Romanian Reports in Physics **69**, 504 (2017)

REDUCTION OF FREESTANDING GRAPHENE OXIDE FILMS USING CONTINUOUS WAVE LASER

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Received December 15, 2015

Abstract. This paper describes a novel approach to the preparation of reduced graphene oxide films. Freestanding reduced graphene oxide (rGO) films were obtained by exposing graphene oxide films to a continuous wave laser diode and were investigated by Fourier transform infrared spectroscopy (FT–IR), scanning electron microscopy (SEM) and X–ray diffraction (XRD) to observe their different structural properties (existence of oxygen-containing functional groups, or defects). Thermal, optical, and electrical properties were also discussed along with the potential applications of reduced graphene oxide (rGO) freestanding films.

Key words: graphene oxide, reduced graphene oxide, continuous wave laser diode.

1. INTRODUCTION

Research on graphene is a fast developing field that can open up new possibilities in both fundamental research and applications [1]. Graphene is a single sheet of sp^2 bonded carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice [2, 3].

Graphene has many properties, such as high surface area, excellent electrical conductivity and electron mobility at room temperature [4] and measurements show that single layer graphene possesses a unique combination of electrical, mechanical, optical, and thermal properties [5]. These unique properties of graphene are promising for applications in various fields such as nanoelectronics, nanocomposites, gas sensors, and batteries [6].

GO is similar to graphene, but presents oxygen-containing functional groups [7], such as hydroxyl, epoxy, carbonyl, and carboxylic [8]. The reduction of GO is definitely a key topic and different reduction processes result in different properties that in turn affect the final performance of materials or devices that contain rGO. With some residual functional groups and defects, the rGO sheets can be considered similar to chemically derived graphene [5]. The most attractive property

of GO is that it can be (partly) reduced to graphene-like sheets by removing the oxygen-containing groups with the recovery of a conjugated structure [9]. GO is a significant and promising candidate as a precursor to graphene, due to its easy production and high solubility in different solvents, including water [6].

In this paper we will present the results of our experiments in developing the process of graphene oxide reduction into graphene by using a continuous wave laser diode. Both GO and rGO are characterized using physicochemical techniques and their properties before and after reduction are discussed in detail.

2. EXPERIMENTAL

2.1. PREPARATION OF GRAPHENE OXIDE

In this experiment we used two batches of GO (concentration: 6.2 g/l) purchased from the same manufacturer, Graphene Laboratories, but in different years. GO films were produced by drop casting 0.4 ml from each of the graphene oxide aqueous solutions on Teflon substrates. Before being covered in the GO solution each of the Teflon substrates was cleaned with acetone and ethyl alcohol and thoroughly wiped several times to prevent contamination with other particles. The samples were left to dry in a Binder vacuum drying oven at a temperature of 30 °C and atmospheric pressure of 1013,5 hPa. After drying, a thin film of graphene oxide was obtained. Each thin film was easily lifted off the Teflon substrate, thus producing freestanding GO films. Preparation of graphene oxide film is presented in Fig. 1.

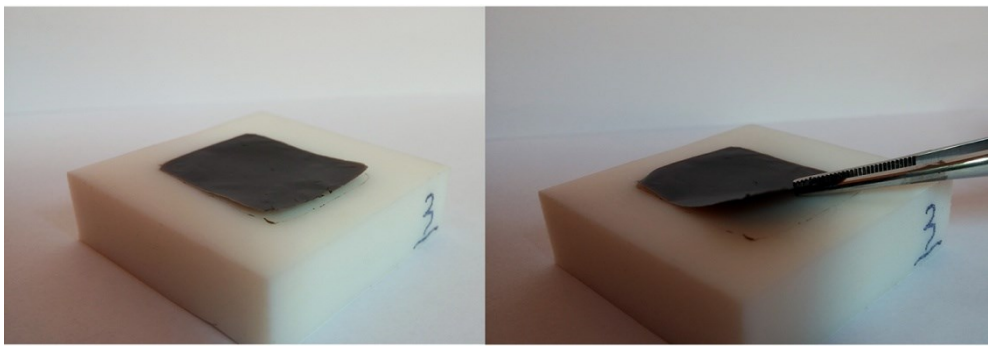

Fig. 1 – The process of obtaining graphene oxide freestanding film.

