Synthetic Metals 221 (2016) 192–200

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Insertion of a biocompatible polymer bewteen graphene and silver nanowires for novel flexible transparent electrode

Qi Zhang[1], Wanyuan Wei[1], Juntao Li, Jie Wei, Jinbao Guo*

College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

ARTICLE INFO

Article history:
Received 4 April 2016
Received in revised form 25 August 2016
Accepted 7 September 2016
Available online 13 September 2016

Keywords:
Flexible transparent electrode
Graphene
Silver nanowire
Biocompatible polymer
Pressure-sensitive liquid crystal device

ABSTRACT

Strongly adhesive and highly stable transparent electrodes based on graphene and silver nanowires (AgNWs) have been developed by embedding biocompatible polylactic acid (PLA) between them. In the process of fabrication of such electrode, instead of removing the supporting PLA layer, this biocompatible polymer layer is sandwiched between graphene and AgNWs, thus simplifying the technology process. In comparison with the traditional graphene/AgNWs hybrid electrode, this novel hybrid electrode exhibits similar optical and electrical properties (around 84.0% at 550 nm, sheet resistance is 13.6 Ω/sq). Remarkably, the surface topography and mechanical flexibility of hybrid film is greatly enhanced due to the introduction of PLA layer. In addition to these, the PLA layer could also provide extra protection to AgNWs locating at the bottom as well as enhanced adhesion force to the substrate, thereby yielding outstanding chemical and electrical stability of the hybrid film. To demonstrate the potential application of the hybrid electrode, a pressure-addressing/electric-erasing liquid crystal device has been constructed, which shows a comfortable optical-electric performance. The strategy demonstrated here could contribute to strong adhesive and highly stable transparent electrodes in flexible optoelectronic devices.

1. Introduction

To adapt the rapid development of flexible electronic devices, high-performance flexible and transparent conductive films (TCFs) have been expected to replace the brittle and expensive indium tin oxide (ITO) electrodes [1,2]. Graphene possesses many extraordinary properties that include high carrier mobility, broadband optical absorption, high thermal conductivity, mechanical strength and so on [3–7]. In addition to this, the emerging of chemical vapor deposition method for the fabrication of large area graphene makes graphene regarded as one of the most potential alternative materials of ITO [8–13]. Therefore, many kinds of electric devices based on transparent graphene electrodes have been extensively investigated [14–17]. However the conductibility of the polycrystalline graphene which have mostly used is limited by high resistance grain boundaries (HGBs) [18]. Besides, line defects and disruptions such as wrinkles, ripples, and folding also adversely affect graphene transport properties through the scattering of the charge carriers [19].

In order to address the problems mentioned above, silver nanowires (AgNWs), which is another superexcellent alternative material of ITO [20–26], have been chosen to enhance the conductibility of polycrystalline graphene by integrating graphene with AgNWs [18,19,27–32]. AgNWs can improve the conductivity of graphene not by increasing the free carrier density but rather by increasing the number of electronic pathways to bridge the percolation bottleneck in theory [18]. Until now, two hybrid structures have been developed to fabricate graphene/AgNWs TCFs. The first one is simply to decorate the surface of graphene using AgNWs, which has been proved to have poor efficiency [27]. Therefore, our group recently attempted to optimize the performance of this type of hybrid TCFs by employing the encapsulation of a silver nanowires (AgNWs) network by polyvinyl alcohol (PVA) on a single-layer graphene. This PVA encapsulated AgNWs/graphene hybrid TCF on a flexible substrate exhibited superior mechanical flexibility, reliability and long-term stability due to the introduction of PVA layer [32]. Another structure has been found to have a better performance, wherein the graphene is on top of the AgNWs layer. In this case, it seems that more intimate contact is achieved between the graphene and AgNWs as well as at the

* Corresponding author.
E-mail address: guojb@mail.buct.edu.cn (J. Guo).
[1] These authors contributed equally to this study.

http://dx.doi.org/10.1016/j.synthmet.2016.09.004
0379-6779/

junctions between AgNWs. However, this current treatment option for graphene-AgNWs hybrid electrode still suffers from certain limitations, such as weak adhesion, chemical instability and large surface roughness.

Here we develop a novel graphene/AgNWs TCF by embedding polylactic acid (PLA) layer between graphene and AgNWs. Different from our previous study, the structure of this TCF is graphene used as top layer and PLA encapsulated AgNWs as the bottom layer. The main feature in this work is that PLA takes the place of polymethyl methacrylate (PMMA) which is the traditional graphene-transfer polymer to form a graphene/polymer hybrid sheet. Under this premise, the supporting PLA layer in modified transfer process doesn't need to remove and instead it is used to act as multi-functional layer between graphene and AgNWs, which simplifies the technology process (without the harsh removal process) and does not suffer from the polymer residuals problem. We chose PLA as the adhesion layer of this TCF based on the following points. First, PLA is an environmentally benign thermoplastic derived from lactic acid, and it has high mechanical properties, thermal plasticity, fabric ability, and biocompatibility [33–36]. Second, acting as adhesion layer between graphene and AgNWs, PLA can afford sufficient adhesion to avoid graphene falling out from AgNWs film, thereby improving mechanical robustness against adhesion, friction, and bending [37]. Third, PLA can also act as inner cushion which can reduce the surface roughness of TCF and protect the completeness of graphene to some extent. Finally, the existence of PLA also inhibits the oxidation of AgNWs. The successful attempt of such hybrid TCF film by integrating polymer layer suggests their potential for a wide range of optoelectronic device applications.

