Highly flexible Ag nanowire network covered by a graphene oxide nanosheet for high-performance flexible electronics and anti-bacterial applications

Hyeong-Min Sim and Han-Ki Kim

School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon-si, Republic of Korea

ABSTRACT
We investigated a flexible and transparent conductive electrode (FTCE) based on Ag nanowires (AgNWs) and a graphene oxide (GO) nanosheet and fabricated through a simple and cost-effective spray coating method. The AgNWs/GO hybrid FTCE was optimized by adjusting the nozzle-to-substrate distance, spray speed, compressor pressure, and volume of the GO solution. The optimal AgNWs/GO hybrid FTCE has a high transmittance of 88% at a wavelength of 550 nm and a low sheet resistance of 20 Ohm/square. We demonstrate the presence of the GO nanosheet on the AgNWs through Raman spectroscopy. Using scanning electron microscopy and atomic force microscopy, we confirmed that the nanosheet acted as a conducting bridge between AgNWs and improved the surface morphology and roughness of the electrode. Effective coverage by the GO sheet improved the conductivity of the AgNWs electrode. Effective coverage of the GO sheet improved conductivity of the AgNWs electrode with minimum degradation of optical and mechanical properties. Flexible thin film heater (TFH) and electroluminescent (EL) devices fabricated on AgNWs/GO hybrid FTCEs showed better performance than devices on bare AgNWs electrodes due to lower sheet resistance and uniform conductivity. In addition, an AgNWs/GO electrode layer on a facial mask acts as a self-heating and antibacterial coating. A facial mask with an AgNWs/GO electrode showed a bacteriostatic reduction rate of 99.7% against Staphylococcus aureus and Klebsiella pneumoniae.

1. Introduction
A flexible and transparent conductive electrode (FTCE) is a thin film with high transparency, high conductivity, and outstanding flexibility [1–3]. Due to the rapid advancements in flexible electronics and wearable devices, FTCEs have gained a great deal of attention as a key component of flexible displays [4–6], flexible touch panels [7–9], flexible thin film heaters (TFHs) [10–16], photoelectric devices [17–20], and wearable electronics [21–23]. Currently, most flexible electronics and wearable devices use Sn-doped In$_2$O$_3$ (ITO) film coated on a flexible substrate through a typical magnetron sputtering process [24–26] owing to the high conductivity and transparency of commercially available ITO films. However, the brittle nature and poor mechanical properties of typical ITO films remain critical problems standing in the way of their use in FTCEs [27–31]. Furthermore, ITO electrodes are usually fabricated through an expensive vacuum process, such as evaporation or sputtering, and indium is very costly because reserves of the element are limited [32–34]. To address the problems of
typical ITO electrodes, various substitutions, such as conductive polymers [35–37], carbon nanotubes [38,39], graphene [40,41], and metal nanowires [42,43], have been extensively investigated. Among several candidates, Ag nanowires (AgNWs) with a diameter of less than 100 nm and a length of several μm are thought to be promising materials to replace ITO films for fabrication of FTCE devices. An AgNWs film with an irregularly connected network has been applied in flexible electronics and wearable devices due to its high conductivity, low sheet resistance, good flexibility and simple solution-based coating process [44–46]. It is possible to produce a cost-effective AgNWs FTCE because it can be printed by spin coating [47,48], bar coating [49], slot die coating [7,50], brush painting [51], and spray coating [52] at room temperature. However, a reduction in the AgNW concentration in ink for the purpose of confirming high transmittance resulted in a reduction in the inter-link connectivity of the AgNWs and increased the sheet resistance. In addition, the high surface roughness and high contact resistance between AgNWs lead to leakage current and local heating of FTCEs. For those reasons, AgNWs still cannot replace commercial ITO film in the FTCE market. Graphene is also a core material for next-generation conductive transparent electrodes. Graphene exhibits a theoretical mobility of 200,000 cm²/V-s, and has high conductivity and excellent transparency due to its 2-dimensional (2D) structure [53]. In particular, its high Young’s modulus, which reaches about 1 TPa, enables outstanding mechanical flexibility [54]. However, the applicability of graphene electrodes in large-area product manufacturing is limited by the high cost of chemical vapor deposition and the complexity of the transfer process [55]. In order to solve these problems, research on graphene oxide (GO) nanosheets obtained through Hummers’ method has actively progressed [56]. Using Hummers’ method, although the sp²-hybrid bond of graphene is broken and shows high resistivity, a GO nanosheet can be obtained in large quantities as a stable solution. Moon et al. have demonstrated that spray coating of GO nanosheets leads to improvements in the surface roughness, haze, and conductivity of AgNWs [57]. They reported the feasibility of a GO nanosheet as an over-coating layer for AgNWs electrodes. However, they did not demonstrate the possible applications of GO over-coated AgNWs electrodes.

In this work, AgNWs and GO were dispersed separately in solution and then airbrushed onto a substrate to create a high-quality FTCE. Spray coating is a well-known method of solution coating in which functional ink is sprayed through a nozzle to deposit a film on a substrate. The spray coating process has a faster coating speed and easier operation than other solution process methods [58,59]. Optimization of the AgNWs/GO hybrid FTCE proceeded by maintaining the high transmittance of the AgNWs and improving the conductivity and surface properties of the electrode by controlling the spray volume of the GO solution. To illustrate the feasibility of the AgNWs/GO hybrid FTCE, we fabricated flexible TFHs, flexible electroluminescent (EL) devices, and an antibacterial facial mask. Successful operation of the flexible TFH and EL devices and antibacterial facial mask indicates that the AgNWs/GO hybrid electrode is a promising substitute for ITO electrodes and solves the critical problems associated with both AgNWs and GO nanosheets.

