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High-performance Bi-stage process in reduction of graphene oxide for transparent conductive electrodes

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A novel and innovative approach to develop reduction of graphene oxide (GO) solution for fabrication of highly and truly transparent conductive electrode (TCE) has been presented. Thanks to outstanding mechanical and electronic properties of graphene which offer practical applications in synthesizing composites as well as fabricating various optoelectronic devices, in this study, conductive reduced graphene oxide (r-GO) thin films were prepared through sequential chemical and thermal reduction process of homogeneously dispersed GO solutions. The conductivity and transparency of r-GO thin film is regulated using hydroiodic acid (HI) as reducing agent following by vacuum thermal annealing. The prepared r-GO is characterized by XRD, AFM, UV–vis and Raman spectroscopy. the AFM topographic images reveal surface roughness almost ~11 nm which became less than 2 nm for the 4 mg/mL solution. Moreover, XRD analysis and Raman spectra substantiate the interlayer spacing between rGO layers has been reduced dramatically and also electronic conjugation has been ameliorated after using HI chemical agent and 700 °C thermal annealing sequentially. Subsequently providing r-GO transparent electrode with decent and satisfactory transparency, acceptable conductivity and suitable work function, it has been exploited as the anode in organic light emitting diode (OLED). The maximum luminance efficiency and maximum power efficiency reached 4.2 cd/A and 0.83 lm/W, respectively. We believe that by optimizing the hole density, sheet resistance, transparency and surface morphology of the r-GO anodes, the device efficiencies can be remarkably increased further.

1. Introduction

In recent years, graphene as a marvelous two dimensional material has allured considerable attention since its breakthrough [1]. Due to the honeycomb lattice structure consisted by sp^2-hybridized carbon atoms, graphene demonstrates fascinating physical properties, including Dirac-Fermi behavior, high carrier mobility, excellent mechanical flexibility, transparency and etc. [1–5]. Therefore, it has been utilized in various application in photonics and optoelectronics area [6] such as field effect transistors [7], photovoltaic cells [8–11], photo detectors [12,13], touch screens [14] and organic light emitting diodes (OLED) [15–20].

In general, Graphene is developed by several techniques, including growth on silicon carbide surface [21–23], mechanical exfoliation [1], chemical exfoliation of graphite [24–27] and growth by chemical vapor deposition (CVD) on metal surfaces [28–31]. Amongst these techniques, chemically converted

Abbreviations: PEDOT: PSS, Poly (3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate); GO, Graphene oxide; r-GO, Reduced graphene oxide; OLED, Organic light emitting diode; CVD, Chemical vapor deposition; TCE, Transparent conductive electrode; HI, Hydroiodic acid; C_r-GO, Chemical reduced graphene oxide thin film; T_r-GO, Thermal reduced graphene oxide thin film; CT_r-GO, Chemical-Thermal reduced graphene oxide thin film; PVK, Poly (9-vinylcarbazole); Alq_3, Tris (8-hydroxyquinoline) aluminum(III); rms, Root mean square.

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graphene from solution-phase graphene oxide (GO) is a well-organized and the most efficient route for synthesizing composites and fabricating optoelectronic devices. In our previous works, we used GO as the dopant in HIL with PEDOT:PSS [32] or a water-soluble conjugated polymer [33] as green HILs to improve the hole injection and balance recombination of electron-hole pairs which showed remarkable results in OLEDs.

GO sheets are composed of planar graphene-like structures are decorated by epoxy, hydroxy, ether, ketone and other oxygen-containing functional groups [34,35], which make GO sheets hydrophilic and insulating in nature. Therefore, the deoxygenating process must be carried out to obtain reduced graphene oxide (r-GO) thin films [35–37]. Recently, many methods proposed for reduction of GO such as using of chemical toxic and friendly reducing agent [24,38], thermal reduction [39,40], electrochemical reduction [41,42], microwave and photo reduction [43,44]. However, each of these methods suffer disadvantages in the pragmatic approach which might decline their being reliability. As a vivid illustration, exposing to hydrazine, although has been introduced as effective chemical way for the de-oxygenation, it is not suitable for the reduction of GO films, due to the stiffening and disintegration of the films during reduction. Moreover, in this manner, electrical conductivity would not significant. Also, hydrazine is an unfriendly and highly toxic chemical agent which might result in some health hazard for users. Therefore, a more effective solution must be considered to reduce GO films into highly stable conductive graphene films. Typically the reduction process of GO consists of low-temperature chemical reduction [24,45–48] and/or high-temperature thermal annealing in different atmospheres. The later method is more effective, but usually needs temperatures above 1000 °C [15,39,49] while the first process can be accomplished at a temperature lower than 100 °C [47,50–52]. It is undeniable that lower working temperature is extremely important for practical applications [53–56] since graphene films are commonly supported on substrates [56] such as plastics that cannot withstand high temperature.

