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Engineering of highly conductive and ultra-thin nitrogen-doped graphene films by combined methods of microwave irradiation, ultrasonic spraying and thermal annealing

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HIGHLIGHTS

- N-doped graphene films were fabricated by combined method.
- Graphene oxide mixed poly(ionic liquids) treated by microwave irradiation was used as an ink.
- High conductivity and high transparency was achieved.
- The film conductivity and level of doping can be controlled by annealing.
- Method is simple, scalable and applicable for broad applications.

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ABSTRACT

We report a new method for the fabrication of highly conductive and transparent ultrathin nitrogen (N) doped graphene films from graphene inks by combining a microwave treatment, ultrasonic nebulizer coating and thermal annealing. The starting graphene oxide (GO) solution was mixed with poly(ionic liquids) (PIL) and treated with microwave (Mw) irradiation to prepare Mw-rGO@PIL inks, which is a gentle reduction of PIL-attached reduced graphene oxide (rGO). In this non-contacting heating method, the PIL was used to not only mediate microwave irradiation and prevent disorder of the graphitic structure, but also repair the lattice defects and introduce nitrogen into the graphitic structure. The ultra-thin graphene films were prepared using the nebulizer for controlling the aerosol droplet distribution of the Mw-rGO@PIL inks coated onto quartz or glass substrates. The prepared films displayed a surface resistance of $\sim 1.45 \times 10^7$ Ω/sq at a transparency of ~87%. A further thermal treatment was conducted to improve the conductivity of the prepared films by annealing at a high temperature (900 °C), which allowed complete reduction of oxygen containing groups, enhanced graphitization, and reordering of the basal graphene plane and N-doping of the carbon lattice (pyrolytic PIL). The resulting thin films significantly reduced the surface resistance in the range of 1.5×10^3 to 6.2×10^3 Ω/sq at a transparency ranging from 68 to 82%, respectively. The presented method involving *in situ* N-doping offers a promising environmentally-friendly, low-cost and scalable manufacture of high-quality conductive N-doped graphene films.

1. Introduction

Graphene films have excellent electrical, mechanical, chemical and optical properties and been explored to design new materials and devices for a broad range of applications including flexible electronics, flexible screens, antennas, chemical sensors, biosensors, energy storage, solar cells, transparent conducting electrodes, and protective coatings [1–6]. Depending on the properties requirements (e.g. conductivity, thickness, transparency and mechanical properties) these films can be fabricated in the form of single layers, thin transparent or thick

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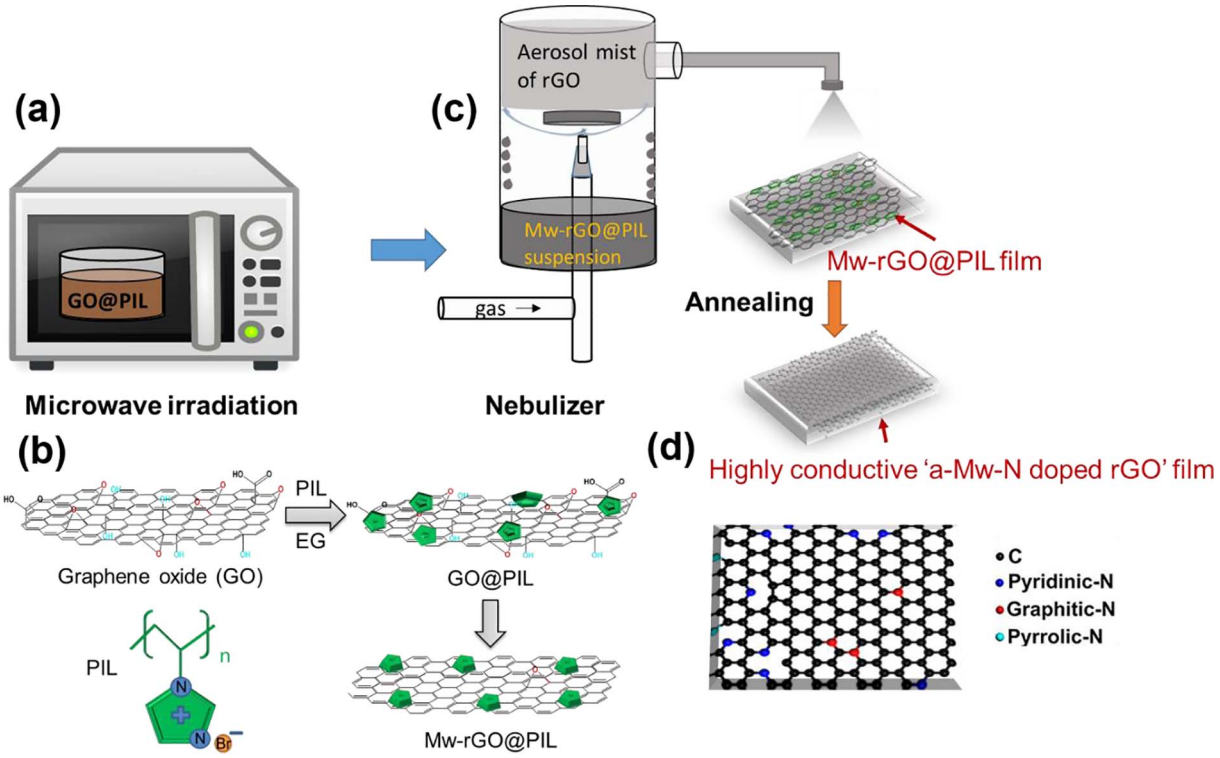