2.2. DIODE LASER TREATMENT

The freestanding GO films were treated using a continuous wave diode laser with the following parameters: optical power 80 mW; wavelength 660 nm;

electrical power supply 314 mW; current intensity of 121 mA and supply voltage of 2.58 V. The graphene oxide films were individually exposed to the continuous wave laser beam and visible changes were observed. Immediate visual analysis of the samples exposed to the laser beam suggests that the process of reducing graphene oxide was successfully completed. Graphene oxide thin films changed color from dark brown to black and increased surface roughness suggesting changes in the number of existing functional groups (Fig. 2).

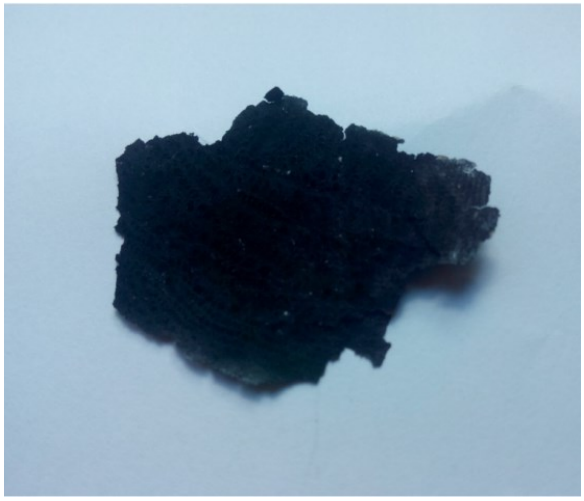

Fig. 2 – Reduced graphene oxide after exposure to continuous wave laser beam.

2.3. CHARACTERIZATION

Both rGO and GO films were characterized using various techniques such as FT-IR, SEM and XRD. IR spectrum measurements were recorded with a Spectrum 100 Perkin Elmer FTIR spectrophotometer, with an ATR accessory with ZnSe crystal and single reflection. All the spectra were recorded at the following parameters: spectral range 4000–600 cm^{-1}, resolution 4 cm^{-1} and acquisition time of three minutes per each sample. AVEGA-TESCAN SEM with a field emission gun was used for investigation of surface morphology changes during laser treatment. XRD spectra were taken to reveal detailed information about the crystallographic structure of GO.

3. RESULTS AND DISCUSSION

The structural evolution process from graphene oxide to reduced graphene oxide is clearly observed in the FTIR spectra in Fig. 3.

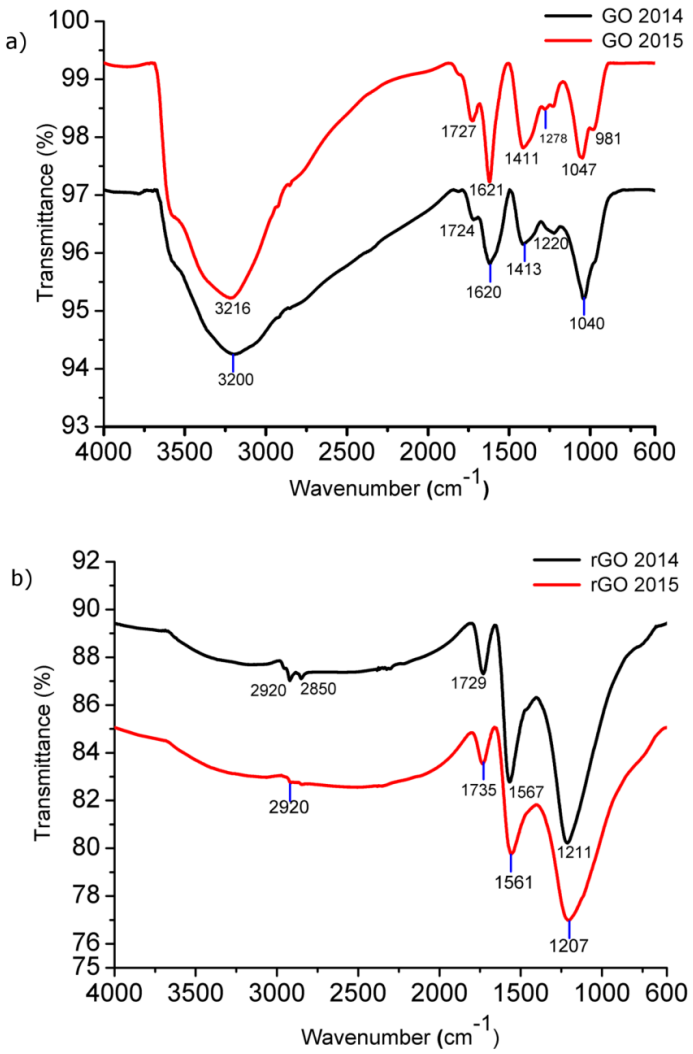

Fig. 3 – FTIR spectra of the a) GO; b) rGO.