2. Experimental procedures

2.1. Spray coating of AgNWs/GO hybrid FTCEs

As shown in Figure 1(a,b), the hybrid FTCE electrode was fabricated by spraying a AgNWs solution (length, 25 μm; diameter, 25 nm; Flexio Co. Ltd) and a GO nanosheet solution (multilayer, Sigma-Aldrich) onto a substrate (1.5 × 1.5 cm²) placed on a rotating platform using a lab-designed airbrush coating system (PS-289, Mr.HOBBY). The AgNWs solution, consisting of 0.125 wt% AgNWs, was dispersed in an isopropyl alcohol solvent and then spray coated onto the substrate. The substrate was allowed to dry at 70°C for 5 minutes on a hot plate. This AgNWs coating process was repeated 3 times. Then, the GO solution was developed by dispersing 0.1 wt% GO in an isopropyl alcohol solvent in a sonicator for 60 minutes. GO solution was spray coated on top of the AgNWs-coated substrate as same spraying condition with AgNWs solution, which was then dried on the hot plate for 5 minutes at 70°C. The transmittance of the optimized AgNWs/GO hybrid FTCE was measured using a UV-vis spectrometer (V-670, Jasco) and the sheet resistance was measured through the four-point probe method (FPF-HS 8, DASOLENG Co. Ltd). The surface morphology and roughness of the optimized FTCEs was analyzed using field emission secondary electron microscopy (FE-SEM; JSM-7600 F, JEOL) and atomic force microscopy (AFM; Nanowizard Ultra Speed, JPK). A micro-Raman spectrometer system (Witec, Alpha 300 M+) was used to analyze the structure of the AgNWs/GO FTCE and confirm the presence of GO.

2.2. Fabrication of flexible and transparent TFHs

The optimized AgNWs/GO hybrid FTCE was used as an electrode for a TFH device. On the spray coated AgNWs/GO hybrid FTCE, an Ag interconnector was sputtered to lower the contact resistance when a direct current (DC) voltage was applied to the electrode. To compare the performance of TFHs with an AgNWs/GO hybrid electrode vs. bare AgNWs electrode, a reference TFH using AgNWs was fabricated under
2.3. Fabrication of flexible EL devices

An EL prepolymer was prepared by mixing ZnS:Cu phosphors (blue color, GG 65) and liquid polydimethylsiloxane in a ratio of 2:1. The flexible EL device was fabricated by spin coating the EL prepolymer on the AgNWs/GO FTCE as the bottom electrode, and contacting another AgNWs/GO FTCE as the top electrode on the EL layer. The fabricated EL device was cured in an oven at 80°C for 1.5 hours. As a reference sample, an EL device with the same structure was fabricated using a single AgNWs electrode. Alternating current (AC) voltage was applied to each sample using a function generator connected to a power amplifier. The luminescence according to the applied AC voltage was measured through a spectroradiometer (CS-2000, Konica Minolta).

2.4. Fabrication of self-heating antibacterial facial mask

The optimized AgNWs/GO hybrid solution was deposited onto the outer surface of the mask to create a self-heating antibacterial mask. In order to check the heat generation characteristics of the fabricated mask, a sample was prepared by attaching Cu tape on both sides of a mask coated with AgNWs/GO hybrid nanoparticles on its outer surface. Then, DC voltage was applied to both sides and the successful operation of the self-heating antibacterial facial mask was visually confirmed through the IR camera. Antibacterial tests were conducted to assess the antibacterial properties of the AgNWs. The KSK 0693 test kit was used to test the self-heating antibacterial mask. Using the kit, the same number of Staphylococcus aureus and Klebsiella pneumonia microbes were incubated with both the normal mask and the antibacterial mask for 18 hours at 37°C.

3. Results and discussion

Figure 2(a,b) show schematic diagrams of the AgNWs TCE fabrication process and the structure of the manufactured AgNWs TCE. In general, important parameters which have been extensively studied for spray coating using an airbrush are nozzle-to-substrate distance, compressor pressure, spray speed, substrate temperature, nozzle diameter and concentration of solution [60–62]. However, the spray speed of the solute is determined by solution concentration and nozzle diameter [63]. Accordingly, the spray speed was accurately controlled by calculating the amount of solution sprayed per unit time by finely adjusting the nozzle valve at a constant solution concentration. Therefore, the electrical and optical properties of AgNWs TCEs were optimized by nozzle-to-substrate distance, compressor pressure, spray speed and substrate temperature. In particular, substrate temperature was applied at a low temperature of 70°C between processes to ensure that the solvent was evaporated without causing...
deformation to the flexible polymer substrate. In consequence, the AgNWs TCE was optimized through measurement of the transmittance, sheet resistance, and figure of merit (FoM) values according to changes in the nozzle-to-substrate distance, spray speed, and compressor pressure, which have a major effect on the reproducibility and properties of the electrode. The FoM is defined by the equation below. The higher the FoM value, the better the performance of the TCE [64].

\[
FoM = 10^3 \frac{T_{av}^{10}}{R_s}
\]  (1)
Here, $T_{av}$ is average transmittance and $R_s$ is sheet resistance. In the process of optimizing the nozzle-to-substrate distance, the spray speed was fixed at 0.10 ml/s and the compressor pressure was fixed at 0.20 MPa. As shown in Figure 2(c) and Table 1, the AgNWs TCE created with a spray nozzle-to-substrate distance of 18.0 cm showed high conductivity and optical transmittance. When the spraying distance is too short, the solution cannot be spread sufficiently and the transmittance decreases due to excessive solution deposition. Conversely, when the spraying distance is too long, the solution spreads well, but the amount of solution that ends up coated on the substrate decreases in comparison to the amount of sprayed solution. So, when the distance between the sample and the nozzle was 18.0 cm, the highest FoM value was obtained due to the high optical transmittance and low sheet resistance. Figure 2(d) and Table 2 show the electrical and optical properties of the spray coated AgNWs TCE according to spraying speed when the nozzle-to-substrate distance and compressor pressure were fixed at 18.0 cm and 0.20 MPa. The spray speed is determined by the amount of a solution sprayed per unit time at a constant air pressure. Sufficient time is required for the solvent to evaporate. Thus, it is essential to control the spray speed in order to find a compromise between the process efficiency that can be obtained by spraying the solution quickly and the quality of the electrode that can be obtained by spraying slowly so that the solvent can evaporate enough. When the spraying speed of the solution is too fast (above 0.10 ml/s), droplets form before the solution dries. As a consequence, solute does not spread uniformly and aggregates, causing a decrease in transmittance. When the spraying speed decreased to 0.05 ml/s, since the solvent had enough time to evaporate, creation of a uniform coating was possible without agglomeration of solution on the substrate, so both transmittance and sheet resistance improved. Even when the spraying speed decreased to 0.03 ml/s, there was no significant change in electrical and optical properties. Thus, the appropriate spraying speed was determined to be 0.05 ml/s in consideration of the efficiency of the process. During the optimization of the compressor pressure, the nozzle-to-substrate distance and the spray speed were fixed at 18.0 cm and 0.05 ml/s. As shown in Figure 2(e) and Table 3, with low compressor pressure, the kinetic energy of the sprayed solution is insufficient, making it difficult to form a uniform AgNWs network. Therefore, the AgNWs TCE showed high sheet resistance. Conversely, when the pressure of the compressor is too high, the solution on the substrate is blown out and the sheet resistance increases. So, when the spray coating was applied with a compressor pressure of 0.20 MPa, the resulting AgNWs TCE showed the highest FoM value. Based on three important spraying parameters, the optimum spraying conditions were determined to be: a compressor pressure of 0.20 MPa, spraying speed of 0.05 ml/s and spraying distance of 18.0 cm.

