filtration, layer-by-layer, and spin coating for the applications in optoelectronics, electromagnetic interference shielding, and electrode.[1,5,6] In addition, the outstanding flexibility of CNT based films as an electrode is essential in the area of flexible electronic systems, such as electronic newspapers, wearable electronic devices, and displays.[1,7]

In this study, flexible CNT based films were fabricated by the immersion of a specific membrane into a multiwalled carbon nanotube (MWCNT) dispersion. In addition, Ag-doped MWCNTs were prepared using a simple method utilizing the functional groups of MWCNTs. A CNT based film containing the Ag-doped MWCNTs was also made to obtain the CNT based film with unusual properties. The electrical properties, flexibility, and electrochemical properties of the films were examined. The results show that a CNT based film containing Ag-doped MWCNTs can serve as a flexible electrode in electronic devices.

## 2. EXPERIMENTAL DETAILS

### 2.1. Materials

The MWCNTs (JEIO Co., Incheon, Korea) synthesized by a thermal chemical vapor deposition (CVD) method was used. The purity of the pristine as received MWCNTs was >95%. Silver nitrate ($AgNO_3$, 99.9999%) was purchased from Aldrich. $N,N'$-dimethylformamide (DMF) was purchased from DC Chemical Co. (Seoul,

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Korea). Cetyl trimethylammonium bromide (CTAB) was used as a cationic surfactant. The bacterial cellulose membrane was synthesized from *Acetobacter xylinum* BRC 5.

### 2.2. Preparation of Purified MWCNTs and Ag-Doped MWCNTs

The MWCNTs were acid-treated to remove impurities, such as metallic catalysts, and to introduce functional groups, such as carboxylic acid and hydroxyl groups, to their surfaces. The MWCNTs were suspended in a mixture of $H_2SO_4$ and $HNO_3$ (3/1, vol/vol) and heated to 60 °C under reflux for 3 h, washed with deionized water until the rinsing water was neutral, and dried in a vacuum oven at 25 °C for 48 h.

To attach silver nanoparticles onto MWCNT surfaces, 5 mM $AgNO_3$ was added to a uniform MWCNT dispersion that had previously been prepared by dispersing the acid-treated MWCNTs in DMF by ultrasonication without surfactants. After stirring at 60 °C for 20 min, the MWCNTs were coated with silver nanoparticles (Ag-doped MWCNTs) that formed *in situ*, without a post-process, due to the ability of DMF to reduce the silver ions.[3]

### 2.3. Fabrication of CNT Based Films

To form single phase MWCNT aqueous solution, either purified MWCNTs or Ag-doped MWCNTs were dispersed in deionized water (0.03 wt%) with CTAB as a surfactant (0.3 wt% in water). Ultrasound was then applied to the purified MWCNT or Ag-doped MWCNT dispersion using an ultrasonic generator (Kodo Technical Research Co., Japan) with a nominal frequency of 28 kHz and a power of 600 W for 4 h at 25 °C.

After obtaining a homogeneous aqueous dispersion of MWCNTs, a highly swollen gel-like bacterial cellulose membrane was immersed in a bath containing the MWCNTs dispersion with CTAB for 24 h at room temperature. To remove the residual surfactants, a bacterial cellulose membrane absorbed with MWCNTs or Ag-doped MWCNTs was withdrawn from a bath, and rinsed several times in deionized water. After vacuum-drying at room temperature overnight, the MWCNT based film and Ag-doped MWCNT based film were obtained.

### 2.4. Characterization

Transmission electron microscopy (TEM, CM200, Philips, Netherlands) equipped with an energy-dispersive X-ray (EDX) was operated at an acceleration voltage of 100 kV. The Ag-doped MWCNT based film was verified by X-ray diffraction (XRD, Model DMAX-2500, Rigaku Co., Japan) at a scan speed of 2°/min from 10 to 85°. Elemental analysis was performed using an EA1112 (CE instrument, Italy). The water contact angle measurements were carried out using a contact angle meter (Digidrop, GBX-Instrumentation Scientifique, France), at ambient temperature. A water droplet (0.8 $\mu$L) was used as an indicator to characterize the wetting properties of the sample surface. The electrical conductivity of both MWCNTs and CNT based films was measured using a four-point probe (FPP) apparatus (Hiresta-up MCP-HT450, Mitsubishi Chemical, Japan). An Ag/AgCl reference electrode and a coiled Pt counter electrode were employed in the electrochemical measurements. A 1.0 mM KOH aqueous solution was used to characterize the CNT based films.