The FTIR spectra of GO, which is shown in Fig. 3a, reveals the presence of oxygen-containing functional groups. The presence of different types of oxygen functionalities in GO was confirmed at 3200 cm^{-1} (O–H-stretching vibrations), at 1724 cm^{-1} (stretching vibrations from C=O and C–H), at 1620 cm^{-1} (C=C skeletal vibrations from unoxidized graphitic domains), at 1413 cm^{-1} (C–OH-stretching vibrations), and at 1040 cm^{-1} (C–O-stretching vibration).

After reduction of graphene oxide with the continuous wave 660 nm laser diode, the FTIR spectrum is visibly changed. FTIR peak of rGO film suggests that the O–H-stretching vibrations observed at 3200 cm^{-1} were significantly reduced and only a weak band of epoxy group at 1211 cm^{-1} is still present in the rGO.

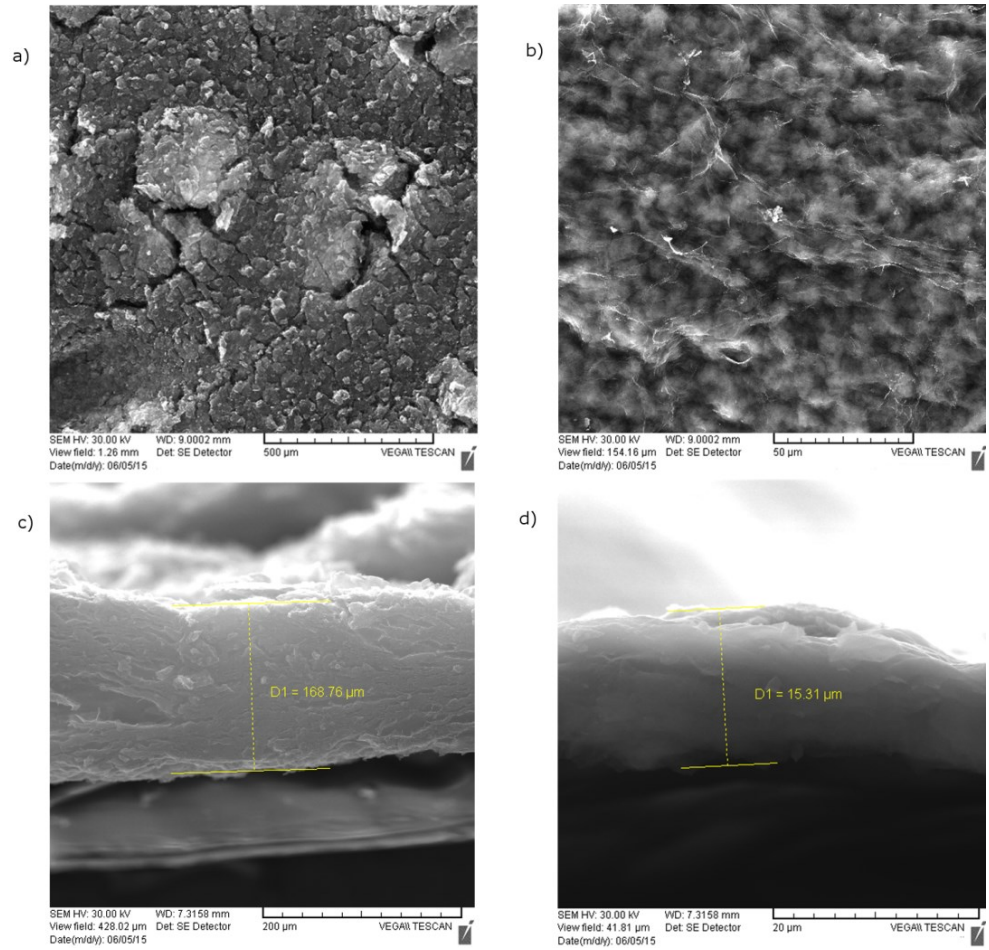

Fig. 4 – SEM image of: a) rGO; b) GO; c) sectional view of rGO; d) sectional view of GO.

