



# Influence of the laser irradiation on the electrochemical and spectroscopic peculiarities of graphene-chitosan composite film

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## ABSTRACT

Activation of the chitosan-modified graphene cast on indium-tin-oxide electrodes was performed with laser irradiation. The composite electrodes were characterised spectroscopically and electrochemically applying Fourier transform infrared and Raman spectroscopies, cyclic voltammetry and electrochemical impedance spectroscopy, respectively. Significant rise in the double-layer capacitance was obtained after the laser irradiation of the modified graphene film formed from its dispersion in chitosan solution. Effect of the laser irradiation depended on a load of the modified graphene in the film. The laser treatment improved electrochemical properties of the electrodes made of the modified chitosan-graphene-film due to creation of edge defects and formation of nanocrystalline structures from graphene flakes.

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## 1. Introduction

Graphene is an attractive material since its discovery by Novoselov et al. in 2004 [1]. Its unique structural, mechanical and electronic properties determine broad application possibilities [2–6]. Use of graphene in electrochemical applications is a complicated task due to the requirements of a stable layer on an electrode surface.

Lasers are yet not widely applied for graphene activation. So far, this method was used for graphene synthesis [7,8], reduction of graphene oxide (GO) to graphene [9–11], reduction of graphene film down to a monolayer [12], modification of graphene [13,14] and laser patterning [15]. Graphene reduced from GO using a femtosecond laser can also be applied to electroanalysis, for instance, to the sensitive hydrogen peroxide detection [11].

Chitosan is a versatile biological compound obtained from chitin and it is widely used in many fields due to its intrinsic properties

allowing fabricate membranes, thin films, three-dimensional structures as well as immobilise graphene and carbon nanotubes [16–18].

Influence of the laser treatment on carbon composites was recently reported in the literature. Carbon composites for optical fibres presented much better mechanical properties after the laser treatment than untreated ones [19]. Dittmar et al. applied nanosecond UV-laser ablation of carbon and glass fibre reinforced epoxy resin [20]. Results showed that nanosecond laser is suitable tool for carbon reinforced plastics machining, however laser fluence and pulse overlap must be chosen carefully to achieve desirable process quality and reduce thermal effects. The pulse laser ablation of bulk graphite in tetraethyloxysilane under rather long pulse duration and low power density caused the simultaneous formation of polyynes and carbon nanoplates/ribbons composed of graphene-based lamellae with Si–H dopant [21]. Effect of the laser interaction on carbon composite most depends on laser parameters such as energy, power and pulse duration [22].

In the present work, a strategy of the graphene film activation with a picosecond laser is described. The homogeneous dispersion of the functionalised-graphene in aqueous chitosan solution was chosen as a matrix as its advantages were shown in the previous work [23]. Graphene dispersion in chitosan solution was cast on ITO surface by spin-coating technique and treated with a picosecond laser in order to reduce the film thickness and increase its

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electrochemical activity. The efficiency of the laser activation was evaluated spectroscopically and electrochemically.

## 2. Experimental

### 2.1. Materials and Chemicals

Graphene flakes with thickness of 8 nm were obtained from Graphene Supermarket (USA). Indium-tin-oxide (ITO) glass slides  $100 \times 100 \text{ mm}^2$ , resistivity  $12 \Omega \text{ cm}^{-2}$  were purchased from Optical Filters (UK). The slides were laser cut into square electrodes with the size of  $20 \times 20 \text{ mm}^2$ .

$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ ,  $\text{CH}_3\text{COOH}$ , KCl, and chitosan from shrimp shells were obtained from Sigma Aldrich (Germany).  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{Na}_2\text{HPO}_4$ , and NaOH were obtained from ROTH GmbH (Germany). All reagents used were of analytical grade. All solutions were prepared using ultrapure MilliQ-water (resistivity of  $18.2 \text{ M}\Omega \text{ cm}$ ) directly taken from the Synergy 185 unit equipped with a UV lamp (Millipore, USA).

### 2.2. Methods and apparatus

The laser activation of the films was performed with the picosecond laser Atlantic (Ekspla, Lithuania) with the pulse duration of 10 ps and pulse repetition rate of 100 kHz. The wavelength of the radiation was 1064 nm. Focused laser beam was scanned over the sample surface. Beam spot diameter at the focus was  $20 \mu\text{m}$ . The scanning speed was varied from 50 to  $300 \text{ mm s}^{-1}$ , and the applied mean laser power was varied from 50 mW to 200 mW, exceptional cases are specified in the text. These two parameters controlled the laser irradiation dose of the film. The accumulated laser irradiation dose in  $\text{J cm}^{-2}$  was estimated from a laser fluence, which was proportional to the mean laser power at the fixed pulse repetition rate and spot diameter, multiplied by the number of laser pulses (depending on the scanning speed) affecting the sample.

