



Long-term air-stable Au doping of graphene by layer-by-layer assembly with graphene oxide for flexible transparent electrodes



Su Jin Lee ^{a, b, 1}, Yi Rang Lim ^{a, c, 1}, Seulgi Ji ^a, Seong Ku Kim ^a, Yeoheung Yoon ^d,
 Wooseok Song ^{a, *}, Sung Myung ^a, Jongsun Lim ^a, Ki-Seok An ^a, Jin-Seong Park ^{b, **},
 Sun Sook Lee ^{a, ***}

^a Thin Film Materials Research Center, Korea Research Institute of Chemical Technology, Yuseong Post Office Box 107, Daejeon 305-600, Republic of Korea

^b Division of Materials Science and Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul 04763, Republic of Korea

^c School of Electrical and Electronic Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 03722, Republic of Korea

^d Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon 34141, Republic of Korea

ARTICLE INFO

Article history:

Received 28 June 2017

Received in revised form

23 September 2017

Accepted 29 September 2017

Available online 13 October 2017

Keywords:

Graphene

Graphene oxide

Doping

Flexible transparent electrodes

ABSTRACT

In order to realize the most suitable hybrid structure for air-stable graphene-based transparent and flexible electrodes, we systematically compared graphene oxide (GO)/Au/graphene and graphene/Au/GO hybrid films fabricated by layer-by-layer assembly. The sheet resistance of graphene/Au/GO was proportional to the concentration of AuCl₃ (1–5 mg/ml), which can be understood by a significant blue-shift in the G-band associated with the phonon stiffening. The size and density of formed Au nanoparticles strongly influenced their reduction reaction, which is a crucial factor for maximizing the doping effects. The optimized optical transmittance and sheet resistance of GO/Au/graphene were 94.9% and 198 ± 29 Ohm/sq, respectively. Furthermore, the hybrid films revealed stable doping effects (sheet resistance variation: 23–55%) against ambient conditions after 1 month. The variation in sheet resistance for GO/Au/graphene hybrid films corresponds to 30% with a bending radius of 10 mm after repeated bending tests (bending cycles of 10⁵).

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Graphene has sparked a huge potential for multifaceted applications such as touch screen, smart window, flexible OLED, and solar cells due to its intriguing electrical, optical, and mechanical properties associated with low-dimensional electron systems [1–6]. However, in order to practically utilize the graphene in above-mentioned electronic devices, improvement in electrical conductivity of graphene is a prerequisite because the sheet resistance of monolayer graphene on synthesized Cu using conventional thermal chemical vapor deposition has been reported to be 500–1000 Ohm/sq [7–10], which is comparatively higher than that of conventional indium tin oxide (ITO). Fortunately, because

graphene possesses linear dispersion with electron energy $E(k) = \hbar v_F k$, where v_F is the Fermi velocity and k is the electron wave vector, the low density of states near the Fermi level in graphene permits the highly effective manipulation of carrier concentration via chemical doping. Consequently, numerous approaches have been devoted to tune the type and concentration of charge carrier in graphene, such as the hybridization with atoms, molecules, nanoparticles (NPs) and nanostructures [11–16]. Among them, it is well-established that the doping of Au NPs on graphene is the most effective technique for p-type doping of graphene [7,14,15,17]. However, this route seems to be unstable in atmospheric conditions, resulting in inevitable deterioration of electrical conductivity of doped graphene [18].

Here we present a facile route for hybridization of graphene oxide (GO) with Au NPs-doped graphene by layer-by-layer assembly for developing air-stable graphene-based transparent and flexible electrodes that complement the previous approaches. To maximize the doping influence of Au NPs on graphene, we particularly considered the hybrid nanostructures with two-types of stacking sequence: graphene/Au NPs/GO and GO/Au NPs/graphene.

* Corresponding author.

** Corresponding author.

*** Corresponding author.

E-mail addresses: wssong@kRICT.re.kr (W. Song), jsparklime@hanyang.ac.kr (J.-S. Park), sunsukl@kRICT.re.kr (S.S. Lee).

¹ These authors contributed equally to this work.

2. Experimental

2.1. Synthesis of hybrid films

In order to maximize the influence of Au NPs doping on graphene, the optimization of sequential stacking methods was conducted. 2 mg/ml GO in methoxyethanol obtained from modified Hummer's method [19] was spin-coated onto a hydrophilic-treated SiO₂ (300 nm)/Si(001) substrate, in which the substrate rotational speed of 2000 rpm for 60 s. 1, 2, 3, and 5 mg/ml AuCl₃ (Sigma Aldrich, 99.8% purity) dissolved in nitromethane was coated on the GO/SiO₂ using spin-coating with a rotational speed of 3000 rpm for 30 s and immediately heated at 100 °C to remove the solvents. Graphene was synthesized using a conventional thermal chemical vapor deposition system (TCVD). A 25 μm-thick Cu foil (Alfa Aesar, 99.8% purity) was utilized as a catalytic substrate for graphene synthesis. The Cu foil was located onto the TCVD chamber, followed by pre-annealing at 1050 °C with introducing H₂ (200 sccm) under a pressure of ~5 Torr for 2 h in order to reduction and surface flattening of the Cu catalyst. After the pre-annealing process, graphene was immediately synthesized with introducing CH₄ (5 sccm) and H₂ (200 sccm) for 3 min. The TCVD reactor was cooled down to room temperature with H₂. The synthesized graphene was transferred onto the Au/GO/SiO₂ by a poly (methyl methacrylate) (PMMA)-assisted wet transfer technique [20]. The fabrication of a GO/Au NPs/graphene electrode was carried out as follows. Graphene was synthesized under the same TCVD conditions as for graphene/Au NPs/GO. After the transfer of graphene on SiO₂/Si, AuCl₃ and GO were sequentially spin-coated onto the graphene/

SiO₂/Si under the same conditions mentioned above.

