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Influence of Oxidation and Deposition Process on Electrical Properties of Graphene Films

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Abstract: The influence of reducibility of graphene oxide (GO) by hydrazine hydrate on their electrical properties was investigated. Reduced GO (rGO) films were obtained by mixing of graphene oxide (GO) solution with hydrazine hydrant (HH) (10% and 50% of concentration) and final dropping on Si substrate or by dropping of GO solution on Si substrate already covered by HH (10% or 50% of concentration). Electrical measurements show semiconductor value ofelectrical conductivity for the samples with high concentration of HH (10^{-4} A at applied ±10 V). At the same time low concentration of HH leads to much smaller value of conductivity (10^{-7} A at ± 10 V).

Key words: Graphene oxide, process preparation, electrical properties.

1. Introduction

Graphene (reduced graphene oxide, rGO) is a two-dimensional material with unique transport and physicochemical properties and potential applications in sensors, super-capacitors and hydrogen storage, etc. [1]. Graphene can be obtained from graphene oxide (GO) and a lot of preparation techniques have been reported [2]. By nature, is electrically insulating and thus cannot be used, without further processing, as a conductive nanomaterial, graphene-based platelets on a large scale [1], in composites [3], paper-like materials and thin films [4], as a coating layer [5], and as transparent conductive films [6]. However, GO has a wide range of oxygen functionalities, such as 1,2-epoxide and alcohol groups on the basal planes, and carboxyl and ketone groups at the edges [7, 8]. In addition, the presence of the oxygen functional groups makes GO thermally unstable, as it undergoes pyrolysis at elevated temperatures [9, 10]. Notably, it has been demonstrated that the electrical conductivity of GO can be restored close to the level of graphite by chemical reduction [11-14]. Due to that hydrazine was proposed as an efficient reducing agent for obtaining grapheme [15]. However, influence of hydrazine hydrate on electrical properties of graphene has not been studied in great detail.

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2. Experiments

Solution of graphene oxide (GO) were prepared by dissolving of GO powder (obtained by Hummer-based method) in water. Reduction of GO was achieved by using hydrazine (N_2H_4) hydrate (HH) in two different concentrations: 10% and 50% and in two different ways. For first two samples GO + 10%N_2H_4 or GO + 50%N_2H_4 solutions (1:1) were dropped on Si substrates after long ultrasonic stirring and dried (samples GO + 10%N_2H_4 and GO + 50%N_2H_4, respectively). And for the next two samples solution of

GO was dropped on Si substrate preliminary covered by thin layer of N_2H_4 with concentrations 10% or 50% (samples GO on 10%$N_2H_4$and GO on 50%N_2H_4).The obtained samples were studied by powder X-ray diffraction (XRD) at room temperature in a continuous scanning mode (step: 0.02 and time: 10 s) on a Siemens D500 diffractometer with secondary monochromator CuKα X-radiation in the range (2θ: 5-60°), 40 kV, 30 mA. Morphology of the obtained samples was checked using a Scanning Electron Microscope. The current-voltage (I-V) cycles were obtained using a Keithley Source Meter 2410C and manual probes with tungsten tips at room temperature.

3. Results and Discussion

XRD spectra of studied samples present broad peak and its position (about 25-30°) is similar for all analyzed films (Fig. 1). Such peak corresponds to peak in reduced grapheme [17] and it is possible to say, that all analyzed samples represented really rGO films.

Scanning electron microscope (SEM) analyze of samples of reduced GO that obtained by using of HH with concentration 50% (GO + 50%N_2H_4 in Fig. 2 and GO on 50%N_2H_4 in Fig. 3) does not show significant difference. In both cases the reduced GO films are transparent and continue.

The main difference between studied films was found during the measurements of electrical properties (volage-current dependency). It was found that reducing of GO by HH with high concentration (50%) (sample GO + 50%N_2H_4) leads to semiconductor behavior of graphene and show high value of current (10^{-4}A) (Fig. 4a). At the same time, reducing of GO by HH with low concentration (10%) (sample GO + 10%N_2H_4) leads to much smaller value of conductivity (current 10^{-6} A) (Fig. 4b). However, samples obtained by dropping of GO solution on preliminary covering of Si substrate by N_2H_4 with concentration equal 50% (sample GO on 50%N_2H_4) shows value of the current about 10^{-4} A that is similar to sample GO + 50%N_2H_4 but form of the curve is more linear (Fig. 4c). Fig. 4d shows the behavior of current for the samples obtained by dropping of GO solution on covered substrate by HH with 10% (sample GO on 10%N_2H_4) and this value of the current is the lowest one in comparison to others films (10^{-7}A).

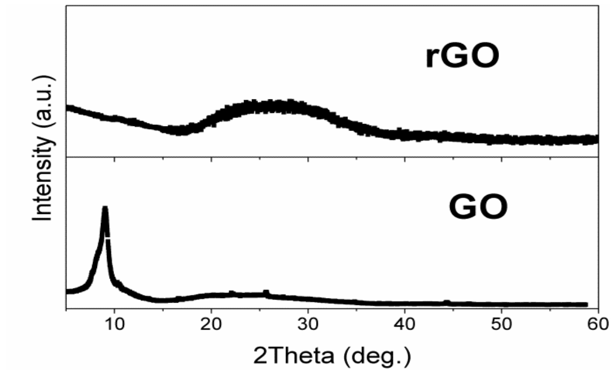

Fig. 1 Typical spectra for graphene oxide (GO) and reduced graphene (rGO) films studied in the current work.

