

Structural investigation of the graphite oxide and thermal reduced graphite oxide with terahertz spectroscopy

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This work presents optical properties of graphite oxide and thermally reduced graphite oxide for five different temperatures: 100, 125, 150, 175, 200 °C. Molecular absorption spectra of the carbon structures were obtained using Time-Domain Spectroscopy (THz-TDS) Kit from EKSPLA Company. Usable spectral range from 100 GHz to 5 THz with spectral resolution 50GHz. Results obtained in THz spectroscopy showed that the carbon structure with different concentrations of oxygen have unique molecular spectrum.

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1. Introduction

The THz radiation are electromagnetic waves this is found between microwave and infrared (IR) light of the electromagnetic spectrum. THz radiation is defined by the frequency range of 0.1 to 10 THz.

So far the researches effectuate showed that THz rays can be used in molecular spectroscopy and imaging, that because THz rays can penetrate nonmetallic materials.

THz time-domain spectroscopy is a recent technique is termed THz time-domain spectroscopy (THz-TDS). THz-TDS uses short pulses of broadband THz radiation, which are typically generated using ultrafast laser pulses. THz spectroscopy allows a material's far-infrared optical properties to be determined as a function of frequency.

THz Time Domain Spectroscopy provides information about the phase and amplitude the THz ray after propagation through the sample THz ray. In this technique can provide more information than conventional Fourier-transform spectroscopy spectroscopy, which provides information only about the amplitude.

Using the TDS-THz spectroscopy in the characterization of different carbon structures (GO) has the following advantages: this technique is nonionizant and non contact (non-destructive technique) the spectra are unique molecular fingerprints.

Graphite-like nanomaterials, graphene and related oxygenate structure as graphite oxide have recently attracted attention as viable and inexpensive filler in the composite materials with many applications in mechanical, thermal and electrical engineering.

Graphite oxide is, in general, obtained by three principal methods proposed by Brodie [1], Hummers [2,3] and Staudenmeier [4]. In graphite oxide, the layered structure of the graphite is still retained, but is much lighter than in the raw material. According to the most recent studies graphite oxide consist of oxidized graphene sheets, having their basal plane decorated with oxygenate functional groups (epoxide, hydroxyl, carbonyl and carboxyl). The oxygenate functional groups are grafted on the edge and on the inner part of the graphene planes. The oxygenate functional groups grafted to the graphitic structure bring new properties as: hydrophilic instead of hydrophobic properties and insulating instead of conductive properties.

The hydrophilic properties bring new possibilities in the further processing route making the homogenization process easier by formation of a stable colloidal suspension with water and other polar solvents. The insulating properties of the graphite oxide are uncalled, and thus cannot be used, without further processing, as a conductive nanomaterial.

In addition, the presence of the oxygenate functional groups make the graphite oxide thermal instable at elevated temperature. This means that the production of composite materials with thermal processes is improper. In order to restore the conductive properties reductive methods as chemical and thermal reduction are used. The extent of reduction and expansion of the graphite oxide is dependent on the type of the raw material used and thermal treatment parameters (duration, final temperature and type of reduction).

Here we describe in short the synthesis process of graphite oxide and a thermal reduction of it, at different temperature in the oxygenated atmosphere and structural investigation by terahertz spectroscopy of these materials.

In this paper we characterize graphite oxide samples with different concentrations of oxygen flat using Time-Domain Spectroscopy (THz-TDS) Kit from EKSPLA Company, Latvia.

2. Basic system description

The standard Time-Domain Spectroscopy (THz-TDS) Kit from EKSPLA Company consists of photoconductive antenna THz emitter and detector, pump laser beam guiding optics, motorized delay line and bias power supply, THz beam guiding mirrors, sample holder and lock-in amplifier, Labview based software for data acquisition and femtosecond laser. All the components are assembled and tested on the baseplate of 60×80 cm dimensions.

The ultrafast laser generates pulses (150fs pulse duration) with repetition rate of 76 MHz.

These pulses pass through is splitted into two paths, one ray goes to detector photoconductive antenna and the other passes through a system of mirrors (M, optical delay line) reaches the antenna photoconductive emitter

Photoconductive antenna emitter generates frequency range (0.1THz-5THz) when laser pulse interacts with emmitter anena. The complete time resolved electrical field amplitude is collected by varying the optical path length of the probe beam via a motor controlled delay stage.

This optical delay line (computer controlled) is used to measure the transmitted terahertz pulse profile at a discrete number of time points to provide temporal information.

