



High electrical conductivity and oxygen barrier property of polymer-stabilized graphene thin films



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ARTICLE INFO

Article history:

Received 23 May 2017

Received in revised form

18 September 2017

Accepted 22 September 2017

Available online 22 September 2017

ABSTRACT

Next-generation electronics require mechanical flexibility and durability as well as electrical conductivity. In this report, few-layer graphene and polyelectrolytes were assembled into ultrathin films on flexible plastic substrates by a simple and cost-effective layer-by-layer technique. This technique integrated high electrical conductivity and excellent oxygen barrier property into a single film. These characteristics have been rarely reported for other types of thin films prepared by solution processing. The optical properties, film thickness, and mass of the films were precisely controlled by the number of bilayers. After a brief exposure to nitric acid (HNO₃) vapor, the films exhibited much improved electrical conductivity while preserving their other properties. Raman, x-ray photoelectron, and FT-IR spectroscopy proved that the effects of the HNO₃ treatment were due to the removal of polymeric components and restricted to the film surface, and not due to the chemical doping of graphene.

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1. Introduction

Carbon nanomaterials have received increasing attention over the past two decades since the discovery of fullerenes, carbon nanotubes, and graphene [1–3]. Their outstanding electrical, thermal, and mechanical properties have driven research into thin films for electronics [4–6], high-toughness composites [7,8], energy devices [9,10], and biomedical applications [11,12]. Many studies have recently focused on thin films consisting of graphene, a two-dimensional layer of sp²-hybridized carbon atoms arranged in a hexagonal lattice. Along with its outstanding electrical conduction, graphene is known as a perfect barrier for various gas molecules in the direction perpendicular to the plane [13], which is its most distinctive feature compared with other carbon nanomaterials. In

many studies, functionalized graphenes derived from natural graphite have been preferred because of their good solubility in various solvents and lower costs than graphene prepared by chemical vapor deposition (CVD). Graphene oxide (GO), an oxidized derivative of graphene, has been widely used for the fabrication of thin films owing to its water solubility and low material cost [14–22]. Coupled with its planar shape, highly oriented GO and reduced GO (rGO) films exhibit excellent gas barrier property or gas selectivity [15–20]. It was also reported that gas barrier membranes with good mechanical properties were fabricated in the form of sandwich-architected polymer/graphene composite [21].

However, little research has been conducted on the integration of gas barrier property and electrical conductivity into graphene thin films. Apart from this, without consideration of gas permeation, conductive graphene films have been prepared by the chemical, electrochemical, and thermal reduction of GO films [22–29] or carbonization of organic layers [30]. It was found that the high UV–visible light absorption by graphene [31] is unfavorable for meeting the required optical transparency in transparent

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conductors. In addition, the electrical conductivity is limited compared with carbon nanotube thin films [32–39]. A recent study attempted to apply thermal annealing to chemically reduced GO films under an inert gas atmosphere to remove residual functional groups [22,23]. The electrical conductivity was improved by thermal annealing owing to greater recovery of the graphitic structure [40].

In addition, environmental stability can be achieved by minimizing undesirable gas permeation. For example, organic layers within optoelectronic devices are susceptible to degradation induced by oxygen [41]. The exposure of organic solar cells to oxygen results in a substantial reduction of the short-circuit current by the deterioration of charge separation in the active layer [42]. This has been attributed to chemical reactions of the active layer and/or electrodes with oxygen diffusing into the devices [43]. On the other hand, degradation in small-molecule and organic light-emitting diodes by oxygen is still a complex problem and has only been studied recently [44]. In short, it should be noted that next-generation electronics require mechanical flexibility and durability as well as high electrical conductivity. Moreover, packaging for electronic devices or parts could be plausible by using electrically conductive plastic films with gas barrier property to protect them from electrostatic discharge and undesirable gases such as oxygen or moisture.

Here, we integrated high electrical conductivity and oxygen barrier property into multilayer graphene thin films. The films were fabricated by direct deposition of polymer-stabilized graphenes onto flexible poly (ethylene terephthalate) (PET) substrates via layer-by-layer (LbL) assembly to avoid post treatments for reducing pre-deposited GO. Depending on the number of layers, the film growth and corresponding optoelectronic and oxygen barrier property could be precisely controlled. As a post treatment, the LbL-assembled graphene films were exposed to nitric acid (HNO_3) vapor. Detailed analysis demonstrated that the HNO_3 treatment effectively removed polymeric components, thereby improving the electrical conductivity, while maintaining the oxygen barrier property of the films.