Fig. 1. Schematic diagram of the fabrication approach of highly conductive N-doped graphene thin films that combines 3 steps. In the first step (a – b), the GO modified with PILs was heated under microwave irradiation to make well-dispersed Mw-rGO@PIL inks. In the second step (c), the ink was used for the preparation of thin films by an aerosol mist coating using a nebulizer. In the final step, these coated films were thermally annealed to achieve highly conductive and transparent N-doped graphene thin films.

graphene films using various deposition and coating techniques including chemical vapour deposition (CVD), sputtering, solution spraying, drop casting, dip coating, spin coating, and printing [1,5,7]. Among them, a solution-processed fabrication based on the dispersion of exfoliated graphene in a certain solvent with or without surfactants, called graphene inks, is the most desirable method for rapid manufacturing of low-cost thin and thick graphene films [3,8–10]. For example, Li et al. reported transparent films grown through Langmuir-Blodgett (LB) assembly achieved a sheet resistance (Rs) of 8 kΩ/sq at corresponding optical transmittance (T) of ~83% [11]. De et al. have demonstrated graphene-based films with Rs of 10^3–10^6 Ω/sq at transmittance values ranging from 35 to 90% [12]. A Rs of 9900 Ω/sq at T of 93.7 for rGO film reduced by sodium borohydride ($NaBH_4$) and doped by gold trichloride ($AuCl_3$) [13], and a film with Rs of 3110 Ω/sq at T of 90% for edge-selective functionalization of graphite with thermal reduction [14]. However, graphene inks used for thin film preparations have a number of limitations due to the various printing rheological requirements (density, surface tension, viscosity) and the use of additional ingredients and binders that have an impact on the electrical conductivity and surface properties [15,16].

Another approach to prepare graphene thin films is to use graphene oxide (GO) as pre-coatings as it has better adhesion and binding properties to common substrates (glass, plastic, textile, Si wafer, etc). Unfortunately, GO contains abundant oxygen functional groups on its basal plane and edges that create structural defects and result in large energy band gaps in the electron density states, and consequently lowers the film's conductivity. In order to restore the structural and electronic properties of GO, conventional chemical routes with reducing agents were generally used. However, they are restricted from toxicity or negative environmental impact, and lack of complete removal of oxygen groups from the structure [17,18]. To address this problem, a new reduction method of GO based on microwave treatment has been recently introduced [19,21–23]. The advantage of electromagnetic radiation is that the energy is directly converted into heat that is distributed uniformly, which enables rapid heating of reactant without interaction with the surrounding [20,24]. Thus, the irradiation method has been demonstrated as less destructive, economical, ultrafast and eco-friendly for the controllable reduction of GO (rGO) [20,25,26]. Nevertheless, the development of these methods has not been translated for practical applications of transparent conductive graphene films since the reduction efficiency is still low, and there are limitations of producing reproducible rGO films under an ambient condition (burn) or even protective environment [26–28].

Recently, spray pyrolysis has been introduced, in which the mist of aqueous suspension of GO from an ultrasonic nebulizer is transported in a tube furnace at high temperature by the N_2 gas carrier [29–31]. During the process, droplets containing GO sheets accumulated at the surface shrinks as solvents evaporate when they pass through the furnace that results in the collapse of the rGO sheet to form a crumpled ball structure. This coating layer with 3D texture or crumpled topographies allow high surface area electrodes for battery and supercapacitor applications [30,32,33]. However, this method is not applicable for the fabrication of transparent thin graphene films since they provide negative affect to the optical transparency and high contacting resistance between the crumpled graphene balls. Therefore further improvements and the development of new methods that are simple, scalable and provide highly conductive and transparent graphene films specially for nitrogen (N)-doped graphene films is still open and needs to be solved.

In this work, considering these limitations and disadvantages we present a simple and scalable route to fabricate transparent and highly conductive N-doped graphene films from GO by combining microwave irradiation, ultrasonic spray coating and thermal annealing. This concept is schematically presented in Fig. 1 showing a three-step process. In the first step, a microwave treatment of GO combined with poly (ionic liquids) (PIL) is proposed to prepare a special graphene ink (referred to as Mw-rGO@PIL) in order to achieve several tasks. The use of PILs is to not only improve structural integrity and repair the lattice