Fabrication of transparent flexible electrodes on polyethylene terephthalate substrate with high conductivity, high transmittance, and excellent stability

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Abstract:

Transparent flexible electrodes based on silver nanowires (AgNWs) have great potential for practical applications and many studies have been carried out to improve their conductivity, transparency, and surface roughness. In this study, we demonstrate a new approach for the fabrication of high-performance transparent flexible electrodes based on AgNWs and graphene oxide (GO) on polymer substrates using the pressing method. The surface morphology of the pressed AgNW/GO electrode was characterised by atomic force microscopy (AFM) and observed by scanning electron microscope (SEM). The electrode had a low surface roughness with the root mean square (Rq) of 7 nm. The electrode exhibits a low sheet resistance of 22 Ω/sq, a high transmittance of ~88%, resulted in a figures-of-merit (FoM) value of ~12.6. The optical and electrical properties of the electrode are comparable to that of the flexible ITO electrode. In addition, the electrodes also displayed outstanding durability and mechanical stability. This simple and scalable fabrication method is expected to contribute to future studies on flexible transparent conductive electrodes.

***Keywords*:** **flexible conducting electrodes, graphene oxide, pressing method, silver nanowires.**

Classification numbers: **2.2, 2.3**

1. Introduction

Transparent electrodes are an important element of various optoelectronic devices such as organic light-emitting diodes (OLEDs) and organic solar cells (OSCs) [1]. So far, indium tin oxide (ITO) is the most common material utilized for transparent electrodes because of its low sheet resistance (<20 Ω/sq) and high transmittance (~90%) [2]. However, it has several disadvantages including brittleness, necessity for high-temperature treatment, and limited optical transmittance in near-infrared (NIR). The brittle property of ITO makes its unsuitable for flexible optoelectronic devices. In addition, the depletion of indium sources is also a major problem for the production of ITO electrodes. Therefore, the development of new flexible materials at low cost to replace ITO has become an important subject [3].

Nowadays, several types of materials can be used to fabricate transparent electrodes such as metal nanowires, graphene, carbon nanotubes, and conductive polymers [4, 5]. Among these, AgNWs have attracted significant attention and are studied extensively. AgNW electrodes show excellent electrical conductivity and transparency, which are comparable to ITO electrodes. Moreover, AgNW electrodes are flexible and have low manufacturing costs and a low level of inherent toxicity. Nevertheless, AgNW electrodes have two main disadvantages: (i) high surface roughness (Rq) due to pile-up at cross points and (ii) weak adhesion between the AgNWs and its polymer substrate. In order to increase the contact between the AgNWs as well as its interaction with the substrate, the spin-coated electrode is usually thermally annealed. However, the annealed electrodes still have large surface roughness, which hampers their applications. Furthermore, the thermal annealing process may cause damage to polymer substrates such as polyethylene terephthalate (PET) or polyethylene naphthalate (PEN). In order to solve this problem, a researcher successfully fabricated AgNW electrodes by mechanical pressing at room temperature [6, 7]. However, in that study, the AgNW had a large diameter (about 70 nm), resulting in fabricated electrodes with low transmittance, resulting in a low figures-of-merit (FoM) value even when they were fabricated on a glass substrate. Lately, many studies have also used GO to improve electrical conductivity and the surface roughness of AgNW electrodes [8-10]. However, this solution only partially overcomes the problems mentioned above. Therefore, in this paper, we fabricated flexible electrodes with small-diameter AgNWs (~35 nm) and GO using a mechanical pressing method. The obtained electrode displayed high electrical conductivity, low surface roughness, and excellent stability.

2. Materials and methods

2.1. Materials

Silver nitrate ($AgNO_3$): purity ≥99.8% (Fisher Scientific); ethylene glycol (EG): 99% purity (Fisher Scientific); nickel(II) chloride: 99% purity (Sigma); graphite (size less than 20 µm, Sigma); polyvinylpyrrolidone (PVP) M_w=360,000 Da, purity 99% (Sigma); isopropanol: 99.7% purity (Sigma); sheet of

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PET: size 300×300×0.25 mm (Sigma); absolute alcohol, sodium nitrate, potassium permanganate, hydrogen peroxide, concentrated hydrochloric acid solutions were used without further purification.

