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Finding optimal HBr reduction of inkjet printed graphene oxide for flexible electronics

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HIGHLIGHTS

- The process of reduction of graphene oxide inkjet printouts by HBr is investigated.
- Impact of parameters of reduction on the chemical structure of printout is studied.
- Impact of parameters of reduction on the sheet resistance of printout is studied.
- Optimal parameters of reduction are proposed.

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ABSTRACT

In this article we present the results of our investigations of reduction of graphene oxide overprints, deposited by ink-jet method, by hydrobromic acid. Our study presents impact of different parameters of reduction, such as a temperature and time of the process on the chemical composition and electrical conductivity of the resulting material – reduced graphene oxide. Our results show the outstanding potential of this method for use in the production of flexible and elastic electronics and indicate the optimal parameters of reduction, which allow producing the optimal product.

1. Introduction

Graphene attracts significant attention of both scientific and industrial communities. Its popularity is caused by its unique properties, such as two-dimensional crystallographic structure [1], high physical durability [2] and electronic structure characterized by unique dispersion relation of the charge carriers [1]. Those exceptional properties ensure many potential applications for this material, such as electronics [3], light emitting diodes [4] or photovoltaics [5]. In particular, recent reports show that graphene has been successfully used in production of flexible devices such as electrodes [6,7] and field-effect transistors [8].

There are several methods of production of graphene, such as mechanical exfoliation or chemical vapor deposition (CVD) [9,10]. Both offer high quality of the material – in the former case the characteristics are closest to the theoretical predictions [11], and in the latter, the properties can be tailored by controlling parameters of the deposition process [12]. However, both of them offer limited production capabilities of high quality graphene, and thus, do not meet the economical expectations of the industry.

One of the most resource efficient and scalable method of production of graphene is fabrication and subsequent reduction of graphene oxide (GO) [13]. In this process the graphite crystals are

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first subjected to the oxidative treatments, which also lead to the intercalation. Next, the obtained GO is exfoliated to the form of monolayers or few-layers stacks [14]. The material prepared this way is later deoxidized forming reduced graphene oxide (rGO). While it is not possible to fully restore the structure to its original configuration, several properties such as the electrical conductivity may reach satisfying levels [15]. Furthermore, rGO can be produced in large quantities at relatively low cost [16]. GO before reduction processes, can also form stable dispersions far more easily than pristine graphene [17,18]. Because of this, GO can be deposited over very large areas using printing methods, such as inkjet [19] or screen printing, which are already widely used in production of broad range of devices, such as light emitting diodes (LED), photovoltaics (PV), flexible electronics or memory devices [4,18,20–25]. The inkjet method has been shown to allow for direct deposition of graphene or graphene oxide materials on surfaces with varying curvatures [26], while providing high parameters of conductivity or electron mobility [27].

One of the biggest issues of the rGO production methods is the restoration of the graphene structure. Initially the material is heavily functionalized by carboxyl, hydroxyl, ether and epoxy groups and the carbon atoms are dominantly in sp^3 hybridization [28]. These groups can be partially removed and partially it is possible to restore sp^2 in few types of processes, such as thermal treatment, UV irradiation or chemical reactions [29–33]. The selection of the proper GO reduction method is crucial due to possibly destructive influence of the reducing factor on the substrate. For instance, it is not possible to use the thermal reduction in case of GO on PET substrate as PET is damaged at 120 °C, while GO reduction become efficient at much higher temperatures [34]. The last of these methods attracts the most attention due to the high degree of control of the process. To procure it several factors can be adjusted, such as temperature and time of the procedure. The most important, however, is the right selection of the reducing agent, as it allows to remove the oxygen groups selectively [10]. What is more, the selection of proper reagent is crucial to avoid the degradation substrate of rGO.

Several reductants are commonly used to reduce graphene oxide – hydrazine (N_2H_4) [13], aluminium hydride ($LiAlH_4$) [13] or sodium borohydride ($NaBH_4$) [13]. However, recently, hydrohalic acids, such as hydrogen iodide (HI) [35], hydrogen chloride (HCl) [36] and hydrogen bromide (HBr) have attracted a growing attention due to the fact that they remove a wide range of oxygen-containing groups [37]. In particular, HBr seems very promising. It is, unlike most of the listed previously agents, one of the few able to remove hydroxyl groups from graphene oxide, allowing for much higher degree of restoration of sp^2 bonds in the rGO structure [37]. Furthermore, it does not decrease the wettability of reduced material, as residual oxygen can be found on the surface of rGO prepared as such [38,39]. What is more, HBr influences PET substrates in only a small degree, thus, it increases the range of applications, where it can be used, to flexible electronics, photovoltaics and sensors. At the same time it is much safer than one of the strongest reductants – N_2H_4 [13].