2. Experimental section

2.1. Materials

AgNWs ink was purchased from Zhejiang Kechuang Advanced Materials Co., Ltd. (average size: ave. diameter D = 35–45 nm, ave. length L = 10–20 μm). Graphene on Cu copper was purchased from Hefei Vigon Material Technology Co., Ltd. PLA was purchased from MakerBot. The T_g of the PLA was around to be 62 °C and its melting point is around 150 °C. Nematic liquid crystal (N-LCs), SLC-1717 (Shijiazhuang Chengzhi Yonghua Display Materials Co. Ltd.), the photo-polymerizable monomer, isobornyl methacrylate (IBMA) (Sartomer Company Inc.), 1,6-hexanediol diacrylate (HDDA) (Sartomer Company Inc.), the chiral dopant, R811 (Beijing Bayi Space LCD Technology Co., Ltd) and 2,5-bis-[4′-(hexyloxy)–phenyl −4-carbonyl]-1,4,3,6-dianhydride-D-sorbitol, ISO-(6OBA)$_2$, and the photoinitiator, 2,2-dimethoxy-2-phenyl-acetophenone (Irgacure 651, TCI Co., Ltd.) were used. All other materials, solvents and reagents were obtained from commercial sources and used without further purication.

2.2. Fabrication of the AgNWs film

The AgNWs films were prepared by spin-coating on PET. PET was pre-treated by deionized water, acetone, and isopropyl alcohol, respectively. Then AgNW ink (1.0 mg/ml) was deposited on the surface of PET matrix. There are two kinds of AgNWs films fabricated with different AgNWs deposition density. The low AgNWs deposition samples were formed by controlling the rotation speed at 2500 rpm and lasting 30 s. While the high AgNWs deposition samples were treated twice in same procedure. All the samples were placed on 80 °C hot plate for 10 min to remove residual solvent.

2.3. Preparation of graphene sheet with PLA

As mentioned above, the polymer used to transfer graphene is PLA. The PLA solution was obtained by dissolving 2 g PLA in 200 ml trichloromethane. Then the PLA solution was spin-coated upon the graphene grown on the copper foil. After that, the Cu/graphene/PLA hybrid film could be placed in Cu etchant without further treating processes. The Cu etchant we used was ammonium peroxodisulfate (APS) solution which was obtained by dissolving 1 g APS in 50 g H_2O. When Cu was completely etched away, the graphene/PLA hybrid sheet was rinsed in de-ionized water for several times to wash away etchant residues.

2.4. Preparation of traditional graphene/AgNWs TCF

The AgNWs film was put into de-ionized water and located under the graphene. After one side of graphene/PLA hybrid sheet was adhered to AgNWs film, we slowly lifted the AgNWs film from one side so that the PLA-coated graphene sheet could comfortably transfer onto the AgNWs film. Then the PLA/graphene/AgNWs film was dried by air. Next, an appropriate amount of PLA solution was spin-coated on the cured PLA layer again, dissolving the pre-coated PLA. The re-dissolution of the PLA tends to mechanically relax from the underlying graphene, leading to a better contact with the substrate. After that, the PLA was dissolved in trichloromethane, and it just took several seconds to remove the PLA layer totally. At last, the AgNWs zone non-coated by graphene should be chipped off. Two kinds of traditional graphene/AgNWs TCF with different AgNWs deposition density were fabricated by integrating graphene with different AgNWs samples.

2.5. Preparation of graphene/PLA/AgNWs TCF

First, the AgNWs film was put into de-ionized water, here the side with surface deposited AgNWs was placed in the face of the graphene/PLA sheet floating on water. Then let the AgNWs film close to the graphene sheet with PLA, and when the PLA/graphene hybrid film adhered to AgNWs film, lowering the AgNWs film fully immerse into the water. The previous step should be processed carefully to make sure the graphene/PLA hybrid film could be transferred to AgNWs film flatly and integrally. After that, the hybrid film was lifted, followed by emerging from de-ionized water. Subsequently, the hybrid film was placed on hot plate, then after a hot pressing process at 120 °C with the help of super-flat PDMS film, the graphene/PLA/AgNWs TCF could be achieved.

2.6. Fabrication of ch-LCs devices

The Ch-LCs mixture was prepared by mixing the photo-polymerizable monomer, photoinitiator, the N-LCs, chiral dopants, and 6 μm spherical spacers in a vial at room temperature, followed by blending the LC mixture with the addition of a few drops of dichloromethane. After the evaporation of the solvent under reduced pressure, Ch-LCs mixture was prepared, in which the weigh ratio is IBMA (10.0%), HDDA (5.1%), SLC1717 (68.1%), ISO-(6OBA)$_2$ (2.1%), R811 (14.2%) and Irgacure 651(0.5%). After that, the Ch-LCs mixture was laminated between two graphene/PLA/AgNWs hybrid films on PET substrates. Subsequently, the material was polymerized under a UV source at 2.0 mW/cm^2 intensity for approximately 10 min and a simple pressure-addressing/electric-erasing LCs device was fabricated.

2.7. Measurements

Sheet resistance (R_S) was measured using a SB118 DC voltage and current source in conjunction with a Jandel 4 point probe unit.