# Graphite oxide based targets applied in laser matter interaction

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**Abstract.** In the present work, we propose the production of a hybrid graphene based material suitable to be laser irradiated with the aim to produce quasi-monoenergetic proton beams using a femtosecond laser system. The unique lattice structure of the irradiated solid thin target can affect the inside electron propagation, their outgoing from the rear side of a thin foil, and subsequently the plasma ion acceleration. The produced targets, have been characterized in composition, roughness and structure and for completeness irradiated. The yield and energy of the ions emitted from the laser-generated plasma have been monitored and the emission of proton stream profile exhibited an acceleration of the order of several MeVs/charge state.

## 1. Introduction

Graphene exhibits unique electronic band structure, thermal conductivity and excellent electronic transport properties indeed electrons in graphene often are indicated as " massless"[1]. Since the first publication in 2004 [1], when Geim's group plucked monolayer graphene sheets from graphite by adhesive tape, one of the foremost challenge is to functionalize its band gap as it is crucial for a controllable manipulation of its atomic and electronic properties. Extensive research had been conducted to investigate the applicability of graphene based material in medicine[2], energy storage[3], fundamental research [4-5], and others, but its suitability in laser matter interaction, in order to improve the ion acceleration from plasma, has been about ignored in literature despite the manufacturing of graphene sheets in a composite material is an indicated way to enhance its properties [6]. Recently, graphene has been produced on a sufficient scale and homogeneously incorporated in a polymeric matrix [7] to be irradiated by laser, exploiting its properties, optical, conductive and mechanical, with the aim to generate hot and dense plasmas in vacuum from which protons and carbon ion beams can be extracted and accelerated at high energy for many applications: hadrontherapy [8], astrophysical studies, laser-driven ion acceleration [9], inertial confinement fusion [10], and others. In the present work, we followed up the increasing demand of advanced target engineering in laser matter interaction, proposing a hybrid graphene based material fabricated to be irradiated by sub-picosecond high intensity laser, taking into account the significance of target composition, geometry, resistivity, roughness and thickness for the electron propagation and the production of sharp proton bunches; we paid attention to the close dependence between the electron spatial distribution and the features of emitted ions plasma laser-generated. It is well established that the conductivity of a material is strictly connected to its lattice. In the case of high current of electrons propagating in a solid target, as a consequence of high energy sub-picosecond laser pulse, due to charge neutrality, an "inverse" current of thermal electrons will induce the heating of a wide volume of the target generating a non equilibrium state of warm dense matter consisting of hot electrons and cold ions which are temporarily in the same position where they were in the condensed matter state. In this situation the target conductivity depends on its ability to maintain its lattice structure. Over a plethora of members in the graphene-like materials family, the one, emerging for the ability of tailoring its mechanical, electrical and optical properties, is graphite oxide. It is a layered material produced by oxidation of graphite and consisting of hydroxyl and epoxide functional groups as basal planes and carbonyl and carboxyl groups at the edges [11] and, it is an insulating material [12] as most of the carbon atoms are sp3-hybridized. A systematic study of compositional, structural, optical properties of graphene based material, correlated to its response, is essential for understanding as various topological defects and

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chemical functionalization can modify the properties of the initial graphene system and for reproducibility of the sample production. To understand the potentiality of the prepared target, the emission of energetic ions induced under laser bombardment was detected online by semiconductor SiC detectors. The structural, compositional and optical properties of the samples have been performed at Tandetron laboratory of the Nuclear Physics Institute, CAS, in Rez (Czech Republic).

## 2. Experimental setup

Despite of the Hummers method is one of the oldest preparation techniques, it is one of the most suitable methods for the formation of bulk graphene.
In this study, fresh graphene oxide (GO) foil was synthesized like-Hummers method as reported in Ref. [13] to prepare GO thin foils. The evaluation of GO density was carried out by a Mettler Toledo Micro-Balance with ± 1μg absolute accuracy in standard microbalance weighing technique. A small square of GO foil was cut and its area was accurately determined by through a digital microscope image analysis. In Fig.1 the typical image of the cross sectioned GO observed by optical microscopy reports the measures of the thickness foil in several positions: 5.95μm, 5.98μm, 5.90μm, 6.20 μm. The evaluated thickness was 6 μm and the density was 0.72 gr/cm$^3$, with an error of 2%.
Two samples have been fabricated, both 1x1 cm$^2$ of size: graphene oxide foil 6 μm thick (labeled as GO) and graphene oxide covered by 200 nm gold film (labeled as Au+GO) by PVD technique.

