Silver Nanowire Embedded Colorless Polyimide Heater for Wearable Chemical Sensors: Improved Reversible Reaction Kinetics of Optically Reduced Graphene Oxide

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Optically reduced graphene oxide (ORGO) sheets are successfully integrated on silver nanowire (Ag NW)-embedded transparent and flexible substrate. As a heating element, Ag NWs are embedded in a colorless polyimide (CPI) film by covering Ag NW networks using polyamic acid and subsequent imidization. Graphene oxide dispersed aqueous solution is drop-coated on the Ag NW-embedded CPI (Ag NW-CPI) film and directly irradiated by intense pulsed light to obtain ORGO sheets. The heat generation property of Ag NW-CPI film is investigated by applying DC voltage, which demonstrates unprecedentedly reliable and stable characteristics even in dynamic bending condition. To demonstrate the potential application in wearable chemical sensors, NO₂ sensing characteristic of ORGO is investigated with respect to the different heating temperature (22.7–71.7 °C) of Ag NW-CPI film. The result reveals that the ORGO sheets exhibit high sensitivity of 2.69% with reversible response/recovery sensing properties and minimal deviation of baseline resistance of around 1% toward NO₂ molecules when the temperature of Ag NW-CPI film is 71.7 °C. This work first demonstrates the improved reversible NO₂ sensing properties of ORGO sheets on flexible and transparent Ag NW-CPI film assisted by Ag NW heating networks.

1. Introduction

Wearable electronics are getting intensive attention in recent years for real-time monitoring of external environment as well as internal state of object. [1–6] Numerous types of wearable electronics have been invented such as tactile sensor,

strain sensor, energy storage, and memory devices. [7–13] Recently, wearable chemical sensors are gaining much interest considering their potential application in real-time monitoring of environmental air quality. [14–18] Among the various sensing layers, graphene-based derivatives such as graphene oxide (GO) and reduced graphene oxide (RGO) have been regarded as potential candidate for integration with wearable electronics due to their mechanical flexibility and transparency. [19–22] For this reason, diverse processing strategies including pattern transferring or ink jet printing have been proposed to integrate graphene layers on flexible and transparent substrates. [23, 24] However, the integration of high quality GO or RGO sheets on a plastic substrate frequently accompanies very complex process or induces damage to the plastic substrate. In addition, graphene-based sensing layers have inherent irreversible sensing properties in which the baseline resistance drifts from the initial value. [25–27] The irreversible sensing characteristics were attributed to slow desorption or permanent adsorption properties of gas
molecules on graphene surface. To address the irreversible sensing properties, operating the sensor at an elevated temperature is the most effective approach by accelerating the desorption process. For example, Choi et al. demonstrated fast recovery and reversible NO₂ sensing properties assisted by graphene heater with the recovery time of around 11 s.[20] In addition, Kim et al. proposed self-heating of graphene to induce high response and reversible recovery toward NO₂ molecules by applying high voltage to the graphene sensing layer.[21] However, stable heating property as well as facile integration of graphene sensing layer should be achieved, which is the critical challenges for its commercialization as a portable sensor.

Silver nanowire (Ag NW) networks have been demonstrated as an essential component to generate heat on a plastic substrate for wearable heater application.[29–32] In previous studies, Celle et al. first investigated the flexible and transparent heater using Ag NW networks on poly(ethylene naphthalate) (PEN) substrate by heating the substrate up to ≈55 °C with the applied voltage of 7 V for application in thermochromic display.[33] In addition, Hong et al. also proposed stretchable and transparent heater using Ag NWs on polydimethylsiloxane (PDMS) substrate with stable operation at 60 °C, which can be potentially applicable in wearable electronics.[34] However, to the best of authors’ knowledge, integration of graphene-based sensing layer on Ag NW network-embedded flexible and transparent substrate, and investigation of reversible chemical sensing properties toward analyte molecules have yet been demonstrated. To achieve graphene-based chemical sensors on the flexible and transparent heating substrate, simple and robust integration method should be established with minimal complexity in fabrication process as well as negligible damage to the plastic substrate.