## 3. RESULTS AND DISCUSSION

### 3.1. Preparation of Ag-Doped MWCNTs and CNT Based Films

The purified MWCNTs were treated with a strong acid mixture. The acid treatment introduces carboxylic acid functional groups to the surface of the MWCNTs.[8] When preparing the Ag-doped MWCNTs, the purified MWCNTs were dispersed in DMF, followed by the addition of $AgNO_3$. In this case, DMF was not only a good reducing agent for silver ions but also a dispersive solvent for the acid-treated MWCNTs.[9] The affinity of silver ions and reduced silver nanoparticles to carboxylic groups means that these groups would capture the silver ions or nanoparticles.[10,11] As shown in Figure 1(a), the surface of the MWCNTs was covered with black spots, which were clearly identified as silver nanoparticles from the EDX spectrum (Fig. 1(b)).



When the swollen bacterial cellulose membrane was embedded into a homogeneous MWCNT dispersion for the adsorption of MWCNTs, the individual MWCNTs were depressively adhered to the bacterial cellulose nanofibrils without aggregation. The bacterial cellulose membrane has the ability to be a template and has structural similarity between the bacterial cellulose nanofibrils and MWCNTs, which would allow the individual MWCNTs to be adsorbed uniformly over the bacterial cellulose nanofibrils.[12] TEM showed that the MWCNTs were entangled with the nanofibrils in the interior of the bacterial cellulose membrane as well as on the surface (Fig. 2(a)). In terms of electrical conductivity, it is important that the MWCNTs adsorbed on the cellulose network can from an electrical pathway. The adsorption aspect of the Ag-doped MWCNTs was equivalent to that of the purified MWCNTs. The Ag-doped MWCNTs were well adhered to the bacterial cellulose membrane without the loss of silver nanoparticles. XRD confirmed the presence of all materials. The peaks related to bacterial cellulose membrane were observed at 14.4° and 22.7° $2\theta$. The peak at 25.5° $2\theta$ corresponds to the (002) planes of crystalline graphite-like materials, such as MWCNTs.[11] The silver particle reflections show face-centered cubic silver crystals on the surfaces of the MWCNTs, corresponding to

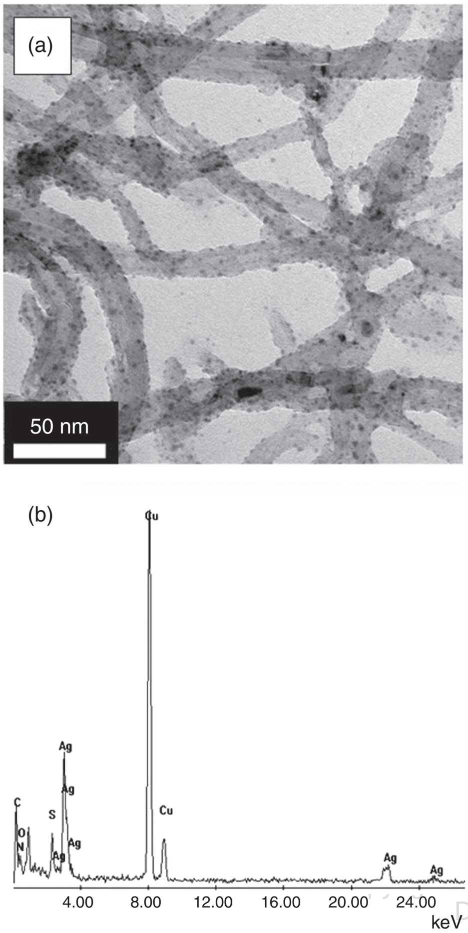


Fig. 1. (a) TEM image and (b) EDX spectrum of Ag-doped MWCNTs on copper grid.



