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Flexible transparent electrodes made of core-shell-structured carbon/metal hybrid nanofiber mesh films fabricated via electrospinning and electroplating

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ABSTRACT

The development of practical flexible transparent electrodes is one of the major core technology fields for future nanoscale optoelectronics. Despite the many efforts to replace the indium tin oxide (ITO) electrode, preparing practical alternatives that satisfy the essential requirements of flexible transparent electrodes remains a challenge. In this work, core-shell-structured carbon/metal hybrid mesh (CS-CMHM) films, comprised of a metal layer coated onto conductive carbon nanofiber network structures, were fabricated using electrospinning and electroplating and demonstrated potential for use as flexible transparent electrodes. In contrast to previously described techniques that use conventional polymer fibers as sacrificial structures, the conductive carbon nanofibers used in the current technique that we developed provided bi-functionality: they formed conductive core channels and artificial supports of the metal structures. The CS-CMHM films displayed superior optoelectrical, mechanical, and thermal properties: they transmitted ~91% of visible light, showed a low sheet resistance of ~2.7 Ω/sq, and displayed excellent mechanical stability even after 10000 cycles of bending the films to a radius of 5 mm; also, applying a voltage of only 3 V to a transparent heater based on CS-CMHM films resulted in the temperature of the film surface increasing very rapidly in the first 20 s, and soon thereafter reaching ~280 °C. Based on these results, we believe that the use of CS-CMHM films and the process we developed to fabricate them open up great opportunities for high-performance flexible transparent electronics.

1. Introduction

Flexible transparent electrodes have attracted intensive attention in various existing and emerging applications, including future optoelectronic devices such as touch panels [1], organic light-emitting diodes [2,3], solar cells [4–6], wearable electronics [7–9], display devices [10] and automobile applications [11,12]. Developing transparent electrodes that combine low electrical resistance, high optical transmittance, and mechanical flexibility is an ultimate goal in this field. Indium tin oxide (ITO) has been the predominant commercial transparent electrode used in industry and applications since it provides an optimal tradeoff between resistance and transmittance and mechanical stability. However, its general use is critically limited by its rising cost due to the low abundance of indium; moreover, its application in practical flexible electronics is limited by its inherent brittleness.

As a result of these limitations, diverse ITO replacement candidates, such as carbon nanotubes (CNTs) [3,6,13,14], conducting polymers [5,15–17], graphene [1,18–20], metal nanowires [21–23], and metal nanofiber meshes [24–28] have been widely explored for application in flexible transparent conductors. Among them, metal meshes of electrospun metal nanofiber webs are considered to be particularly promising candidates: the electrospun nanofibers can span an extremely long distance with a continuous 1-dimensional (1-D) shape and realize highly uniform nanoscale metal networks with a low percolation threshold [29]; moreover, as a result of these properties, these meshes can achieve excellent optical transparency and electrical conductivity as well as flexibility when composed of nanosized metal structures.

Recently, many efforts have been made to develop high-

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performance transparent electrodes by utilizing the electrospinning process for obtaining advanced interlinked nanofiber meshes. Cui's group [26,27] used electrospinning and metal deposition via thermal evaporation to fabricate a new type of highly flexible transparent electrode of metallic nanofiber networks. Although the network films displayed highly enhanced optoelectronic performance, the metal deposition method used to interconnect the nanofibers is a high-vacuum process and is not practical for low-cost production. Furthermore, the thermal post-treatment inhibits the wider use of flexible polymer-based substrates for flexible optoelectronics. In order to overcome these limitations, Yoon's group [28] introduced Cu-electroplated electrospun nanofiber mesh films, produced using low-temperature and non-vacuum processing. These films exhibited exceptional optoelectrical properties and mechanical stability due to the remarkably reduced contact resistance between intersecting fibers caused by their self-fused junctions formed by electroplating. However, despite the excellent optoelectrical properties of these films, multiple steps are required to make the fibers conductive for facilitating the electroplating, with these steps including adding supplementary Ag nanoparticles and depositing a noble-metal seed layer. Also note that the above-mentioned research groups employed electrospun polymer nanofiber templates used only as sacrificial frameworks for forming the metal fiber and that were fully removed or left in place without any use after coating of the metal layer. Hence, the resultant metal fibers showed hollow or polymer-filled tubes [28], or curved-ribbon structures [26], and such structures are apt to cause mechanical or thermal failures, resulting in electrical disconnection or thermal deformation of the fiber channels.

