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Flexible, transparent, and conductive defrosting glass

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ABSTRACT

Flexible and transparent electronics play a predominant role in the next-generation electrical devices. In this study, a printable aqueous graphene oxide (GO) ink that enables direct deposition of GO onto flexible glass substrates is demonstrated and its application on fabricating a transparent, conductive, and flexible glass device by solution coating process is investigated as well. A uniform GO layer is formed on the flexible glass through Meyer-rod coating followed by an annealing process to reduce GO into graphene. The obtained thermally reduced graphene oxide (RGO) flexible glass has a transmittance of over 40%, as well as a sheet resistance of ~5×10^3 Ω/sq. In addition, a defrosting window fabricated from the RGO coated flexible glass is demonstrated, which shows excellent defrosting performance.

1. Introduction

Flexible glass is a promising substrate for transparent conductive electrodes (TCEs) since high flexibility allows efficient and scalable roll-to-roll manufacturing of thin films [1]. In the past few years, extensive research was based on the utilization of common plastics such as polyethylene terephthalate and poly(ethylene naphthalate) (PEN) to fabricate flexible TCEs [2,3]. However, they cannot withstand thermal annealing above 200 °C during device fabrication, which limits the device performance in terms of electrical conductivity. As an example reported recently [4], a flexible transparent heater was fabricated using PEN as the substrate. However, a failure mode related to temperature was encountered since PEN substrates were prone to tearing after heating. This drawback sets an obstacle for its large-scale application in TCEs. To overcome this challenge, common glass was employed as an alternative substrate to obtain better mechanical stability under heat treatment [5]. The low flexibility of typical glass substrates (>0.3 mm thick), however, cannot satisfy the requirements for flexible TCEs. From this perspective, flexible glass is a more suitable substrate as compared with plastics and rigid glass substrates. Its transparency, low thickness, heat-resistance, and mechanical reliability features make it promising to be used in large-scale production of TCEs.

Currently, the deposition of graphene on flexible substrates has been widely investigated due to its superior electrical conductivity, mechanical stability, and ultra-high transparency [6–11]. Direct deposition of uniform graphene nanoflakes by scalable methods is still challenging, which hinders its application in thin film industry [12–14]. The advancement of roll-to-roll coating processes provides a route in solving this issue since it is efficient, simple and controllable [15,16]. The utilization of Meyer-rod coating opens an alternative route for large-scale production of TCEs since it enables a uniform deposition of conductive material by roll-to-roll production. For instance, transparent silver nanowire electrodes with superior optoelectronic performance were recently obtained by Meyer-rod coating on flexible plastic substrates [7].

In this study, we utilize Corning® Willow® Glass as a flexible substrate to fabricate transparent, conductive, and flexible graphene oxide (GO) films using Meyer-rod coating processes. The flexible glass substrates were 100 μm in thickness and 100 mm × 200 mm in size. An efficient and uniform solution coating process is demonstrated with the addition of surfactant to the aqueous GO ink. After annealing directly on the flexible glass substrate, the as-prepared reduced graphene oxide (RGO) film shows improved conductivity and high optical transmittance. Its performance in terms of sheet resistance and optical transmittance is investigated. In addition, we demonstrate a concept of flexible thin film heaters using conductive RGO film. It shows great potential to be window defrosters due to its excellent heating performance.

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2. Experiment details

2.1. Synthesis of GO powder

All chemicals were purchased from Sigma-Aldrich and used as received. Graphene oxide is prepared using a modified Hummer's method [17]. A mass of 1 g $NaNO_3$ is added to 2 g Johnson Matthey graphite powder in 46 mL concentrated sulfuric acid. The mixture is stirred in 0 °C ice bath. Then 6 g $KMnO_4$ is added very slowly while the reaction container is kept in the ice bath. The temperature is increased to 35 °C and kept for 30 min after removing the ice bath. A volume of 90 mL de-ionized water is added to the paste and the temperature is allowed to reach 98 °C for 12 h. A volume of 280 mL warm water is used to dilute the products and 50 mL 30% H_2O_2 is added. The solution turns golden and the solid particles are dark brown. The filtration is done using a Büchner's funnel and filter paper. The solid is washed by 100 mL warm water 3 times and dried in vacuum overnight. The obtained powder is brown.