In this work, we propose a flexible and transparent chemical sensing platform by combining Ag NW network-embedded colorless polyimide (CPI) film as a heating substrate and optically RGO (ORGO) directly formed on the CPI film as a chemical sensing layer. To achieve Ag NW-embedded CPI (Ag NW-CPI) substrate, Ag NWs were randomly dispersed on a glass substrate using vacuum filtration and transferring methods. After screen printing of polyamic acid (PAA) solution on the Ag NW networks and subsequent imidization of PAA, highly conductive and flexible Ag NW-CPI film can be obtained. Then, very thin-layered GO sheets were coated on the Ag NW-CPI substrate by simple drop-coating of GO solution. The GO sheets were reduced by the direct exposure of optically intense pulsed light (IPL) onto the Ag NW-CPI film within a few milliseconds to minimize the damage on the CPI film as well as Ag NWs. The ORGO sheets on Ag NW-CPI heating substrate exhibited temperature dependent NO₂ sensing characteristics with high reliability and reversibility at an elevated temperature of 71.7 °C even in mechanically bending condition.

2. Result and Discussion

The fabrication process of Ag NW-CPI film was illustrated in Figure 1a. The Ag NWs were prepared by a conventional polyl synthesis method as described in the Experimental Section. (i) The Ag NW dispersed solution was filtrated using a vacuum pump on a nylon filter paper. (ii) Then, the Ag NWs were transferred on a rigid glass substrate by pressing the nylon filter paper on the glass substrate. (iii) A solution mixture of PAA comprising 4,4’-(hexafluoroisopropylidene)-diphenyl hydride (6FDA) and 3,3’-diaminodiphenyl sulfone (APS) was prepared and printed on the Ag NW distributed glass substrate using a doctor blade. (iv) After subsequent imidization process at elevated temperatures, Ag NW-CPI film was peeled off from the glass substrate, resulting in the free-standing and flexible film. The Ag NWs were successfully transferred on the top surface of CPI film because the Ag NW networks were embedded in the CPI film during the imidization. The surface and cross-sectional structures were observed using scanning electron microscopy (SEM) (Figure 1b-d). It was revealed that Ag NW networks were successfully embedded in the CPI film (Figure 1b). In addition to the embedded Ag NWs, partially extruded Ag NWs were observed on the surface of CPI film (Figure 1c). Furthermore, cross-sectional observation revealed the interconnected Ag NWs, which were embedded in the CPI film as well as extruded on the surface (Figure 1d). The unique structure of Ag NWs-CPI film can enhance stability and reliability of Ag NW-based flexible heater by encapsulating the Ag NWs in CPI film and inhibiting surface contamination. In addition, thermally robust CPI film can sustain thermal stress induced by IPL irradiation during the optical reduction process preventing thermal deformation. High optical transmittance of 89.5% at the wavelength of 550 nm was obtained using pristine CPI film without embedding Ag NWs in CPI film (Figure 1e). Only 8.6% reduction in transparency was observed even after embedding the Ag NW networks in the CPI film, exhibiting transparency of 80.9% at the same wavelength. After embedding the Ag NWs, the CPI film became highly conductive with the sheet resistances in the range of 8–11 Ω sq⁻¹.