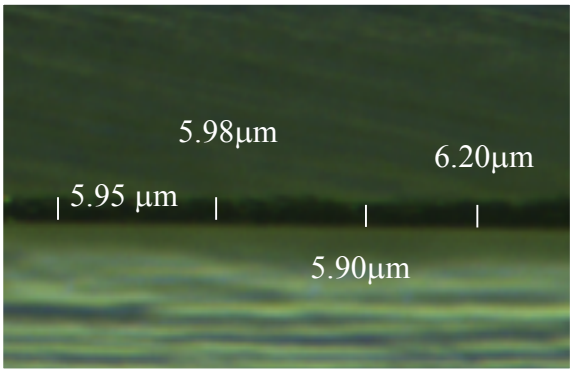


**Fig. 1.** Optical microscope image of the graphene oxide foil section.

The AvaSpec-2048 spectrophotometer with UB-600 lines/mm grating and a bandwidth of 195–757 nm has been employed to carry out optical measurements in reflectance mode. The adopted incidence angle and the investigated wavelength range were 15° and 175–2500, nm respectively. The source designed by Avantes was a deuterium halogen lamp AvaLight-DH-S with an integrated TTL-shutter and filter holder for filters of up to 50x50x5.0 mm. An area of 1.8 mm$^2$ is analysed using a probes of 1.5 mm in diameter and equipped with a setscrew to place the probes into suitable positions.

The morphology of the substrates was studied by atomic force microscopy (AFM) analysis [14] using a NTEGRA AURA instrument (NT-MDT) in the tapping mode in the ambient atmosphere, and a chip (NSG01) with the radius less than 10 nm. The arithmetic average height ($R_a$) and the mean roughness (RMS) for pristine and irradiated polymers with three different ion fluences were estimated and their error does not exceed 10%. Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) measurements have been conducted using both a FIB-SEM system LYRA3 (TESCAN ORSAY HOLDING a.s.) and an EDS Aztec X-MAX 80 (Oxford Instruments plc). In order to probe the relative amounts of carbon and oxygen present in the sample, 5 kV and 20 kV voltages electronic microscope [15] and the detectors of secondary electrons (SE) and of the backscattered electrons (BSE) for a better z material contrast have been adopted.

An InVia Raman microscope (Renishaw, England) supplied with a spectrometer operating in backscattering geometry has been employed to estimate the structural properties of the substrates. The system consists of a CCD detector and a Nd-YAG laser operating at 532 nm of wavelength, 50× of magnification objective and at no more than 5% of the max power output (50 mW) to avoid the sample damage. In this context, the characteristic Raman band of Silicon at 520 cm$^{-1}$ has been adopted as calibration reference.

Preliminary ion beam irradiation of GO foil was performed at Helmholtz-Zentrum Dresden-Rossendorf to characterize the changes in a set of GO foils under ion irradiation in different conditions. The composition of the foils in the most superficial layer ( ~1 μm) has been evaluated by Rutherford Backscattering Spectrometry(RBS) and Elastic Recoils Detection( ERD) analyses at Tandetron laboratory in the Czech Republic. In both cases, a beam of 2.9 MeV protons has been used as projectile at incident angles of 0°. Solid state detectors placed at 160° and 35° for each analysis, monitored the backscattered and forward recoiled atoms.

After the characterization, thy have been laser irradiated by a multi-TW femtosecond laser at the Institute of Plasma Physics and Laser Microfusion (IPPLM) in Warsaw. The central laser wavelength is 810 nm, the pulse duration is ~ 40 fs, the maximum energy of the output pulse is 500 mJ, the contrast is $10^{-9}$ , the power density is $10^{18}$ W/cm$^2$, 10 μm focal spot diameter, and operating in single-pulse mode or at 10 Hz repetition rate. A high resolution CCD camera evaluates the laser focal position (FP) on the surface of the target and presently was +150 μm (i.e. inside the target) and the main plasma stream was generated close to the target surface. The laser-target interaction give rise to complex phenomena and ends with the emission of protons and heavier ions driven by electrons. Because of the ion acceleration is strictly connected to electrons, the fast electron transport has been analyzed by the monitoring of the proton bunch profile as a function of both space and intensity in the rear side of the target[16]. The online bunches monitoring was performed in Time of Flight (TOF) approach where ions propagate over a known

distance and then revealed by Ion Collectors and robust semiconductor SiC detectors[17] placed at 0° with respect to the normal to the target surface, in the forward direction.