2.2. The preparation of GO ink

The GO ink is prepared by dissolving 150 mg graphite oxide in 150 mL distilled water. The solution is then sonicated using the horn sonicator for 30 min and water bath sonicator for 2 h. After that, the centrifugation is done at 6000 rpm for 30 min. The supernatant is collected. A commercial surfactant Zynol (DuPont) was added to the GO ink to reduce its surface tension enabling the aqueous GO solution to easily spread on the surface of the glass. The surfactant (0.01 wt.% based on GO) was added to GO ink (0.5 mg/mL) by pipette to reduce the surface tension of GO ink, and was then dispersed with the aid of bath sonication for several minutes.

2.3. Meyer-rod coating with GO ink on flexible glass

To coat the Willow Glass substrate, a volume of 80 μL of the GO ink was dropped on the gap between the Meyer rod (35#) and the edge of the flexible glass. The Meyer rod was then used to remove the excess solution on the surface of flexible glass. A uniform wet film was formed that was then oven dried at 50 °C to 80 °C for less than 1 min. Depending on the number of layers applied, the thicknesses of the dried films was in the range of 5–25 nm as measured by atomic force microscopy (AFM).

2.4. Thermal reduction of GO film

After coating with GO ink, the flexible glass samples were put into a tube furnace fitted with controlled gas flows. The GO films were thermally annealed with a ramp rate of 5 °C/min and kept at 650 °C for 5 h under Ar/H_2 gas (95%/5%) flow to form RGO film. The system was cooled down to room temperature during duration of 2 h. Upon removing the flexible glass samples from the furnace, no physical deformation of the substrate was observed.

2.5. Material characterizations

Scanning electron microscopy (SEM) images were taken by Hitachi SU-70 analytical ultra-high resolution SEM (Japan). The applied voltage of SEM is 10 kV. AFM images were taken by Digital Instruments (Veeco) Multimode AFM with nanoscope III controller10 micron scanner. Raman measurements were performed on a HORIBA Jobin Yvon LabRAM ARAMIS using a 532 nm diode-pumped solid-state laser, attenuated to give ~900 μW power at the sample surface.

3. Results and discussion

Fig. 1(a) shows the high flexibility of the Willow Glass used in this study. Such a flexible substrate is promising for the next generation flexible electronics and displays. Fig. 1(b) displays a schematic of a typical Meyer-rod coating of GO films on the flexible glass substrate. The transparency of GO films can be controlled simply by the amount of layers deposited on the substrate. Fig. 1(c) shows three GO films coated on flexible glasses by depositing different layers of GO ink. As more layers of GO ink were coated, it formed a thicker, darker, light yellow film on the flexible glass. The additional films were coated onto the flexible glass substrate after oven drying. The multi-layer films went through a single reduction step at the end. The transmittance of these three GO films was determined to be 70%, 50%, and 30% respectively. Their different transparent properties can be identified by the visibility of UMD logo underneath the glass.

The molecular structure of Zynol is illustrated in Fig. 2(a), which includes a stable C – F hydrophobic chain and – OH hydrophilic groups. Fig. 2(b) shows that as-prepared GO ink is a clear, brown aqueous suspension. Fig. 2(c) displays a typical coating that results when the GO ink droplets could not be spread to wet the whole glass. This phenomenon is ascribed to large surface tension of water-based GO ink. After the addition of Zynol surfactant to GO ink, a uniform coating is achieved as demonstrated by Fig. 2(d). The crucial effect of Zynol is thus revealed for the coating process. Zynol is a non-ionic surfactant and reduces the surface tension of GO ink. The Zynol molecules have strong affinity with water molecules, resulting in the decrease of interaction between water molecules on the surface and their surroundings. Therefore, Zynol surfactant controls the surface tension of water-based GO ink and a uniform coating can be achieved.

