Electrical and mechanical properties of graphene oxide on flexible substrate

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Graphene oxide (GO) was deposited via the electrophoretic deposition (EPD) method to lower the oxygen concentration of graphene sheets for large-scale production. In addition, the direct synthesis of large-scale GO films using transfer processes on a polydimethylsiloxane (PDMS) substrate was conducted. The thickness of the GO films was controlled to adjust the optical, electrical, and mechanical properties. The Young's modulus values of films with thicknesses of 100–200 nm were 324–529 GPa. Moreover, the GO films exhibited excellent conductivity, with a sheet resistance of 276–2024 Ω/sq at 23–77% transparency. Experiments show that transfer processes for flexible substrates can produce high-quality cost-effective transparent conductive films.

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1. Introduction

The unique physical properties of graphene make it of interest for electronic and optoelectronic devices. Graphene is a one-atom-thick layer of bonded-sp 2 carbon atoms packed into a two-dimensional honeycomb lattice [1]. Graphene has an electron mobility of up to 15,000 cm 2/V s at room temperature and 60,000 cm 2/V s at 4 K [2,3]. Graphene has high optical transparency and can absorb \( \alpha \alpha \) of white light, where \( \alpha \alpha \) is the fine-structure constant [4].

Graphene oxide (GO), a non-conducting material, has been extensively studied [5–7]. Many kinds of oxygenation/reduction processes are used for GO structures for application in hybrid materials [8], transparent conductive films (TCFs), battery electrodes, and sensors. Graphene sheets have been used to create new composites [9,10]. Simple methods for the synthesis of graphene sheets have been investigated, including electropolymerization deposition and electrochemical processes [11,12]. Lee et al. [12] chemically prepared graphene paper via the electrochemical exfoliation of graphite in an electrolyte. Although a number of studies have investigated the chemical structure of GO, no complete model exists. The most probable structural models are the Lerf–Klinowski model [13] and the Dékány model [14], which consider the structure and hydration behavior of GO. Fig. 1 shows the carbon plane decorated with hydroxyl and epoxy (1, 2-ether) functional groups. There are a number of carboxylic acids along the sheet edge, with organic carbonyl defects within the sheet.

Electrophoretic deposition (EPD) is an economical and versatile method that is widely applied to films coatings [15]. EPD has many advantages, including a high deposition rate, high throughput, high uniformity, and controlled thickness of the obtained films [16]. Hilder et al. [17] described the direct electrochemical reduction of GO to graphene from aqueous suspension by the application of reduction voltages exceeding 1.2 V. Wu et al. [18] obtained cyclic voltammograms for electrochemically deposited Cu on reduced GO (r-GO) electrodes in a 10 mM CuSO 4 solution with various pH values at a scan rate of 20 mV s \(^{-1}\). Their research provides an electrochemical platform based on r-GO electrodes for sensing, optoelectronics, and energy harvesting applications. An et al. [19] reported the deposition of films composed of overlapped and stacked platelets of GO reduced by an EPD process. Wu et al. [20] showed the fabrication and field-emission properties of single-layer graphene films by EPD from a stable suspension of isopropanol-alcohol-dispersed graphene prepared by chemical exfoliation. They obtained good field-emission properties with a low turn-on electric field, a low threshold field, and good uniformity.

Graphene/GO is strong and can thus be processed into sheets as thin as paper. Graphene is thus suitable for nanoelectromechanical systems applications. The present study uses nanoindentation to measure the mechanical properties of GO films. Although many
in the liquid induced by an applied electric field. The streaming potential of water was found to be $2.5 \mu V m V^{-1} s^{-1}$ from the Helmholtz–Smoluchowski formula [21]:

$$u = \frac{\varepsilon_0 V_{ac}}{\eta_{H2O}} \zeta_{GO}$$

(1)

where $u$ is the streaming potential at zero net current conditions ($V$), $\varepsilon_0$ is the electrical permittivity of a vacuum ($F m^{-1}$), $\eta_{H2O}$ is the relative permittivity of the liquid (dimensionless), $\zeta$ is the zeta potential ($V$), and $\eta_{H2O}$ is the dynamic viscosity of the liquid ($kg m^{-1} s^{-1}$).

Fig. 3 shows a schematic illustration of the major steps in the transfer processes for patterned graphene films. The deposition of GO/ITO films is schematically shown in Fig. 3(a). As shown in Fig. 3(b), PDMS (evenly mixed with a hardening agent at a ratio of 10:1) was poured onto a GO/ITO substrate. The GO/ITO substrate assembly was transferred to a furnace and heated to a temperature of 65 °C for 4 h to solidify the PDMS. As shown in Fig. 3(c), the GO films were separated from the GO/ITO substrate and transferred to a PDMS substrate. A lift-off operation was then performed to remove the ITO glass substrate, leaving just the GO films on the PDMS substrate. The finished flexible substrates for samples 1–4 are shown in Fig. 3(d and e).