## 3. Results

SEM analysis conducted at 20 keV electron beam on GO foil in the Au side (b, c) as well as in the GO side (a) reveals in the latter case (Fig. 2a) as main elements, for C, O and S, the mass concentrations of 0.62, 0.35, 0.02 respectively and also minor elements in traces of Cl, Al, Mn and K.

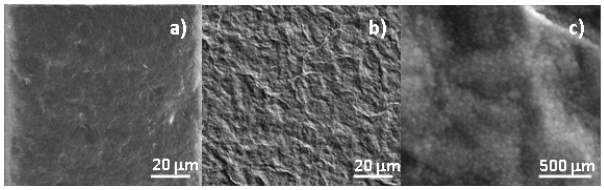


**Fig. 2.** SEM images of virgin GO foil 100 µm field view a) Au on GO foil 100 µm b) and 2 µm field views c).

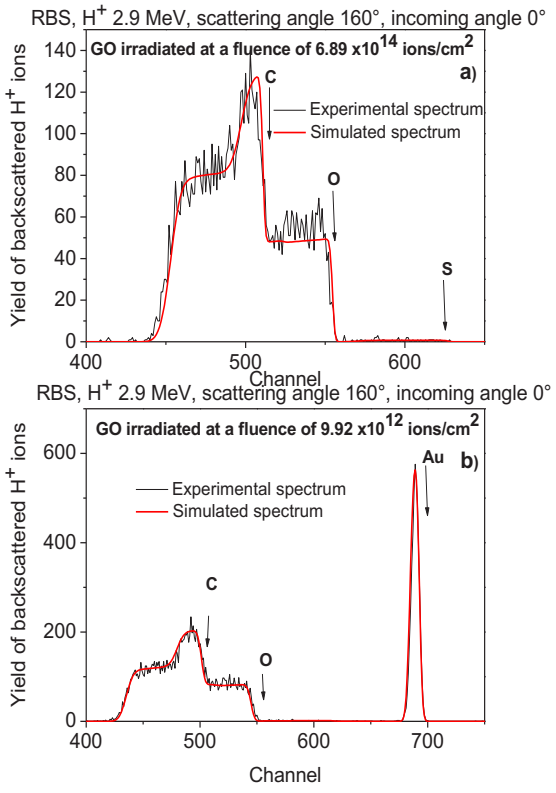


**Fig. 3.** RBS spectra for GO a) and for GO-Au b).

In the former (b, c), Au as main element and C as contaminant have been revealed with the morphology reported in Fig. 2b. Au microstructures on top of the underlying surface are observed from Fig. 2c. RBS and ERDA analyses have been performed to evaluate the composition of GO and GO covered by gold and typical spectra are reported in Fig. 3 and Fig. 4.

