

## HYBRID COMPOUNDS BASED ON GRAPHENE OXIDE AND THEIR COMPOUNDS WITH METALS

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### Abstract

The paper describes the preparation and identification of hybrid compounds based on graphene oxide, graphene oxide - fullerene C<sub>60</sub>, graphene oxide CF<sub>x</sub>, graphene oxide-biochar and graphene oxide-MWCNT.

Chemical modification procedures of the foils and its compounds with nanoparticles of metals (oxides) are further described. In conclusion, alternative applications of hybrid foils and synthesized compounds are proposed.

**Keywords:** Graphene oxide, nanoparticles, composites, hybrid compounds, toxicity

### 1. INTRODUCTION

Graphene oxide (GO) is prepared by the oxidization of graphite with strong oxidization agents. GO is also a precursor for the chemical preparation of graphene [1]. A complete and current overview of the possibilities of further processing and usage of suspensions of graphene oxide is presented in the article 'A manufacturing perspective on graphene dispersion' [2]. In our previous publications [3,4] common graphite oxidization with fullerene C<sub>60</sub> were described at the various weight ratios [5]. This work broadens on common graphite oxidation reaction with fluorine graphite, Biochar and multnanotubes (MWCNT) in order to prepare the hybrid compound into the form of foil. Biochar is a product of pyrolysis of the waste after a fermentation process of biomass [6].

The surface of the carbon nanotubes can be functionalized and in case of the formation of covalent bonds between the surface of nanotubes and by substituent or non-covalently and with modifications of macromolecule (hybrid composite) or the physical adsorption of molecules on the surface of nanotubes. Responses to enable a covalent binding to nanotube include: oxidization (can take place in a solution, gas phase or in plasma), halogenation (iodation, bromination, chlorination, fluorination of reactions with BrF<sub>5</sub>, XeF<sub>2</sub>), and reaction with diazonium salts (ArN<sup>2+</sup>). Non-covalent modification of the nanotubes is managed primarily by interactions π-π, π-stacking, electron transfer and hydrophobic interaction. It concerns, for example, pyrene derivatives, composites with polymers, biological molecules, DNA, proteins etc. The composite graphene (rGO)-MWCNT can be included among these reactions. The principle of the published preparation of these composite is that graphene oxide and MWCNT are mixed in a specific weight ratio, the mixture is sonicated and then reduced by e.g. ascorbic acid [7]. Thus prepared composites of rGO-MWCNT have application utilization in supercapacitators [8], or after morphological adaptation become ideal adsorbents of organic substances, especially oils [9]. In our case GO was not mixed with MWCNT, but a common oxidation of mixtures of graphite and MWCNT was done by the classic method according to Mr. Hummers, the same way as was managed with graphite-C<sub>60</sub>, graphite-CF<sub>x</sub>, graphite-biochar [10].

### 2. METHODOLOGY

#### 2.1. The employed chemicals

*Grafit PM*: very fine, crystalline, powder graphite, mesh diameter 0.025 mm, the supplier KOH-I-NOOR, Netolice, Czech Republic; *Fullerene C<sub>60</sub>*: 99.5 % purity, purchased by SES Research, Houston, USA; *MWCNT*: Joint research Centre, Institute of Health and Consumer Protection, Via. E. Fermi 2749, I-21027 Ispra (VA) Italy; *Albumin*: bovine, Initial Fraction by Heat Stock, Fraction V (Sigma, A-6793); *Hemoglobin*: hemoglobin

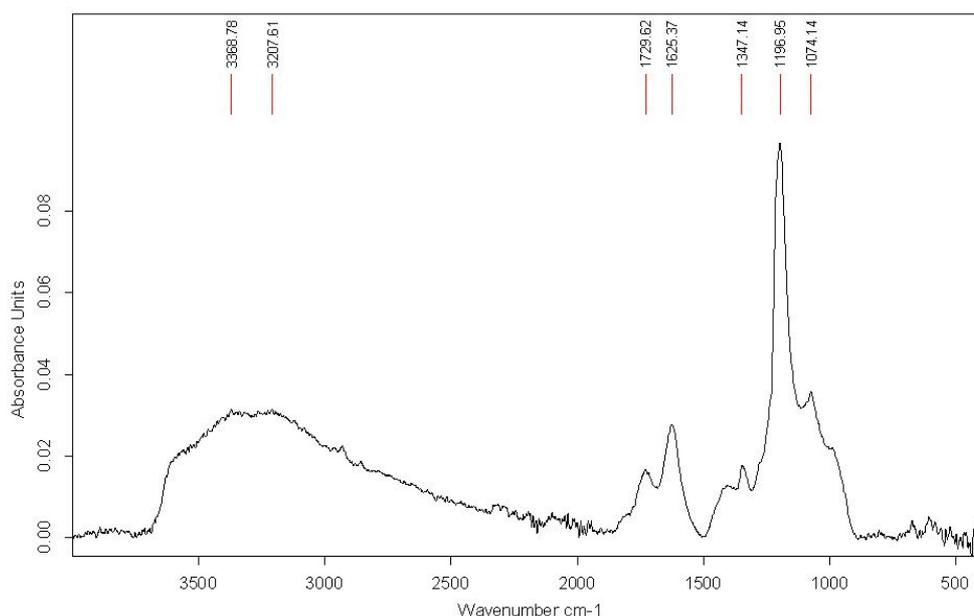
powder (Himedia, FD 022); Sulfuric acid, hydrochloric acid, sodium nitrate, potassium permanganate, hydrogen peroxide, copper sulfate, silver nitrate - supplier Sigma-Aldrich.