2.2. Synthesis of AgNWs

AgNWs were synthesised by the polyol method, using EG as a reducing agent in the presence of PVP surfactant [11, 12], with some modifications from the procedure reported in 2013 [10]. Firstly, 1.02 g $AgNO_3$, 1.66 g PVP, 200 ml EG, and 3.12 mg $NiCl_2$ were added to a flask and well-mixed under stirring. The mixture was heated and kept at 140ºC for 6 h. After the reaction, the AgNWs were filtered and washed several times with isopropanol by centrifugation and then dispersed in 100 ml of isopropanol to obtain an AgNWs dispersion with a concentration of 4 mg/ml. The synthesised AgNWs had an average diameter of 35 nm and an average length of 20 µm.

2.3. Synthesis of GO

GO was synthesised from graphite by the Hummer method [13]. The specific procedure included the following steps. Firstly, 48 ml of concentrated H_2SO_4 was cooled to below 5ºC, then 1 g of graphite and 0.5 g of $NaNO_3$ were added. The mixture was stirred at 5ºC for 60 minutes. Then, 6 g of $KMnO_4$ was slowly added to peel off the graphene layers. Finally, 10 ml H_2O_2 was added to the reaction to reduce excess Mn^{+7} ions to Mn^{+2} ions. The resultant GO was filtered and washed with distilled water by centrifugation to obtain a final solution with a concentration of 0.05%. The GO solution had high transparency and high durability, suitable for use in electrode fabrication.

2.4. Electrode fabrication

Four types of electrodes were fabricated: electrodes E1 (AgNWs) and E2 (AgNWs pressed) were fabricated by spin-coating only the AgNW dispersion onto the PET substrate (2000 rpm, 40 s) and electrodes E3 (AgNW/GO) and E4 (AgNW/GO pressed) were fabricated with a layer-by-layer spin-coating method using the AgNW dispersion and GO solution (2000 rpm, 40 s). After spin-coating, electrodes E2 and E4 were pressed at a pressure of 10 MPa for 20 s.

2.5. Characterisation

The surface morphology of the electrodes was characterised by atomic force microscopy (AFM, XE-100) using non-contact mode. The size and distribution of AgNWs on the electrode were observed by scanning electron microscope (SEM, S-4800, Hitachi, Japan). The sheet resistance of the electrode was measured with a Jandel RM3000 four-probe wafer resistance meter at 5 random positions on the electrode surface, then the average value was taken as the sheet resistance. The transmittance of the fabricated electrode was determined using a UV-Vis spectrophotometer (SP-3000 nano). Bending tests were carried out using a thin film bending tester that was custom-built. This tester allowed for control of the bending radius and number of bends with great precision. For testing the adhesion of the nanowire network and the PET substrate, 3M Scotch tape was attached to the surface of the electrode and then peeled off. The sheet resistance of the electrode was measured before and after attaching it with 3M scotch tape. The stability of the electrode in solvent was studied by placing the electrode in an ethanol solution and then sonicating for 10 min, drying completely, and then re-measuring the conductivity of the electrode.

3. Results and discussion

3.1. Surface morphology of the electrodes

The morphology and surface roughness of the fabricated electrodes were studied by AFM.

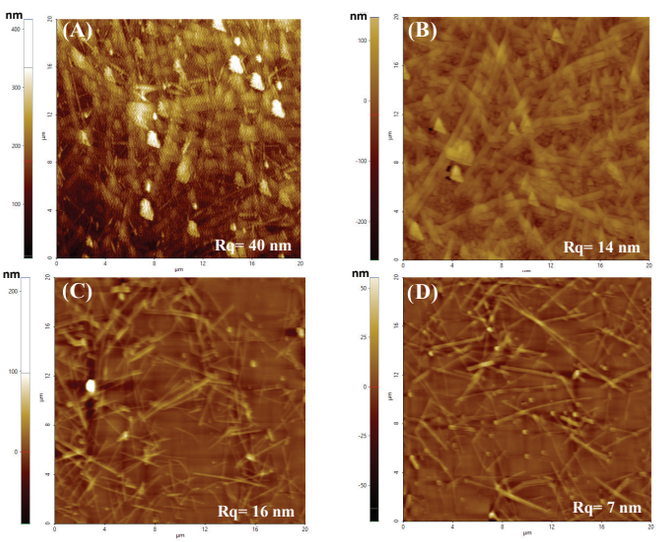

Fig. 1. Surface image of electrodes analysed by AFM. (A) Electrode E1, **(B)** Electrode E2, **(C)** Electrode E3, **(D)** Electrode E4.