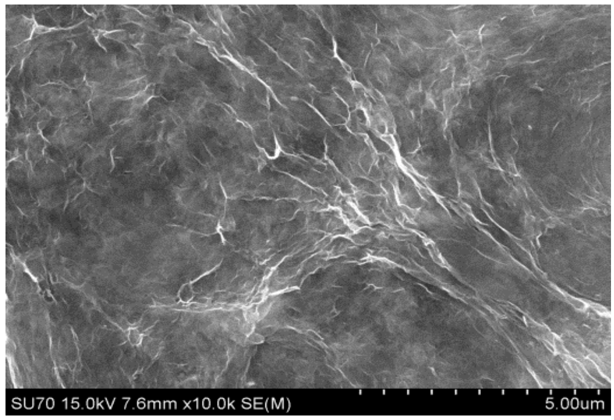

Fig. 2 SEM picture of reduced graphene, obtained by mixing of graphene oxide solution with hydrazine hydrate with concentration equal to 50% (GO + 50%N_2H_4).

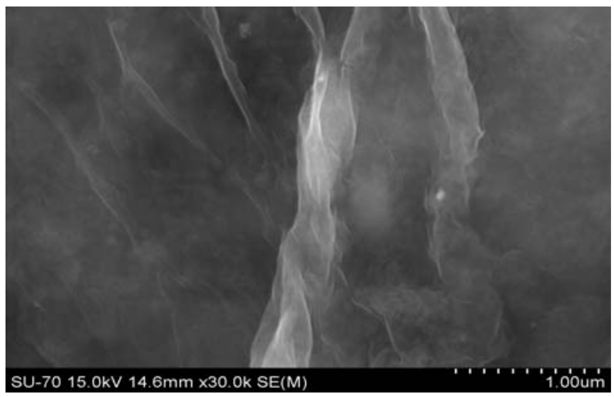

Fig. 3 SEM picture of reduced graphene, obtained by deposition of graphene oxide solution on thin layer of hydrazine hydrate with concentration equal to 50% (GO on 50%N_2H_4).

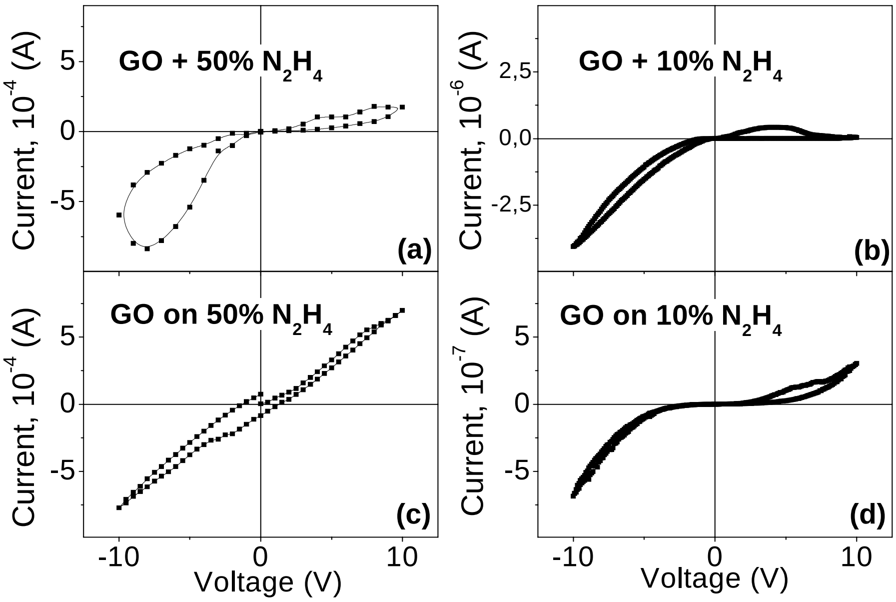

Fig. 4 I-V data of graphene films obtained by mixing GO (a) with HH 50%, (b) with HH 10%, by deposition of GO (c) on thin layer of HH 50% and (d) on HH 10%.

Such structural results clearly show that reduction of the exfoliated GO results in considerable removal of oxygen. The same conclusion can be reached through the electrical conductivity measurements since the observed increase in conductivity upon reduction of GO requires that conductive pathways of conjugated carbon atoms be re-established. Thus, the characterization of the reduced GO indicates that the hydrazine treatment results in the formation of unsaturated and conjugated carbon atoms, which in turn imparts electrical conductivity and it is in agreement with published already [18]. Moreover, covering of substrate by hydrazine hydrate before deposition of GO films leads to more homogeneous distribution of hydrazine between surface of substrate and GO film that could lead to better reducing of graphene oxide top filmand results in the higher value of electrical conductivity. Moreover, according to the better electrical results obtained for films deposited on substrate with layer of hydrazine hydrant, it is possible to suppose, that during the such way of preparation of samples all bonds (C-O-C, OH, C=O) are well reduced in opposite to reducing by simple mixing of GO and HH [16].

4. Conclusions

According to the obtained results, hydrazine with high concentration in 50% leads to fast reducing of GO and these samples shown semiconductor behavior with current about 10^{-4} A and deposition of GO on covered substrate by HH with 50% could be perspective.

Acknowledgments

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