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The stopping power and energy straggling of light ions in graphene oxide foils

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ABSTRACT

Energy-loss and straggling experiments were performed using 2–4 MeV $^{1}H^{+}$ and 7.4–9.0 MeV $^{4}He^{2+}$ ions in graphene oxide foils by the transmission technique. The thickness of the graphene oxide foils was determined using a detailed image analysis of a graphene oxide cut, which was used to refine the graphene oxide density. The density was determined by the standard technique of micro-balance weighing. The stoichiometry of the graphene oxide foils before the irradiation was determined by Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA) using 2 and 2.5 MeV $^{4}He^{+}$. The measured energy stopping powers for hydrogen and helium ions in graphene oxide were compared with the predictions obtained from the SRIM-2013 code. The energy straggling was compared with that calculated using Bohr's, Bethe-Livingston and Yang predictions.

The results show that the stopping power of graphene oxide foils irradiated by both ion species decreases with increasing energies, the differences between the measured and predicted values being below 3.8%. The energy straggling determined in our experiment is higher than Bohr's and Bethe-Livingston predicted values; the predictions by Yang are in better agreement with our experiment.

1. Introduction

The stopping power and energy straggling of energetic ions in carbon-based materials have been studied both theoretically [1] and experimentally [2–6]. The understanding of deceleration processes in graphene-based materials is of high interest as data are scarce and there are only a few publications on energy loss in graphene [2].

The knowledge of the ion stopping power in graphene oxide is important to many application fields such as e.g. microelectronics and optoelectronics prepared by ion implantation [7,8]. Graphene can be used as semi-conductors because of their extraordinary conducting properties [9,10]. The great significance of graphene-based devices is in space application [11], in particular graphene solar cells [12], and the stability of this equipment in the space environment is best studied by the interaction of MeV ions with graphene [13–15]. Graphene is an interesting material with great electronic [7], mechanical [16] and thermal properties [17]. It has excellent optical properties, with a band gap value of ~0–0.25 eV, with high carrier mobility, high Young's modulus etc. Due to high quality sheets of graphene is often prepared by chemical vapor deposition [18,19], which demands expensive equipment; many groups have looked at using graphene oxide as a solution processable alternative for the preparation of graphene- like materials [20–22]. Graphene oxide foils are used for the fundamental studies of graphene based structures, as the chemical or physical based reduction of oxygen lead to graphene synthesis. Our work is focused on the energetic ion interaction with the graphene oxide foils as a base for the further functionalizing of graphene oxide using ion beams.

The experimental data of the stopping power and energy straggling of ions in such an extraordinary material as graphene base structures (graphene oxide) are fundamental for checking the reliability and validity of existing theoretical and semi-empirical approaches (SRIM-2013 [23], Bragg's formula [24], and the Core-and-Bond approach [23] – see our work [25] for details). The simple theoretical models, for instance Bohr [26] or Bethe-Livingston [27], are used only for collisional energy straggling. Bohr's theory depends on the atomic number of the medium penetrated by ions and its thickness, not on the energy of the incident ions. The Bethe–Livingston theory moreover takes into account the binding of target electrons within atomic shells. Yang [28] takes into account

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the charge-exchange energy straggling component resulting from fluctuations in the charge state of the ion during its passage through the target foil.

In the present work, the stopping powers and energy straggling of hydrogen and helium ions in graphene oxide (GO) were investigated in the reference ion energy range of 1.6–7.4 MeV. This ion energy range was selected for the sake of comparison with our previous experiments with polymers and mainly to investigate the electronic energy loss, thus the ion energy range was chosen such a way to achieve the prevailing electronic stopping over the nuclear energy loss. The experimental stopping powers were compared to the predicted values of the electronic energy loss using semi-empirical approaches implemented in SRIM. The experimental energy straggling were compared to the theoretical and semi-empirical simulations based on the models of Bohr, Bethe–Livingston and Yang.

2. Experimental details

2.1. GO foil thickness, volume density and composition determination

The present experiment used two graphene oxide foils prepared by graphite oxidation utilising the permanganate oxidation method. 3 g of graphite (2–15 μm, 99.9995%, Alfa Aesar) were mixed with 360 mL H_2SO_4 (96 wt%) and 40 mL of H_3PO_4 (85 wt %). Subsequently, 18 g of $KMnO_4$ were added and the reaction mixture was heated at 50 °C for 12 hours. Afterwards, the reaction mixture was quenched in ice (400 g) with 20 mL of hydrogen peroxide (30 wt%), and the formed graphene oxide was separated by centrifugation. GO foils were prepared by suction filtration using a polycarbonate membrane (Nucleopore 0.45 μm) and graphene oxide suspension. The GO1 foil was prepared using 20 mL of aqueous suspension with a concentration of 1.7 mg/mL and the GO2 foil was prepared using aqueous suspension with a concentration of 6.7 mg/mL.