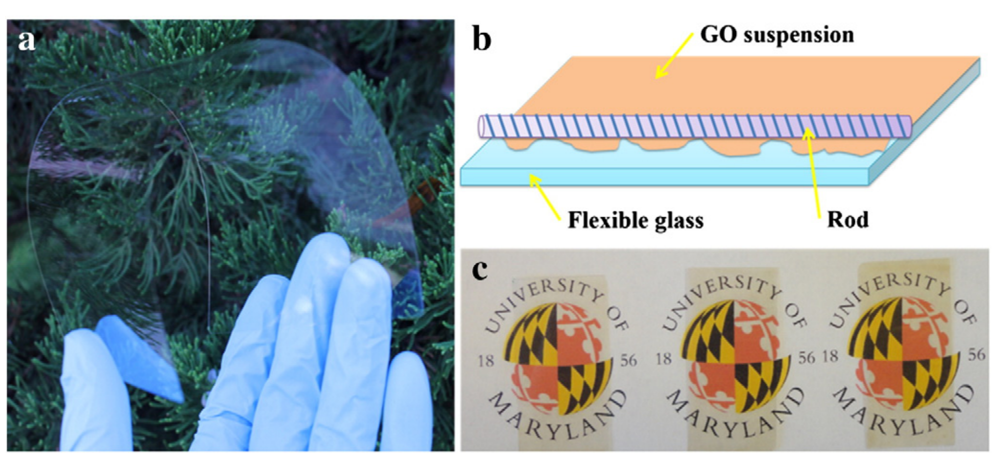

Fig. 1. (a) Flexibility of the transparent glass. (b) The schematic procedure of producing transparent and flexible GO coated glass by Meyer rod coating. (c) Uniform printing with GO ink on flexible glasses (transparency from left to right: 70%, 50%, and 30%).

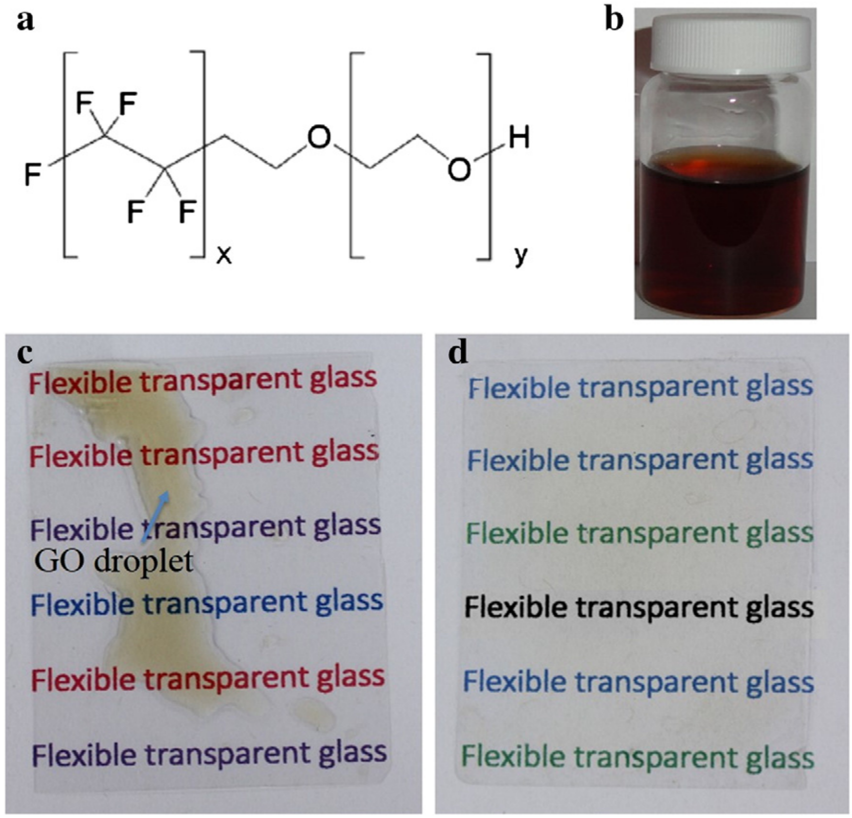

Fig. 2. (a) Molecular formula of the chosen Zynol surfactant. (b) Water-based graphene oxide ink containing Zynol surfactant. (c) Agglomeration occurs for an ink without Zynol additive. (d) Uniform coating of GO ink with Zynol on flexible glass.