After optimization of the AgNW network, the GO nanosheet was sprayed on the AgNW network electrode. Schematic illustrations of the AgNWs/GO FTCE fabrication process and structure are shown in Figure 3 (a–c) and Table 4 exhibit the electrical and optical properties according to the amount of GO solution sprayed onto the optimized AgNWs electrode. In the optimal coating process for the AgNWs TCE, the nozzle-to-substrate distance, spray speed, and compressor pressure were adjusted to avoid agglomeration of the solution and improve uniformity. Because both the GO solution and the AgNWs solution have similarly low solute concentrations and the same isopropanol solvent, there is no significant difference in viscosity or volatility (see supplementary materials 1). Through the FE-SEM analysis (Figure S1), it was confirmed that GO was uniformly deposited without non-uniform parts due to droplet formation when the GO solution was sprayed under the same conditions as the optimal AgNWs TCE spraying conditions. Subsequently, to control only the amount of GO deposited to reach the optimum FoM value while the parameters that ensure

### Table 1. Electrical and optical properties of the AgNWs TCE according to nozzle-to-substrate distance.

| Distance [cm] | Average transmittance [%] | Transmittance at 550 nm [%] | Sheet resistance [Ohm/square] | FoM $[10^{-9} \text{Ω}^{-1}]$ |
|--------------|---------------------------|----------------------------|-------------------------------|--------------------------------|
| 15.0         | 66                        | 69                         | 7                             | 2.2                            |
| 16.5         | 73                        | 76                         | 10                            | 4.2                            |
| 18.0         | 79                        | 81                         | 16                            | 5.7                            |
| 19.5         | 85                        | 93                         | 51                            | 3.8                            |
| 21.0         | 92                        | 93                         | 236                           | 1.8                            |

### Table 2. Electrical and optical properties of the AgNWs TCE according to spraying speed.

| Speed [ml/s] | Average transmittance [%] | Transmittance at 550 nm [%] | Sheet resistance [Ohm/square] | FoM $[10^{-9} \text{Ω}^{-1}]$ |
|--------------|---------------------------|----------------------------|-------------------------------|--------------------------------|
| 0.10         | 79                        | 81                         | 15                            | 5.9                            |
| 0.07         | 80                        | 82                         | 14                            | 7.6                            |
| 0.05         | 81                        | 83                         | 14                            | 9.2                            |
| 0.04         | 81                        | 83                         | 14                            | 9.2                            |
| 0.03         | 81                        | 83                         | 14                            | 9.2                            |

### Table 3. Electrical and optical properties of the AgNWs TCE according to compressor pressure.

| Pressure [MPa] | Average transmittance [%] | Transmittance at 550 nm [%] | Sheet resistance [Ohm/square] | FoM $[10^{-9} \text{Ω}^{-1}]$ |
|---------------|---------------------------|----------------------------|-------------------------------|--------------------------------|
| 0.15          | 90                        | 91                         | 53                            | 6.2                            |
| 0.18          | 89                        | 92                         | 53                            | 8.1                            |
| 0.20          | 90                        | 91                         | 35                            | 9.5                            |
| 0.23          | 90                        | 91                         | 43                            | 8.2                            |
| 0.25          | 91                        | 92                         | 76                            | 5.0                            |
uniformity are fixed, the volume of the GO solution was adjusted as a new parameter. Notably, the sheet resistance decreased slightly when the GO solution was sprayed on the AgNWs electrode. In particular, when 1.0 ml of GO solution was sprayed, the AgNWs/GO hybrid electrode showed a sheet resistance of 20 Ohm/square and optical transmittance of 86%, which could make it applicable to flexible TFHs and EL devices. When more GO solution was sprayed, the sheet resistance decreased very slightly, but the transmittance further decreased, so the FoM rapidly decreased. Therefore, the optimal AgNWs/GO hybrid FTCE was produced by spraying of 1.0 ml of GO solution.

To demonstrate the flexibility of the AgNWs/GO FTCE, we measured the change in resistance as the bending radius decreased. Figure 4(a) shows the change in resistance during the inner and outer bending test for the AgNWs/GO FTCE. In general, application of tensile stress (outer bending) to an FTCE causes a greater change in resistance than application of compressive stress (inner bending) [65]. However, the AgNWs/GO FTCE showed no difference in resistance regardless of the bending mode (inner vs. outer bending). Even at an inner and outer bending radius of 2 mm, the AgNWs/GO FTCE shows no resistance change, indicating excellent flexibility. Due to the limits of our bending test system, a further decrease in the inner bending radius of the AgNWs/GO FTCE was not possible. Figure 4(b) shows the dynamic bending test results for the AgNWs/GO FTCE. At a fixed bending radius of 3 mm, the AgNWs/GO FTCEs were subjected to 10,000 cycles of inner and outer bending. Following repeated inner and outer bending, we observed no change in resistance due to the outstanding flexibility of the AgNWs/GO FTCEs. Based on the results of the mechanical tests, the AgNWs/GO FTCE has sufficient mechanical flexibility for applications in flexible electronics without degrading the mechanical properties of AgNWs TCE (Figure S2).