The configuration of the kit can be easily modified, for example, sample holder can be mounted on motorized X-Y stage for imaging experiments.

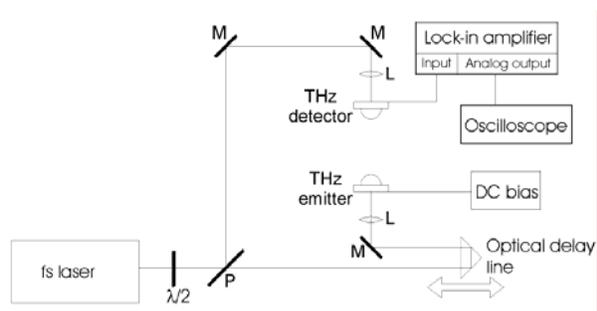


Fig. 1. Schema bloc a Kit THZ-TDS.

Typical emitted THz radiation power from EKSPLA Company is around $10 \mu\text{W}$ when pumped by mode-locked ultrafast laser with 100 mW output power and 150 fs pulse duration. The Fourier transform of waveform gives the spectral content of THz radiation.

2. Experimental

2.1 Sample preparation

Synthesis of the graphite oxide: Commercially available microcrystalline graphite powder Ramnicu Valcea ($>600 \mu\text{m}$, with 99 % C, and with the crystallographic properties are presented in the Table 1) was used as raw material to produce graphite oxide. The graphite was subjected to extreme oxidizing conditions to obtain GO, by using modified Hummer's method [3, 4]. In this method graphite is treated with potassium permanganate (KMnO_4) and sodium nitrate (NaNO_3) in concentrated H_2SO_4 (98%). The resulted solution was washed with peroxide water (H_2O_2), and 5% chloric acid (HCl), filtered, and dried for 100°C .

The colloidal suspension of graphite oxide before filtration presents a yellow-brown color (Picture 1 – left.). After filtration of the colloidal suspension of graphite oxide and draying process a material was obtained with paper like aspect with brown dark color (Picture 1 - right.).

Thermal reduction of graphite oxide: Four pieces of the graphite oxide paper was thermal reduced in the oxygenate atmosphere at 125, 150, 175, 200°C .

Table 1. Crystallographic parameters of raw graphite.

Sample	La [Å]	Lc[Å]	D ₀₀₂ [Å]	N
Graphite	600	873	3.367	180

Where La is basal planes diameter, Lc is high stack, d_{002} is interlayer spacing and N is the number of graphitic planes.



Picture 1. Left –colloidal suspension of graphite oxide and right-graphite oxide paper like.

After the thermal reduction of graphite oxide papers every sample present a mass loss which is proportional with the temperature of thermal reduction process. The experimental results are presented in the Table 2. These transformations (mass loss) are associated with two distinct processes.

First process is associated to elimination of the physically absorbed water (hygroscopic humidity). And, second process is associated to the pyrolysis of the labile oxygenate functional groups such as epoxy (-O-), hydroxyl (-OH), carbonyl (>CO), carboxyl-COOH, which are yielding CO , CO_2 and steam.

First was eliminated the physically bonded water, and after was broke the epoxy, hydroxyl and related functional groups.

Table 2. The mass loss during the thermal reduction treatment of graphite oxide.

Sample	T [°C]	t [hours]	η [%]
Go 100	100	5	-
Go 125	125	1	16
Go 150	150	1	32
Go 175	175	1	37
Go 200	200	1	40

Where the T is the temperature of the thermal reduction, t is the duration of the thermal reduction treatment, and η is the mass loss yield after the thermal reduction treatment.

2.2 THz spectroscopy

Different chemical substances (or mixtures) have unique spectral “fingerprint” when using the THz spectroscopy. The convolution spectrum in the THz domain obtained from scanning a substance has 2 contributions to the absorption spectrum: one from the atmospheric air, and one from the substance of interest. The first one contributions form what is known as “the reference spectrum”. Knowing the reference spectrum, a pure individual spectrum can identify the substance of interest.

Using THz-TDS spectroscopy from EKSPLA Company we obtained THz power spectra of some carbon structures. The power spectra are obtained from 0.1 to 5 THz with a resolution of 0.05 THz and scanning time of one minute. A comparison of the spectra with and without sample inserted into THz beam path gives the power spectra of the sample under investigation. Using Bert-Lambert law (1) we obtain absorption spectra for different materials:

$$Abs_{spectra} = -2 \ln \cdot \frac{P}{P_0} \quad (1)$$

P = power spectra radiation

P_0 = spectra power reference

Using THz-TDS spectroscopy, we obtained absorption spectra for graphite oxide and partially reduced graphite oxide having different oxygen concentration. The experiments were carried out at normal atmospheric pressure and room temperature. In the scanning process with THz-ray the power spectrum depends of thickness and absorption proprieties of the materials. Air absorption could be a source of noise so it will be better to subtract the nitrogen spectrum from the spectrum obtained in air.