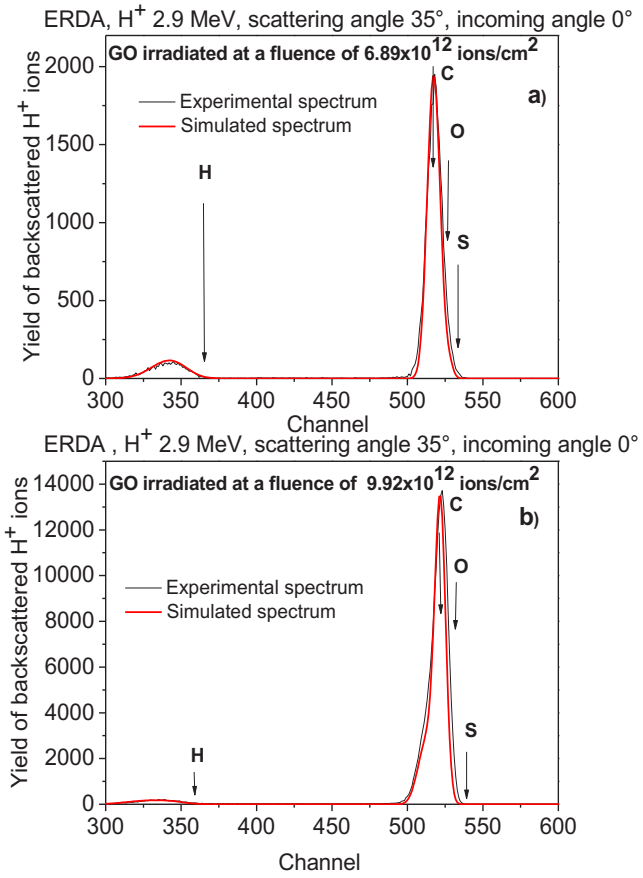


**Fig. 4.** ERDA spectra for GO a) and for GO-Au b).

In both samples, the main components are carbon, oxygen, hydrogen and trace elements, such as sulphur. This last component is present as a consequence of the chemical synthesis of GO. The ERDA spectrum reports a value of hydrogen content of 17.4% for GO foil and 22.6% for GO Au foil, gathering the final increment of 23 %, as reported in Fig. 3b. carbonization effects occurring during the GO foil irradiation. Because of RBS provides information about the presence of heavy ions, whereas ERDA about the presence of light ions, by the comparison between the obtained atomic concentrations we obtained the overall consistency of analyses. From such ion beam analyses was possible to find out the hydrogen/oxygen (H/O) and the C/O ratios, of about 1.68 and 0.572 for GO and 1.59 and 0.766 for GO Au, respectively.

Table I reports the values of the C, O, H, C/O and H/O atomic value determined by the ion beam analyses. The enhancement of C of about 9.1 % (0.47-0.513)/0.47) was a consequence of the thin gold coverage of the GO substrate.

**Table I.** The composition of GO and GO Au foils.

| COMPOSITION OF THE GO FOILS [atm%] | | | |
|---|---|---|---|
| Sample/ Ions | C | O | H |
| GO | 51.3± 0.5 | 30.4± 0.3 | 17.4± 0.2 |
| GO_Au | 47± 0.5 | 29.5± 0.3 | 22.6± 0.2 |

The optical characterization of the prepared thin foils was studied by the reflectivity-curves for all the samples as a function of the wavelength, as reported in Fig. 5. It shows a reflectivity decreasing going from Au+GO to Go virgin and to GO+Au sample with seven main peaks at 370.7, 465.7, 486.4, 581, 610.3, 656, 674.8 and 691 nm. The direct evaluation of the reflectivity of the samples, performed at room temperature and in the range of wavelength of 300-760 nm, reports a good agreement between the experiment and literature. The highest reflectivity is presented for Au+GO foil illuminating the Au side, due to the contribution of the gold film which gives high an high reflectivy of about 98-99% in the near infrared region, but a limited and very low reflectivity at wavelengths shorter than ~ 400 nm.

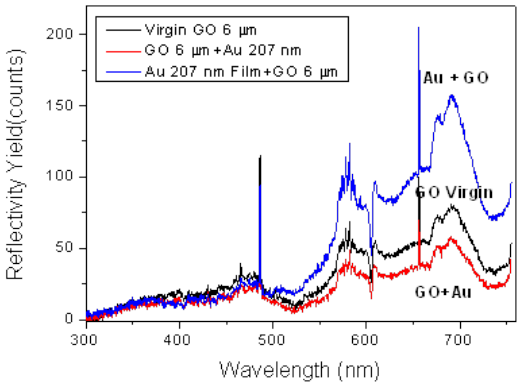


**Fig. 5.** Optical measurements in reflection mode for graphene oxide, graphene oxide coated with thin gold film illuminated on the graphene oxide surface side and then, on the gold surface side.

The reflectivity of GO is slightly higher in the near UV region and markedly lower in the near IR region due to its unique electronic structure [18]. For completeness the reflectivity of the Au+GO foil illuminating the GO face (i.e. GO+Au) has been evaluating, exhibiting the lowest value caused by the opacity of the foil, which increases with the membranes' thickness. Thus, also if the graphene is constituted by a monoatomic layer, it is found that it absorbs a significant ($\pi\alpha$= 2.3%) fraction of the incident visible light, according to literature [18].