Figure 5(a,c) and Figure S1 show surface FE-SEM images of AgNWs and the optimized AgNWs/GO FTCE. In the case of bare AgNWs, the FE-SEM image showed a percolating AgNW network structure, as in previous reports [66–68]. The randomly percolating network provides a conduction path for current. Figure 5(b) illustrates the small contact region between

![Figure 3](image-url)

Figure 3. (a) Schematic diagram of spray coating of GO solution on AgNWs and (b) structure of the AgNWs/GO FTCE. (c) Transmittance according to the volume of sprayed GO solution and FoM values calculated from the average transmittance and sheet resistance.

| GO [ml] | Average transmittance [%] | Transmittance at 550 nm [%] | Sheet resistance [Ohm/square] | FoM [10⁻³Ω⁻¹] |
|--------|--------------------------|----------------------------|-----------------------------|---------------|
| 0      | 91                       | 92                        | 42                          | 9.8           |
| 0.2    | 91                       | 92                        | 38                          | 9.9           |
| 0.4    | 90                       | 91                        | 35                          | 10.1          |
| 0.6    | 90                       | 91                        | 34                          | 10.4          |
| 0.8    | 89                       | 90                        | 30                          | 11.0          |
| 1.0    | 86                       | 88                        | 20                          | 11.4          |
| 1.2    | 82                       | 84                        | 15                          | 8.8           |
AgNWs. However, in the case of the AgNWs/GO hybrid electrode, GO covered the AgNWs network and acted as a conductive bridge between AgNWs. As illustrated in Figure 5(d), the GO layer helps to decrease the high contact resistance caused by the small contact area of AgNWs by covering the disconnected part of the network, thus enhancing the electrical conductivity. In addition, there is excessive deposition of the relatively low-conductivity GO layer, the excess results in a loss of optical transmittance.

Figure 5(e,f) and show the peak shifts of Raman spectra of the bare GO and optimized AgNWs/GO FTCE. Both samples showed clear D, G, and 2D peaks, indicating the presence of GO on AgNW network. D peak is a peak activated by a structural defect in GO. The G peak is a peak generated by the first order double-generated scattering process due to the $E_{2g}$ symmetry of the $sp^2$ carbon lattice. The 2D peak is a peak arisen by the second-order phonon mode between two in-plane transverse optical phonons \[57,69-71\]. Studies on the interaction of Raman effect occurring in the hybrid system of silver nanostructures and graphene have been extensively reported \[72-74\], and AgNWs are known to have more influence on mechanical strain than charge transfer to graphene \[75\]. Unlike graphene deposited on a flat substrate, the graphene deposited on a rough surface such as Ag NWs network suffers tensile stress by the curvature of AgNWs. As shown in graphs, when GO was deposited on AgNWs, the D and G bands redshifted by 20 and 24 cm\(^{-1}\). Especially the 2D band, which is most sensitive to the strain effect \[76\], showed a redshift of 32 cm\(^{-1}\). The shift rate of the Raman D, G, 2D band position ($\omega_p$) with strain ($\epsilon$) applied to graphene can be expressed by the following two equations \[76,77\].

\[
\Delta \omega_p = -\gamma_p^{uax} \omega_p^0 (1 - v)\epsilon 
\]

\[
\gamma_p^{uax} \text{ represents the Grüneisen parameter under uniaxial strain for each Raman band, and } \omega_p^0 \text{ is the Raman band position at zero strain, which are all positive value. } v \text{ is the Poisson’s ratio of the substrate. } \omega_{G^-} \text{ and } \omega_{G^+} \text{ were not considered because the uniaxial strain caused by the AgNWs was not high enough to separate the G peak into G$^-$ and G$^+$ peak [77].} 
\]

\[
\Delta \omega_p = -\gamma_p^{bax} \omega_p^0 (\epsilon_l + \epsilon_t) 
\] (3)

In terms of the TCE of AgNWs/GO FTCE, the measured TCE is \[-0.1\% K^{-1}\] at 20 °C. This indicates that AgNWs/GO FTCE has a low planar anisotropy. The high TCE of AgNWs/GO FTCE is attributed to the pure AgNWs side, which is highly conductive and less affected by the anisotropy of the GO layer. In addition, the sheet resistance of AgNWs/GO FTCE was 7.6 Ω\(\text{sq}^{-1}\) at 20 °C, indicating the potential for using AgNWs/GO FTCE as a TCE material.
The TFH with the AgNWs TCE showed a saturation temperature of 111°C at a voltage of 5 V, while the TFH using AgNWs/GO TCE showed a saturation temperature of 119°C at a voltage of 5 V; based on Joule’s law, the relationship between sheet resistance of TFH ($R$) and the generated temperature ($\Delta Q_s$) can be expressed as equation

$$\Delta Q_s = \frac{V^2}{R} \Delta t = Q_{\text{conv}} = h_{\text{conv}} A_{\text{conv}} (T_s - T_i)$$

where $V$ is input voltage and $t$ is heating time; $Q_{\text{conv}}$ is heat loss due to convection in air; $h_{\text{conv}}$, $A_{\text{conv}}$, $T_s$, and $T_i$ are convective heat transfer coefficient, surface area, saturation temperature, and initial temperature, respectively [82,83]. In this experiment, the heating time and applied voltage for each TFH are the same. From this equation, it is clear that the saturation temperature of TFH is inversely proportional to the sheet resistance of TFH. Since the sheet resistance of AgNWs/GO FTCE is lower than AgNWs TCE, AgNWs/GO FTCE-based TFH showed better performance than AgNWs TCE-based TFH. Spraying of the GO solution improved the connectivity and surface morphology of the AgNWs network. Therefore, spraying of GO on AgNWs helps to improve the performance of AgNWs-based TFHs. In general, the non-

![Figure 5](https://example.com/figure5.png)

Figure 5. (a) FE-SEM image of the AgNWs TCE with (b) schematic illustration of contact area between AgNWs. (c) FE-SEM image of the AgNWs/GO FTCE with (d) schematic illustration of contact area between AgNWs under the overcoated GO nanosheet. Raman spectra of (e) GO and (f) AgNWs/GO FTCE.
uniform distribution of AgNWs in a TFH leads to Joule heating at the narrow contact area between the nanowires due to the localized current density, which results in the failure of the nanowire network. However, as shown in Figure 6(d), even in the heat stability test, which was repeated 10 times under the same conditions, the FTCE showed excellent stability without any change in heating performance. The IR image of the TFH during operation in Figure 6(e) allows for visual observation of uniform heat generation due to the excellent characteristics of the AgNWs/GO FTCE.

