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Silver nanowire/carbon nanotube/cellulose hybrid papers for electrically conductive and electromagnetic interference shielding elements

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ABSTRACT

We report the microstructures, electrical conductivity, and electromagnetic interference (EMI) shielding effectiveness of a series of hybrid cellulose papers coated alternatively with silver nanowire (AgNW) and multi-walled carbon nanotube (MWCNT), which are fabricated by controlling the dip-coating sequence and cycle. SEM images and EDS data reveal that AgNWs and/or MWCNTs are sequentially coated on the surfaces of the cellulose papers with increasing the dip-coating cycle and the coating density of the particles decreases gradually in thickness direction of the papers. This result is supported by the anisotropic apparent electrical conductivity of AgNW/MWCNT/cellulose hybrid papers in in-plane and thickness directions. In addition, the apparent electrical conductivity of the hybrid papers in the in-plane direction increases significantly from 0.17–0.22 S/cm to 2.55–2.83 S/cm with increasing the coating cycle from 2 to 10, although it is higher for the hybrid cellulose papers with AgNW top-coating layers than the hybrid papers with MWCNT top-coating layers at the same coating cycle. This result indicates that a highly effective and conductive AgNW/MWCNT network is formed on the cellulose fibers in a layer-by-layer manner. For the hybrid papers with 2.55–2.83 S/cm, high EMI shielding effectiveness of ~23.8 dB at 1 GHz is achieved.

1. Introduction

Electronic and communication devices are now essential not only in our daily lives but also for military purposes. However, high frequency electronics generate electromagnetic (EM) waves that are harmful to human body and cause malfunction to other electronics close to them by EM interference (EMI) [1–4]. In general, EMI shielding is attained by reflecting and/or adsorbing EM waves in a space with barrier materials made of conductive or magnetic materials [5,6]. The degree of EMI shielding depends strongly on the materials used, its thickness, the EM frequency of interest, etc.

It is known that both reflective and absorptive EMI shieldings are proportional to $\log(\sigma/f)$ and $(\sigma f)^{1/2}$, respectively [2,7], where σ is electrical conductivity and f is frequency. The conductive particles, carbon nanotubes (CNTs) [8], and silver nanowires (AgNWs) [9,10], can be advantageous for creating conductive paths for electron transfer in polymer matrix, due to high electrical conductivity and aspect ratio. Therefore, EMI shielding materials based on the conductive nanoparticles are designed in a way of enhancing their electrical conductivity, that is, inducing electrical percolation [11,12].

Although AgNW is promising due to high electrical conductivity, flexibility, and effectiveness for EMI shielding applications, it is susceptible to be oxidized in air ambient [13,14]. On the other hand, since CNT possesses a high level of resistance to oxidant and corrosive substances such as oxygen, acids, and salts, it has been applied as a protective coating material against oxidation and corrosion [15,16]. Therefore, it can be drawn that a hierarchical structure of AgNWs and CNTs could be very promising for high performance EMI shielding materials with a long life cycle in uses. Although polymer composites reinforced with AgNWs or CNTs have been widely investigated, AgNW/CNT/polymer hybrid composites have not been investigated for the high performance EMI shielding applications before now.

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Cellulose as a naturally abundant polymer with remarkable mechanical strength has been widely processed to papers, films, textile fibers, and nanofillers [17–20], which are potential substrate materials for the advanced applications such as electric heaters [8], supercapacitors [21], sensors [22], composite materials [23], EMI shielding materials [24], and parts of electronics and communication devices [25].

In this research, to attain high performance EMI shielding materials with multi-functionality, a cellulose paper is chosen as an eco-friendly substrate. In addition, dip-coating process is adopted to generate electrically conductive and anti-corrosive coating layers composed of AgNWs and multi-walled CNTs (MWCNTs) on the cellulose paper. For the purpose, we have fabricated a series of AgNW/MWCNT/cellulose hybrid papers coated with different layer sequences and numbers of MWCMTs and AgNWs via an efficient dip-coating process and have investigated their microstructures (coating thickness, density, and porosity) and electrical conductivity in the in-plane and thickness directions as function of dip-coating sequence and cycle. The EMI shielding performance of AgNW/MWCNT/cellulose hybrid papers is evaluated in the frequency range of 0.5–1.0 GHz, which is a part of ultra-high frequency (UHF) used widely for the communication devices such as mobile phone [26], automobile [27], and local area network [28]. In addition, the experimental EMI shielding performance is also discussed in comparison with the values calculated from a theoretical model. The concept of this work on synergistic effect of MWCNTs and AgNWs is created out of curiosity drawn from our previous studies on MWCNT/cellulose paper [8] and AgNW/cellulose paper [10].

2. Experimental

2.1. Materials

A commercially available cellulose paper (model #541, Whatman Com.) with average pore size of ~22 μm, diameter of 150 mm, and thickness of ~154 μm was used as a substrate for hybrid composite papers. Pristine MWCNT (CM-250, Hanwha Chemical Co., Ltd.) with diameter of 10–15 nm and length of ~100 μm was chosen as a carbon nanomaterial. Sodium dodecyl benzenesulfonate (SDBS, Sigma-Aldrich Com.) was used as a surfactant to disperse the pristine MWCNT in distilled water. An aqueous suspension including 0.5 wt% AgNW was obtained from Aiden Com (South Korea). The diameter and length of AgNW in the aqueous suspension are 19.5 ± 1.6 nm and 18.2 ± 7.3 μm, respectively.

