High-Performance Graphene-Based Transparent Flexible Heaters

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Supporting Information

ABSTRACT: We demonstrate high-performance, flexible, transparent heaters based on large-scale graphene films synthesized by chemical vapor deposition on Cu foils. After multiple transfers and chemical doping processes, the graphene films show sheet resistance as low as ∼43 Ohm/sq with ∼89% optical transmittance, which are ideal as low-voltage transparent heaters. Time-dependent temperature profiles and heat distribution analyses show that the performance of graphene-based heaters is superior to that of conventional transparent heaters based on indium tin oxide. In addition, we confirmed that mechanical strain as high as ∼4% did not substantially affect heater performance. Therefore, graphene-based, flexible, transparent heaters are expected to find uses in a broad range of applications, including automobile defogging/deicing systems and heatable smart windows.

KEYWORDS: Graphene, transparent, flexible, heater, chemical vapor deposition, layer-by-layer doping

Graphene has attracted a tremendous amount of attention over the past few years because of its outstanding electrical, mechanical, and chemical properties. Various efforts have been made to use these fascinating properties for macroscopic applications, such as transparent conducting films that can replace indium tin oxide (ITO). Recent advances in graphene growth techniques have enabled the roll-to-roll synthesis of high-quality graphene films as large as 30 in. in diagonal, and the field expects to soon realize the industrial production of graphene conducting films for macroscopic applications, including displays, solar cells, and transparent heaters.

A transparent heater is very useful for clearing automobile windows, mirrors, and displays, as well as ensuring the fast response of electronic devices under extreme environmental conditions. ITO film has been widely used as a transparent heater, but it not only exhibits a slow thermal response but also requires complicated fabrication processes that rely on rare indium sources, resulting in higher production costs. For this reason, there have been many efforts to replace ITO films with a new type of transparent conducting film, such as single-walled carbon nanotube (SWNT) sheets, as demonstrated by Yoon et al. While transparent SWNT films show a rapid thermal response and have a better heating performance than ITO films, their dispersion process requires strong acid treatments and surfactants, which limit the conductivity of SWNT-based conducting films. In addition, the difficulty in removing semiconducting SWNTs hinders the enhancement of their optical transmittance (Tr) at a given sheet resistance (R_s = ∼180 Ohm/sq at Tr = 90%). Thus, we suggest the use of large-scale graphene films synthesized by chemical vapor deposition (CVD) methods for transparent heaters. Graphene demonstrates exceptional optoelectronic properties that are superior to those of previously used transparent conducting materials (R_s = ∼43 Ohm/sq at Tr = 89%). The outstanding thermal conductivity of graphene films provides another advantage for using graphene in transparent heaters; it quickly delivers heat to the environment. This results in a faster heating rate and a more homogeneous temperature distribution. In addition, the flexibility of graphene further allows its facile application to a curved window surface or as arollable screen because it can be prepared as an attachable film structure combined with polymer substrates.

For the large-scale production of high-quality graphene films for heater applications, the CVD system is used, allowing the synthesis of a monolayer graphene film on a roll of Cu foil. Figure 1 shows a schematic of the fabrication procedure for transparent flexible graphene films with layer-by-layer doping.

Received: July 7, 2011
Revised: November 8, 2011
A roll of Cu foil is inserted into a quartz tube and heated to 1000 °C with H2 flowing at 2 sccm at 20 mTorr. After annealing for 30 min without changing the flow rate or pressure, a gas mixture of CH4 and H2 is flowed at 400 mTorr with rates of 28 and 2 sccm for 30 min, respectively. Finally, the sample is rapidly cooled to room temperature with a mixed flow of H2 and He under a pressure of 400 mTorr. After growth, the graphene film grown on the Cu foil is transferred to the target substrate by using a roll-to-roll process, as suggested by a previous paper.