Among numerous applications of graphene, manufacturing it as a transparent conductive electrode (TCE) is one of the most noteworthy strategy to soar the performance of electronic devices. There are a wide variety of materials with different physical properties which are used as TCEs [57]. The common materials used so far for TCE are including indium tin oxide (ITO) [58], fluorine doped tin oxide (FTO) [59], cadmium oxide [60], doped zinc oxide and aluminum doped zinc oxide (AZO) [61–63]. The ITO glass has been commonly used as the anode for OLEDs, because ITO simultaneously provides good transparency and conductivity [64]. Nonetheless, it has many disadvantages like the high price of indium, low throughput deposition process, inflexibility and brittleness under bending [15,65,66]. Owing to its 2D structure, astounding electronic, impressive optical and mechanical properties, graphene can be considered as a reliable, thriving and low cost TCE for optoelectronic devices.

In this work, we present a novel and remarkable approach to reduction GO efficiently in terms of chemically and thermally stages which is amiable, eco-friendly and feasible to fabricate highly performance conductive thin films. It is momentous point to mention that the GO has been synthesized with narrow size/shape distribution based on modified Hummer method and then was spin-coated from 2, 4, 6 and 8 mg/ml GO dispersion in air and dried at 50 °C for 1 min to remove the solvent. Afterward, we have exposed GO thin films to HI fume and then used thermal treatment to acquire best result. In order to analyze the conductive layers, UV–vis absorption, AFM, XRD and Raman spectroscopy especially physical phenomena in anharmonic interactions are discussed on detailed to compare different reduction methods. According to this analysis, we present the best method to attain the high quality GO thin films to achieve high transparency along with the superior conductivity and adhesion. Finally, we examine the PLED devices made from these reduced GO electrodes with reasonable efficiencies.

2. Experimental

2.1. Synthesis of GO and GO spin-coating

We used the Hummer method [67] to oxidize the starting crystalline graphite for the synthesis of GO as previously used in our last work [32]. Briefly first, 2 g crystalline graphite, 1 g sodium nitrate and 46 mL of sulfuric acid were mixed and strongly stirred at 0 °C for 15 min in a 500 mL reaction flask immersed in a water-glycol bath (DFY-5 L/25). Then 6 g potassium permanganate was added slowly to the above solution and cooled for 15 min. After this, the suspended solution was stirred continuously for 1 h, and 92 mL of water was added slowly to the suspension for 10 min. Subsequently, the suspension was diluted by 280 mL of warm water and treated with 10 mL of H_2O_2 (30%) to reduce residual permanganate to soluble manganese ions. Finally, the resulting suspension was filtered, washed with water, and dried in a vacuum oven at 60 °C for 24 h to obtain GO.

Herein we have made thin films of GO using large surface area GO spin-coated at 2, 4, 6 and 8 mg/ml concentrations. The homogeneous GO suspension was deposited on quartz slides at the size of 2.5 × 2.5 cm. Before coating, the quartz substrates were ultrasonically cleaned in organic solution baths (NaOH 10%, followed by acetone, isopropanol and finally deionized water) each for 15 min, and then dried under the nitrogen stream and stored in the oven at 60 °C until use. Aqueous solutions of GO were deposited on the prepared quartz slides and allowed to wet the surface for about 2 min. Initially, to find the optimized rotational spin-coating speed resulting in appropriate thin films, GO solution with 8 mg/ml concentration had deposited on quartz slide, with different sequential rotational speed. The substrate was entirely covered with the adequate amount of GO solution. Based on surface uniformity and transparency measurement of the prepared films, we finally selected this procedure: 600, 800, and 2000 rpm each for 30s. For r-GO 2 sample (2 mg/ml), this procedure was repeated twice. Analyzing all films deposited at different weight ratios, it is discovered that GOs with 4 mg/ml and 2 mg/ml concentrations produce more reliable uniform, homogeneous and transparent films than 6 and 8 mg/ml. At 2 mg/ml of GO due to its lower concentration, film thickness can be controlled by repeating its spin-coating cycle. Increasing film thickness will reduce the transparency and eventually deteriorate sheet resistance. Briefly, the best deposition rate for an effective transparent electrode would be once acquired 3 significant parameters: film uniformity, lower sheet resistance and higher optical transparency [39]. Evaluating GO deposition with different concentration and spin coating rotational speeds and duration, we discovered the optimized layers with 4 mg/ml GO concentration.

2.2. Reduction of GO thin films and characterization techniques

In this project, reduction of GO thin films carried out in two steps: chemical reduction followed by thermal annealing. We have proposed using an acidic agent, hydroiodic (HI) acid, to efficiently reduce the GO films and subsequently in the next part, we applied thermal treatment in a vacuumed quartz furnace tube at 700 °C for an hour. To assess the effects of reduction process on GO thin films, we classified our experiments on thin films in 4 categories: 1) graphene oxide thin films (GO); 2) chemical reduced graphene