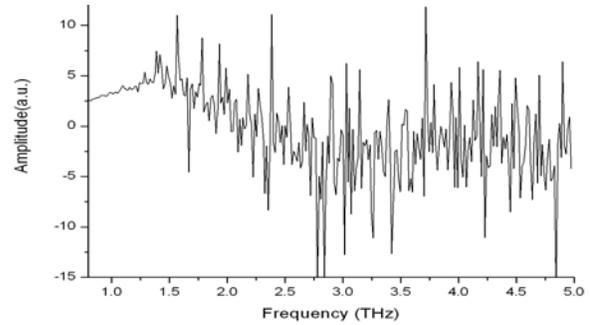


Fig. 2. Graphite oxide (GO100).

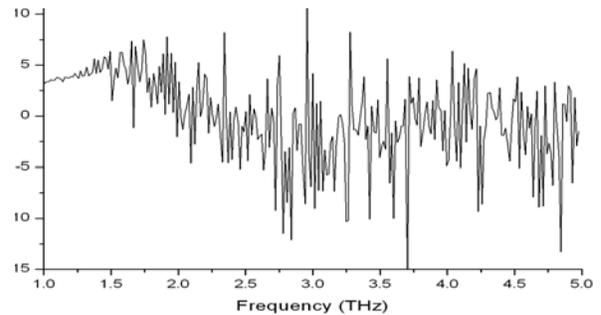


Fig. 3. Graphite oxide (GO125).

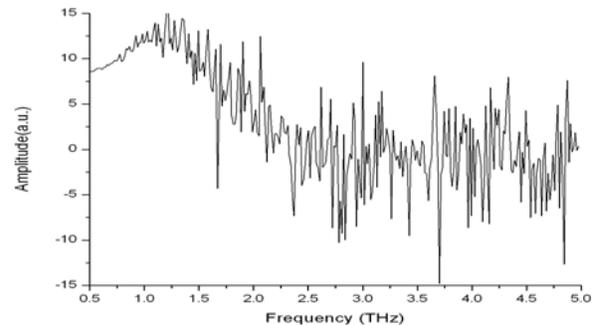


Fig. 4. Graphite oxide (GO150).

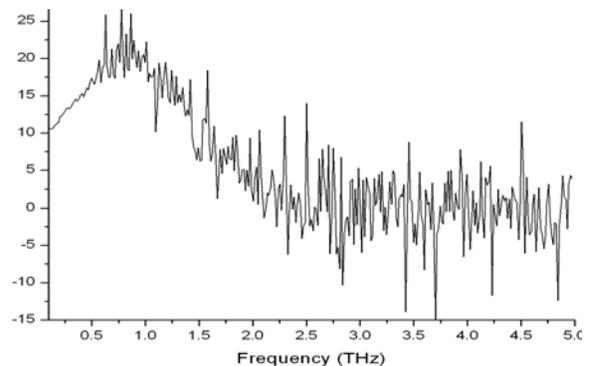


Fig. 5. Graphite oxide (GO175).

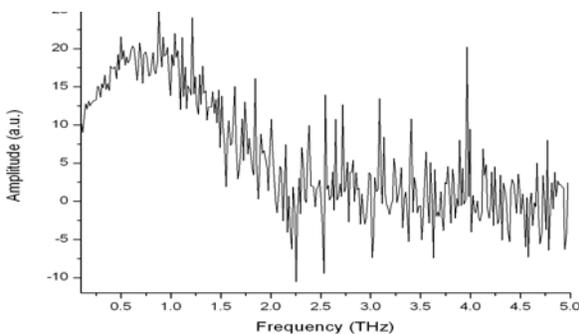


Fig. 6. Graphite oxide (GO200).

4. Conclusion

The work has provided good evidence that the optical properties (0.1THz - 5THz) of the graphite oxide and partially reduced graphite oxide structures are strongly influenced by the oxygenate functional groups quantity.

The quantity of the oxygenate functional groups has a key role in the optical properties of the studied materials and is an important parameter in the future design of new materials.

Acknowledgments

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