2. Experimental

2.1. Materials

Poly (vinyl alcohol) (PVA) (MW = 89,000–98,000) and poly (4-styrenesulfonic acid) (PSS) (MW = 75,000) were purchased from Sigma-Aldrich and used as received. Few-layer graphene (N002-PDR, XY < 10 μm , thickness < 1 nm), a commercially available reduced GO prepared by chemical exfoliation and thermal reduction, was purchased from Angstrom Materials. The graphene dispersion and PVA solution were prepared by the following procedures: graphene (0.1 wt%) and PSS (0.1 wt%) were dispersed in deionized water and subsequently sonicated with a probe sonicator (Sonoplus Homogenizer 2070, Bandelin, power: 70 W) for 3 h. It was confirmed that sonication for 3 h was advantageous for breaking graphene agglomerates into individual graphene sheets, while possessing the lateral dimension of a few micrometers (Fig. S1). PVA (0.25 wt%) was dissolved in water at 80 °C and sonicated for 30 min in a bath sonicator. The pHs of PVA solution and graphene dispersion were 6.0 and 2.7, respectively. PET films (thickness = 80 μm) and thermally oxidized Si wafers (thickness of oxidized layer = 300 nm) were used as the substrates for LbL assembly.

2.2. Layer-by-layer assembly and HNO_3 treatment

Conformal multilayer coatings were deposited on the PET

substrates or thermally oxidized Si wafers using the LbL assembly technique. The substrates were first cleaned by probe sonication (Sonoplus Homogenizer 2070, Bandelin, power: 70 W) in isopropyl alcohol for 20 min and O_2 plasma treatment for 10 min. They were then immersed in the PVA solution for 5 min, rinsed with deionized water, and air-dried. Subsequently, the substrates were dipped into the graphene dispersion for 5 min, followed by rinsing and drying. Alternating these processes yields a complete deposition cycle for one bilayer of PVA and PSS-stabilized graphene. This cycle was repeated to deposit the desired number of bilayers. For the HNO_3 vapor treatment, the LbL-assembled graphene films were maintained in a saturated HNO_3 vapor environment. After exposure to HNO_3 vapor at 55 °C for 5–25 min, the films were rinsed with deionized water then dried with compressed air.

2.3. Characterization

To be used as TEM specimens, the LbL-assembled graphene films were embedded in an epoxy resin. The films were sectioned at room temperature with a diamond knife and placed on Cu grids. SEM micrographs were obtained using a field-emission scanning electron microscope (Sirion, FEI) operated at 10.0 kV, after coating 10 nm of Pt on the film surface. The optical absorbance and transmittance were measured between 300 and 700 nm with a UV–vis spectrometer (Cary 100, Varian). All absorbance and transmittance values in this study are for one-sided coating. The sheet resistance was measured by the four-point probe method with a resistivity meter (Loresta-GP MCP-T610, Mitsubishi). The thickness of the films deposited on the thermally oxidized silicon wafers was determined using a spectroscopic ellipsometer (M2000D, Woolam). The mass of the deposited layers per unit area was calculated by the Sauerbrey equation [45] using a quartz crystal microbalance (QCM) (eQCM 10 M, Gamry). For the QCM measurement, a 10 MHz Au-coated quartz crystal was alternately immersed in the PVA solution and the graphene dispersion according to the same procedure as described in the fabrication of the LbL-assembled graphene films on PET. The morphology of graphene sheets and the LbL-assembled graphene films was observed by using a scanning electron microscope (SEM) (S4700, Hitachi) after coating their surfaces with 2 nm-thick Iridium. The surface roughness of the films was measured by using an atomic force microscope (AFM) (XE-100, Park Systems) in non-contact tapping mode. Raman spectra were recorded using a Raman spectrometer (NTEGRA Spectra, NT-MDT) with a Nd:YAG 532 nm laser. XPS spectra were obtained with a Sigma Probe spectrometer (Thermo Scientific) using an AlK α X-ray source. The atomic concentration was calculated from the peak areas and relative sensitivity factors. For Fourier transform-infrared spectroscopy (FT-IR) analysis, PVA and PSS bulk films were prepared by solution casting. The films were exposed to HNO_3 vapor at 55 °C for 5 and 25 min, rinsed with deionized water, and dried with compressed air. FT-IR spectra were recorded on a Nicolet Magna IR 760 spectrometer (Thermo Scientific). The oxygen transmission rate (OTR) was measured at 23 °C and 0% relative humidity by an oxygen transmission rate testing system (OX-TRAN 2/21 MH, Mocon). The ASTM D-3985 standard was used for the measurement, with a detectable limit of 2.5 cc/m² day atm.

3. Results and discussion

LbL assembly is a simple and cost-effective nanoscale fabrication technique to produce conformal multilayer thin films with molecular-level control over the film thickness and chemistry [46]. It allows for the use of a wide range of materials, including organic compounds [46–48], inorganic nanoparticles

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