To demonstrate the Ag NW-CPI film as a flexible heater for application in chemical sensor, heat generation property was investigated in terms of reliability and stability (Figure 2). The amount of current was measured with respect to the applied voltage when the Ag-CPI film was in flat and bending state (Figure 2a). The current was steadily increased up to 268 mA at the applied voltage of 2.2 V in the flat state. In addition, minor difference in current was observed with 249 mA at 2.2 V when the Ag-CPI film was in concave bending state with the bending angle of 30° (Supporting Information, Figure S1). The slightly decreased current at the relatively high voltage range was mainly attributed to local breakdown of Ag NW networks induced by bending stress. A heat generation property of Ag NW-CPI film in flat and bending state was investigated using an IR camera (E8, FLIR) (Figure 2b,c). In the flat state, Ag NW-CPI film exhibited heating temperature of 75.7 °C with the applied voltage at 2.2 V (Figure 2b). In the case of bending state, temperature of the film was 79.5 °C at the same applied voltage (Figure 2c). In the case of heating time, it was confirmed that 133 s was required for heating Ag NW-CPI film to 75 °C from room temperature under the applied voltage.
of 2 V (Supporting Information, Figure S2). In addition, the maximum temperature of the film was \(\approx 100 ^\circ C\) just before the breakdown of Ag NW-CPI heater. Dynamic long-term stability of the Ag NW-CPI film was investigated in a continuous operation to understand feasibility of the Ag NW-CPI film as a heater for wearable chemical sensors (Figures 2d,e). A constant voltage of 2 V was applied to Ag NW-CPI film while the current transition was monitored in real-time (Figure 2d). The current started from 222 mA just after applying 2 V to the Ag NW-CPI heater. However, first sudden drop in current was observed at 205 mA after 15 min. In addition, the current slowly decreased to 193 mA after 20 h, which later exhibited the film temperature of 85.9 \(^\circ C\). After continuous operation for 75 h, \(\approx 19\%\) reduction in current was observed with 179 mA. However, the temperature of Ag NW-CPI film was maintained at 86.2 \(^\circ C\). The current was further decreased to 162 mA after 120 h continuous operation, exhibiting slightly increased Ag NW-CPI film temperature of 90.3 \(^\circ C\). The increase in film temperature can be explained by the local breakdown of Ag NW networks during the continuous operation, thereby increasing current through the undamaged Ag NWs. The current was maintained relatively stable until 180 h. However, second sudden drop in current was observed after 190 h, which was related to the major breakdown of Ag NW networks. Then, the current was finally saturated at 30 mA after 220 h with the Ag NW-CPI film temperature of 50.3 \(^\circ C\). Dynamic current transition during the cyclic bending with the bending angle of 60\(^\circ\) was investigated by applying constant voltage of 2.3 V (Figure 2e). The current was stably maintained in the range of 208–214 mA.

Figure 1. a) Schematic illustrations of fabrication process for silver nanowire (Ag NW)-embedded colorless polyimide (Ag NW-CPI) film; (i) Ag NW filtration, (ii) Ag NW transfer on a glass substrate using a pressing machine, (iii) screen printing of PAA solution on the Ag NW dispersed glass substrate using doctor’s blade, and (iv) imidization of PAA to form Ag NW-CPI film and lift-off the Ag NW-CPI film from the glass substrate. SEM images of b) embedded Ag NW in the CPI film, b) partially extruded Ag NW on the CPI film, and d) cross-sectional observation of Ag NW-CPI film. e) Optical transmittance of bare CPI film and Ag NW-CPI film.
for ≈165 min under the continuous applied voltage and the mechanical bending stress (Supporting Information, Videos). The temperature of the Ag NW-CPI film was 76.4 and 73.5 °C after 5000 and 7000 bending cycles, respectively (Figure 2f,g). However, the current was suddenly dropped to 0.4 mA after 7200 bending cycles and the temperature was returned to 30.6 °C (Figure 2h). It was revealed that the current drop resulted from a crack induced by mechanical bending stress (red arrow) (Figure 2i). The heat generation property of Ag NW-CPI film as well as dynamic long-term stability in flat and bending state demonstrate potential feasibility of flexible and transparent heater for application as a substrate in wearable chemical sensors. In addition, the present study first demonstrated the robustness of Ag NW-based heater in terms of long-term stability and reliability in mechanical stress (Table 1).

Figure 2. a) Current–voltage relationship of Ag NW-CPI film in flat and concave bending states with bending angle of 30°. IR temperature images of Ag NW-CPI film in b) flat and c) concave bending states with the bending angle of 30°. d) Long-term stability of Ag NW-CPI film with real-time current monitoring in a continuous heating operation. e) Dynamic current monitoring of Ag NW-CPI film under applied voltage and mechanical bending stress. IR temperature images after f) 5000 bending cycles, g) 7000 bending cycles, and h) 7200 bending cycles. i) Camera image of Ag NW-CPI film after 7200 bending cycles. (Scale bar: 1 cm).
The integration of sensing layer on the Ag NW-CPI heating substrate was achieved by optical reduction process using IPL on GO sheet (Figure 3a). The intensive flash irradiation has been demonstrated as a fast and simple reduction technique to obtain RGO sheets.[36,37] In this study, a xenon lamp was used to generate visible light pulse and the light was guided through a quartz crystal. Very short and intense light pulse was irradiated to the GO sheets directly on Ag NW-CPI substrate. The current–voltage (I–V) characteristic revealed that ≈1000-fold enhanced electrical conductivity was observed with ORGO sheets after IPL irradiation (Figure 3b).