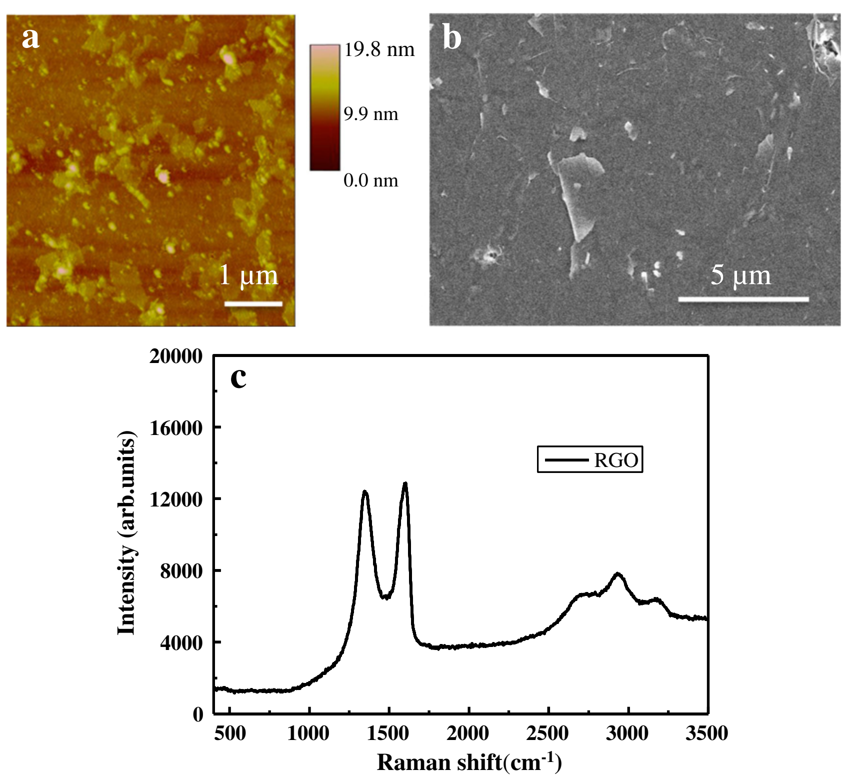

Fig. 3. (a) The AFM image of GO flakes. (b) The SEM image of a typical RGO flake deposited on flexible glass substrate. (c) Raman spectrum of RGO film excited with a laser wavelength of 514 nm.

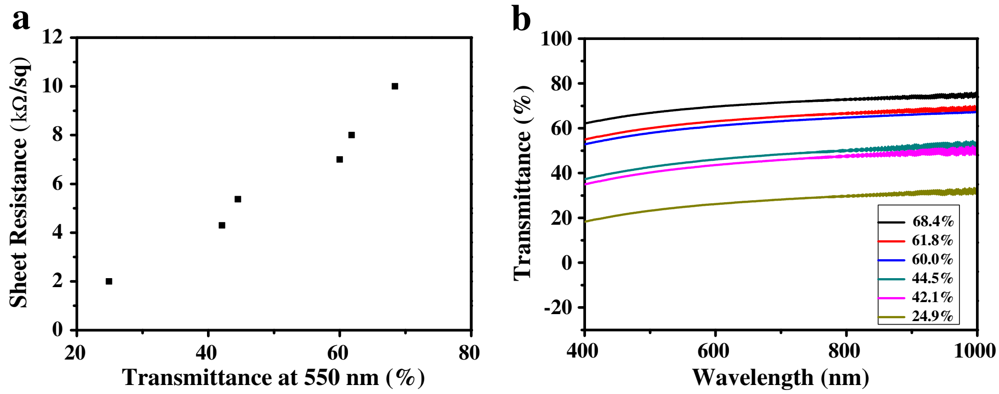

Fig. 4. (a) Sheet resistance versus optical transmittance at 550 nm for RGO film. (b) Optical transmittance of different RGO films on flexible glasses (the numbers showed in the box are the transmittances of RGO films at the wavelength of 550 nm).

Fig. 3(a) displays an AFM image of the GO flakes. A typical RGO flake diameter is determined to be ~1 μm. This is further confirmed by the SEM image of GO flakes (Fig. 3(b)). Fig. 3(c) shows a Raman spectrum of RGO film. It consists of a G-band located at ~1580 cm^{-1}, D-band at ~1350 cm^{-1} and 2D-band at ~2700 cm^{-1}. As reported by previous papers, a typical Raman spectrum of graphene includes G and 2D bands with a negligible D band [18,19]. The G-band is designated as the in-plane vibration of sp^2-bonded carbon atoms. The D-band is related to vibrations of carbon atoms with sp^3 electronic configuration of a disordered carbon plane. The 2D band is the second order of the D peak. The Raman spectrum of RGO film deposited on flexible glass shows typical G and 2D peaks of graphene, indicating the completeness of our thermal reduction. The RGO film is a multilayer as we coated several layers of graphene oxide before annealing, the 2D peak becomes shorter and wider as compared with that of single-layer graphene. The broad peaks between 2500 cm^{-1} and 3300 cm^{-1} include 2D, D + G and G + D′ bands due to the disorder in the as-prepared RGO film [20]. The relatively high intensity of the D peak shows the existence of defects in the structure of RGO.

