In situ elastic recoil detection for graphene oxide analysis

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Abstract

Thin graphene oxide films were irradiated with 12.5, 18 and 23 MeV iodine beams. At the same time, stoichiometry changes have been monitored by the *in situ* time-of-flight elastic recoil detection analysis. Final state of the irradiated films indicated their reduction is similar to the reduction of samples undergoing classical thermal annealing procedure. Nuclear energy loss was identified as the main force driving reduction process, although electronic energy loss seems to play an important role in behaviour of the hydrogen under irradiation.

Keywords: graphene oxide, ion irradiation, elastic recoil detection

1. Introduction

Graphene oxide (GO) is a graphene with added oxide functional groups, whose abundance is heavily dependent on the preparation method [1,2]. It is the most widely researched derivative of the graphene [3,4]. Compared to the pristine graphene, it has much lower electrical conductivity, as it is almost an insulator. The reason can be found in sp^2 hybridized carbon atoms in carbon backbone that become sp^3 hybridized due to the functional groups which change their π-π electronic conjugation. One of the most promising methods for GO modification is ion beam irradiation [5-7]. Changes in chemical [8] and structural [9] properties have been observed, sometimes causing a reduction process [10]. Actually, a plethora of structural modifications and

defects have already been established, such as bond breaking [11], production of point/line defects and vacancies [12], amorphization [13,14], rippling [15] and formation of nanochannels [16]. The ion irradiation method is also very practical as it is very easy to control applied ion fluence, beam energy, and type of the ion being used. Also, access to small accelerator facilities capable of delivering ion beams with MeV energies is not difficult and can provide means of modifying GO via nuclear energy loss of the used ion beams. Versatility of this method also means that diverse applications can be easily targeted with ion irradiated GO, such as sensing [17,18], dosimetry [19,20], filtration [21], microelectronics [22-24] and even accelerator technology [25]. Filtration in particular can benefit from ion irradiation processing, which has already been demonstrated well in the case of the graphene [26-29].

High-energy heavy ion irradiations can offer some additional options due to specifics of the ion-matter interactions at MeV energies. Such ions travel through the material in a straight line, causing damage along their path due to intense interaction between ion and electron subsystem of the target material, also known as the electronic energy loss. Hot electrons produced in the wake of the ion cause rapid warming of the material due to electron-phonon coupling, that can easily exceed melting temperature. This way, hot matter formed along the ion trajectory acts as a seed for damage formation, which (upon rapid cooling) results in permanent damage known as an ion track. Studies of the high-energy heavy ion irradiation of GO have not been many, and were geared mostly toward possible applications [10,15-19,21,24,30]. Therefore, it remains of interest to study the basics of the high-energy heavy ion irradiation interaction with the GO. To achieve this, in the present work we used iodine beams with energies between 12.5 – 23 MeV, used both for GO modification and simultaneous *in situ* time-of flight elastic recoil detection (ToF-ERD) measurements. Reduced graphene oxide (rGO) obtained by the means of autoclave heating in vacuum at high temperature was used as a benchmark for efficiency of reduction with ion beams.

2. Experimental methods

At Ruđer Bošković Institute (RBI), GO samples were prepared from the GO powder, which was purchased from Graphenea (Spain). The GO powder was dissolved in distilled water in concentrations from 100 mg/L to 500 mg/L, after which a concentration of 300 mg/L was

determined as ideal for preparation of a thin GO film on a silicon substrate. In order to obtain a homogeneous and stable dispersion of the aqueous solution of GO, it was necessary to apply the ultrasonification with several repetitions. Each repetition lasted ~ 15 min. Between repetitions it was necessary to wait for the cooling of the solution. After the sonification process was completed, magnetic stirring was carried out for about 24 hours, resulting in preparation of ~ 100 ml of solution. This GO solution was stored in hermetically sealed containers and put aside in order to determine its stability. If visible sedimentation didn't occur within time frame of several days (up to one week), the stability of the solution was confirmed. Such a solution was used for the preparation of thin GO films.

