Flexible Transparent Conductive Films with High Performance and Reliability Using Hybrid Structures of Continuous Metal Nanofiber Networks for Flexible Optoelectronics

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Supporting Information

ABSTRACT: We report an Ag nano fiber-embedded glass-fabric reinforced hybrimer (AgNF-GFRHybrimer) composite film as a reliable and high-performance flexible transparent conducting film. The continuous AgNF network provides superior optoelectronic properties of the composite film by minimizing transmission loss and junction resistance. In addition, the excellent thermal/chemical stability and mechanical durability of the GFRHybrimer matrix provides enhanced mechanical durability and reliability of the final AgNF-GFRHybrimer composite film. To demonstrate the availability of our AgNF-GFRHybrimer composite as a transparent conducting film, we fabricated a flexible organic light-emitting diode (OLED) device on the AgNF-GFRHybrimer film; the OLED showed stable operation during a flexing.

KEYWORDS: transparent conducting electrode, silver nanofiber, glass-fabric reinforced plastic, all-in-one TCE/substrate platform, flexible organic light-emitting diode

In a world where flexible and wearable electronics have become commonplace, optoelectronic devices such as displays, touch screen panels, organic light-emitting diodes (OLEDs), and solar cells (SCs) have been demanding flexibility and stretchability.1,2 To keep pace with this trend, transparent conducting electrode (TCE), which is the essential and crucial component of optoelectronic devices, is also expected to have flexible and stretchable properties.3–5 The most commonly used TCE material is indium-doped tin oxide (ITO). Its high transparency (~90%), low sheet resistance (15 Ω sq−1), and chemical stability allow it to be widely used in modern electronics. However, the fragile nature of an oxide material and its high-cost vacuum-deposition process preclude it from being applied to next-generation flexible electronics. To replace ITO, various candidate materials have been proposed: graphene, carbon nanotubes (CNTs), conducting polymers, metal grids, and metal nanowires (NWs).6–8 Carbon materials such as graphene, CNTs, and conducting polymers have improved flexibility over ITO, but they have poor electrical conductivity and stability. Periodic metal grids have excellent conductivity because of their junction-free networks and metallic nature, but moiré pattern issue is inevitable.9,10 In this respect, random network metal NWs are considered the most promising candidate for flexible TCE materials. Because of their mechanical flexibility, high transparency with 100% trans-

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mittance from the empty space between NWs, the metal NWs have been extensively studied.\textsuperscript{11−13} However, metal NWs still have problems to be solved. When NWs are connected to form a conductive path, junctions between the NWs cause surface roughness and junction resistance. When applied to electronic devices, surface roughness might induce a device short, which is directly related to the reliability of the device, and the junction resistance degrades the electrical property of the TCE. On the basis of these considerations, studies on a reduced number of junctions or junction-free metal network TCEs have attracted much attention.\textsuperscript{14} For example, Ko et al. synthesized long Ag NWs by using multistep growth method to reduce the number of junctions.\textsuperscript{15} Recently, Song et al. proposed an electro-welding method to eliminate junctions, and Hauger used mechanical pressing to remove junctions.\textsuperscript{16,17} Furthermore, the surface roughness and poor adhesion to the substrate still need to be addressed for sufficient reliability.

In this study, we report on a high-performance all-in-one flexible TCE film (AgNF-GFRHybrimer) using a surface-embedded continuous network of Ag nanofiber (NF) in thermostable and mechanically durable glass-fabric reinforced composite (GFRHybrimer) film.\textsuperscript{18,19} A single-line AgNF network effectively reduces the number of junctions, providing superior optoelectrical property ($T_{\text{tot}} \approx 91\%$ and $R_{\text{sh}} = 3 \Omega \text{sq}^{-1}$). Moreover, the embedded structure with transparent and thermostable GFRHybrimer film not only solves surface roughness and poor adhesion problems but it also improves the thermal (60 h at 250 °C) and environmental stability (120 h at 85 °C/85% RH) by minimizing the exposure area of AgNF network. AgNF-GFRHybrimer composite film also shows outstanding mechanical durability and dimensional stability.

Figure 1. (a) Schematic illustration of the electrospun AgNF embedded GFRHybrimer composite film fabrication procedure, and (b) the synthesis process of hybrimer resin with chemical structures. (c) A digital photograph of the AgNF-GFRHybrimer film, showing flexible and transparent properties. (d) Tilted and (e) surface SEM images of the AgNF-GFRHybrimer composite film. AFM images of electrospun AgNF (f) on a donor substrate and (g) embedded in GFRHybrimer matrix.
To demonstrate the potential of the AgNF-GFRHybrimer as a next-generation flexible TCE film, we fabricated a flexible OLED on the film.