## 2.2. The employed instruments

Analysis SEM: Scanning Electron Microscope FEI Quanta 650 FEG FEI (USA); Incorporated-THASS, analytical scale SUMMIT, SI 234-4, at flow rate 20 mL·min<sup>-1</sup>, heating rate °C·min<sup>-1</sup>, ceramic crucible, diameter 5 mm and height 8 mm, degradation medium air; Measurement FTIR spectra: Bruker spectrometer alpha / FT-IR software OPUS 6.5, range 375-4000 cm<sup>-1</sup>; Spectrophotometre NanoDrop 1000 Spectrophotometer (Thermo SCIENTIFIC).

## 2.3. Realized reactions

Fluorine graphite (graphite fluoride) of the composition CF<sub>0.8-0.9</sub> was prepared by direct fluorination of graphite with diluted elemental fluorine from the electrolyser at 450-500 °C in a Monel reactor [11]. Biochar was prepared by pyrolysis at 470 °C from the digestate composition of 80 % corn silage, 20 % cellulosic fiber [14], supplier Biouhel.CZ. s.r.o., J. Káňa. Progressive common oxidation of graphite (1.5 g), firstly with C<sub>60</sub>, secondly with CF<sub>0.8-0.9</sub> and finally with Biochar (the sample weight amounted to 0.7 g) was performed in a mixture of NaNO<sub>3</sub> (3.0 g), KMnO<sub>4</sub> (7.0 g) in concentrated H<sub>2</sub>SO<sub>4</sub> (52 mL). The oxidation mixture was stirred for 2.5 h at 55 °C. Before distribution, it was left for 72 hours at room temperature. The decomposition was carried out with distilled water, decanted and H<sub>2</sub>O<sub>2</sub> and HCl were added. This was followed by repeated centrifugation and repeated decantation until neutral pH and a negative reaction to sulfate ions. In the oxidation of the graphite itself, the portion of the oxidation mixture was reduced about 30 %, concentrated foil enabled application on the teflon pad or nano fibers and followed by successive drying. Graphite (0.2 g) and MWCNT (0.1 g) were put into an Erlenmeyer flask, then H<sub>2</sub>SO<sub>4</sub> (10 ml) and NaNO<sub>3</sub> (0.52 g) were added and the reaction mixture was cooled to 10 °C H<sub>2</sub>O +ice. Afterwards KMnO<sub>4</sub> (1.1 g) was gradually added and the water bath temperature was raised to 55-60 °C, the mixture was stirred for 3.5 h. The mixture was subsequently left for 72 hours at room temperature, finally 10 ml of HCl and 10 ml H<sub>2</sub>O<sub>2</sub> were added. Progressive decantation and centrifugation followed, with the aim of obtaining the thickened suspension to prepare foils, which are spotted onto a teflon substrate and subsequently dried out. The foils were tested for the presence of functional groups and thermal stability by using electron microscopy through which the foil cuts and their surfaces were analyzed.