Raman measurements were performed with the Raman microscope inVia (Renishaw, UK) equipped with the thermoelectrically cooled CCD detector using four different excitation wavelengths: 442 nm (0.8 mW) line from a He-Cd laser, 532 nm (0.6 mW) from a diode-pumped solid state laser, 633 nm (0.5 mW) from a He-Ne laser, and 785 nm (1.8 mW) from a diode laser. Raman spectra were taken using a  $50\times/0.75 \text{ NA}$  objective lens. Integration time was 50 s. Wavenumber axis was calibrated according to the Si line at  $520.7 \text{ cm}^{-1}$ . Raman measurements were carried out in  $180^\circ$  (backscattering) geometry. Frequencies and intensities of the Raman bands were determined by fitting the experimental contour with the Gaussian-Lorentzian form components. Spectral analysis was performed by using GRAMS/A1 8.0 (Thermo Scientific, USA) software.

FTIR spectra were measured with the Nicolet 8700 spectrometer (Thermo Scientific, USA) in the range of  $500\text{--}7400 \text{ cm}^{-1}$  in transmission mode with subtraction of the polyethylene film absorption.

The scanning electron microscope JSM-6490 LV (JEOL, Japan) was used for investigation of surface morphology before and after the laser treatment. Samples were investigated by SEM without any additional pre-treatment. The thickness measurements were performed with a Dektak 150 + stylus profiler (Veeco, USA).

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were conducted with the CompactStat potentiostat/galvanostat with impedance module (Ivium Technologies, The Netherlands). The three-electrode system was used employing the bare or graphene modified ITO as a working electrode, Pt wire was as a counter electrode and Ag/AgCl (KCl sat.) served as a reference. EIS was performed with the same

equipment at a constant applied potential in a frequency range from 100 kHz to 0.1 Hz, with potential perturbation of 10 mV.

CVs at the bare and modified ITO were recorded in the potential range from -1.0 to 1.0 V with the start potential at 0 V in 0.1 M KCl. Potential sweep rate was  $0.1 \text{ V s}^{-1}$ . EIS spectra were recorded at the bare and modified ITO before and after their irradiation with the picosecond-laser at various potentials in the whole potential range used in CV investigation: -0.75; -0.50; 0.00; 0.50; 0.75; 1.00 V. The lowest potential -1.00 V was not applied because the spectra were scattered due to the hydrogen evolution at this potential. The graphene load was varied from 0 to  $3 \text{ mg mL}^{-1}$ .

### 2.3. Preparation of graphene-chitosan film

Graphene flakes were additionally exfoliated to thickness of 2–3 nm and functionalised with hydroxy- and carboxy-groups by sonication 50 mg of graphene flakes in the mixture of  $5 \text{ mol L}^{-1}$   $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  3:1 (V:V) at  $40^\circ\text{C}$  for 20 h. The mixture was filtered and washed excessively with the MilliQ water. Finally, a solid precipitate was dried at  $80^\circ\text{C}$  for 24 h.

Aqueous solution of 0.5% chitosan was prepared as described elsewhere [24]. Chitosan was dissolved in aqueous 1%  $\text{CH}_3\text{COOH}$  solution; then pH was adjusted to 5.0 with 20% NaOH solution. Then functionalised graphene was added to the solution and sonicated for 2 h to reach a homogeneous dispersion. Suspensions of appropriate concentrations ( $10 \text{ pg mL}^{-1}$ ,  $10 \mu\text{g mL}^{-1}$ ,  $1 \text{ mg mL}^{-1}$ , and  $3 \text{ mg mL}^{-1}$ : G1, G2, G3, and G4, respectively) were prepared in this way. One of these suspensions was spin-coated on the indium-tin-oxide (ITO) square electrode with the WS-650-23 spin-coater (Laurell Technologies Corporation, USA), at the 700 rpm rotation speed for the period of 1 min and then 1800 rpm for 30 s. The electrodes were left to dry overnight and then the characterisation was conducted applying CV and EIS. Thickness of the graphene-chitosan film was  $\sim 1 \mu\text{m}$ .

The control sample for the FTIR measurement was prepared as follows: solution of chitosan and suspension of G2 in chitosan solution (as described above) were covered on the framed  $16 \mu\text{m}$ -thick polyethylene film and dried in air. The thickness of the deposited film was measured with the bench micrometer and the thickness of 10 and  $6 \mu\text{m}$  was found for chitosan and G2-Chit films, respectively.

## 3. Results and discussion

### 3.1. Optical investigation of graphene-chitosan film modified ITO electrodes

#### 3.1.1. Raman spectroscopy

Raman spectroscopy is a non-destructive and highly sensitive technique for characterisation of the structure and defectiveness of carbon materials [25,26]. The characteristic D, G and 2D bands are visible in Raman spectra around 1333, 1580, and  $2680 \text{ cm}^{-1}$ , respectively, using excitation with the wavelength of 633 nm. The G band of  $E_{2g}$  symmetry was assigned to in-plane relative motion of pairs of carbon atoms in  $sp^2$  hybridization [25]. The D mode has  $A_{1g}$  symmetry and arises from the breathing vibration of aromatic rings. Defects are required for activation of this mode, while, no defects are necessary for the activation of the second order of D peak, the 2D mode. Position of both D and 2D modes depends on the excitation wavelength [25–28]. The ratio of the intensity of the D and G bands,  $I(D)/I(G)$  is useful for characterisation of the defect content in the sample. Development of two kinds of defects might be responsible for increase in  $I(D)/I(G)$  ratio; i.e. the point defects associated with changes in  $sp^2$  hybridisation in the carbon lattice plane, and formation of new edges due to the reduction of average size of the graphene flake [29,30].

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