Figure 1a illustrates the fabrication procedure of the AgNF-GFRHybrimer composite film. First, two sheets of glass-fabric were placed on a hydrophobic-treated glass substrate and impregnated with hybrimer resin. The synthetic process for the hybrimer resin is depicted with chemical structures in Figure 1b. Subsequently, the electrospun AgNF network was transferred from a donor substrate to the surface of the hybrimer resin impregnating glass-fabric sheets. This sandwich-structured composite is pressed under vacuum-bag molding (~14 MPa) and then exposed to UV light for 10 min to induce curing of the hybrimer resin. By removing the glass and donor substrate, a freestanding, transparent and flexible AgNF-GFRHybrimer composite film was fabricated, as seen in Figure 1c (see also Supporting Information for the experiment details). The surface topography of the film is depicted by scanning electron microscopy (SEM) and atomic force microscopy (AFM) analyses. A tilted SEM image (Figure 1d) showed that glass-fabric sheets were sufficiently impregnated with hybrimer resin, and the continuous AgNF network is embedded into the surface of the hybrimer matrix without any disconnection. AFM images represent the surface morphology before (Figure 1f) and after AgNF embedding (Figure 1g). As seen in the AFM images, the AgNF-GFRHybrimer film exhibited a smooth surface profile, and the surface roughness was reduced by 11 times compared to before embedding (see also Figure S2).

The most common way to evaluate the optoelectrical property of transparent conductor is by using a figure of merit (FoM). This performance index includes the physical expression of a transmittance and sheet resistance term so that it can help to assess and compare the performance of TCEs. Generally, the FoM for nanomaterial TCEs is calculated using the following relation

$$ T = \left(1 + \frac{Z_0 \sigma_{\text{dc}}}{2R_{\text{sh}} \sigma_{\text{dc}}} \right)^{-2} $$

where $T$ is total transmittance at 550 nm wavelength, $R_{\text{sh}}$ is sheet resistance, $Z_0$ is impedance of free space (377 $\Omega$), and $\sigma_{\text{dc}}/\sigma_{\text{op}}$ is FoM. According to the equation, a larger FoM value indicates the better optoelectrical properties. The UV–vis transmittance spectra of the AgNF-GFRHybrimer film with a variation of sheet resistance were displayed in Figure S3. By substituting the transmittance ($T_{\text{tot}}$ at 550 nm) and corresponding sheet resistance ($R_{\text{sh}}$) values in the above equation, we calculated the FoMs for the AgNF-GFRHybrimer. The results are summarized in Table 1; the performance index of the AgNF TCE showed the highest value of 1298 at $R_{\text{sh}} = 3$ $\Omega$ sq$^{-1}$, and average value was about 1200.

<table>
<thead>
<tr>
<th>AgNF area fraction</th>
<th>$R_{\text{sh}}$ (U/sq)</th>
<th>$T_{\text{tot}}$ at 550 nm (%)</th>
<th>FoM ($\sigma_{\text{dc}}/\sigma_{\text{op}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>7 ± 0.53</td>
<td>95.81</td>
<td>1244</td>
</tr>
<tr>
<td>0.24</td>
<td>5 ± 0.60</td>
<td>93.48</td>
<td>1100</td>
</tr>
<tr>
<td>0.32</td>
<td>3 ± 0.48</td>
<td>90.98</td>
<td>1298</td>
</tr>
<tr>
<td>0.43</td>
<td>2.2 ± 0.40</td>
<td>87.32</td>
<td>1221</td>
</tr>
</tbody>
</table>

For the comparison of optoelectrical properties, we display the latest Ag-based transparent conductors with the AgNF-GFRHybrimer in the transmittance versus sheet resistance graph, as detailed in Figure 2.8,15,21–23 The AgNF-GFRHybrimer exhibited exceptionally superior optoelectrical property. This outstanding performance index results from an inherent continuous network of AgNF TCE; charge transport occurs along the one-dimensional (1D) metallic pathways, and thus ultralong length of conductive AgNF facilitates the reduction of sheet resistance by minimizing the number of junctions between the metal lines. Therefore, continuous network of 1D AgNF with ultrahigh aspect ratio can be a potential alternative to overcome the current limit of metal NWs.24–27