In this article we investigate one of the most important issues of the reduction of GO with HBr from the industrial point of view – the efficiency of the process of the graphene oxide printouts prepared with the industrial methods. We correlate the parameters of the reduction, such as time or temperature with the changes in the chemical structure of the material. This knowledge might give the control over the chemical composition of rGO, which in turn is related to the final characteristics of the material. In particular, we concentrate on the electrical conductivity of the overprints. Presented results will shed more light on the process of the chemical reduction of GO by HBr and be a contribution into the scientific trend of the graphene oxide reduction. They will also be important to the applications of printed GO/rGO materials providing both possibility of achieving the desired parameters of the output material and the optimal conditions at which the process should be held.

2. Experimental

The graphene oxide was prepared by modified Hummers method [40]. The graphite sample (Asbury Carbons, particle diameter: 300–425 μm) and potassium nitrate (POCh, pure) were added to a beaker containing concentrated sulphuric acid (POCh, 96–98%, analytical grade). The beaker was cooled in an ice bath to under 5 °C and potassium permanganate (POCh, pure) was gradually added. After delivering the last portion, the ice bath was removed, replaced by water (25 °C) and left in that state for 16 h. The beaker was once more put into ice bath and deionized water (DI) was slowly poured into suspension. The mixture was then heated to 95 °C for 15 min, further diluted by addition of DI water and cooled to room temperature. Then, small amount of 30% hydrogen peroxide was added. The oxidized graphite was purified by centrifugation, firstly in HCl solution and next by multiple centrifugations in water. Finally, pure graphite oxide was exfoliated by sonication in water (500 W, 30 min) to obtain a stable suspension of GO flakes. In order to select the fragment sizes which are compatible with GO deposition setup used in our experiments the material was filtered using 1 μm glass filter, which limited the sizes of the GO flakes (see SEM and AFM images in Supplementary Material). As a result we developed the ink based on the mixture of GO water dispersion and propylene glycol $C_3H_8O_2$. Such liquid is characterized by the 1/Oh = 2.33 (see Table S1 in supplementary materials) and its other properties (as viscosity, surface tension etc. – see Table S1 in supplemental materials) are close to that measured for a commercial color ink which is dedicated for our printer and printhead [28].

The material was deposited using a commercial Mimaki GP 604 S printer onto 125 μm polyethylene terephthalate (PET) foil substrates. The printer was equipped with the Epson DX4 printhead with 2 × 180 matrix of 20 μm nozzles and table heater allowing for controlled temperature of deposition in range of 20–60 °C. Using this setup a series of 1 × 1 cm^2 graphene oxide printouts, with thicknesses of about 15 nm, was prepared.

Printouts were reduced using HBr acid diluted in water (48% HBr). The process was conducted on a heat plate, allowing for adjustment of the temperature in wide range. Uniformity of both temperature and chemical composition of the solution was ensured by using magnetic stirrer. Using this method two series of samples were prepared. First series was reduced over 90 min time span at temperatures of 40 °C, 50 °C, 60 °C, 70 °C and 90 °C. The second one was reduced at 90 °C over time spans 15, 30, 45, 60, 300, 600, 900, 1800, 2700, 3600, 4500, 5400, 7200, 10800 and 14400 s. Each of the samples was reduced in the single, continuous process. After the process, samples were cleaned using deionized water and dried in ambient conditions.

The chemical analysis of the reduced GO printouts was conducted using X-Ray Photoemission Spectroscopy (XPS) in ultra-high vacuum (UHV) conditions with EA 125 hemispherical analyzer, which is a part of Omicron GmbH Multiprobe P system. X-Ray radiation, generated by magnesium anode (non-monochromated Mg Kα line - 1254.6 eV) was used. The spot size was set to 3 mm diameter.

Electrical conductivity of the reduced printouts was investigated with Hall measurements in Van Der Pauw configuration and using resonant microwaves with the use of MICROWAVE FREQUENCY Q-METER. The Van Der Pauw measurements were conducted using