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Transparent and flexible cellulose nanofibers/silver nanowires/acrylic resin composite electrode

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ABSTRACT

In this study, we report a novel, eco-friendly and simple method to fabricate cellulose nanofibers (CNFs)/silver nanowires (AgNWs)/acrylic resin (AR) composite electrode. CNFs with average diameter of 15 nm were disintegrated only by one time-pass grinding. Aqueous dispersion of AgNWs was embedded onto the surface of CNFs film by simple vacuum filtration. The final composite electrode was obtained by impregnating CNFs/AgNWs film to AR with the assist of adhesive tape. This electrode with AgNWs density of 134 mg/m^2 showed low sheet resistance (4 Ω/sq), and high light transmittance (85%) which was 6% lower than that of neat AR. The coefficient of thermal expansion of the composite electrode was as low as 25.32 ppm K^{-1}. The tensile strength and Young's modulus of CNFs/AgNWs/AR composite film were 35.71 MPa and 1.63 GPa, which were about 8 and 5.8 times larger than neat AR film, respectively.

1. Introduction

Transparent conductive electrodes have played essential roles in various electronic applications, including rollable electronic displays and solar cells [1]. Recently, flexible electronics has become the focus of major research, due to that it offers new possibilities for next-generation devices with lightweight and portable electronics. Indium tin oxide (ITO) is a typical transparent conductive material, and is traditionally used for widespread applications [2–4]. However, ITO is difficult to use in flexible electronics, because it is brittle and breaks easily after bending [5]. Therefore, enormous efforts have been made in the research and development of alternative conductors, examples including conductive polymers, carbon nanotubes, grapheme, metal grids, and random networks of metallic nanowires [6,32–37]. Among these contenders, silver nanowires (AgNWs) show optoelectronic properties very close to that of ITO and are regarded as the leading candidate material to replace ITO [7,16–18].

In general, conductive nanomaterials, including the AgNWs and CNT, are dispersed in solvents using dispering agents or chemical medication, and are then coated on the substrate. As we know, the most common substrate to host flexible electronics is plastic [6,8]. However, recent studies reported cellulose nanopaper substrates with translucence that were amenable to hosting printed electronics [9,10]. Cellulose nanofibers (CNFs) are the main component of plant and wood pulp fibers. Printing flexible electronics on CNFs paper rather than plastic substrates further bolsters economical production due to the renewable, environmentally friendly, light-weight, mechanically flexible, and disposable properties of paper [11–13]. However, there are following two critical issues that currently prohibit AgNWs films from large scale applications: optical and mechanical properties of composite films are poor, and AgNWs networks deposited on bare substrates are highly coarse and can be easily removed by adhesion or friction [14,15].

In this work we introduce a novel transparent conducting electrodes structure that consists of an Ag NW network embedding onto the surface of a translucent CNFs paper substrate through a simple filtration process without the need for any pre-treatments, and impregnating the CNFs/AgNWs nanopaper into matrix-AR with the assistant of adhesive tape. Then, the composite film was cured using UV curing equipment and peeled the adhesive tapes to obtain the final composite transparent electrode. The AgNWs network was buried just below the surface of a transparent polymer to form a transparent surface conducting film. On the other hand, acrylic resin was selected as the matrix because of its high optical transparency. The refractive index of cellulose nanofiber is 1.618 along the fiber and 1.544 in the transverse direction, and that of impregnated acrylic resin is 1.536 [19–21]. Compared with a AgNWs film on a bare CNFs substrate, three improvements were significantly observed in respect of regular transmittance, electrical stability, and surface roughness. The

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conductive networks of the composite electrode showed strong adhesion to the nanopaper, and maintained their excellent conductive properties even after folding, indicating new possibilities for future foldable electronics. This AgNWs composite electrode is low cost, renewable, durable, and demonstrates high optoelectronic performance. This method might boost large-scale applications of CNFs, AgNWs and acrylic resin in future flexible optoelectronic devices.

2. Experimental section

2.1. Materials

Wood powder from Hevea *brasiliensis* sieved under 60 mesh was used to make CNFs. AgNWs (average diameter of 70 nm, and average length of 40 um) with appearance of gray suspension were purchased from Suzhou Coldstones Nanomaterials Technology Co., Ltd. Acrylic resin(ABPE 10) with refractive index of 1.536 was purchased from Shin-Nakamura Chemical Co., Ltd. All chemicals used for purification were purchased from Nanjing Chemical Reagent Company. All reagents were of analytical grade.

2.2. Methods

Cellulose nanofibers were obtained from wood power by chemical and mechanical process. First, lignin in the sample was removed with a certain concentration of sodium chlorite solution at 75 °C for 1 h, and the process was repeated several times until the product became white. Second, the sample was treated using 5 wt% potassium hydroxide overnight at room temperature and then the same concentration at 90 °C for 2 h in order to remove hemicelluloses [22,23]. Then, the sample was washed with distilled water until reaching neutral pH, and it was kept in a never dried state. Finally, we passed the slurry of 0.7 wt% purified cellulose through a grinder (MKCA6-2, Masuko Sangyo Co., Ltd., Japan) at 1500 rpm [22,24–26]. Width and length of the obtained CNFs were average of 15 nm and more than several micron, respectively.