The hybrid GO material was characterized by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Raman measurements were taken using a micro-Raman system (Renishaw, Vendor) with a wavelength of 514 nm. XPS measurements were taken in a JEOL JAMP-9500F system using a monochromatic Al-Kα X-ray source with a photon energy of 1486.6 eV. The microstructures of the deposited materials were measured by scanning electron microscopy (SEM, Zeiss Auriga FIB-SEM system), scanning confocal microscopy (SCM, Keyence VK-X200), and transmission electron microscopy (TEM, Philips Technai G2F20). The deposited materials were investigated by analyzing selected area electron diffraction (SAED) patterns and energy-dispersive X-ray spectroscopy (EDS).

Atomic force microscopy (AFM, NT-MDT SFC050L) was used to determine the layer thickness at the nanometer scale and the surface morphology. The AFM measurements were made using a probe with radius of 20 nm. A constant normal force of 5 nN was maintained between the tip and the sample surface in contact mode. A nanoindentation device (Hysitron Triboscope, TI 700 Ubi) equipped with a Berkovich diamond probe with a radius of approximately 100 nm was used to measure the nanomechanical properties in the experiment. The hardness, $H$, was determined as the maximum indentation load $F_{max}$ divided by the actual projected contact area $Ac$:

$$H = \frac{F_{max}}{Ac}$$

(2)

The hardness and Young's modulus as functions of the displacement of the indenter were measured from the loading–unloading curve [22]. The hardness of a material is defined as its resistance to plastic deformation. In depth-sensing nanoinindentation, the composite modulus $E'$ is calculated as:

$$E' = \frac{\pi S}{2\beta \sqrt{Ac}}$$

(3)

where $S$ is the measured stiffness and $\beta$ is a shape constant (1.034 for the Berkovich tip).

Hot plate heating was used to clean formvar/carbon films to obtain support-free films on a 200-mesh Cu grid (Pelco Int., USA). The ITO substrate layers were etched and free-standing GO films were transferred to the grid, whose holes were 97 µm × 97 µm (thickness of 10 µm). After ITO films were etched with 3.4 wt% researchers have determined the mechanical properties of a monolayer, few studies have investigated EPD GO films by nanoindentation.

The present study deposits GO onto an indium tin oxide (ITO) substrate via an electrochemical processing method. A soft lithography technique is employed using a polydimethylsiloxane (PDMS) mold to deposit the GO films. The mold makes contact with the substrate, leaving behind GO films on the surface. The mechanical properties of the deposited GO on the flexible PDMS substrate are investigated.

2. Experiments

GO was deposited via EPD, as shown in Fig. 2. The EPD system comprised an ITO cathode, a highly oriented pyrolytic graphite (HOPG) anode, and graphite powder (1 g) as the electrolyte (in 100 ml of water). In the anodizing process, negatively charged material was deposited onto the positively charged electrode (anode). A direct-current (DC) voltage of 10 V was applied for 0.5, 1, 3, and 5 min (samples 1, 2, 3, and 4, respectively) to an electrolyte in contact with the ITO surface to generate a GO film. Samples 1, 2, 3, and 4 had average thicknesses of 100, 150, 180, and 200 nm, respectively.

The distance between electrodes, applied voltage, and deposition time for GO sheets deposited on ITO substrates were measured. EPD uses charged particles and the electrophoretic mobility...
H$_2$C$_2$O$_4$, the free-standing GO films were separated from the substrate and floated on the surface of the solution. The films were then ready to be transferred to the Cu grid for nanoindentation to measure mechanical properties.

The current–voltage ($I$–$V$) characteristics of the GO films were measured using a digital sourcemeter (Keithley 2400). The absorbance and reflectivity of the GO films were examined under various wavelengths using an ultraviolet–visible (UV–vis) spectrophotometer (Jasco V-670).

3. Results and discussion

3.1. Surface morphology of GO films

Fig. 4(a) shows that the GO sheets became randomly dispersed on the ITO substrate at 0.5 min. Fig. 4(b) shows GO films electrophoretically deposited on carbon and oxide substrates for 1 min. Fig. 4(c) shows that the GO film thickness increased with deposition time, becoming 180 nm thick at 3 min. Fig. 4(d) shows that
reported the formation of a nanocomposite comprised of chemically converted graphite and carbon nanotubes. The sheet resistance was 2024 Ω/sq at 77% transmittance. The present study enhanced the TCs by controlling the film formation process [29]. GO film can replace ITO electrodes in the future.

4. Conclusion

Films composed of stacked layers of GO sheets were deposited via EPD. The GO films exhibited excellent conductivity (sheet resistance of 276–2024 Ω/sq at 23–77% transparency). The EPD method can be used to obtain GO with a low oxygen concentration and high electrical conductivity. The GO film had excellent mechanical properties. The Young’s modulus values of films with thicknesses of 100–200 nm were 324–529 GPa. The experiments show that transfer processes for flexible substrates can produce high-quality cost-effective TCs.

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References


