Ink-jet printed highly conductive pristine graphene patterns achieved with water-based ink and aqueous doping processing

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ABSTRACT

We report an efficient inkjet printing of water-based pristine GNPs graphene ink and a facile aqueous halogen doping process that provides significant and thermally stable conductivity enhancement of printed patterns. Highly concentrated aqueous graphene ink populated by few-layer pristine graphene flakes is obtained by means of scalable shear exfoliation process with the aid of bromine intercalation. The as-printed GNP films which has been merely treated by drying at 100 °C exhibits DC conductivity (σ_{DC}) of ~1400 S/m likely due to bromine doping effect. This value is significantly increased to ~3 × 10^4 S/m when an additional treatment by means of dipping in aqueous iodine solution is applied prior to the drying. As contrast, σ_{DC} is increased to ~2.4 × 10^4 S/m when a mere annealing at elevated temperature in air is employed. When the aqueous iodine doping process and annealing at elevated temperature is combined, an unprecedented value of σ_{DC} ~10^5 S/m is achieved. The availability of water-based GNPs inks and low-temperature doping scheme for efficient and reliable conductivity enhancement has offered a pathway for the application of GNPs in different printed electronics devices.

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1. Introduction

Printed electronics provides an alternative to the conventional technologies by enabling low cost, large area, flexible devices [1]. Electrical interconnections are one of the main challenges in the printed electronics, to connect different functional units of an electronic device. With the progressive advancement of large area and low cost printed electronic devices, the requirement for reliable interconnections with lower power consumption fabricated at low temperature is necessary. The conventional copper based interconnections suffer severe problems in terms of cost efficiency when they are processed with photolithography technique [2]. Therefore, there is being a copious amount of research to find alternative interconnect materials to overcome such problems. The required characteristics needed for such alternative materials are

their high electrical conductivity, excellent reliability, good mechanical strength and printability. Graphene, a carbon sheet with atomic thickness [3,4], is being widely studied as an ideal alternative material for the aforementioned areas due to its unique inherent properties like higher electrical conductivity and mechanical strength. Among the available printing methods (ink-jet printing, nozzle printing, spray printing), inkjet printing enables additive patterning, reduction in material waste, direct writing, compatibility with a variety of substrates and scalability to large area manufacturing [5–9]. Inkjet-printing of pristine graphene nano-platelets (GNPs) is proven to be a promising approach since it combines the attractive features of graphene as well as the drop-on-demand inkjet fabrication process [9]. Although, several strategies for inkjet printing of GNPs are reported widely in literature, they are mainly limited by the key issues, namely, long processing time for pristine graphene exfoliation (typically requires many hours of operation), low ink concentration (usually ~1 mg/mL) and low electrical conductivity (σ_{DC} ~100 S/m) of the printed films without any further post-treatment process [6,9]. From processing aspect, they suffer from the use of unfriendly organic solvents for ink formulation and high temperature treatment (>250 °C) for improved electrical performance. The conventional method of

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annealing at elevated temperature is incompatible with a wide range of unconventional polymer and cellulose substrates [5–7,9,10].

Due to the requirement of environmental benign and material compability, water based inks are preferred for real application. One example is the generation of printed sensors with graphene on paper with special coatings for food packaging for which organic solvent is unwelcome. To our best knowledge, inkjet printable water based inks have been so far formulated using graphene oxide (GO) flakes but no pristine GNPs yet [11,12]. Compared to pristine GNPs, reduced graphene oxide (rGO) flakes contain high density of various defects. This present work is motivated to formulate water based inks with pristine GNPs instead of using rGO flakes. From the post-processing aspect, chemical doping provides a promising low-temperature processing method for conductivity enhancement. Among all the available resources for doping agents, e.g., I_2, Br_2, alkali metal based dopants, HCl, HNO_3; iodine is considered to be an efficient and practical dopant and widely employed for doping graphene and carbon nanotubes (CNTs) through physisorption [13–15]. However, chemical doping with physisorption generally suffers from rather poor thermal stability. As an example, iodine species detach from surfaces of graphene and carbon nanotubes at temperature at around 100–150 °C or under vacuum condition [13,14]. This creates reliability problems in many real life applications, for example if Joule heating starts to play a role. Therefore, doped graphene films of with high thermal stability are required.