**Figure 1** IR spectrum of the products of oxidation of GO-CF

### 3. CHARACTERISTICS OF THE PRODUCED FOILS

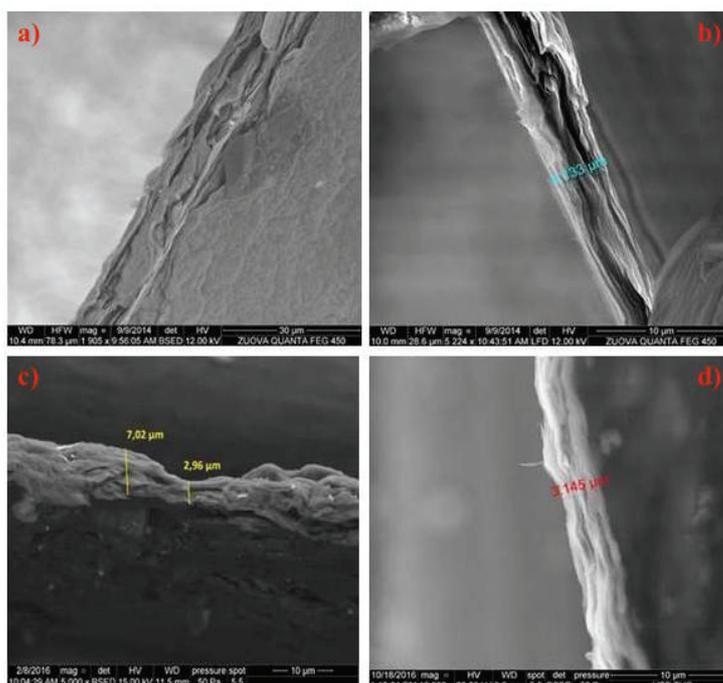
#### 3.1. Analysis of the functional groups by FTIR

Infrared spectroscopy was used to identify the functional groups of prepared film. Selected spectrum is reported for illustration in **Figure 1**. The dominant feature in the spectra of all products is a broad absorption peak extending from 2500-3500  $\text{cm}^{-1}$ , which belongs to the group -OH. The vibration of the oxo-groups predominates in all the measured spectra. Examples of allocation with values of wave numbers are provided in **Table 1**. A very strong vibration which occurs only in the case of hybrid foil GO-CF has a value of 1197  $\text{cm}^{-1}$  and corresponds to the valence vibration bond -C-F, see **Figure 1**.

**Table 1** Wavenumbers characteristic of vibration linkages and functional groups

Probable allocation, [functional group]	Product/ wavenumber, intensity		
	GO	GO-C60	GO-CF
vs (C-O-C)	1068 (s)	1054 (vs)	1074 (m)
vas (C-O-C)			
v (C-O)	979 (m)	979 (s)	
[RCO-OR, -O-, =C-O-C, R-CO-C]			
v (C=C)	1613 (s)	1607 (vs)	1625 (m)
v (C=O)			
[ > C=C <, -C=C-C=C-, elol.β diketones]			
v (C=O)	1723 (w)	1727 (w)	1729 (w)
[O=CR-O-, R1R2-C=O, -COOH, α, β, ketones]			

#### 3.2. The SEM pictures of cuts of hybrid foils



**Figure 2** SEM cut of foils a) GO, b) GO-C<sub>60</sub>, c) GO-CF d) GO-MWCNT

By plating a thickened suspension after centrifugation, film with a layer structure can be prepared, see **Figure 2 (a, b, c, d)**. Identified film thickness of GO-MWCNT was 3.1-3.5  $\mu\text{m}$  (**Figure 2d**), while in the GO-C<sub>60</sub> film, the thickness of 4.133 microns appeared (**Figure 2b**). The GO-CF and GO films (**Figures 2a** and **2c**) do not have a constant thickness.

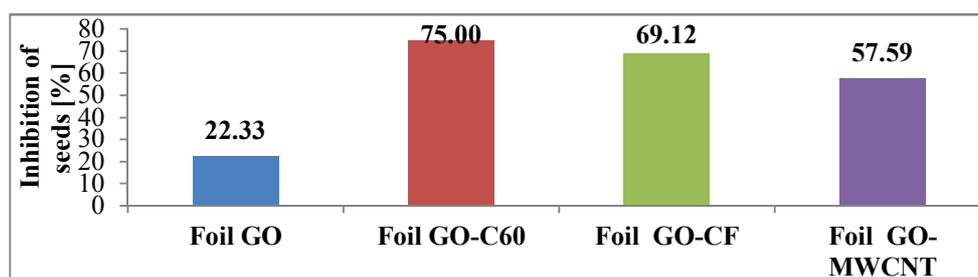
### 3.3. Toxicity of hybrid foils

The ecotoxicity of selected nanofoils was examined by means of a contact germination seed test on white mustard *Sinapis alba* L. (OECD Guidelines 208/1984) which is used as a standard test in Europe. The contact germination seed test on *Sinapis alba* L. onto the foil is to monitor the inhibition (stopping of the growth of seeds) for the time period of 72 hrs. The experiment takes place in the dark at a temperature of  $(20 \pm 2) ^\circ\text{C}$ . During the experiments, 10 seeds were seeded onto the sample (nanofoils) and 10 seeds of mustard outside the sample in a total of 20 seeds per one sample. There was made two parallel determinations. For one type of foil, two samples with the dimensions of 20x20 mm were always cut. It was pipetted 2.5 mL of diluent. The purpose of the test was to determine the inhibition of seeds both outside and onto the foil [12]. The calculation of root growth inhibition when applied to the film or outside of the foil consists in measuring the length of the root (root elongation) after the test by computing the relation (Equation 1):