In addition, the color of GO was changed from brown to dark after IPL irradiation, which clearly reveals the optical reduction of GO sheets.[36] The in-situ observation on the electrical property of GO sheets revealed a sudden increase in electrical current during the IPL irradiation (Figure 3c). It was only 22 ms to reach the maximum current up to ≈3 mA with the constant applied voltage of 1 V. Subsequently, the current rapidly decreased and saturated at a certain value around 1.9 mA after 5 s later. The evidence of ORGO formation was confirmed by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) when it was compared with that of pristine GO sheets (Supporting Information, Figure S3). A substantial decrease in intensity of D band peak of ORGO as compared to that of pristine GO indicates the elimination of functional groups and defects in ORGO sheets.[38] In addition, high resolution XPS analysis for Cls revealed the noticeable reduction in the intensity of C=O bonding due to the reduction of GO by IPL irradiation.

To investigate the effect of IPL irradiation on Ag NW networks, the in-situ current transition was observed with respect to time during the IPL irradiation at the constant applied voltage at 1 V (Figure 3d). A sudden drop in current was observed from 32 to 23.6 mA within 20 ms. However, the current was slowly recovered to 28 mA after 4 s later. The current transitions with the different applied voltages were evaluated to understand the effect of IPL (Figure 3e). The current was decreased ≈1.8-fold from 231 mA before IPL irradiation to 128 mA after IPL irradiation at 1.8 V in flat state. The noticeable decrease in electrical current of Ag NW-CPI film was attributed to the partial disconnections of Ag NWs after IPL irradiation. In the previous studies, nanowelding between Ag NWs after optical treatment can enhance electrical conductivity, which is identically observed in our work[39] (blue circles in Figure 3f).

However, locally disconnected Ag NWs (yellow circles in Figure 3f) were formed in excessive thermal stress,[35,40] thereby leading to the reduction in electrical current. This result implies that electrical conductivity of Ag NW networks is easily affected by IPL irradiation and careful control of total energy for the reduction of GO sheets on Ag NW-CPI substrate is required to maintain consistent current of Ag NW networks after IPL treatment. Although the electrical conductivity was decreased after IPL irradiation due to the formation of disconnected Ag NWs, Ag NW-CPI film exhibited stable current transitions with respect to the applied voltages with minor current changes between flat and bending state (bending angle of 30°) (Figure 3e). In addition, Ag NW-CPI film was observed to be intact by the IPL irradiation without noticeable damage and any thermal deformation, which was attributed to the high thermal stability of CPI film.

The tunable baseline resistance of ORGO sensing layers with respect to the controlled heating using Ag NW-CPI heater was demonstrated (Figure 4). The baseline resistance was monitored in two different physical states of Ag NW-CPI substrate, i.e., flat and bending state with the bending angle of 30° (Figure 4a). The temperature modulation of Ag NW-CPI film was achieved by applying voltage in the range of 0–1.8 V to the Ag NW networks. The electrical properties of ORGO sheets on Ag NW-CPI film were affected by the applied voltage to Ag NW networks. The result revealed that step-wise decrease in resistance of ORGO sensing layer was observed while voltage was increased with 0.2 V step from 1 kΩ at 0 V to 0.68 kΩ at 1.8 V in the flat state, which reveals the effective baseline resistance modulation by Ag NW-CPI heater. On the other hand, increased baseline resistance was observed when the Ag NW-CPI film was in the bending state. The initial baseline resistance was 2 kΩ without applying voltage in bending state, which was two-fold increased baseline resistance as compared with the flat state. The baseline resistance modulation dependent on the applied voltage was achieved as well in bending state up to 1.8 V. The baseline resistance was dropped to 1.25 kΩ with the applied voltage of 1.8 V. The increased baseline resistance in the bending state as compared with the flat state was mainly attributed to the

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^4iTest under continuous heating operation.
bending stress that induces cracks on ORGO sheets (Supporting Information, Figure S4).