The E1 electrode has a root mean square roughness (Rq) of 40 nm. The white areas protruding in the topography image (Fig. 1A) correspond to the intersection points of the AgNW network. These areas have high elevations that were caused by overlapping AgNWs. This issue was improved on the remaining electrodes (Figs. 1B, 1C, 1D). As shown in Fig. 1, the root means square roughness of the electrode decreases to 14 nm (E2), 16 nm (E3), and 7 nm (E4). This result indicates that the GO coating layer and the mechanical pressing method both make the AgNW electrode surface smoother.

The morphology of the electrodes was also studied by SEM images. For the E2 electrode, the AgNWs were tightly connected instead of overlapping as before pressing (Fig. 2A). The compressed connection points can be seen as shown in Fig. 2B. In the case of the E3 electrode, Fig. 2C exhibited GO covering the AgNW junctions. The thin GO layer contributes to tightly pressing the AgNW network onto the PET substrate surface, making the film electrode smoother and more stable.

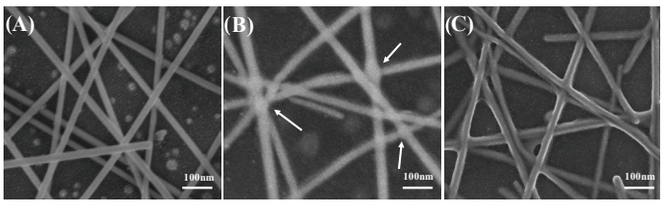

Fig. 2. SEM image of electrode surface in the top view. (A) Before, **(B)** After pressing (white arrows indicate junctions that have been pressed tightly by the pressing method) of AgNW electrodes, **(C)** AgNW/GO electrode.

The off-angle cross-sectional view shows that the AgNWs are not only tightly connected, but also sank into the PET substrate after the pressing process (Fig. 3B).

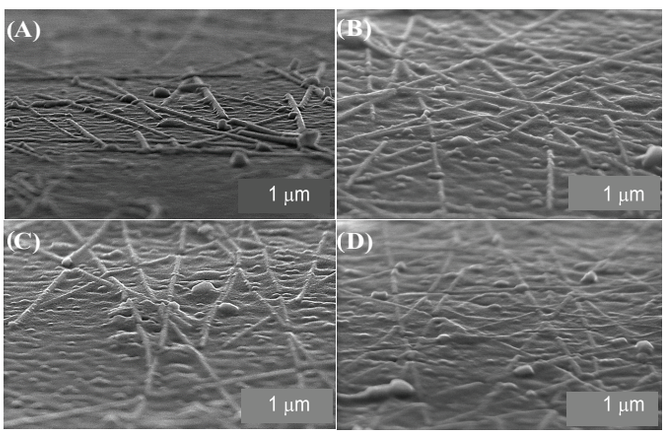

Fig. 3. SEM image of four electrode surfaces with tilt angle. (A) Electrode E1; **(B)** Electrode E2; **(C)** Electrode E3; **(D)** Electrode E4.

For the E3 electrode, GO was coated onto the AgNW network, thereby decreasing the surface roughness of the electrode. Therefore, the E3 electrode surface is smoother than that of E1, as shown in Fig. 3C. The E4 electrode is fabricated by combining both methods and it has a surface roughness value of only 7 nm. This result is better than that of the recently published AgNW/GO electrodes [3, 8, 14]. Off-angle FE-SEM observation indicated that the nanowires networks are tightly pressed onto the substrate, which reduces the protrusion of AgNWs (Fig. 3D).

3.2. Optical and electrical properties of electrodes

The results in Table 1 indicate that the resistance value after pressing the AgNWs and AgNW/GO electrodes significantly decreased from 120 to 33 Ω/sq and from 38 to 22 Ω/sq, respectively. Meanwhile, the transmittances of these electrodes were almost unchanged. After pressing, the conductivity of the electrodes improved significantly because the junctions were tightly bonded, allowing the charge to move easier in the silver nanowire network.

Table 1. Value of resistance, transmittance, and FoM index of 4 electrodes.

Electrode	E1	E2	E3	E4
R (Ω/sq)	120	33	38	22
T (%)	90	89	89	88
FoM×1000	2.9	9	8.2	12.6

As shown in Fig. 4, after pressing, the transmittance of the electrodes tends to decrease in the short wavelength range and increase in the long wavelength range. Fig. 5 illustrates the shape change of the AgNWs after pressing. The pressing method leads to a higher coverage ratio of the AgNW network on the electrode thus the absorption in the short-wavelength range increased. In contrast, after pressing, the AgNWs are thinner. Thus, long-wavelength light can pass through with lower loss. High transmittance in the near IR region in this electrode is an advantage for optoelectronic applications such as OSC devices.