After a stable solution of GO was prepared, droplets of solution were applied to Si substrates with a micropipette, and if necessary, heating and the spin coating were applied. A temperature controller ensured that the heating temperature did not exceed ~ 50°C at any time (to eliminate the possibility of reduction), so as a rule of thumb, heating was kept within 30°C - 50°C range. Spin coating was carried out in several iterations. Each subsequent series of spin coating had, as a general rule, a higher number of revolutions per minute (rpm) than the previous one and a shorter duration, since amount of remaining liquid on the surface was decreasing with increase in rotation speed. In the first step, spin coating speed ranged between 200 - 300 rpm, and was done in intervals of ~ 10 minutes. Later, faster rotation (500 - 600 rpm) and shorter durations (several minutes) of spin coating were used. The film making process would be finalized with rotation speed of 800 rpm and exposures for about one minute. If needed, the process could be concluded with 1000+ rpm in very short film exposures, within ten seconds, solely for the purpose of removing excess residual liquid. From these samples, rGO films have also been prepared by a reduction process which took place independently and subsequently. These films were placed in an autoclave, and heated at 1000 °C for at least one hour in a vacuum.

Prepared GO and rGO films, few hundred nanometers thin, have been subjected to high-energy heavy ion irradiation and simultaneous *in situ* ToF-ERD analysis using 12.5 MeV, 18 MeV and 23 MeV iodine beams. The irradiation parameters are given in Table 1., assuming GO density of 1.5 g/cm^3 [25] and using its stoichiometry as measured by ToF-ERD in this work. Ion beams were delivered by 6 MV EN Tandem Van de Graaff accelerator, and irradiation with *in situ* measurement was accomplished at the ToF-ERD beamline [31]. The measurements were performed at 20° incidence angle with respect to the sample surface, with spectrometer positioned

at the angle of 37.5° towards the beam direction. All acquired ToF-ERD spectra were collected in a list mode and were analysed offline using POTKU code [32].

Table 1. High-energy heavy ion irradiation parameters obtained by the SRIM code [33], assuming GO density of 1.5 g/cm^3 [25] and stoichiometry as measured by the ERD (C = 57%, H = 16%, O = 24%, N = 2%).

Ion beam	Electronic energy loss S_e (keV/nm)	Nuclear energy loss S_n (keV/nm)	Range (μm)
12.5 MeV I	2.53	0.29	5.96
18 MeV I	3.55	0.22	7.63
23 MeV I	4.38	0.19	8.82

3. Experimental results and discussion

Results of the *in situ* ToF-ERD measurements are shown in Fig. 1, with the spectrum obtained by 23 MeV I beam shown in Fig. 1(b). In the spectrum, all constituent elements of the GO film can be observed, while the primary iodine beam is not scattered into the detector. Since the spectra have been recorded in the list mode (i.e. event-by-event recording), it was possible to monitor changes in the stoichiometry of the GO films with increasing ion fluence. Experimental data were fitted to the Poisson law [34], from which cross sections σ for a single ion impact modification were evaluated. In this way, for each ion beam, cross sections for each element in the GO have been obtained. Furthermore, as shown in Fig. 1, it can be observed that the GO films are stoichiometrically unstable up to a fluence of 5×10^{11} cm^{-2}, but attain new stable stoichiometry for high fluences (typically above 1.5×10^{12} cm^{-2}). These results (elemental cross sections and irradiated GO composition) are shown in Fig. 2.