Gas sensing characteristics were evaluated using the ORGO sheets on Ag NW-CPI heater substrate to demonstrate improved reversible reaction toward NO$_2$ (Figure 5). The operating temperatures were controlled by applying voltages of 0, 1, and 1.8 V to maintain the temperature of Ag NW-CPI heater at 22.7 °C (room temperature),

Figure 3. a) Schematic illustration of IPL irradiation to GO sheets on Ag NW-CPI film, b) $I$–$V$ characteristic of pristine GO sheets and ORGO sheets after IPL irradiation, c) in-situ current transition of GO sheets during IPL irradiation, d) in-situ current transition of Ag NW networks in CPI film, e) current–voltage correlation of Ag NW networks, and f) SEM image of Ag NW networks after IPL irradiation.

Figure 4. a) Schematic illustrations of ORGO sensing layer integrated on Ag NW-CPI film in flat and bending states with the bending angle of 30°. b) Temperature-dependent baseline resistance modulation with different applied voltage in the range of 0–1.8 V with 0.2 V step in flat and bending states.
35.3 °C, and 71.7 °C, respectively (Figure 5a). The sensing results of ORGO sheets toward NO2 molecules in flat and bending state were presented in Figure 5b and c, respectively. The resistance changing properties of ORGO sheets in flat state were observed at room temperature in a concentration range of 5–20 ppm (Figure 5b). However, irreversible recovery processes resulted in the severe drift of baseline resistance to lower resistance value. Large deviations from the initial baseline resistance were observed with 1.6%, 2.1%, and 2.5% at room temperature toward 20 ppm of NO2. On the other hand, remarkably improved reversible reaction properties were identified with the increased voltage to Ag NW-CPI heater. In the case of applying 1 V, the deviations were in the range of 1.1%–1.3% toward 20 ppm of NO2. Further decrease in drift of baseline resistance from the initial resistance was achieved with the deviation range of 1%–1.1% with the applied voltage at 1.8 V. The reversible resistance changes to NO2 were evaluated in the concave bending state as well with the bending angle of 30° (Figure 5c). The irreversibility of baseline resistance was even severe in the bending state particularly at room temperature in which the deviation from the initial baseline resistance was observed to be 2.3%, 2.4%, and 4.1% toward 20 ppm of NO2. However, applying voltage to the Ag NW networks can induce lower deviation ranges of 1.7%–2.5% at 1 V and 1.5%–2.4% at 1.8 V toward the same NO2 concentration.

The sensitivity (\(S = \frac{[R_0 - R]}{R_0} \times 100\%\), where \(R_0\) is the initial baseline resistance and \(R\) is the resistance of the sensor in NO2 ambient) results revealed that the ORGO sensor exhibited the highest sensitivity of 2.85% at the first reaction to NO2 without applying voltage (at room temperature) in flat state (Supporting Information, Figure S5a). However, ORGO sensor at elevated temperatures with applied voltage to the Ag NW-CPI heater exhibited more reliable and stable response and recovery characteristics toward NO2. Similarly, NO2 sensing characteristics in the bending state showed the most stable response and recovery properties at elevated temperatures even though ORGO sheets exhibited the highest sensitivity of 3.8% at room temperature in the first reaction (Supporting Information, Figure S5b).

The reversibility in response and recovery processes was quantitatively analyzed based on the adsorption and desorption kinetics at different operating temperatures. In the previous studies, desorption rate constant (\(k_{des}\)), adsorption rate constant (\(k_{ads}\)), and equilibrium constant (\(K = k_{ads}/k_{des}\)) were calculated by fitting the sensitivity curves to Equations (1) and (2), as shown below

\[
S(t) = S_0 \exp[-k_{des}t]
\]

\[
S(t) = S_{max} \frac{C_a K}{1 + C_a K} \left(1 - \exp \left[- \frac{1 + C_a K}{k_{ads}} \right]\right)
\]