Figure 7(a) shows the structure of the EL devices with the AgNWs TCE and AgNWs/GO hybrid FTCE. The EL layer was coated between the top and bottom electrode and AC voltage was applied to each electrode. Figure 7(b) shows photographs of the EL devices with the AgNWs TCE and AgNWs/GO FTCE at an AC voltage of 200 V, and Figure 7(c) shows the change in luminance when 0 to 225 V was applied to each device. The relationship between AC voltage and luminance is as follows [84].

\[
L = L_0 \exp \left( -\frac{\beta}{V^2} \right)
\]

Here, \(L\) is the luminance, \(V\) is the applied voltage, and \(L_0\) and \(\beta\) are constants determined by the device. As shown in Figure 7(c), each sample shows a sharp increase in luminance as the applied voltage increases, and the EL device with the GO layer on top of the AgNWs shows higher luminance when the voltage is applied due to the higher conductivity and reduced surface roughness of the electrode.

Figure 6. (a) Schematic illustration of the structure of the AgNWs/GO FTCE-based TFH. Temperature change over time when DC voltage is applied to the TFH with (b) AgNWs TCE and (c) AgNWs/GO FTCE. (d) Thermal stability of the TFH with AgNWs/GO FTCE. (e) Photograph and IR image showing heating of the TFH with AgNWs/GO FTCE when power is applied to the electrode.
The optimized AgNWs/GO FTCE was coated on the facial mask to assess the efficiency of its antibacterial effect and demonstrate stable heat generation under application of DC voltage. Figure 8(a) shows a schematic diagram of the fabrication process and surface structure of the self-heating antibacterial mask with the optimized AgNWs/GO FTCE. The AgNWs/GO FTCE was spray coated on the surface of the mask filter. Cu tape was attached to both ends of the mask to serve as a contact electrode for application of DC voltage. Figure 8(b) and supplementary material 2 shows an IR image and video of successful heat generation by the self-heating antibacterial facial mask. Even on a curved sculpture similar to a human face, the self-heating antibacterial mask with the AgNWs/GO FTCE showed uniform heat generation over the entire mask surface. This photograph and Figure 4 demonstrate that the AgNWs/GO FTCE deposited on the mask maintains stable performance even under the bending that occurs when the mask is actually worn on the face based on its excellent mechanical and electrical properties. The mechanism for the antibacterial action of silver has not yet been clearly elucidated, though many studies have been conducted over the past 60 years in attempts to clarify this issue [85,86]. One of the most convincing potential mechanisms holds that silver ions released from the surface of silver damage the structure of membranous enzymes [87]. Several studies have addressed the change in antimicrobial activity according to the surface area of silver, which showed that nanometer-sized silver with an extremely wide surface area allows for better contact with microorganisms and thus excellent antibacterial activity [88–90]. AgNWs, which have nanometer-sized wires, also have very large surface areas. An antibacterial test was conducted to assess whether the excellent antibacterial activity of AgNWs was maintained even in the mask with the AgNWs/GO FTCE coating on its surface. Figure 8(c,d) shows the results of the antibacterial test for a self-heating antibacterial mask, which was conducted using the KSK 0693 kit. This test method measures the number of bacteria that remain after 18 hours following inoculation of antibacterial fibers and ordinary fibers with the same number of bacteria. Figure 8(c) shows the number of Staphylococcus aureus microbes that remained 18 hours after 7.2 × 10⁴ bacteria were applied to a mask coated with the AgNWs/GO FTCE and an uncoated mask. After 18 hours, the number of bacteria on the normal mask increased to 3.7 × 10⁵, while the number of bacteria on the antibacterial mask decreased to 1.2 × 10³. These data indicate that the self-heating antibacterial mask has good antibacterial properties, as it was associated with a bacteriostatic reduction rate of 99.7 according to the following equation.
Here, $R_{bac}$ indicates a bacteriostatic reduction rate. $N_{nor}$ indicates the number of viable bacteria after 18 hours on the normal mask and $N_{ant}$ indicates the number of viable bacteria after 18 hours on the antibacterial mask. Similarly, Figure 8(d) shows the number of bacteria remaining on each mask after an 18-hour incubation with $1.3 \times 10^5$ Klebsiella pneumonia bacterial cells. After 18 hours, the normal mask showed $8.8 \times 10^5$ bacteria, while the antibacterial mask showed just $2.3 \times 10^3$, for a bacteriostatic reduction rate of 99.7%. The results of the antibacterial tests using both bacteria indicate that the self-heating antibacterial mask exhibits excellent antibacterial activity. The optimized AgNWs/GO FTCE retained the benefits of the large nano-silver particle surface area when spray-coated on the mask due to its excellent uniformity. Furthermore, the mechanism of microbial inactivation of Ag is also highly correlated with temperature [91]. This self-heating antibacterial mask, which combines stable heat generation performance and good antibacterial activity, not only exhibits strong antibacterial power, but also allows hygienic reuse by effectively removing moisture and bacteria adsorbed on the mask through heat.

### 4. Conclusion

In order to fabricate a high-performance cost-effective FTCE, a AgNWs/GO hybrid film deposited through a simple spray coating process was applied to flexible devices to show the feasibility of the AgNWs/GO electrode. The AgNWs/GO electrode was optimized by controlling the distance, spray speed, compressor pressure and spraying volume of GO solution. In the optimized AgNWs/GO FTCE, GO improved the surface roughness of the AgNW network and widened the contact area between AgNWs. The optimized AgNWs/GO FTCE showed a high transmittance of 88% at a wavelength of 550 nm and a low sheet resistance of 20 Ohm/square. The flexible TFH with the AgNWs/GO FTCE showed a stable saturation temperature of 119°C when a DC voltage of 5 V was applied; its performance was superior to that of a TFH with a single AgNWs TCE. The flexible EL device with AgNWs/GO FTCE showed better luminance than the EL device with a single AgNWs TCE when the same AC voltage was applied. The facial mask sprayed with the AgNWs/GO FTCE showed stable heat generation based on the excellent flexibility, conductivity, and uniformity of the electrode and showed a bacteriostatic reduction rate of 99.7% against both Staphylococcus aureus and Klebsiella pneumonia. Based on the excellent
electrical, optical, and mechanical properties of the AgNWs/GO FTCE and the successful operation of TFH and EL devices, this study confirmed that the AgNWs/GO hybrid electrode is a promising substitute for conventional ITO electrodes in FTCEs.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

**Funding**

This work was supported by the Ministry of Education, Korea [2019R1A6C1010031]; Ministry of Trade, Industry and Energy [20004934].