CNFs nanopaper with diameter of approximately 38 mm was prepared by filtration. The obtained CNFs suspension was slowly vacuum filtered into wet CNFs sheets using a membrane filter (membrane pore size: 0.22 um). Fig. 1 schematically illustrates the production process of the composite electrode. For CNFs/AgNWs composite film, an aqueous suspension of AgNWs at a specific concentration (10 mg/ml) was added on the top of above mentioned CNFs nanopaper, and filtered in the same manner [6]. The wet sheet was treated by hot pressing at 110 °C for 10 min (1 MPa) and then peeled from the membrane [22–24]. The deposition density was controlled by the volume and concentration of filtered AgNWs dispersion [13]. For CNF/AgNWs/AR composite film, as shown in Fig. 1, the CNFs/AgNWs sheet was firstly put adhesive tape on both sides of the film surface, and impregnated in matrix acrylic resin ABPE10. (In this step, the purpose for using adhesive tape was that preventing the two areas were not impregnated by acrylic resin, as a barrier layer effect. And they act as the conductive ports of the composite electrode.) Then, the sheet was kept under vacuum at a pressure of 0.01 MPa for 12 h. The resin impregnated sheet was sandwiched between glass slides and was immediately cured using UV curing equipment [23,27–31]. Finally, the two side of adhesive tapes were peeled to obtain the composite electrode.

2.3. Properties evaluation

2.3.1. FE-SEM observations

A field emission scanning electron microscope (FE-SEM, S-4800, HITACHI, Japan) was used to investigate the morphological features of CNFs after one time-pass grinding. The samples were treated respectively by ethanol, acetone and *t*-butyl alcohol to solvent-exchange, and then freeze dried to prevent structural collapse during dehydration. It was also used to examine the surface and cross-section morphology of the composite films. All the samples were coated with platinum by an ion sputter coater and then observed with the FE-SEM operating at 3.0 kV.

2.3.2. Sheet resistance measurement

A layer of AgNWs network with thickness more than 70 nm was deposited on the CNFs nanopaper. Sheet resistance values were measured using a 4-point probes resistivity measurement system (RTS-8, 4 PROBES TECH, CHINA).

2.3.3. Light transmittance

Light transmittances were measured at wavelengths of 200–1000 nm using a UV–visible spectrometer (U-4100, HITACHI, Japan) with an integrating sphere of 60 nm in diameter. Each sample was placed 25 cm away from the entrance port of the integrating sphere. The total diffuse optical hazes of these films were measured with an integrating sphere of the UV–Vis spectrometer.

2.3.4. Thermomechanical analysis (TMA)

The coefficients of thermal expansions (CTE) of CNFs nanopaper, CNFs/AgNWs and CNF/AgNWs/AR composite films were measured by a thermo mechanical analyzer (TMA 402 F1, NETZSCH, Germany). Specimens were 25 mm long and 4 mm wide with a 20 mm span. The measurements were carried out three times with a heating rate of 5 °C min^{-1} in a nitrogen atmosphere, under a load of 29.4 mN in tensile mode. The CTE values were determined as the mean values at 20–150 °C in the second run.

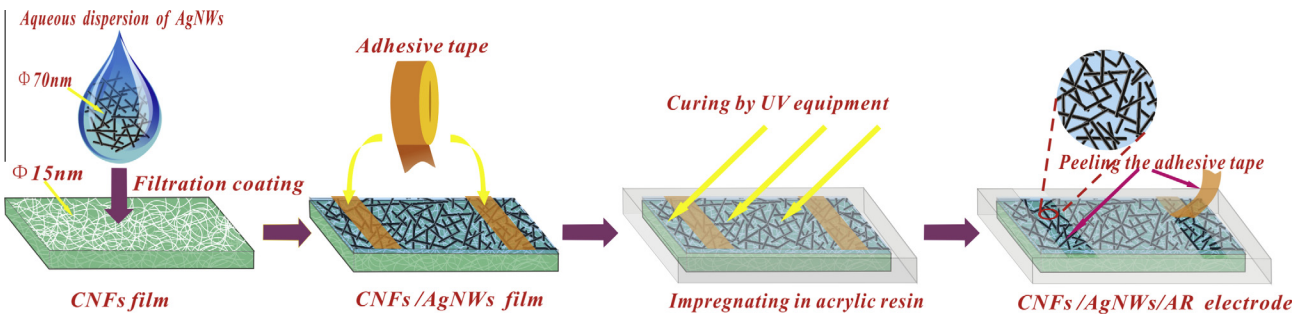

Fig. 1. Schematic of the fabrication of CNFs/AgNWs/AR composite electrode. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)