One of the primary considerations for applying TCEs to various applications is thermal stability. This is because a device is accompanied by high temperature in the process of fabricating or operating, such as annealing treatment and joule heating.28 In this work, we conducted elevating temperature tests with a 5 °C/min ramp rate to demonstrate thermal stability of the AgNF-GFRHybrimer film. For the comparison, an AgNF on a glass substrate was adopted as a reference. As seen in Figure 3a, the AgNF-GFRHybrimer endured higher temperature than the reference without resistance change. The AgNF-GFRHybrimer film maintained its initial resistance until 430 °C, whereas the AgNF on glass started to increase its resistance at 300 °C. This resistance increase in the reference sample is due to thermal instability of AgNF; at high temperature, AgNF melted down and coalesced, so the conductive path was broken, resulting in a resistance increase (see Figure S4d).29 However, the resistance of the AgNF network embedded in GFRHybrimer is retained even above 400 °C; the thermostable resin tightly holds and encapsulates the AgNF after curing to improve morphological instability of AgNF from melting down and coalescing. As a consequence, AgNF in the GFRHybrimer exhibited better thermal stability. Above 430 °C, the resistance of the AgNF-GFRHybrimer film increased because of the decomposition of the hybrimer matrix.8 The decomposition of hybrimer matrix induces cracks, which cut off the conductive path of AgNF (Figure S4c). In an additional thermal aging test, the AgNF-GFRHybrimer film showed stable electrical properties under 250 °C for 60 h as displayed in Figure S5a.

![Figure 2](image-url)
Corrosion resistance of Ag-based TCEs is also of importance because Ag is easily corroded by sulfur gas in atmosphere. We used 5 wt % K$_2$S aqueous solution to demonstrate corrosion stability of the AgNF-GFRHybrimer film. The K$_2$S solution, like sulfur gas, reacts with AgNF and forms silver sulfide. This silver sulfide is an insulator, so the conductivity of the transparent conductor reduces as Ag$_2$S particles surround the AgNF network. Figure 3b reveals that AgNF on the glass rapidly lost its conductivity after 150 s, whereas AgNF buried in GFRHybrimer retained its initial resistance value for 450 s; the initial conductivity of the AgNF-GFRHybrimer lasted three times longer than that of the reference. The formation of Ag$_2$S was confirmed by X-ray diffraction (XRD) and SEM images. After exposure to K$_2$S solution, both the AgNF on the glass and the AgNF-GFRHybrimer showed silver sulfide peaks in the XRD data, and silver sulfide particles surrounding the AgNF in SEM images (see Figure S6). However, the exposure area of AgNF to the K$_2$S solution determines corrosion stability. By minimizing the exposure area of AgNF with the hybrimer matrix, the composite film can improve corrosion stability.

Oxidation-resistance of the AgNF-GFRHybrimer was also tested under high temperature and high humidity condition. The test was carried out in an environmental chamber of 85% relative humidity at 85 °C; coexistence of high temperature and
high humidity accelerates the oxidation reaction of AgNF. As seen in Figure 3c, embedded AgNF in GFRHybrimer presented stable electrical property even after 120 h. On the other hand, AgNF on the glass showed a dramatic increase in resistance after 30 h. From XRD data (Figure S7b) and SEM images of the reference sample, the resistance increase was due to the formation of silver oxides. The formation of Ag2O nanoparticles along the AgNF broke the conductive network on the glass substrate (Figure S7d). In contrast, the AgNF-GFRHybrimer film still had a smooth surface, with an intact conductive path after 120 h, as shown in Figure S7c. The embedded structure of the AgNF-GFRHybrimer film allows minimal exposure of the AgNF network to the external environment; the low oxygen transmission rate (2.95 × 10−2 day−1 @ 34.8 °C 100% O2) and water transmission rate (1.77 × 10−2 gm mil m−2 day−1 @ 37.8 °C under 90% RH) of hybrimer resin effectively protects the embedded AgNF, so enhanced oxidation stability of the AgNF TCE was achieved.29

The mechanical durability of a TCE film is another important requirement to verify the reliability when applied to flexible devices. For evaluating the mechanical durability of the composite film, we conducted bending, adhesion, and abrasion tests with a lab-made bending machine, a sticky tape, and an eraser, respectively.