Returning to the application of the thin GO foil to prepare advanced target for laser irradiation in target-normal-sheath acceleration (TNSA) regime, there is a reason of the correlation between proton stream properties and electron beam transport. Protons have been exploited to diagnose the behaviour of electron beam laser accelerated into the target. Fig. 6 shows a typical SiC spectrum recorded in time-of-flight (TOF) approach [17] for ions emitted irradiating with the IPPLM of Warsaw terawatt laser the GO+Au target. The focal position was optimized to obtain dense and hot plasma from the target and to maximize the ion acceleration in the forward direction. The data were collected using a fast storage oscilloscope (TekTronix DPO2024, 200 MHz, 1GS/s).

UV and X-ray laser plasma generated are indicated by the first peak, 3 ns wide in Fig. 6, followed by faster ions at 34.4 ns, 47 ns and 50 ns corresponding to protons, carbon and oxygen ions, with kinetic energies of about 2.7 MeV, 17 MeV and 20.5 MeV, respectively. The wide peak starting at 50 ns to 76 ns is due to the emission of low energetic Carbon and Oxygen. The peak at 81 ns is due to the contribution of gold ions. This acceleration increment is due to the thin Au coverage enhancing the electron density of the plasma and the electric field driving the ion acceleration regime[19].

This interesting result can be ascribed also to the reduction of the target reflectivity, the lattice of the GO foil, the enhancement of the electron density due to the presence of gold all together providing better transferring of the laser energy to the target and decreasing of the electron energy loss through the target. Since a high intensity laser at $10^{18}$ W/cm$^2$ and 39 fs pulse duration interacts with a thin solid target, a high fraction of laser energy is absorbed by the target surface electrons, producing high current of relativistic accelerated electrons.

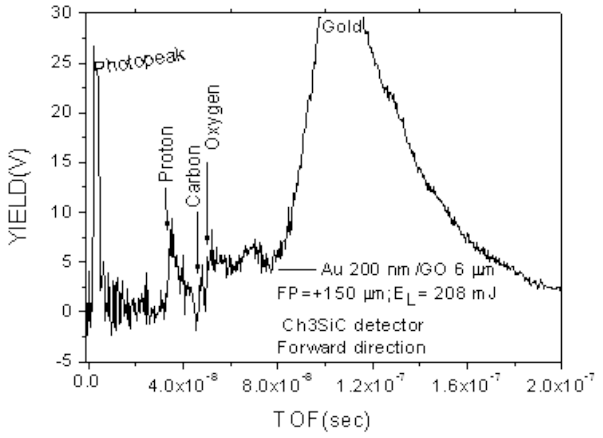


**Fig. 6.** SiC spectrum in the forward emission irradiating GO foil with a gold film 200 nm thick

This effect induces a significant enhancement of the target temperature (~ 10 keV) and an high electric field developed in the rear side of the thin irradiated foil. In this step, in facts, it is generated a "non-equilibrium state of dense matter", consisting of hot electrons and cold ions, generating an electron cloud out of the target and a high positive target surface in which ion acceleration take place. The developed electric field, direct orthogonally to the target surface, is of the order of tens GV/m, as reported in literature [20].

Conventionally, the ion acceleration per charge state can be evaluated by the maximum proton energy detectable from TOF measurements, reaching a value of about 3.2 MeV relatively to the TOF spectrum of Fig. 6, in well agreement with literature [20].

## 4. Summary and conclusions

Universally is recognised that conductive targets, laser irradiated at high intensities, induce the emission of smooth proton stream profiles, while insulator generate non-homogeneities in the proton density. The electron current is undergone to electromagnetic instabilities which split the flow of hot electrons into filamentations [22]. In this work, hybrid GO based materials have been employed to be laser irradiated and their response were surprising if compared with experiments conducted in the same laser facility, at optimized laser conditions, but using different targets. GO is an insulator material and it has been simply coated with gold to enhance its electron density. The main purpose of this work is to perform a comparative study of structural, compositional and optical of graphite oxide based materials properties to potentially implement design and fabrication of advanced targets usable in laser matter interaction for too long overlooked in literature. Certainly the achieved result can be maximized changing the laser parameters (focal position, laser energy, contrast, pulse duration..) and this is our proposed approach. The emerging preparation of sophisticated targets leads to a high level development of ions sources laser plasma generated useful for many applications and the use of graphene based materials arises several issues such as: what does occur increasing the number of the graphene layers? would be better to use lower thickness of metallic substrate to enhance the electron density and to reduce the electron energy loss? How the optical properties of graphene control the laser-plasma interaction?. Work is in progress to reply to these questions.

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