**ORCID**

Han-Ki Kim [http://orcid.org/0000-0003-4650-6245](http://orcid.org/0000-0003-4650-6245)

**References**

[1] Liu H, Avrutin V, Izumskaya N, et al. Transparent conducting oxides for electrode applications in light emitting and absorbing devices. Superlattices Microstruct. 2010;48:458–484.

[2] López-Naranjo EJ, González-Ortiz LJ, Apáñiga LM, et al. Transparent electrodes: a review of the use of carbon-based nanomaterials. J Nanomater. 2016;2016. DOI:10.1155/2016/4928365.

[3] Cao W, Li J, Chen H, et al. Transparent electrodes for organic optoelectronic devices: a review. J Photonics Energy. 2014;4:040990.

[4] Hwang I, Seong M, Yi H, et al. Low-resistant electrical and robust mechanical contacts of self-attachable flexible transparent electrodes with patterned circuits. Adv Funct Mater. 2020;30:1–12.

[5] Wang J, Zhang Z, Wang S, et al. Superstable copper nanowire network electrodes by single-crystal graphene covering and their applications in flexible nanogenerator and light-emitting diode. Nano Energy. 2020;71:104638.

[6] Zhang Z, Xia L, Liu L, et al. Ultra-smooth and robust graphene-based hybrid anode for high-performance flexible organic light-emitting diodes. J Mater Chem C. 2021;9(6):2106–2114.

[7] Kim DJ, Shin HJ, Ko EH, et al. Roll-to-roll slot-die coating of 400 mm wide, flexible, transparent Ag nanowire films for flexible touch screen panels. Sci Rep. 2016;6;1–12.

[8] Kim DJ, Kim HJ, Seo KW, et al. Indium-free, highly transparent, flexible Cu2O/Cu/Cu2O mesh electrodes for flexible touch screen panels. Sci Rep. 2015;5:1–10.

[9] Shin YH, Cho CK, Kim HK. Resistance and transparency tunable Ag-inserted transparent In2ZnO films for capacitive touch screen panels. Thin Solid Films. 2013;548:641–645.

[10] Park JH, Seok HJ, Kamaraj E, et al. Highly transparent and flexible Ag nanowire-embedded silk fibroin electrodes for biocompatible flexible and transparent heater. RSC Adv. 2020;10:31856–31862.

[11] Choi S, Han SI, Jung D, et al. Highly conductive, stretchable and biocompatible Ag–Au core–sheath nanowire composite for wearable and implantable bioelectronics. Nat Nanotechnol. 2018;13:1048–1056.

[12] Choi DH, Seok HJ, Kim DH, et al. Thermally evaporated C60/Ag/C60 multilayer electrodes for semi-transparent perovskite photovoltaics and thin film heaters. Sci Technol Adv Mater. 2020;21:435–449.

[13] Lim SH, Kim HK. Deposition rate effect on optical and electrical properties of thermally evaporated WO3–x/Ag/WO3–x multilayer electrode for transparent and flexible thin film heaters. Sci Rep. 2020;10:1–13.

[14] Lee JE, Kim HK. Self-cleaning, waterproof, transparent, and flexible Ag networks covered by hydrophobic polytetrafluoroethylene for multi-functional flexible thin film heaters. Sci Rep. 2019;9:1–11.

[15] Seok HJ, Jang HW, Lee DY, et al. Roll-to-roll sputtered, indium-free ZnSnO/AgPdCu/ZnSnO multi-stacked electrodes for high performance flexible thin-film heaters and heat-shielding films. J Alloys Compd. 2019;775:853–864.

[16] Park JY, Kim HK. Flexible metal oxide/metal/metal transparent electrodes made of thermally evaporated MoO3/Ag/MoO3 for thin film heaters. Phys Status Solidi Appl Mater Sci. 2018;215:1–4.

[17] Khachatryan H, Kim DJ, Kim M, et al. Roll-to-Roll fabrication of ITO thin film for flexible optoelectronics applications: the role of post-annealing. Mater Sci Semicond Process. 2018;88:51–56.

[18] Raman V, Jo J, Kim HK. ITO and graphene-covered Ag grids embedded in PET substrate by thermal roll imprinting for flexible organic solar cells. Mater Sci Semicond Process. 2020;120:105277.

[19] Yoon S, Kim YJ, Lee YR, et al. Highly stretchable metal-polymer hybrid conductors for wearable and self-cleaning sensors. NPG Asia Mater. 2021;13. DOI:10.1038/s41427-020-00277-6.

[20] Yoon S, Sim HM, Cho S, et al. Highly stretchable, conductive polymer electrodes with a mixed AgPdCu and PTFE network interlayer for stretchable electronics. Adv Mater Interfaces. 2020;2001500:1–11.

[21] Ko KJ, Lee HB, Kang JW. Flexible, wearable organic light-emitting fibers based on PEDOT:PSS/Ag-fiber embedded hybrid electrodes for large-area textile lighting. Adv Mater Technol. 2020;5:1–8.

[22] Jin W, Ovhal MM, Lee H, et al. Scalable, all-printed photocapacitor fibers and modules based on metal-embedded flexible transparent conductive electrodes for self-charging wearable applications. Adv Energy Mater. 2021;2003509:1–10.

[23] Lim Y, Jin J, Bae B. Optically transparent multiscale composite films for flexible and wearable electronics. Adv Energy Mater. 2020;1907143:1–15.

[24] Choi KH, Kim HK. Effect of Ar Ion beam pre-treatment of poly(ethylene terephthalate) substrate on the mechanical and electrical stability of flexible InSnO films grown by roll-to-roll sputtering system. Jpn J Appl Phys. 2013;52:10MA14.

[25] Bok S, Seok HJ, Kim YA, et al. Transparent molecular adhesive enabling mechanically stable ITO thin films. ACS Appl Mater Interfaces. 2021;13:3463–3470.

[26] Lee SM, Park JY, Kim HK, et al. Deformable, and multifunctional AgPdCu/ITO/PTFE hybrid films for self-cleaning, flexible, and energy-saving smart windows. Adv Mater Interfaces. 2018;5:1–12.
Park S, Park H, Seong S, et al. Multilayer substrate to use brittle materials in flexible electronics. Sci Rep. 2020;10:1–8.

Bi YG, Liu YF, Zhang XL, et al. Ultrathin metal films as the transparent electrode in ITO-free organic optoelectronic devices. Adv Opt Mater. 2019;7:1–23.