First, the bending test was performed in two ways with a 1 mm bending radius; the electrode surface was under compressive stress in inner bending, and under tensile stress in outer bending. To compare bending durability, we performed the bending tests with commercialized ITO/PET film. As illustrated in Figure 3d, the AgNF-GFRHybrimer film exhibited highly stable electrical performance over the 2000 repetitive bending cycles in both inner and outer bending. By contrast, the resistance of ITO/PET dramatically increased by 80 times in the outer bending and by 20 times in the inner bending after only five bending cycles, respectively. This stable bending performance of the AgNF-GFRHybrimer composite film is caused by the mechanical durability of GFRHybrimer, the flexibility of AgNF, and the tightly encapsulated structure. The embedded structure also eased the delamination problems between the TCE and the substrate. As the hybrimer resin underwent a photo cross-linking process, it anchored the AgNF network firmly in the surface of the hybrimer matrix. As a result, unlike AgNF on the glass substrate, the AgNF-GFRHybrimer composite film can preserve its electrical property even in a 100 repeatable tape test, without detaching the conductive network (see Figure 3e).

We also evaluated the abrasion-resistance of the AgNF-GFRHybrimer film by using an eraser. As seen in Figure 3f, the AgNF embedded in GFRHybrimer tolerated 30 erasing cycles without a resistance change, while the AgNF on the glass lost its conductivity after erasing one time only; the eraser scrubbed off the AgNF from the glass substrate. The smooth topography of embedded structure with the hybrimer matrix and encapsulation of AgNF improved the abrasion resistivity of the AgNF-GFRHybrimer film.

To verify the availability of the AgNF-GFRHybrimer composite film as a flexible TCE substrate, we fabricate a flexible OLED on the AgNF-GFRHybrimer film. Figure 4a illustrates a schematic diagram of the flexible OLED device structure. In this approach, the top surface of AgNF-GFRHybrimer film was spin-coated with a layer of poly-(ethylenedioxythiophene):polystyrenes sulfonate (PE-DOT:PSS) doped with dimethyl sulfoxide as a second transparent electrode for matching the work function. After coating a hole transport layer of PEDOT:PSS there, a light-emitting polymeric layer of PDY-132 (a green polymer known as ”super yellow”, Merck & Co.) and an electron transport layer of poly [((9,9-bis(3’-(N,N-dimethylamino)Propyl)-3,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) were coated subsequently. Then, the thermal evaporation of a 100 nm thick, Al cathode completed the OLED fabrication. Here, all layers except the Al cathode were formed using solution processing.
without any vacuum process. Figure 4b shows a photograph of the flexible OLED device using the AgNF-GFRHybrimer film. No significant degradation in the light emission of this flexible device occurs for bending to radii of curvature as small as 3.1 mm, as shown in Figure 4b. Figure 4c presents the curves on its current density versus the applied voltage (J−V) and its luminance versus the applied voltage (L−V), indicating the stable operations of this OLED with a turn-on voltage of 2 V and a maximum luminance of 59 918 cd/m2. Figure 4d exhibits the curve on its external quantum efficiency (EQE) with 4.57%, and Figure 4e shows the normalized electroluminescence (EL) spectrum of this OLED. AgNF encapsulated with hybrimer matrix solves the problem of shorting by providing smooth surface topography and thus enhances the reliability of OLED device. In addition, AgNF-GFRHybrimer allows the strong adhesion between TCE and the substrate, so that bending reliability of OLED devices can be improved. On the basis of these results, we demonstrated the potential of AgNF-GFRHybrimer composite film as a robust and reliable TCE platform for next-generation flexible optoelectronics.

In summary, we fabricated AgNF-GFRHybrimer composite film as a next-generation flexible TCE/film platform. The continuous network of AgNF provides excellent optoelectrical properties of the composite film by forming a 1D conductive path with reduced number of junctions. A transparent and thermostable GFRHybrimer improves the stability of AgNF TCE in high temperature, corrosive, and oxidative environments by minimizing the exposure of the AgNF network. In addition, this embedded structure addresses the surface roughness and adhesion issues of AgNF TCE in an effective manner. The stable performance of flexible OLED fabricated on AgNF-GFRHybrimer demonstrated the availability of the composite film as a promising flexible TCE platform in future optoelectronics.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b04314.

Experimental Section, AFM and SEM images, XRD patterns and transmittance graph of AgNF-GFRHybrimer film (PDF)

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Notes
The authors declare no competing financial interest.

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