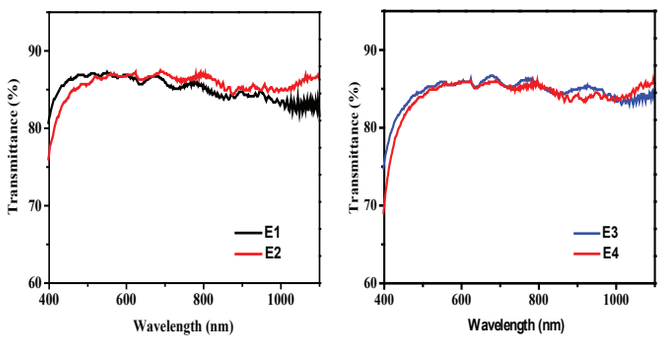

Fig. 4. The transmittance of the electrodes.

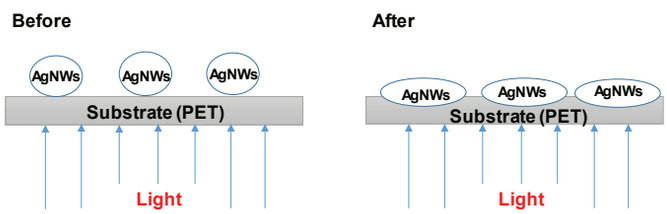

Fig. 5. Illustration the shape of AgNWs before and after pressing.

The FoM value of electrodes was evaluated to compare their performance. The FoM value represents the optimisation between the optical and electrical properties of the electrode and the classical FoM definition of Haacke is commonly used: $FoM = \frac{T^{10}}{R}$ (where T is the optical transmittance measured at a wavelength of 550 nm and R is the resistance value of the electrode) [15-18]. Calculation results (Table 1) show that the AgNW/GO electrode after pressing (E4) has the highest FoM value with an FoM×1000 value of 12.6. The FoM values of the remaining electrodes are 9 (E2), 8.2 (E3), and 2.9 (E1). Thus, the E4 electrode has the best balance between electrical and optical properties. With a FoM value of ~12.6 (sheet resistance value of 22 Ω/sq and a transmittance of 88%), the optical and electrical properties of the E4 electrode in this study are comparable to that of the flexible ITO electrode and higher than some recently announced flexible electrodes [2, 16].

3.3. Investigation of electrode durability

When the E1 electrode was bent with a curve radius of 4 mm, its resistance value increases by 60% after bending 2000 times. For E2 electrodes, which were pressed, their durability increased as shown in Fig. 6A.