Huang S, Liu Y, Jafari M, et al. Highly stable Ag-Au core–shell nanowire network for ITO-free flexible organic electrochromic device. Adv Funct Mater. 2021;2010022:1–11.

Alzoubi K, Alkhazali AS, Choi G, et al. Comparisons of the thermal stability of Poly(3,4-Ethylene dioxythiophene) (PEDOT) and ITO on flexible substrates. IEEE Trans Components, Packag Manuf Technol. 2020;10:1259–1265.

Wang X, Jin H, Nagiri RCR, et al. Flexible ITO-free organic photovoltaics on ultra-thin flexible glass substrates with high efficiency and improved stability. Sol RRL. 2019;3:1–7.

Mahani FF, Mokhtari A. Enhancement of ITO-free organic solar cells utilizing plasmonic nanohole electrodes. Proceedings of the 7th International Conference of Nanotechnology; 2017 Sep 7–8; Tbilisi, Georgia.

Lahtela V, Virolainen S, Uwaoma A, et al. Novel mechanical pre-treatment methods for effective recovery from end-of-life liquid-crystal display panels. J Clean Prod. 2019;230:580–591.

Christodoulou C, Wolter B, lokeimidis A, et al. Surface analysis and surface doping of graphene on indium-tin-oxide. Thin Solid Films. 2019;682:57–62.

Kim JH, Kang SB, Lee JH, et al. Buffer and anode-integrated WO3-doped In2O3 electrodes for PEDOT:PSS-free organic photovoltaics. Org Electron. 2013;14:1305–1312.

Lee JH, Shin HS, Noh YJ, et al. Brush painting of transparent PEDOT/Ag nanowire/PEDOT multilayer electrodes for flexible organic solar cells. Sol Energy Mater Sol Cells. 2013;114:15–23.

Seo HJ, Lee JE, Heo SB, et al. P-type Sn-doped Cu2O hole injection layer integrated on transparent ITO electrode for acidic PEDOT:PSS-free quantum dot light emitting diodes. Phys Status Solidi Appl Mater Sci. 2019;216:1–8.

Cho DY, Eun K, Choa SH, et al. Highly flexible and stretchable carbon nanotube network electrodes prepared by simple brush painting for cost-effective flexible organic solar cells. Carbon N Y. 2014;66:530–538.

Mclean B, Kauppinen EL, Page AJ. Initial competing chemical pathways during floating catalyst chemical vapor deposition carbon nanotube growth. J Appl Phys. 2021;129. DOI:10.1063/5.0030814

Seo K-W, Lee J-H, Cho NG, et al. Simple brush painted Ag nanowire network on graphene sheets for flexible organic solar cells. J Vac Sci Technol A Vacuum, Surfaces, Films. 2014;32:061201.

Jung YU, Oh SI, Cho SH, et al. Electromechanical properties of graphene transparent conducting films for flexible electronics. Curr Appl Phys. 2013;13:1331–1334.

Lan S, Shin HI, Kim HK. Electrically stable Ag nanowire network anodes densely passivated by a conductive amorphous InSn2TiO layer for flexible organic photovoltaics. Appl Phys Lett. 2020;117:73–8.

Im HG, Jeong S, Jin J, et al. Hybrid crystalline-ITO/metal nanowire mesh transparent electrodes and their application for highly flexible perovskite solar cells. NPG Asia Mater. 2018;10:e282–e282.

Kim DJ, Hwang DY, Park JY, et al. Liquid crystal-Based flexible smart windows on roll-to-roll slot die–Coated Ag nanowire network films. J Alloys Compd. 2018;765:1090–1098.

Lee SM, Kim SH, Lee JH, et al. Hydrophobic and stretchable Ag nanowire network electrode passivated by a sputtered PTFE layer for self-cleaning transparent thin film heaters. RSC Adv. 2018;8:18508–18518.

Lim JE, Lee SM, Kim SS, et al. Brush-paintable and highly stretchable Ag nanowire and PEDOT:PSS hybrid electrodes. Sci Rep. 2017;7:1–12.

Kim HK, Chung KB, Kal J. Comparison of ZnO buffer layers prepared by spin coating or RF magnetron sputtering for application in inverted organic solar cells. J Alloys Compd. 2019;778:487–495.

Kim SK, Seok HJ, Kim DH, et al. Comparison of NiO:x thin film deposited by spin-coating or thermal evaporation for application as a hole transport layer of perovskite solar cells. RSC Adv. 2020;10:43847–43852.

Hwang BY, Choi SH, Lee KW, et al. Highly stretchable and transparent electrode film based on SWCNT/Silver nanowire hybrid nanocomposite. Compos Part B Eng. 2018;151:1–7.

Wang BY, Lee ES, Lim DS, et al. Roll-to-roll slot die production of 300 mm large area silver nanowire mesh films for flexible transparent electrodes. RSC Adv. 2017;7:7540–7546.

Kim YJ, Kim G, Kim HK. Study of brush-painted Ag nanowire network on flexible invar metal substrate for curved thin film heater. Metals (Basel). 2019;9:1073.

Lin S, Wang H, Zhang X, et al. Direct spray-coating of highly robust and transparent Ag nanowires for energy saving windows. Nano Energy. 2019;62:111–116.

Du X, Skachko I, Barker A, et al. Approaching ballistic transport in suspended graphene. Nat Nanotechnol. 2008;3:491–495.

Jiang JW, Wang JS, Li B. Young’s modulus of graphene: a molecular dynamics study. Phys Rev B - Condens Matter Mater Phys. 2009;80:15–18.

Vlassiouk I, Regmi M, Fulvio P, et al. Role of hydrogen in chemical vapor deposition growth of large single-crystal graphene. ACS Nano. 2011;5:6069–6076.

Marcano DC, Kosynkin DV, Berlin JM, et al. Improved synthesis of graphene oxide. ACS Nano. 2010;4:4806–4814.

Moon IK, JI K, Lee H, et al. 2D graphene oxide nanosheets as an adhesive over-coating layer for flexible transparent conductive electrodes. Sci Rep. 2013;3:1–7.

Woo JS, Lee GW, Park SY, et al. Realization of transparent conducting networks with high uniformity by spray deposition on flexible substrates. Thin Solid Films. 2017;638:367–374.