Fig. 4 shows the optical transmittance spectra of different RGO films and the relationship between sheet resistance and optical transmittance. The lowest sheet resistance obtained was 2 kΩ/sq with a transmittance 24.9% at 550 nm. The extent of GO reduction determines the electrical conductivity of the RGO film. Graphene oxide can be reduced completely by annealing at 1100 °C or with the treatment of hydrazine [21]. However, the utilization of toxic hydrazine is not suitable for large-scale applications. Therefore, an annealing of the GO film is carried out directly on flexible glass, which can tolerate a high temperature of 650 °C. Such a facile fabrication process of conductive RGO films makes it promising for scalable production of transparent electrodes. The improvement of its performance in terms of sheet resistance and optical transmittance is under investigation.

Since our RGO coated glass is transparent and conductive, a possible application is defrosting glasses for vehicle windows. Fig. 5 illustrates

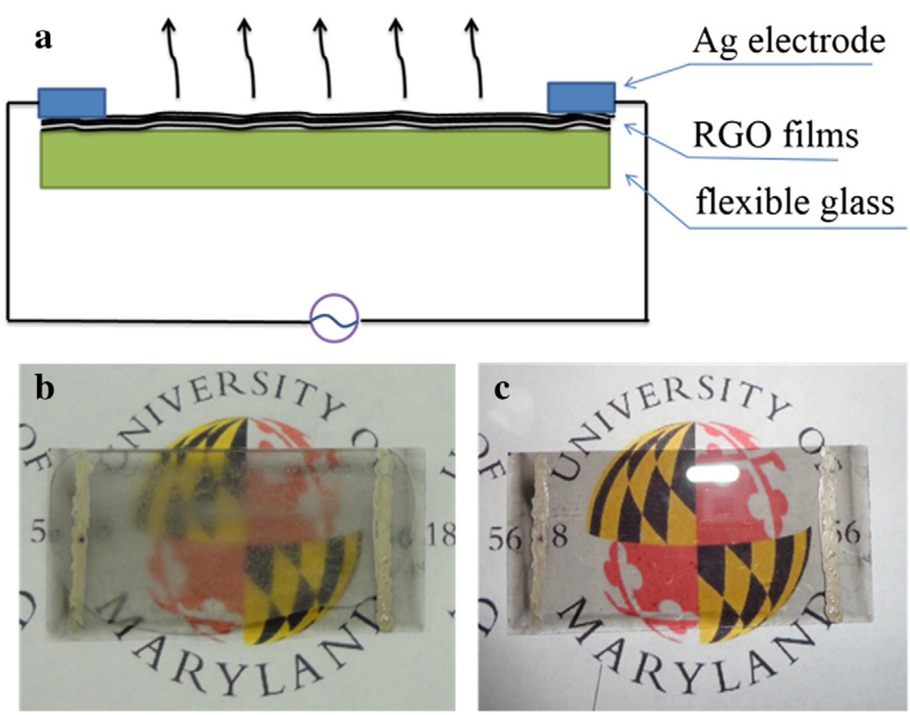

Fig. 5. (a) Schematic diagram of RGO films on flexible glass with an electrode pair. Defrosting results (b) before and (c) after annealing process of the RGO film with transparency 45% and sheet resistance 5370 Ω/sq.

the defrosting demonstration test. Firstly, the RGO film with a transparency of 45% and a sheet resistance of 5370 Ω/sq is selected as a potential window defroster. Secondly, some silver gel is pasted on two sides of the RGO deposited glass. A Keithley instrument is used to apply a 10 V voltage across the glass via Ag electrodes. To simulate a real frosting process for vehicle windows, we put the glass into freezer for 2 h to grow frost. As shown from Fig. 5(a), the UMD logo under our RGO deposited glass is not clear and hard to recognize. After applying a 10 V voltage for 80 s, the frost is removed and thus the UMD logo is visible again. The control experiment shows that such a defrosting process takes 120 s without the deposition of conductive RGO films on the substrate. The shorter defrosting time demonstrates its potential to be utilized as a window-defrosting device. Its high electrical conductivity enables a heating process after applying 10 V voltage, leading to the rise of temperature and the elimination of grown frost on flexible glass.

4. Conclusion

We demonstrate a transparent, conductive, and flexible glass coated with RGO film. A printable aqueous GO ink was made with the addition of a non-ionic surfactant. This solution was then uniformly spread on the surface of flexible glasses by Meyer-rod coating followed by a post-treatment of annealing at 650 °C for 2 h. The RGO coated glass achieved a transmittance of 45% and a sheet resistance of 5370 Ω/sq, which displayed excellent defrosting performance when it was used to assemble a defrosting device.

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