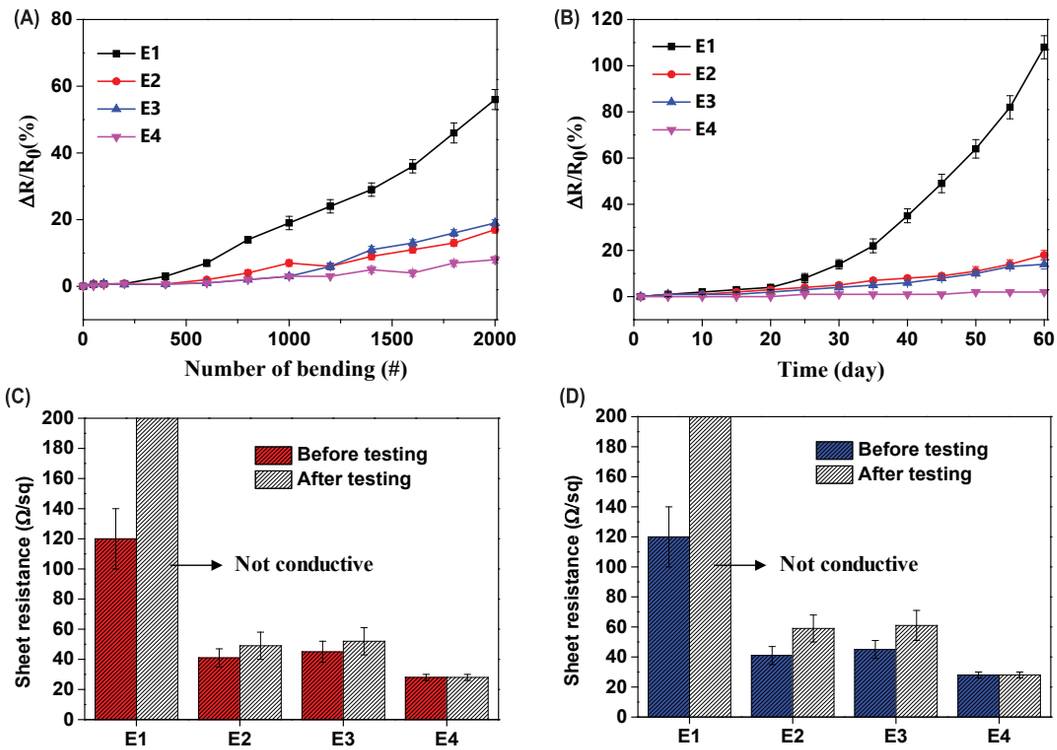

Fig. 6. Resistance changes of the 4 electrode types in the tests. (A) Bending with a radius curve of 4 mm; **(B)** Exposing the electrode to the normal environment; **(C)** Attaching 3M scotch tape to the electrode surface and then tape removal; **(D)** Rinsing the electrode in ethanol and subjecting it to ultrasonic vibration for 10 min.

Through 2000 bends, the resistance value of the E2 electrode rises slightly by 17%, which proves that the pressing method creates a strong interaction between AgNWs as well as the adhesion between the AgNW network and the PET substrate. For that reason, after the pressing process, the AgNW network was less damaged when subjected to mechanical impact. After coating with GO, the sheet resistance of the E3 electrode increased by 19% after 2000 bends. This phenomenon demonstrates that the GO layer also increases the adhesion of the AgNW network to the PET substrate. The E4 electrode has the highest mechanical durability. The sheet resistance of the pressed AgNW/GO electrode was almost unchanged after bending 2000 times. As shown in Fig. 6B, the sheet resistance value of the E1 electrode rapidly increased from 120 to 250 Ω/sq after 60 d of storage. For the E2 electrode, the sheet resistance value only increases by 18% under the same conditions. This demonstrates that the tight contact between the AgNWs makes the electrode more stable. In the case of the E3 electrode, the sheet resistance increased by 14% after the test period. It was reasoned that the coating of GO on AgNWs as a protective layer shielded the AgNWs from the effects of oxidation and humidity. Therefore, GO layers improve the stability of the electrodes. This phenomenon is consistent with the some published results [14, 19]. In this experiment, the E4 electrode still shows superior durability. After 60 d of storage, the sheet resistance value of the E4 electrode remained constant.

In order to study the adhesion between the AgNWs and the PET substrate, 3M Scotch tape was applied to the electrode and then pulled off (Fig. 6C). For the E4 electrode, the sheet resistance value was unchanged. Meanwhile, the sheet resistance value of the remaining electrodes all increased. In particular, in the case of electrode E1, after pulling the tape, this electrode showed very high resistance. In addition, the E4 electrode also exhibits high stability when rinsing and subjecting it to ultrasonic vibration in ethanol (Fig. 6D). The application of the mechanical pressing method and GO layer not only increases the conductivity but also improves the stability of the AgNW electrode.

4. Conclusions

The AgNW/GO transparent flexible hybrid electrode on a PET substrate has been successfully fabricated at room temperature by a simple pressing method. This electrode fabrication method has significantly decreased the surface roughness of the electrode, which was a chronic drawback of silver nanowire electrodes. This pressed AgNW/GO hybrid electrode displayed a low surface roughness, a low sheet resistance of 22 Ω/sq, and a high transmittance of 88% at 550 nm, which are all comparable to the ITO electrodes. Moreover, the electrode shows high mechanical and chemical stability. Thus, this AgNW/GO hybrid electrode could be used to fabricate flexible OSCs.

CRediT author statement

Tien Dat Doan: Conceptualization, Methodology, Writing - Original draft preparation; Nhung Hac Thi: Data curation, Visualisation; Ho Thi Oanh: Conceptualisation, Methodology; Tuyen Nguyen Duc: Investigation; Dong Hoon Choi: Reviewing and Editing; Mai Ha Hoang: Supervision. All authors have read and agreed to the published version of the manuscript.

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COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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