There are three steps in the roll-to-roll transfer as illustrated in Figure 1. First, the thermal release tape (Nitto Denko Co.) is attached to the graphene film on the Cu foil. After etching the Cu foil in a bath filled with Cu etchant, the graphene film is then rinsed with deionized water to remove residual etchant. The graphene film on the polymer support is inserted between the rollers, together with a target substrate, and exposed to mild heat (140 °C), resulting in the transfer of the graphene film from the polymer support to the target substrate. In order to improve the electrical quality of graphene films with high optical transmittance, we carried out multiple stacking processes and a wet-chemical doping process. We used gold(III) chloride-nitromethane (AuCl3−CH3NO2, 0.025 M) and nitric acid (HNO3, 16 M) on graphene films to compare the difference in their heating performance after treatment. First, graphene film on a polyethylene-terephthalate (PET) substrate was immersed in the dopant solution for 5 min. After the doping process, the graphene film was placed with another graphene film on thermal release tape and exposed to heat, fabricating multiple stacked graphene films. By repeating these steps on the same substrate, interlayer-doped graphene films can be prepared by a roll-to-roll process, as demonstrated by Bae and colleagues. Supplementary Figure S1 shows the electrical and optical characterizations of graphene films as a function of layer-by-layer doping with (a) AuCl3−CH3NO2 and (b) HNO3. The optical transmittance at λ = 550 nm is usually decreased by 2.3% for each additional transfer. Finally, we fabricated a sheet with a resistance as low as ~43 Ohm/sq and a transmittance of ~89%.
Figure 3. The temperature profiles of graphene-based heaters with two different doping agents and an ITO-based heater, measured by (a) an infrared scanner (Testo 881) and (b) a thermocouple (K-type).
temperature can be set by modifying the sheet resistance using chemical doping and multiple transfer process, the graphene could be produced into large-scale heater. These results demonstrate that graphene-based heaters could be applied as transparent heaters for a vehicle or a smart window system.

To understand the heat performance of graphene film heaters under bending conditions, we describe experimental results obtained from changing the temperature of the graphene-based heaters and the ITO-based heater under mechanical strain and bending cycles. Figure 4a demonstrates the electromechanical properties of graphene-based heaters and ITO-based heater. Bending strain was applied to four-layer graphene films transferred to a PET (188 μm) and ITO coated on a PET (130 μm). The strain can be calculated from the following equation:

\[ \varepsilon = \left( \frac{\delta_l + \delta_f}{2R_C} \right) \left( \frac{1 + 2\eta + \chi \eta^2}{1 + \eta + \chi \eta + \chi^2 \eta^2} \right) \]  

where \( \eta = \delta_l/\delta_f \), \( \chi = Y_f/Y_s \), and \( R_C \) is the bending radius. \( Y \) is Young's modulus. The subscripts \( s \) and \( f \) indicate the substrate (PET) and film (graphene). Typically, approximately 1.2% strain for an ITO-coated PET sample with a thickness of 130 μm is regarded as a failure strain.24 Unlike an ITO-based heater, which easily breaks at an approximate strain of 1.1%, in our experiments, the graphene-based heater resisted a strain of up to 4%.24 The temperature of the graphene-based heater changed by 9%, which was observed for a range of strains up to ~4% (corresponding to a bending radius of 2.36 mm). In addition to the experiments in the mechanical stability of graphene-based heater we have performed bending stability test (Figure 4b). The bending test was repeated 1000 times during application of the input voltage. The bending rate was one cycle per 20 s (0.05 Hz). The lower inset in Figure 4b shows optical images of the bent device under ~1.1% strain, which was the threshold strain for ITO-coated PET. Only small changes in temperature deviation of approximately 1.02 °C were detected over the complete mechanical stability experiment. Therefore, the excellent mechanical properties of graphene films can be applied to produce transparent, flexible heaters.

In summary, we have developed a flexible and transparent heater composed of graphene films. We fabricated multiple stacked graphene films using a roll-to-roll method and prepared interlayer doped graphene films using two wet chemical dopants, AuCl₃—CH₃NO₂ and HNO₃, resulting in a low sheet resistance ideal for low-voltage heaters. The temperature response and heat distribution results show that the performance of graphene-based heaters is superior to that of conventional ITO-based transparent heaters. In particular, the graphene-based heaters are mechanically stable against large bending deformations, which is suitable for automobile defogging/deicing systems and heatable smart windows.

**ASSOCIATED CONTENT**

Supporting Information. Additional information and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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**ACKNOWLEDGMENT**

This research was supported by Basic Science Research Program (2010K001066, 2011-017587, 2011-006270, 2010-0028037, 2011-0006268), Priority Research Centers Program (2011-0018395) through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science, and Technology. This work (000-437-010-110) was supported by Business for Cooperative R&D between Industry, Academy, and Research Institute funded Korea Small and Medium Business Administration in 2010.

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dx.doi.org/10.1021/nl202311v | Nano Lett. XXXX, XXX, 000–000
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