Park SY, Kang YJ, Lee S, et al. Spray-coated organic solar cells with large-area of 12.25 cm². Sol Energy Mater Sol Cells. 2011;95:852–855.

Aziz F, Ismail AF. Spray coating methods for polymer solar cells fabrication: a review. Mater Sci Semicond Process. 2015;39:416–425.
[61] Madaria AR, Kumar A, Zhou C. Large scale, highly conductive and patterned transparent films of silver nanowires on arbitrary substrates and their application in touch screens. Nanotechnology. 2011;22:245201.

[62] Susanna G, Salamandra I, Brown TM, et al. Airbrush spray-coating of polymer bulk-heterojunction solar cells. Sol Energy Mater Sol Cells. 2011;95:1775–1778.

[63] Walker CE, Xia Z, Foster ZS, et al. Investigation of airbrushing for fabricating microelectrodes in micro-fluidic devices. Electroanalysis. 2008;20:663–670.

[64] Haacke G. New figure of merit for transparent conductors. J Appl Phys. 1976;47:4086–4089.

[65] Cho KS, Kim HK. Transparent and flexible Sb-doped SnO2 films with a nanoscale AgTi alloyed interlayer for heat generation and shielding applications. RSC Adv. 2018;8:2599–2609.

[66] Kim D-H, Ko E-H, Kim K-H, et al. Transparent and flexible ag nanowire network covered by a thin ITO layer for flexible organic light emitting diodes. ECS J Solid State Sci Technol. 2016;5:S124–8.

[67] Seo KW, Kim HK. Plasma damage free sputtering of Ti-doped In2O3 film on Ag nanowire network for transparent and flexible electrodes. Thin Solid Films. 2015;591:301–304.

[68] Jeong JA, Kim HK. Ag nanowire percolating network embedded in indium tin oxide nanoparticles for printable transparent conducting electrodes. Appl Phys Lett. 2014;104:071906.

[69] Sahoo S, Khurana G, Barik SK, et al. In situ Raman studies of electrically reduced graphene oxide and its field-emission properties. J Phys Chem C. 2013;117:5485–5491.

[70] Jaworski S, Wierzbicki M, Sawosz E, et al. Graphene oxide-based nanocomposites decorated with silver nanoparticles as an antibacterial agent. Nanoscale Res Lett. 2018;13:116.

[71] Rahman MT, Kabir MF, Gurung A, et al. Graphene oxide-silver nanowire nanocomposites for enhanced sensing of Hg2+. ACS Appl Nano Mater. 2019;2:4842–4851.

[72] Wu T, Shen H, Sun L, et al. Facile synthesis of Ag interlayer doped graphene by chemical vapor deposition using polystyrene as solid carbon source. ACS Appl Mater Interfaces. 2012;4:2041–2047.

[73] Gong T, Zhang J, Zhu Y, et al. Optical properties and surface-enhanced Raman scattering of hybrid structures with Ag nanoparticles and graphene. Carbon. 2016;102:245–254.

[74] HBin S, Fu C, Xia YJ, et al. Enhanced Raman scattering of graphene by silver nanoparticles with different densities and locations. Mater Res Express. 2017;4:025012.

[75] Lee F, Tripathi M, Lynch P, et al. Configurational effects on strain and doping at graphene-silver nano-wire interfaces. Appl Sci. 2020;10:5157.

[76] Ferralis N. Probing mechanical properties of graphene with Raman spectroscopy. J Mater Sci. 2010;45:5135–5149.

[77] Mohiuddin TMG, Lombardo A, Nair RR, et al. Uniaxial strain in graphene by Raman spectroscopy; g peak splitting, Grüneisen parameters, and sample orientation. Phys Rev B - Condens Matter Mater Phys. 2009;79:1–8.

[78] Li Z, Young RJ, Wilson NR, et al. Effect of the orientation of graphene-based nanoflakes upon the Young’s modulus of nanocomposites. Compos Sci Technol. 2016;123:125–133.

[79] Lee JE, Ahn G, Shim J, et al. Optical separation of mechanical strain from charge doping in graphene. Nat Commun. 2012;3:1024.

[80] Li Z, Kinloch IA, Young RJ. The role of interlayer adhesion in graphene oxide upon its reinforcement of nanocomposites. Philos Trans R Soc A Math Phys Eng Sci. 2016;374:20150283.

[81] Papanastasiou DT, Schultheiss A, Muñoz-Rojas D, et al. Transparent heaters: a review. Adv Funct Mater. 2020;30:1–33.

[82] Bae JJ, Lim SC, Han GH, et al. Heat dissipation of transparent graphene defoggers. Adv Funct Mater. 2012;22:4819–4826.

[83] Ko EH, Kim HJ, Lee SJ, et al. Nano-sized Ag inserted into ITO films prepared by continuous roll-to-roll sputtering for high-performance, flexible, transparent film heaters. RSC Adv. 2016;6:46634–46642.

[84] Alfrey GF, Taylor JB. Electroluminescence in single crystals of zinc sulphide. Proc Phys. Soc Sect B. 1955;68:775–784.

[85] Franke S, Grass G, Nies DH. The product of the ybdE gene of the Escherichia coli chromosome is involved in detoxification of silver ions. Microbiology. 2001;147:965–972.

[86] Ghandour W, Hubbard JA, Deistung J, et al. Applied microbiology biotechnology the uptake of silver ions by Escherichia coli K12: toxic effects and interaction with copper ions. Cell. 1988;28:559–565.

[87] Li WR, Xie XB, Shi QS, et al. Antibacterial activity and mechanism of silver nanoparticles on Escherichia coli. Appl Microbiol Biotechnol. 2010;85:1115–1122.

[88] Rai M, Yadav A, Gade A. Silver nanoparticles as a new generation of antimicrobials. Biotechnol Adv. 2009;27:76–83.

[89] Helmlijnger J, Sengstock C, Groß-Heitfeld C, et al. Silver nanoparticles with different size and shape: equal cytotoxicity, but different antibacterial effects. RSC Adv. 2016;6:18490–18501.

[90] Dong Y, Zhu H, Shen Y, et al. Antibacterial activity of silver nanoparticles of different particle size against Vibrio Natriegens. PLoS One. 2019;14:1–12.

[91] Feng QL, Wu J, Chen QQ, et al. A mechanistic study of the antibacterial effect of silver ions on Escherichia coli and Staphylococcus aureus. J Biomed Mater Res. 2000;52:662–668.