where \(S_0\) is the sensitivity when NO2 is removed, \(S_{max}\) is the maximum sensitivity, and \(C_a\) is the constant NO2 concentration. First, the desorption rate constants were fitted to Equation (1) to investigate recovery characteristics of ORGO sensors at different applied voltages (Supporting Information, Figure S6a–c). Particularly, the fitting curves for the desorption rate constants were focused on the initial desorption process. The results give \(k_{des} = 4.579 \times 10^{-3} \text{ s}^{-1}\) at 0 V, \(k_{des} = 5.454 \times 10^{-3} \text{ s}^{-1}\) at 1 V, and \(k_{des} = 7.731 \times 10^{-3} \text{ s}^{-1}\) at 1.8 V. ≈1.7-fold increase in desorption rate constant was
achieved with the ORGO at 1.8 V as compared with the desorption rate constant at 0 V, which implies fast and reversible recovery property of ORGO at an elevated operating temperature. Second, adsorption rate constants were calculated using Equation (2) at a constant NO2 concentration (C0) of 20 ppm (Supporting Information, Figure S6a–c). The adsorption rate constants (kads) were obtained as 4.649 × 10−2, 5.182 × 10−2, and 6.201 × 10−2 ppm−1·s−1 at applied voltages of 0, 1, and 1.8 V, respectively. In the case of adsorption rate constant, 1.3-fold higher value was observed with the applied voltage of 1.8 V than the adsorption rate constant at 0 V. Therefore, reaction process as well as recovery process was accelerated by increasing operating temperature using flexible and transparent Ag NW-CPI heater.

The sensing mechanism of the ORGO toward NO2 is discussed. In general, analyte sensing property of graphene-based materials is explained by charge transfer mechanism.[41] It has been known that graphene-based sensors exhibit p-type sensing characteristic in which the majority carrier is hole.[42] In this study, the ORGO still contains functional groups and defects even though the reduction was performed by IPL irradiation as confirmed in XPS analysis (Supporting Information, Figure S3). For this reason, hole rich p-type ORGO was maintained at the stabilization in ambient air (Stage (I) in the Supporting Information, Figure S7). The analyte NO2 molecules are oxidizing species behaving like electron acceptor (or hole donor). As a result, decreasing resistance transition occurred on ORGO sensor during the NO2 injections due to the hole injection from NO2 molecules (Stage (II) in the Supporting Information, Figure S7). Finally, excessive holes were eliminated during the injection of ambient air, which resulted in the reversible recovery of baseline resistance (Stage (III) in the Supporting Information, Figure S7).

3. Conclusion

In summary, we developed ORGO sheets on the flexible and transparent heater substrate for application in wearable chemical sensors. For the flexible and transparent heater, Ag NW networks were embedded in the CPI film. The Ag NW-CPI heater exhibited unprecedentedly high mechanical stability even in dynamic bending cycles up to 7200 times under continuous heating operation. In addition, superior long-term stability of Ag NW-CPI heater was observed in a continuous operation for 190 h. The ORGO sheets were integrated on the Ag NW-CPI heater using facile IPL irradiation on GO sheets to avoid thermal damage to CPI film. ~1000-fold enhancement in electrical conductivity was observed after IPL irradiation within 22 ms. The NO2 sensing characteristics were evaluated using ORGO sensors on Ag NW-CPI heater at different applied voltages to investigate improved reversible sensing properties with respect to the operating temperatures. The result revealed that ~1.8-fold improved reversible recovery kinetic was achieved as well as 1.3-fold enhanced reaction kinetic at an elevated operating temperature (71.7 °C) as compared with the sensors operated at room temperature. This work is the first demonstration of reversible NO2 sensing of ORGO sheets on Ag NW-network-embedded CPI film, which can pave a new way for flexible and transparent chemical sensors.

4. Experimental Section

Materials: 6FDA, APS, N,N-dimethylformamide (DMF), potassium bromide (KBr), silver chloride (AgCl), ethylene glycol (EG), silver nitrate (AgNO3), polyvinylpyrrolidone (PVP, Mn = 1300 k g·mol−1), and GO dispersed DI solution (2 mg mL−1) were purchased from Sigma-Aldrich (St. Louis, USA). All chemicals were used without further purification.

Ag NW Synthesis: Ag NWs were synthesized by the polyp method, which is described elsewhere.[40,45] Briefly, a mixture of 6.68 g of PVP, 0.1 g of KBr, and 0.5 g of AgCl was dissolved in 200 mL of EG for 1 h under stirring at 200 rpm and heated up to 170 °C. As a precursor solution for Ag NW growth, 2.2 g of AgNO3 dissolved in 5 mL of EG solution was slowly injected to the mixture solution using a syringe pump for 1 h. After the reaction was complete, the obtained Ag NWs were washed to remove solvent, PVP, and other impurities using DI water for three times and then redispersed in methanol. The Ag NWs exhibited average diameter of 70 nm with the length distribution of 20–50 µm (Supporting Information, Figure S8).