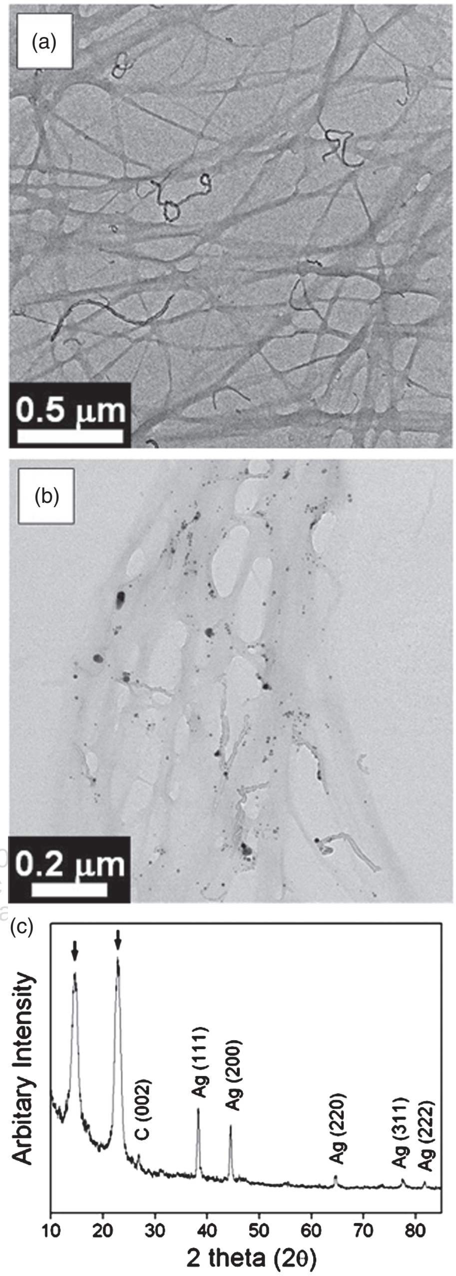


Fig. 2. TEM images of (a) MWCNT based film, and (b) Ag-doped MWCNT based film. XRD pattern of Ag-doped MWCNT based film (The arrows indicate the peaks related to bacterial cellulose).

the (111), (200), (220), (311), and (222) planes of silver crystals (Fig. 2(c)).[3]

The amount of MWCNTs or Ag-doped MWCNTs adsorbed in the bacterial cellulose membrane was determined by elemental analysis. The amount of MWCNTs or Ag-doped MWCNTs was calculated using the increased percentage of carbon atoms compared with that of a pure bacterial cellulose membrane.[13] The MWCNTs and Ag-doped MWCNTs contents in cellulose were 4.77 wt% and 4.80 wt%, respectively. The MWCNTs and Ag-doped MWCNTs showed similar results. This suggests that the amount of MWCNTs adsorbed on the cellulose is independent of the type of MWCNT under identical experimental conditions, such as the immersion time and the initial MWCNT concentration in the dispersion. Therefore, the following data for the CNT based films is not related to the amount of MWCNTs in cellulose.

### 3.2. Characterization of the CNT Based Films

Free-standing conducting films were fabricated by adsorbing the MWCNTs onto a substrate with a membrane shape. They appear black overall and are extremely bendable. While a sheet consisting of only CNTs is fairly brittle, these films are flexible.[14] Their physical properties can allow easy handling of the CNT based films, which can provide many opportunities for a variety of applications.

Areas on both sides of the MWCNT sheets and their derived films were chosen randomly, and the electrical conductivity was measured using a FPP apparatus. For measuring the electrical conductivity of the MWCNTs and Ag-doped MWCNTs, the sheets were fabricated with a diameter of approximately 40 mm by filtering the MWCNT or Ag-doped MWCNT dispersion. As shown

**Table I.** Electrical conductivity of MWCNTs, Ag-doped MWCNTs, and derived films.

| | MWCNTs | Ag-doped MWCNTs | MWCNT based film | Ag-doped MWCNT based film |
|---|---|---|---|---|
| Conductivity (S/cm) | $8.0 \pm 2.6 \times 10^2$ | $5.1 \pm 4.6 \times 10^2$ | $2.5 \pm 1.0 \times 10^{-3}$ | $3.1 \pm 1.9 \times 10^{-3}$ |

in Table I, the electrical conductivity of the MWCNTs only was unchanged regardless of the presence of silver nanoparticles on the MWCNTs. The presence of silver nanoparticles did not affect their inherent electrical property. Moreover, the CNT based films fabricated with two type MWCNTs have comparable electrical conductivity in the order of $10^{-3}$ S/cm, which was attributed to the similar amount of MWCNTs and Ag-doped MWCNTs adsorbed onto the cellulose membrane, as indicated by elemental analysis.

For the as-grown CNT substrate, the surface of the CNT substrate could not be wetted by polar components, such as water, due to their hydrophobicity.[1] However, the CNT based films were still hydrophilic to some extent despite the introduction of MWCNTs because the bacterial cellulose membrane used as a substrate for the MWCNTs is extremely hydrophilic. During the cyclic voltammetry measurements, an aqueous solution containing electrolyte ions was used as the reactive solution. In order to evaluate the performance of the CNT based films accurately, the wettability of the CNT based films with water should be confirmed. The wettability of the CNT based films was sufficient to perform cyclic voltammetry measurements in the aqueous solutions.