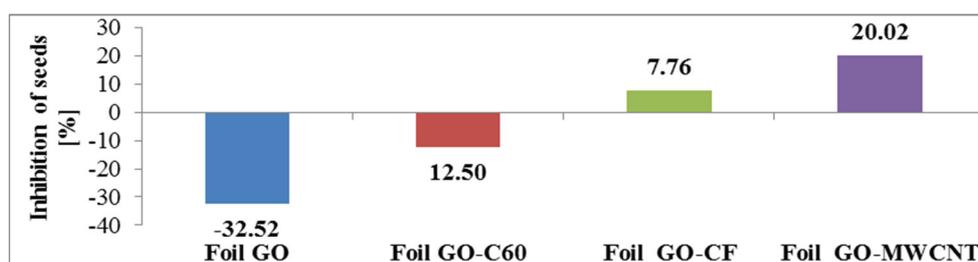
$$IC = \frac{L_c - L_v}{L_c} \cdot 100 \quad (1)$$

The  $IC$  value is the root growth inhibition in %,  $L_c$  is the mean root length of control in millimetres and  $L_v$  is the arithmetic average root length in the test solution in mm.

The final inhibitions of the germination seed tests on white mustard are illustrated on **Figures 3 a, b**. **Figures 3a** and **3b** also show that the highest parallel inhibition was observed onto the foil GO-C<sub>60</sub>, the  $IC$  of this foil was 75.00 %. The lowest average parallel inhibition was detected onto the foil GO ( $IC$  was 22.33 %). For the different inhibitions of the seeds on the foils, see **Figure 3a**. The highest inhibition for mustard seeds placed outside the foil was determined for the foil GO-MWCNT (20.02 %). Mustard seeds located outside foils GO and GO-C<sub>60</sub> grew up, the stimulation of the growth of seed was up to 33 % and 13 % (stimulation GO (-32.52 %), GO-C<sub>60</sub> (-12.5 %)). The lowest average inhibition of seeds outside the foil was determined for the foil GO-CF (7.76 %).



**Figure 3a** Inhibition ( $IC$ ) for materials: the location of mustard seeds on the foil, parallel determination



**Figure 3b** Inhibition ( $IC$ ) for materials: the location of mustard seeds outside the foil, parallel determination

#### 4. THE PARTIAL APPLICATION OF THE PREPARED HYBRID COMPOUNDS FROM GRAPHENE OXIDE (NANOCOMPOSITES, BIOCONJUGATES)

Hybrid GO compounds can also be used for the reaction in the form of water suspension. These suspensions are used e.g. to prepare nanocomposites of metals, particularly copper and silver. In the case of GO-Cu composite, we used an electrochemical voltage series of metals (Becket series of metals) and sonication (the sonication goal was peeling copper *in statu nascendi* from an iron nail surface). In the case of GO-Ag, respectively rGO-Ag, was used ascorbic acid as the reducing agent [13]. There was used bovine serum albumin for the reaction of our hybrid compounds with a biomolecule [14] as a used biological material (Albumin Bovine; blood plasma protein consisting of 583 amino acid wastes; protein which is used in the blood thanks to its hydrophobic pocket on the surface as a carrier for hydrophobic substances, which would otherwise have a low solubility) and hemoglobin (hemoglobin powder; protein containing the protein and non-protein part of the heme group and iron in tetrapyrroles nucleus). Bio conjugate formation was confirmed by using UV spectroscopy whereby the detailed specification did not take place, whether the bio conjugate was with covalent or noncovalent ( $\pi$ - $\pi$  bonds, H-bridges, adsorption, hydrophobic interactions) bonds and that GO reduction of heme iron had taken place.

#### 5. CONCLUSIONS AND DISCUSSIONS

In conclusion, it can be stated that it was managed to chemically prepare graphene oxide and its hybrids with other carbon compounds. The preparation of metal nanocomposites on the carbonaceous carriers gives a wide variety of ways in the area of synthesis, and testing of applications. Currently our interest is to focus on the preparation of composites based on polydimethylsiloxanes.

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