Carbon Materials Nanoengineering for High Performance Optoelectronics

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1. Introduction

Graphene, the genuine two-dimensional hexagonal honey-comb carbon material, has been in the spotlight of academic and industrial societies since its unanticipated exfoliation by a mechanical drawing.[1] The outstanding material properties of graphene have been reported, including extremely high mechanical properties, high thermal conductivity, ballistic mobility of charge carriers, and ultra-large surface to volume ratio.[1-4] Recently, the application of graphene into optoelectronics is attracting a great deal of attentions. The excellent electrical and optical properties of graphene has been evaluated to alternate or complement the high cost, mechanically brittle rare earth elements or materials, which are currently employed for transparent conducting oxides (TCOs).[5,6] In this work, we report an optimized procedure to fabricate reduced and nitrogen (N)-doped graphene electrodes on a glass substrate by spin casting. We also introduce the inverted-type polymer light emitting diodes (iPLEDs) exhibiting the possibility for commercialization as one of the viable applications of highly reduced and N-doped graphene electrodes.

2. Results and Discussion

The fabrication process of N-doped graphene electrode is illustrated schematically in Figure 1a. Firstly, an aqueous dispersion of graphene oxide was prepared by a modified Hummers method.[5] Thin graphene oxide films were spin cast on glass substrates (Corning 1737). After an uniform film deposition, we optimized the reduction condition involved with N-doping to improve the electrical property of the graphene electrodes. It is well-known that foreign element doping intentionally introduces impurities for the purpose of modulating the electrical properties. A doped material may show a promoted electro-conductivity with the enhancement of carrier density. Based on this concept, we developed a doping process involved with hydrazine vapor and thermal treatment under ammonia gas. N with one more electron than C could act as an atomic dopant to enhance electrical conductivity and electron density. First of all, spin-coated graphene oxide samples were divided into two groups. While one group was handled with hydrazine vapor in a sealed vessel, another other group was kept without any treatment.
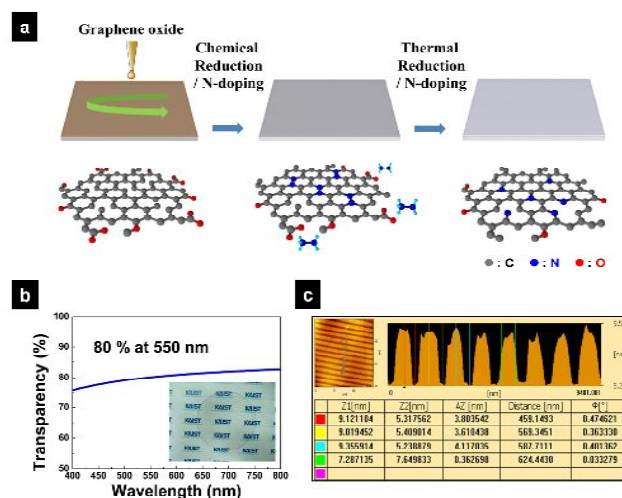

Figure 1. (a) Schematic description of N-doping and the reduction process for a transparent graphene electrode. (b) UV-Vis spectrum of the N-doped graphene film (Inset: Photograph of the N-doped graphene film). (c) Atomic force microscope (AFM) image to confirm N-doped reduced graphene thickness with graphene film patterned by selective etching.

After this selective hydrazine treatment, two groups were thermally reduced and doped under various combinations of H_2 and NH_3 mixture vapor at 750 °C. The optical transparency of N-doped graphene electrodes measured by a UV-Vis spectrophotometer was ~80 % at 550 nm, as described in Figure 1b. The inset image in Figure 1b shows the transparency of highly reduced and N-doped graphene films on a glass substrate. We maintained the film transparency of 80 % at 550 nm by controlling the spinning rate and the concentration of the graphene oxide solution. Since monolayer graphene absorbs ~2.3 % of the visible light, 80 % transparency indicates 8 or 9 stacked layers. Figure 1c shows the atomic force microscope (AFM) thickness profile of the N-doped graphene film. The thickness measurement of the N-doped reduced graphene pattern was obtained after the patterned etching of the graphene film through photopatterned poly (methyl methacrylate) (PMMA) photoresist layer as follows. A PMMA (M_w:

350,000 g/mol) was dissolved in chlorobenzene with the concentration of 4 wt%. After spin casting a PMMA film onto N-doped reduced graphene film, a deep-UV exposure process was carried out with a patterned mask for 2000 s. The exposed area was removed by 4-methyl-2-pentanone, and the graphene film was dry-etched with O_2 plasma. The remaining PMMA was also completely eliminated by 4-methyl-2-petanone. The measured thickness of graphene film was ~4 nm.