The intensity of the peaks related to oxygen functional groups of the rGO decreased dramatically, demonstrating a successful reduction of the GO by using the continuous wave laser beam.

The morphology and structure of the samples were studied using SEM. The differences between GO and rGO films are very well highlighted in SEM analysis

and support the morpho-structural changes that have taken place after the laser based reduction process.

In Fig. 4a,b top views of the films illustrate the difference between the surface structures of both films. Figure 4a but instead the edge of the film has not suffered major changes. Reduction of GO to graphene normally should lead to a decrease in the film thickness. The SEM images show that the samples are formed of multiple two-dimensional sheets layered one on top of the other, more important, the GO films are more ordered and tighter packed, while the rGO films are more textured and present an expanded structure.

Figure 4c,d represents sectional views of the rGO and GO films. It can be observed how the graphene oxide structure has expanded after being exposed to the laser beam with the rGO films being approximately 10 times thicker than the original GO films. Further analysis of the images suggests a more layered structure of the rGO films.

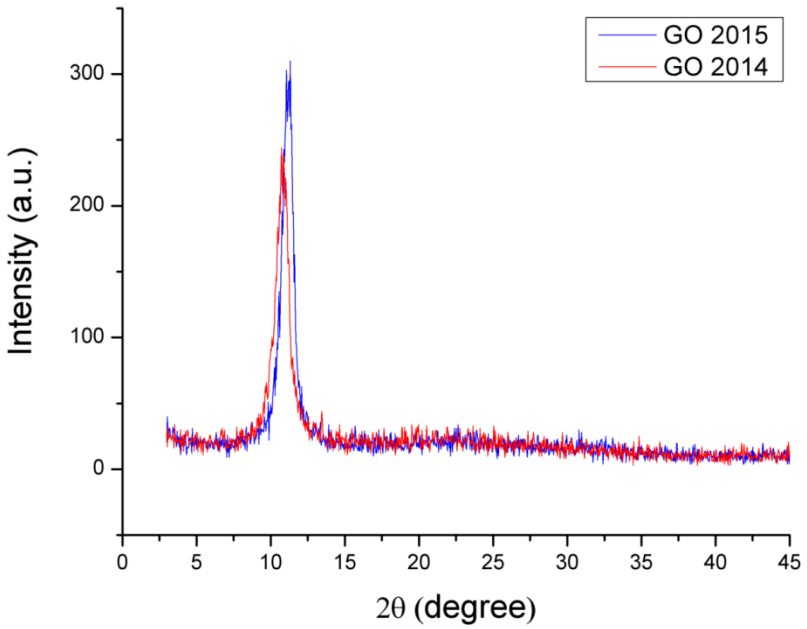

Fig. 5 – XRD for graphene oxide.

XRD is a very useful characterization tool to study the crystallographic structure, chemical composition and physical properties of materials and thin films.

The structural properties of GO were characterized using XRD analysis as shown in Fig. 5, to see if there are differences between the two GO solutions used in this paper. The pattern of GO shows a very intense and sharp peak at $2\theta = 11.7$ corresponding to (002) plane of interlayer distance of 0.74 nm. The larger

interlayer distance of GO suggests the presence of oxygen-containing functional groups, such as hydroxyl, epoxy, and carboxyl.

4. CONCLUSIONS

From the presented experimental results it can be concluded that reduced graphene oxide freestanding films obtained from the exposure of freestanding graphene oxide films to a continuous wave laser, represents a promising start in the structural modification of graphene derivatives. By reducing graphene oxide with laser radiation at a wavelength 660 nm, the FTIR spectrum is visibly changed, as follows carboxyl, hydroxyl and epoxy groups are not present and the new peaks which were assigned to the functional groups as C–H, CH_2 or CH_3 were found.

The SEM analysis revealed that the structure of reduced graphene oxide is comprised of many individual layers or flakes that give it a very large specific surface area, thus being suitable for electrodes, energy storage materials, polymer composites and mechanical resonators.

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