The main premise of this work is to address the above mentioned issues by coupling highly concentrated water-based GNPs ink with a simple and reliable method using aqueous iodine doping to achieve highly conductive and thermally stable graphene films. The approach for GNP production is based on our previously reported shear-exfoliation technique that enables high-concentration graphene dispersions in gram-scale quantities with shorter processing times of only 30 min [9]. Here, the unfriendly organic solvent is replaced with aqueous media containing bromine for intercalation. Successful inkjet printing of highly-concentrated (~8.5 mg/mL) inkjet printable few-layer GNPs ink populated by few layer graphene flakes are achieved. The as-printed GNP films which has been merely treated by drying at 100 °C exhibits a DC conductivity (σ_{DC}) of ~1400 S/m most likely due to the doping effect of Br remaining in the films [16,17]. This value can be further enhanced by 1 order of magnitude, i.e., reaching ~3 × 10^4 S/m, when a subsequent step of dipping the GNPs films in an aqueous iodine solution followed by the drying process is employed. As contrast, the conductivity of an as-printed GNPs film is increased up to a value of ~2.4 × 10^4 S/m merely with a annealing at elevated temperature 250–300 °C in air. When a combination of the aqueous iodine doping process and annealing at elevated temperature is employed, we have achieved an unprecedented value of ~10^5 S/m of conductivity. The results also show a high thermal stability character of iodine doping in the printed GNP films.

2. Experimental

2.1. Exfoliation of GNPs from graphite

GNPs are first exfoliated from graphite powders by aid of bromine intercalation [18] in aqueous media using a water soluble cellulose stabilizer ((Hydroxypropyl) methyl cellulose). Intercalation of molecular Br_2 into the graphite results in decrease in the cohesive forces between the layers in the graphite and thus producing increased number of graphene nano-platelets (GNPs) [18]. Graphite flakes (Sigma Aldrich, initial size < 20 μm) are first immersed in saturated Br_2 water for overnight with initial graphite

concentration of ~50 mg/mL. Saturated Br_2 water is prepared by mixing Br with deionized (DI) water and the solution is kept in dark to avoid light induced reactions. The aqueous cellulose solution is prepared by mixing cellulose with warm DI water and sonicating for 1 h. All the ingredients are mixed together in a large beaker for shear-mixing. The shear-mixer (Silverson L5M) is equipped with a 250 W motor, providing a maximum rotor speed of 8000 r.p.m (6000 r.p.m under full load) and is described in detail elsewhere [9,19]. Two independent parameters, i.e., shear mixing speed (V) and processing time are varied and optimized to obtain the minimum thickness (t_G) and lateral size (L_G) of GNPs. The dispersion is centrifuged in a Thermo Scientific bench top centrifuge setup (5000 r.p.m) in order to remove the thick and large particles. The concentration of the flakes (C_G) is measured by weighing the dried GNPs inside the supernatant.

2.2. Sample preparation for topographical and Raman measurements

To characterize the topographical properties of the GNPs, the supernatant collected right after the centrifugation, is spin-coated and dried on cleaned Si/SiO$_2$ substrates (2.2 × 2.2 cm^2). We use non-contact mode atomic force microscopy (AFM) technique to characterize the thickness and lateral size of the GNPs. Transmission Electron Microscopy (TEM) samples are prepared by drop-casting the dispersion on copper grids with carbon support. All TEM measurements are performed at 80 kV acceleration voltages. For Raman measurements the samples are characterized by RENISHAW "Invia" Raman microscope with 532 nm laser for excitation and 20 × lens. Raman spectra are obtained from randomly chosen 5 spots from each sample.

2.3. Ink formulation and inkjet printing

The aqueous GNPs solution collected right after the centrifugation is used to formulate ink. The ink formulation starts from concentrating the aqueous GNPs solution by boiling the vials for 1 h. It is followed by tuning of the viscosity and surface tension by adding 2, 3-Butanediol with the aid of a mild sonication process. The viscosity of the solution is measured by Brookfield viscometer. The inkjet printability of the produced GNPs ink is tested by the Dimatix (DMP-2831) inkjet printing setup on both glass and Poly-ethylene terephthalate (PET) substrates. During printing, a 10 pL cartridge (DMC-11610) with nozzle diameter of 20 μm is used. The as-printed samples are dried at 100 °C in vacuum oven for 1 h for the subsequent post-treatment and measurement.

2.4. Post-treatment of the printed films

After the aforementioned drying process, the readily available inkjet graphene features are dipped into saturated aqueous iodine solution with the concentration of I$_2$ at 0.5 mM I$_2$ molecules cannot be intercalated into graphite flakes easily during the exfoliation process like Br$_2$ as mentioned above [20]. Therefore, the post-treatment with iodine is chosen right after the preparation of the GNPs films. The reaction times are varied during this process. The samples are subsequently dried at 100 °C in vacuum oven for 1.5 h. Annealing of the samples on glass is conducted in air on hot plate at varied temperature.

2.5. Characterization of the printed films

The sheet resistance (R_S) of the samples is measured by four-point probe station (AIT, CMT-SR2000N). To minimize the errors of the four point probe measurement, geometric correction factors