Table I. Sheet resistance and workfunction values of N-doped reduced graphene films.

750 °C (H_2, NH_3) unit : sccm	Hydrazine pre-treated samples		Hydrazine untreated samples	
	Sheet Resistance (R_s) (unit: kΩ / sq.) (± 0.01)	Work Function (Φ) (unit: eV) (± 0.005)	Sheet Resistance (R_s) (unit: kΩ / sq.) (± 0.01)	Work Function (Φ) (unit: eV) (± 0.005)
(100, 0)	0.51	4.22	1.24	4.41
(80, 20)	0.39	4.27	1.15	4.34
(60, 40)	0.30	4.25	0.89	4.23
(40, 60)	0.36	4.26	1.14	4.35
(20, 80)	0.42	4.27	1.17	4.31
(0, 100)	0.47	4.27	1.20	4.32

Table I shows the variation of sheet resistance (R_s) and the workfunction of N-doped reduced graphene film according to volume fraction of H_2/NH_3 mixture gases. The R_s values were measured with a 4-point probe system (KEITHLEY 2635) by the van der Pauw method. Each minimum R_s value in both hydrazine pre- and untreated samples was positioned at the gas condition of a 6/4 (H_2/NH_3) ratio. Moreover, the lowest R_s value of 300 Ω/□ was obtained with hydrazine pre-treatment. This demonstrates that hydrazine pretreatment plays a significant role optimizing the electrical conductivity of reduced graphene film. More interestingly, the workfunction of graphene electrodes could be precisely tuned with the range from 4.22 eV to 4.41 eV by N-doping and reduction conditions.

The iPLEDs with a green light-emitting polymer, poly(9,9′-dioctylfluorene)-co-benzothiadiazole (F8BT), were fabricated employing the N-doped graphene films as transparent cathodes (Figure 2a). It is noteworthy that N-doped graphene has a relatively lower workfunction (~ 4.25 eV) than that of FTO (4.70 eV). Such a low workfunction provides a unique opportunity as an electron injecting/collecting transparent electrode in inverted-type devices with a minimized electron injection barrier (Figure 2b). This is supported by the current (J) – voltage (V) characteristics of the electron only device (Figure 2c), where the N-doped graphene cathode exhibited excellent electron injection and conduction. Figure 2d presents the luminance (L) as a function of applied voltages (V). The L-V plot of iPLEDs with an N-doped graphene electrode is quite comparable to the device with FTO electrode for $V < 7$ V, featuring a turn-on voltage even lower than that of the FTO (the turn-on voltage defined at a luminance of 1 cd/m^2 was

5.2 V for FTO and 4.8 V for N-doped graphene, respectively). Meanwhile, in the relatively high voltage range ($V > 7$ V), the performance of iPLEDs fabricated with N-doped graphene electrodes is restricted by the rather high R_s of the graphene electrode.
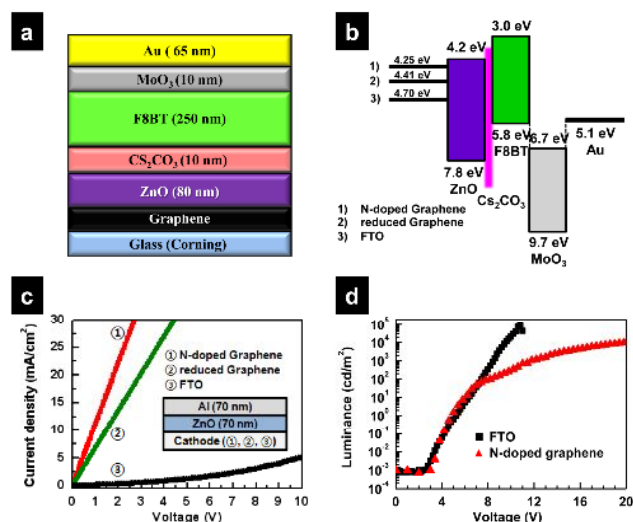

Figure 2. (a) Schematic illustration of iPLEDs based on the graphene electrode. (b) Energy level diagram of iPLEDs. (c) Current density vs voltage (J-V) characteristics of the electron-only devices with the different cathodes to directly compare the injection barrier between the cathode and the ZnO electron transport layer. (d) Luminance vs voltage (L-V) characteristics of iPLEDs fabricated with FTO and N-doped graphene electrode.

3. Conclusions

We have demonstrated highly conductive, N-doped, workfunction tunable graphene films and their application to iPLEDs transparent electrodes. Despite the high R_s values of N-doped graphene, the performance of iPLEDs employing the N-doped graphene electrodes is comparable to those with FTO electrodes. N-doped graphene films would be useful for the manifold purposes in optoelectronics in terms of scalability, mass production, and low cost.

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