Cyclic voltammetry of the CNT based films was performed in an aqueous 1.0 mM KOH solution. There have been many studies on the enhanced electrochemical properties of CNT/silver particle hybrids. Most of these studies reported similar results, which is that CNTs coated with silver particles have improved electrochemical properties.[4, 15, 16] The voltammetry behavior of the Ag-doped MWCNT based film was different from that of the MWCNT based film in Figure 3. In the case of the Ag-doped MWCNT based film, the integrated area was larger than the area of the MWCNT based film, indicating that higher capacitance than the MWCNT based film. The existence of silver nanoparticles in the Ag-doped MWCNT based film could alter their electrochemical properties, as is reported elsewhere.[4, 15, 16] This can pave the way for a wide range of practical applications, such as nano-objects in the area of electrodes, catalytic activity for the oxidation of some materials, and a catalyst for fuel cells.[4, 15, 16]

In addition, a Ag-doped MWCNT based film was fabricated using a bacterial cellulose membrane as a template. As mentioned above, the swollen bacterial cellulose membrane is advantageous to adsorbing the MWCNTs during film preparation, which makes it a suitable template.

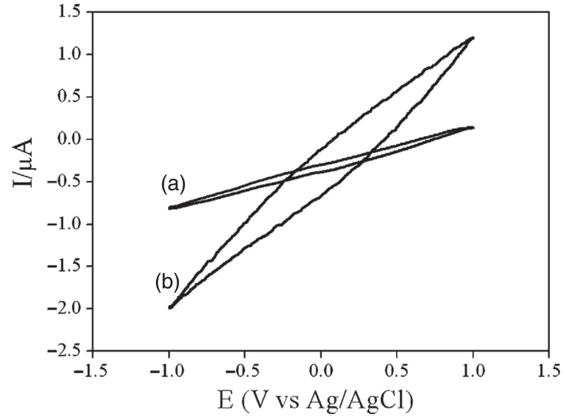


**Fig. 3.** Cyclic voltammograms of 1.0 mM KOH at (a) MWCNT based film, and (b) Ag-doped MWCNT based film. (Scan rate: 50 mV · sec$^{-1}$).

A template-based electrode was fabricated using a bacterial cellulose membrane. Other methods for fabricating the CNT sample for electrochemical applications include directly growing the CNTs on graphite foil or silicon substrate, bucky paper type by filtering CNT suspension, and a CNT film by casting and drying the CNT suspension on a glassy carbon electrode.[4, 17, 18] The process for making CNT based films is a more convenient method compared to other fabrication methods. One of the advantages of the bacterial cellulose membrane is ability to manufacture different shapes or sizes by adjusting the culture dish. This suggests that CNT based films with macroscopic dimensions can be produced as desired. Furthermore, the bacterial cellulose membrane consisting of a nanofibrillar network has a large surface area. The Ag-doped MWCNT based film consisting of a bacterial cellulose membrane has a large surface area. In electrochemical analysis, large surface areas are important because the electrolytes can access a larger CNT surface, which induces the highly efficient electrical activity of the electrochemical specimen. Guo et al. used porous films as a template for fabricating nanoarchitectured metal film electrodes with macroscopic dimensions, which exhibited high electroactivity relative to the corresponding macroelectrode.[19] Li et al. examined three-dimensional CNT electrode. They enhanced the capacitance of the CNT electrode by heat treatment. The heat treatment removed the amorphous carbon materials around the CNTs, which created a highly porous CNT electrode with high electro-efficiency.[20] Therefore, the Ag-doped MWCNT based film can be made into a nanoscopic disk-shaped CNT electrode with macroscopic dimensions and a larger electro-efficiency than that of MWCNT based films.

## 4. CONCLUSION

Two types of CNT based films were fabricated by absorbing MWCNTs or Ag-doped MWCNTs onto a bacterial cellulose membrane template with high surface area. The unique membrane structure is advantageous to the uniform MWCNTs distribution in CNT based films. The CNT based films contained similar amounts of MWCNTs and Ag-doped MWCNTs, which resulted in comparable electrical conductivity and surface states. The presence of silver nanoparticles in the case of the Ag-doped MWCNT based film enhanced their electrochemical properties according to cyclic voltammetry. The flexibility and enhanced electrochemical properties of Ag-doped MWCNT based films make them good novel flexible electrodes.

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