The mass density of graphene oxide foils was determined by the standard technique of microbalance weighing. A piece of sample was cut from the GO foil. The foil area cut was precisely determined using a digital microscope image photograph, on which the image analysis code was applied using polygon selection area routine implemented in the ITAP program (see Section 2.3). Then the sample was repeatedly weighed by means of a Mettler Toledo Micro-Balance with a ±1 μg absolute accuracy. The thickness Δx of the GO foils was determined by microscopic analysis of polished cuts through graphene oxide foils (see Fig. 1.) clamped between two polymer cubes by drenched resin. The cuts were polished perpendicular to the surface of the foils. The GO thickness values are shown in Table 1.

Standard optical microscopy was performed with an Olympus AX70 Provis microscope using 40X Olympus UPlan FL N Ph2 objective (NA 0.75) and an external cold light source (Zeiss KL 1500 LCD with two light guides). Images were acquired with a Lumenera Infinity 2 CCD camera at the pixel size of 176 nm.

The average foil density ρ was determined from the known GO foil cut weight m, area A and thickness Δx (see Table 1).

The stoichiometry of the GO foils was checked by Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA). The RBS measurements were performed using 2.0 MeV $^4He^+$ ions with the detector placed at the backscattering out-of-plane angle of 170°. The ERDA analysis was performed by means of 2.5 MeV $^4He^+$ ions. The hydrogen atoms recoiled under a laboratory angle of 30° from the sample surface were registered by a partially depleted PIPS detector placed at an angle of 75° with respect to the sample surface normal. In front of this detector, a 12-μm-thick Mylar film was mounted to stop forward-scattered $^4He^+$ ions. The recorded spectra were evaluated using the SIMNRA 6.06 code [29]. The final GO foil elemental compositions are shown in Table 1. However, the used analytical methods RBS and ERDA characterize mainly the surface layer of the GO foil, we can expect following the deposition procedure used for GO foil preparation, that the elemental composition doesn't show any significant differences across the depth. At least laterally the elemental composition was checked to be homogeneous. The concentrations of impurities, Mn and S, in the samples are below 1.5 at%.

2.2. Experimental set-up

The energy-loss measurement was provided using the ion beams $^1H^+$ and $^4He^{2+}$ from the Tandetron accelerator at the Nuclear Physics Institute of the CAS, v. v. i. The ion beams were scattered from a thin Au layer and the ions scattered at a scattering angle of 150° were detected by a partially depleted PIPS detector. The analysing detector was covered by an aluminium film with two holes 1 mm in diameter placed in front of the detector, one of which was covered with the investigated GO foil and we can register simultaneously both the primary ions as scattered on Au layer and those slowed down in the foil in the same energy spectrum;

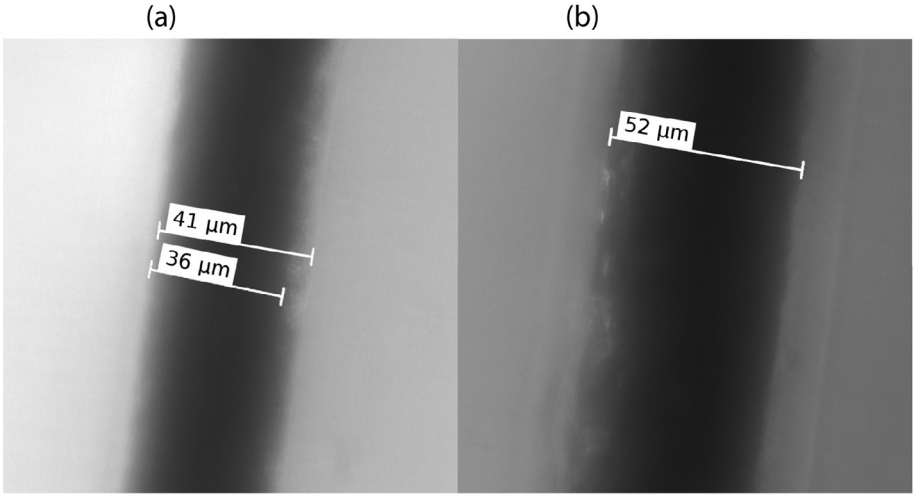

Fig. 1. The visualization of the graphene oxide foil thickness using Optical microscope. The images of a GO1 (a) and GO2 (b) perpendicular cuts, where the indicated line is the measured foil thickness.

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