In this work, we developed a facile process to fabricate core-shell-structured carbon/metal hybrid mesh (CS-CMHM) films, composed of a metal layer covering conductive carbon nanofiber network structures, by combining electrospinning and electroplating. This developed technique is based on controlling the electroplating process to uniformly generate the metal layer on conductive carbon nanofiber seeds. Here, the conductive carbon nanofibers, which were processed using a heat treatment (carbonization), provided bi-functionality: they formed conductive core channels and artificial supports of the metal structures. In the investigations described below, we made technologically important advances to our technique for fabricating conducting core-shell nanostructures: (i) using this method, we were able to fabricate carbon-hybridized metal meshes with core-shell-structured (core: carbon fiber, shell: metal layer) nanofibers over a large area; (ii) these core-shell fiber webs enhanced the electrical, mechanical, and thermal properties of the films, which were shown to be due to the formation of core-area-packed carbon nanofibers having superior mechanical strength and high electrical and thermal conductivity; (iii) complex structures with various sizes were prepared by simply controlling the electrospinning and electroplating conditions; and (iv) we were able to fabricate freestanding transparent flexible thin films that we were able to apply, using the electroplating technique, onto complex surfaces of various metal materials.

To demonstrate this novel approach, core-shell-structured mesh films made of gold layer-coated carbon nanofibers were fabricated for use in flexible transparent electrodes. The resulting CS-CMHM films exhibited a high, ~91%, transmittance of light at a wavelength of 550 nm, a low sheet resistance of ~2.7 Ω/sq, and excellent mechanical stability even after 10000 cycles of bending to a radius of 5 mm. Additionally, a transparent heater consisting of the CS-CMHM films was demonstrated in high operating temperature. These results indicated a significant potential for the use of CS-CMHM films, and the efficient and facile method to make them, in high-performance flexible transparent electrodes and their applications.

2. Experimental

2.1. Fabrication of PAN precursor nanofiber meshes

Polymer mesh structures with nanosized fibers as a precursor of carbon nanofiber meshes (/templates) were prepared by electrospinning (Nano NC Co., Korea, ESN-HV30B) using a polyacrylonitrile (PAN, Mw = 1.5×10^5 g/mol, Sigma Aldrich) solution. PAN with a subunit molecular formula C3H3N can produce carbon fibers with a relatively high carbon yield [30]. The PAN solution was produced by dissolving PAN powder in dimethylformamide (DMF, Sigma-Aldrich), and solutions with 12 wt% PAN were used for fabricating nanosized polymer fibers. The dispersed PAN solution was transferred into a metal-tipped syringe (0.50 mm inner diameter, 21G). The parameters utilized for electrospinning were a pump rate of 0.3 mL/h and an electric field of 7 kV, and the distance between the needle tip and grounded collector was 13 cm. A square steel use stainless (SUS) frame with dimensions of 2.5 cm × 2.5 cm was used as the substrate for collecting the electrospun PAN nanofibers.

2.2. Carbonization, Au electroplating, and transfer to substrates

Carbon nanofiber meshes were produced by heating the electrospun PAN fibers with a two-step process consisting of thermal stabilization and carbonization. PAN precursor fiber webs previously prepared in the SUS frame were placed on an alumina boat and inserted in the heating zone of a furnace. The heating was carried out at 240 °C for 1 h in air (to effect stabilization) and then at 900 °C for 1 h in an Ar gas flow of 1.5 l/min (for carbonization). Next, an 8 wt% PAN solution was electrospun above the carbon nanofiber meshes using a pump rate of 0.3 ml/h at an applied voltage of 8 kV. These nanofibers sustained the carbon nanofiber webs and protected them from being damaged during electroplating. After that, the SUS frame containing collected carbon nanofibers was made to serve as a cathode by immersing it in an Au electroplating solution with a pure Pt anode, and a potential of 0.85–1 V was applied for ~3 min. The SUS frame was then rinsed with DI water. After the rinsing, the layers of PAN nanofibers which were supporting the carbon nanofiber webs were then removed by dissolving them in DMF. Then, finally, Au fiber meshes electroplated on the carbon fiber webs, i.e., the CS-CMHMs, were transferred onto a substrate such as glass and plastic films by spreading several drops of the DMF solution on the substrate. Once DMF evaporated from the substrates, the frame was then raised and removed.

2.3. Characterizations

The surface features and morphology of the CS-CMHMs were characterized by using field emission-scanning electron microscopy (FE-SEM) (Sirion FE-SEM, FEI), and the cross-sectional analysis of the CS-CMHMs was performed by focused ion beam (FIB) (Helios nanolab 600, FEI). The elemental distribution in the fibers was determined by acquiring energy dispersive spectroscopy (EDS) mapping scans. Sheet resistance was characterized by using a four-point probe system (Cascade Microtech, Inc.) with a source measure unit (4200-SCS, Keithley). Transmittance was recorded on a UV–visible/NIR spectrophotometer (Lambda 1050, PerkinElmer). Mechanical stability was analyzed using a bending test system. The system consisted of a two-contact interface serving to induce compressive stress to the sample, where one interface was fixed and immobile, while the other was allowed to move laterally using a motion controller (T-LSR075D, Zaber). The surface temperature of the mesh films resulting from Joule heating was measured by using an infrared (IR) camera (A305sc, FLIR) with a source measure unit (OPS-305, ODA).