2.2. Preparation of AgNW/MWCNT/cellulose hybrid composite papers

For the dip-coating process, an aqueous MWCNT suspension was prepared by dispersing 0.1 wt% MWCNT and 1.0 wt% in distillated water with 1.0 wt% SDBS using a horn-type ultrasonicator (VibraCell 505, 500 W, 20 kHz, Sonics and Materials Inc.) for 40 min. 0.1 wt% AgNW aqueous suspension was also prepared by diluting the commercial AgNW suspension with distilled water. A series of AgNW/MWCNT/cellulose hybrid papers were fabricated by changing dip-coating sequences and cycles, as shown schematically in Fig. 1. To fabricate AgNW/cellulose and MWCNT/cellulose papers, the first dip-coating cycle (1 cycle) was carried out by dipping neat cellulose papers into AgNW or MWCNT aqueous suspension at room temperature for 3 s and drying at 60 °C for 15 min. The second dip-coating (2 cycle) was performed by dipping AgNW/cellulose and MWCNT/cellulose papers into AgNW and MWNT aqueous suspension, respectively, and drying again at 60 °C for 15 min. This dip-coating process was carried out alternatively and sequentially by 10 cycles to control the sequence and number of MWCNT and AgNW layers coated on the cellulose papers. The final cellulose hybrid papers, which were fabricated with different dip-coating sequences and cycles of MWCNT and AgNW suspensions, are named as M, S, MS, SM, MSM, SMS, MSMSM, SMSMS, M(SM)$_4$S, and S(MS)$_4$M, where M and S denote MWCNT and AgNW coating layers, respectively, and the underline (S and M) indicates top-coating layer. M(SM)$_4$S, and S(MS)$_4$M are sample codes for hybrid papers fabricated with 10 dip-coating cycles in the sequences of MSMSMSMSMS and SMSMSMSMSM, respectively.

2.3. Characterization

The apparent thicknesses of AgNW/MWCNT/cellulose papers fabricated with different dip-coating cycles and sequences were measured by using an absolute digital thickness gauge (Model ID-S1012EBS, Mitutoyo). The apparent density and porosity of the papers were evaluated by measured weights and apparent volumes of paper samples with dimensions of 2 cm × 2 cm. All the measurements were carried out more than 5 times at different positions for a given sample and the results were averaged.

The dispersion state and morphology of AgNWs and/or MWCNTs coated on the cellulose papers were characterized by obtaining the surface and cross-section images with aid of a cold-type field emission scanning electron microscope (SEM, S-4800, Hitachi) equipped with energy dispersion spectrometer (EDS). For the cross-section analysis, the neat cellulose and hybrid cellulose papers were cut with a razor blade. In addition, EDS spectra were obtained to identify the atomic composition of the surfaces of hybrid cellulose papers.

The crystalline structural features of neat cellulose paper, AgNW, MWCNT, and their hybrid papers were characterized by using an X-ray diffractometer (D/MAX-2200 Ultima/PC, Rigaku) with Ni-filtered Cu Kα radiation.

The electrical properties of the hybrid cellulose papers were investigated by obtaining current-voltage (*I-V*) curves in the paper

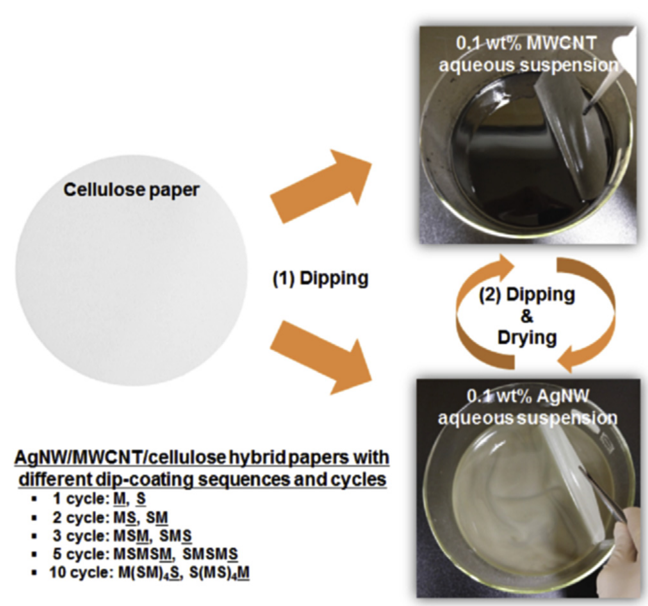

Fig. 1. Fabrication process of AgNW/MWCNT/cellulose hybrid papers with different dip-coating sequences and cycles: (1) dipping a neat cellulose paper in 0.1 wt% MWCNT or AgNW aqueous suspension; (2) repetitive dipping and drying cycle for applying sequential AgNW and MWCNT coating layers on cellulose papers.