Preparation of Ag NW-Embedded CPI Film: To obtain Ag NW-CPI film, the Ag NWs were filtrated on a 0.2 µm pore Nylon membrane filter (Whatman, Germany) and transferred to a glass substrate using the DC power supply. (2.5 × 2.5 cm2) using a pressing machine with a pressure of 2 MPa. The average coverage of Ag NWs on glass substrate was 29%–31% with sheet resistance in the range of 4–8 Ω sq−1 and optical transparency of 74%–75% at 550 nm wavelength. The Ag NW networks that were transferred on the glass substrate were covered by PAA solution. The PAA solution was prepared by dissolving 1.018 g of 6FDA and 0.569 g of APS in 3.5 g of DMF solution. For complete dissolution, the mixture was stirred at 500 rpm with a magnetic stirrer for 5 h at 20 °C. The homogeneously dissolved PAA solution was coated on the Ag NW transferred glass substrate using a doctor's blade with the thickness of 100 µm. The Ag NW-CPI film was achieved after imidization at 100, 200, and 230 °C for 1 h at each temperature in a box furnace with a heating rate of 2 °C min−1. The Ag NW-CPI film was detached from the glass substrate by immersing in DI water for 30 min. The fabricated Ag NW-CPI films exhibited the sheet resistance in the range of 8–11 Ω sq−1.

Stability Test of Ag NW-CPI Heater: The long-term stability and the bending stability were characterized using DC power supply (E3644A, Agilent). For the long-term stability test, constant voltage of 2 V was applied to the Ag NW-CPI heater in the flat state to maintain the initial current of 222 mA. The transition of current of Ag NW-CPI heater was monitored with respect to the time for 220 h. In addition, temperatures of Ag NW-CPI heater were monitored after 20, 75, 120, and 220 h, respectively. During the bending stability test, slightly lower initial current in the range of 208–214 mA was maintained with the applied voltage of 2.3 V to prevent early breakdown of Ag NW-CPI heater. The temperature of Ag NW-CPI film was controlled at around 75 °C under bending stress, where the temperature was similar to the condition of gas sensing characterization. The current transition was measured with a 1 s interval using the DC power supply.
Interdigitated Electrode (IDE) Patterning: IDEs were patterned on CPI film, i.e., the opposite side of the Ag NW networks, to measure resistance changes of ORGO during the exposure to NO$_2$ molecules. The IDEs on CPI film were patterned using shadow mask with finger width of 200 μm, length of 2750 μm, and 200 μm spacing between electrodes. A 10 nm/100 nm thick Cr/Au layer was deposited using e-beam evaporator for IDEs.

GO Coating on CPI Film: The GO coating was performed by a simple drop-coating method on the IDE-patterned CPI film. To mask with finger width of 200 μm molecules. The IDEs on CPI film were patterned using shadow respectively. The operating temperature of the ORGO sensor was

IPL Irradiation: A xenon flash lamp (ILC technology, L675S) was utilized to form ORGO sheets on the Ag NW-CPI film. The spectrum of a light source ranged from about 400 to 1100 nm (Supporting Information, Figure S11a). The pulse light was irradiated to the GO sheets through quartz crystal (Supporting Information, Figure S11b). The light energy was adjusted by modulating the applied voltage, pulse duration, pulse on/off time, pulse gap, and pulse number. The GO-coated Ag NW-CPI film was placed under the quartz with the pulse gap of 5 mm. Then, the pulse on/off time was fixed as 15 ms/30 ms. A constant voltage of 150 V was applied to the flash lamp to maintain the flash light energy as 1.15 J cm$^{-2}$. Single light pulse was irradiated to directly form ORGO sheets on Ag NW-CPI film.

NO$_2$ Sensing Characterization: NO$_2$ sensing characteristics are the sensor’s resistance upon exposure to air and NO$_2$, $R_0$ and $R_1$ are the sensor’s resistance upon exposure to air and NO$_2$, respectively. The operating temperature of the ORGO sensor was controlled by applying DC voltage to the Ag NW-CPI heater using a DC power supply (E3644A, Agilent).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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