2.2. Characterization

The structural feature of the hybrid films was investigated using micro Raman spectroscopy (Renishaw, 514 nm, Ar⁺ ion laser). The chemical identification of the hybrid films was conducted using X-ray photoelectron spectroscopy (XPS, Thermo scientific, ESCA Probe). XPS spectra were acquired with a normal emission geometry using conventional monochromatic Al Kα radiation ($h\nu = 1486.6$ eV). The pass energy was 20.0 eV and the spectra were deconvoluted by a standard non-linear-least-squares fitting procedure using Voigt functions. The structural characterization of the samples was carried out using scanning electron microscopy (SEM, S-4700, Hitach). The sheet resistance of the samples was measured by 4-point probe measurement system (CMT-SR1000 N, Advanced Instrument Technology). The optical transmittance of the hybrid films was examined by UV–visible spectroscopy (UV–2501PC, SHIMADZU).

3. Results and discussion

Fig. 1a provides a schematic representation for the fabrication process of a graphene/Au NPs/GO electrode. Chemically-derived GO and AuCl₃ (1, 2, 3, and 5 mg/ml) solutions were spin-coated onto a hydrophilic-treated SiO₂ (300 nm)/Si(001) substrate sequentially, after which TCVD-grown graphene was transferred onto the Au NPs/GO films. For initial assessment of the structural properties of TCVD-grown graphene and chemically-derived GO, resonant

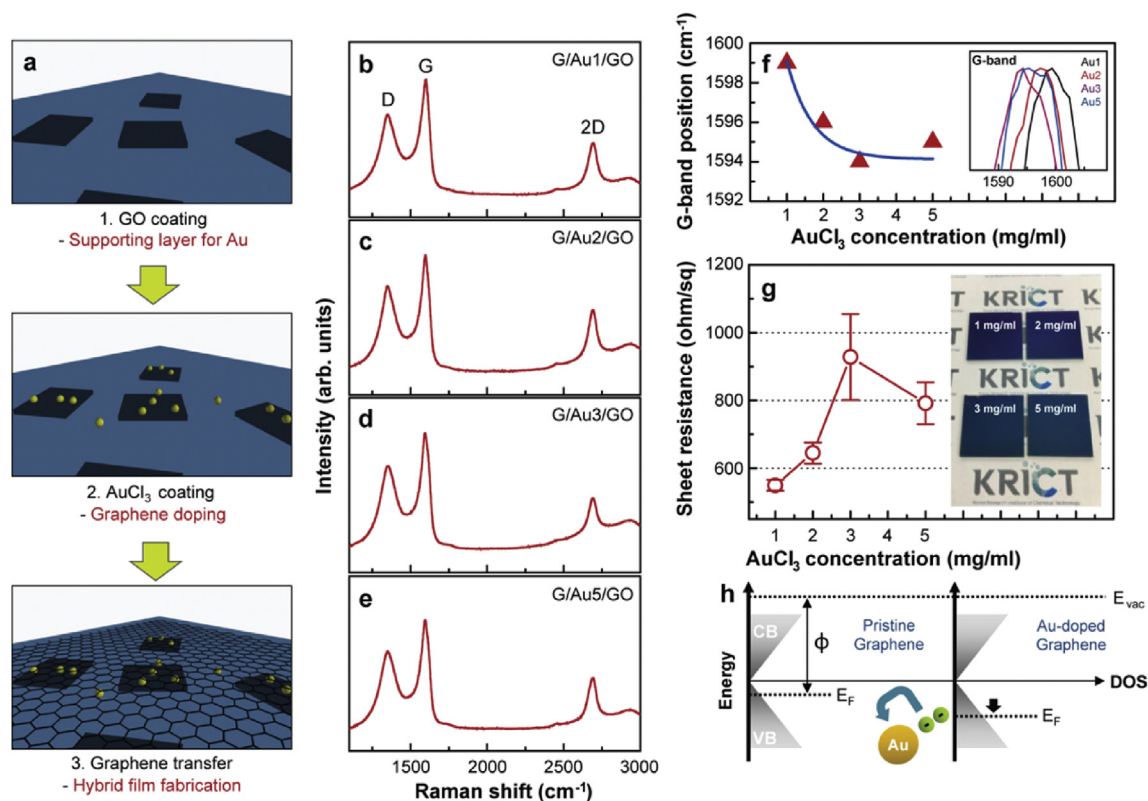


Fig. 1. (a) Schematic representation of the layer-by-layer assembly process for G/Au NPs/GO hybrid films. (b–e) Resonant Raman spectra recorded with an excitation wavelength of 514 nm for G/Au1/GO, G/Au2/GO, G/Au3/GO, and G/Au5/GO hybrid films. (f) Plots of the G-band position and (g) the sheet resistance of the hybrid films as a function of the concentration of AuCl₃. The inset in (f) indicates that the G-band shift as varying the concentration is clearly observed. The inset reveals a photograph of G/Au1/GO, G/Au2/GO, G/Au3/GO, and G/Au5/GO onto SiO₂/Si substrates. (h) The energy band diagrams of pristine graphene and Au-doped graphene hybrid structures. (A colour version of this figure can be viewed online.)

Download English Version:

<https://daneshyari.com/en/article/5431507>

Download Persian Version:

<https://daneshyari.com/article/5431507>

[Daneshyari.com](https://daneshyari.com)