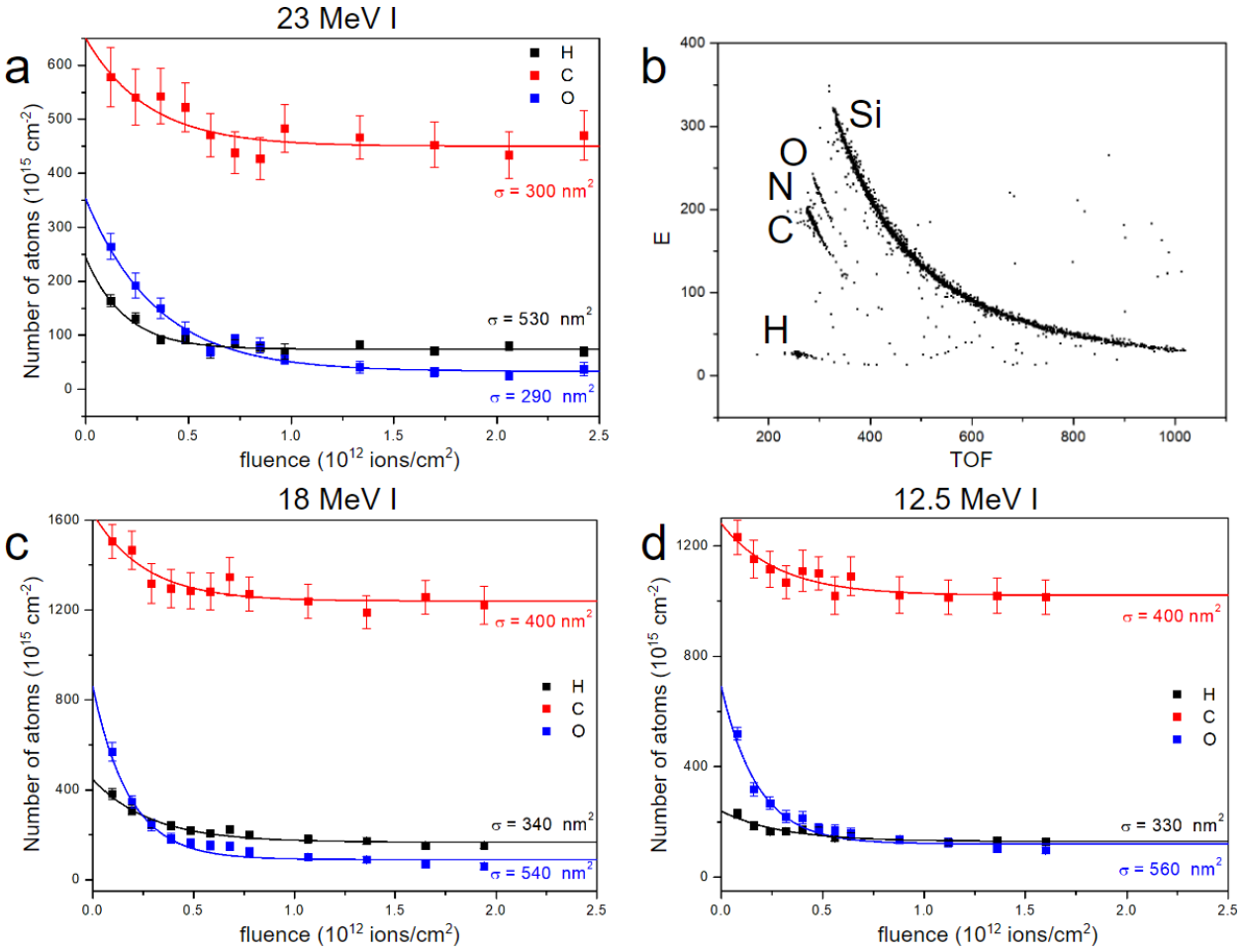

Figure 1. Results of the *in* situ ToF-ERD measurement of GO irradiated with (a) 23 MeV I, (c) 18 MeV I and (d) 12.5 MeV I. (b) ToF-ERD spectrum generated using the 23 MeV I beam.

As shown in Fig. 2(a), decrease of the elemental cross sections with increase in the iodine beam energy identifies nuclear energy loss as the main driver behind GO stoichiometry changes. Only in the case of hydrogen, whose cross section increases when iodine beam energy rises, more significant role of the electronic energy loss is indicated. Figure 2. (b) shows the stoichiometry of GO films after high fluence (i.e. above 1.5×10^{12} ions/cm^2) irradiations, and a comparison with prepared (i.e. non-irradiated) GO and rGO samples. It is observed that the final states of the irradiated GO films are much closer to rGO than GO, indicating that reduction of GO occurs during high-energy heavy ion irradiation. Actually, the most prominent difference between high-fluence irradiated GO and rGO is in the hydrogen content. Higher amount of hydrogen in high-energy

heavy ion irradiated GO could be a consequence of electronic energy loss which redistributes hydrogen around ion trajectory, whereas nuclear energy loss (i.e. direct collisions between iodine ions and constituent atoms of GO) is more likely to drive atoms out of the GO films. We also notice that carbon atoms, which form GO backbone structure, are less scattered, hence its content increases relatively to the other atoms, just like in case of rGO. Finally, we note that the *in situ* ToF-ERD measurements proved rGO film to be stable under ion irradiation (results not shown here). The final stoichiometric values, obtained by the fitting procedure and corresponding to the high fluence limit (i.e. above 1.5×10^{12} ions/cm^2), are also listed in the Table 2.

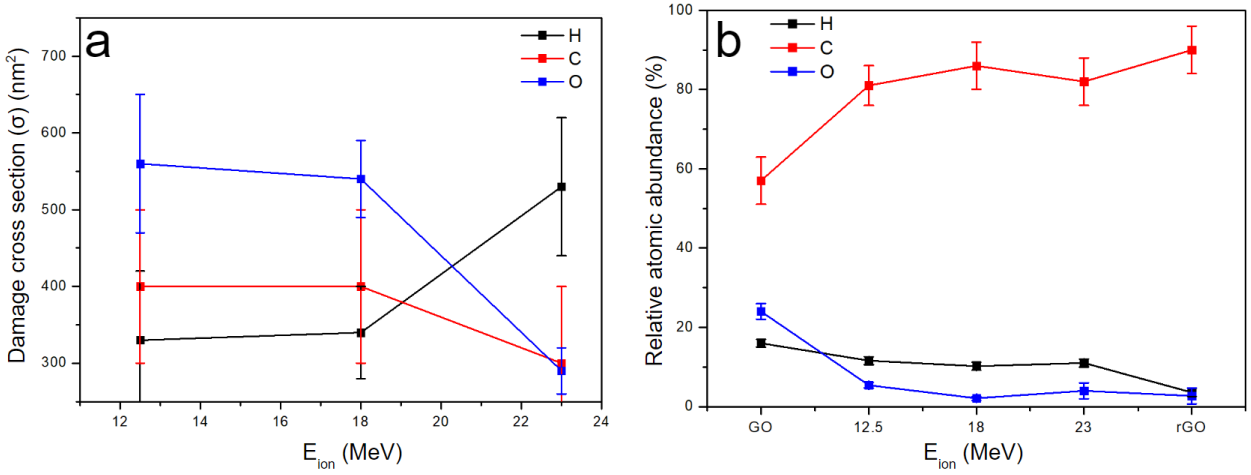

Figure 2. (a) dependence of the damage cross-section σ of GO as a function of the energy of the iodine beam, (b) the stoichiometry (i.e. relative abundance of C, H and O atoms) for as-prepared GO and rGO, and for GO irradiated with 12.5, 18 and 23 MeV I after steady state conditions (i.e. at high fluences, beyond 1.5×10^{12} ions/cm^2) have been reached.

Table 2. Comparison of the stoichiometry of prepared GO and rGO films, together with GO irradiated with iodine beams, obtained by *in situ* ToF-ERD technique.

Atom	**GO pristine**	**GO 23 MeV I**	**GO 18 MeV I**	**GO 12.5 MeV I**	**rGO**
C (%)	57±6	82±6	86±6	81±5	90±6
H (%)	16±1	11±1	10±1	12±1	4±1
O (%)	24±2	4±2	2±1	5±1	3±2
N (%)	2±1	1±1	1.0±0.3	1.0±0.2	2±1

Conclusion

In this work, effects of the high-energy heavy ion irradiation of GO were investigated by *in* situ ToF-ERD. Almost complete reduction of the GO was found for all ion beams used, when applied iodine ion fluence was sufficiently high enough, i.e. above 1.5×10^{12} ions/cm^2. The main factor governing reduction of GO films was nuclear energy loss of the ions, at least for the energy range investigated in this work. Only in the case of hydrogen, whose behaviour was found to be different, role of the electronic energy loss seems to be important. To investigate this further, studies with more energetic ion beams (i.e. with beams having higher electronic energy losses) are needed.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

D. Iveković: Conceptualization, Investigation, Formal analysis, Visualization, Writing – original draft. **S. Kumar**: Investigation, Formal analysis, Writing – review & editing. **Z. Siketić**: Investigation, Formal analysis, Visualization, Validation, Writing – review & editing. **O. Romanenko**: Investigation, Formal analysis, Writing – review & editing. **M. Karlušić**: Conceptualization, Supervision, Resources, Project administration, Funding acquisition, Writing – original draft.

Data availability

Data will be made available on request.

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