CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY

Graphene research in the Center of Physical Sciences and Technology

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Brussels | May 15, 2017

Center for Physical Sciences and Technology

FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRAS

New scientific institution in Lithuania. (www.ftmc.lt)

CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY

Institute of Chemistry

Founded 1945

Organic chemistry, electrochemistry, metallic coatings

Institute of Physics

1956 – Institute of Physics - Mathematics

Founded in 1977

Expertise in:
lasers technologies, nuclear physics, environmental research, molecular physics

Institute of Semiconductor Physics

Founded 1967

Technology Centre - 1981

Science park 1993

Expertise in:
optoelectronics, microwave electronics, electrical engineering, solid state theory, fluctuation phenomena

2010: State Founded Scientific Research Institute

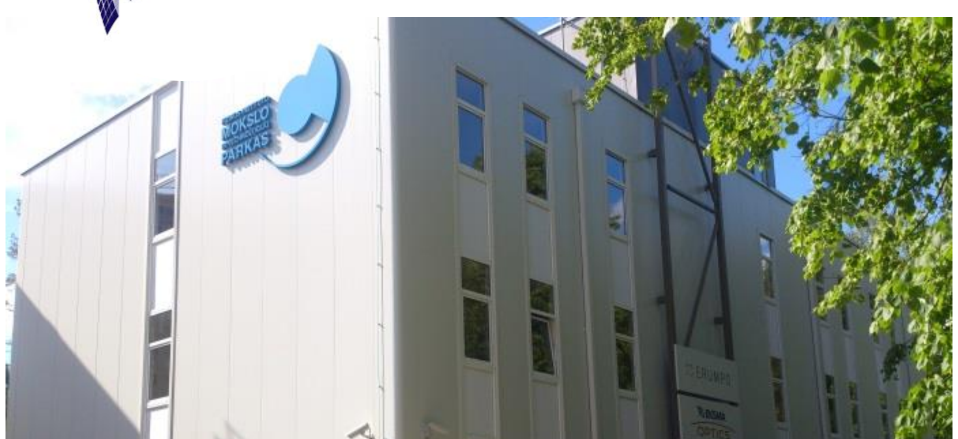
Center for Physical Sciences and Technology

Geography of the Sunrise valley

VU:
Laser technologies:
Naglis

VGTU:
Civil Engineering Research Centre

FTMC



Sunrise (Saulėtekis)
VU+FTMC+VGTU //
East part of Vilnius

FTMC

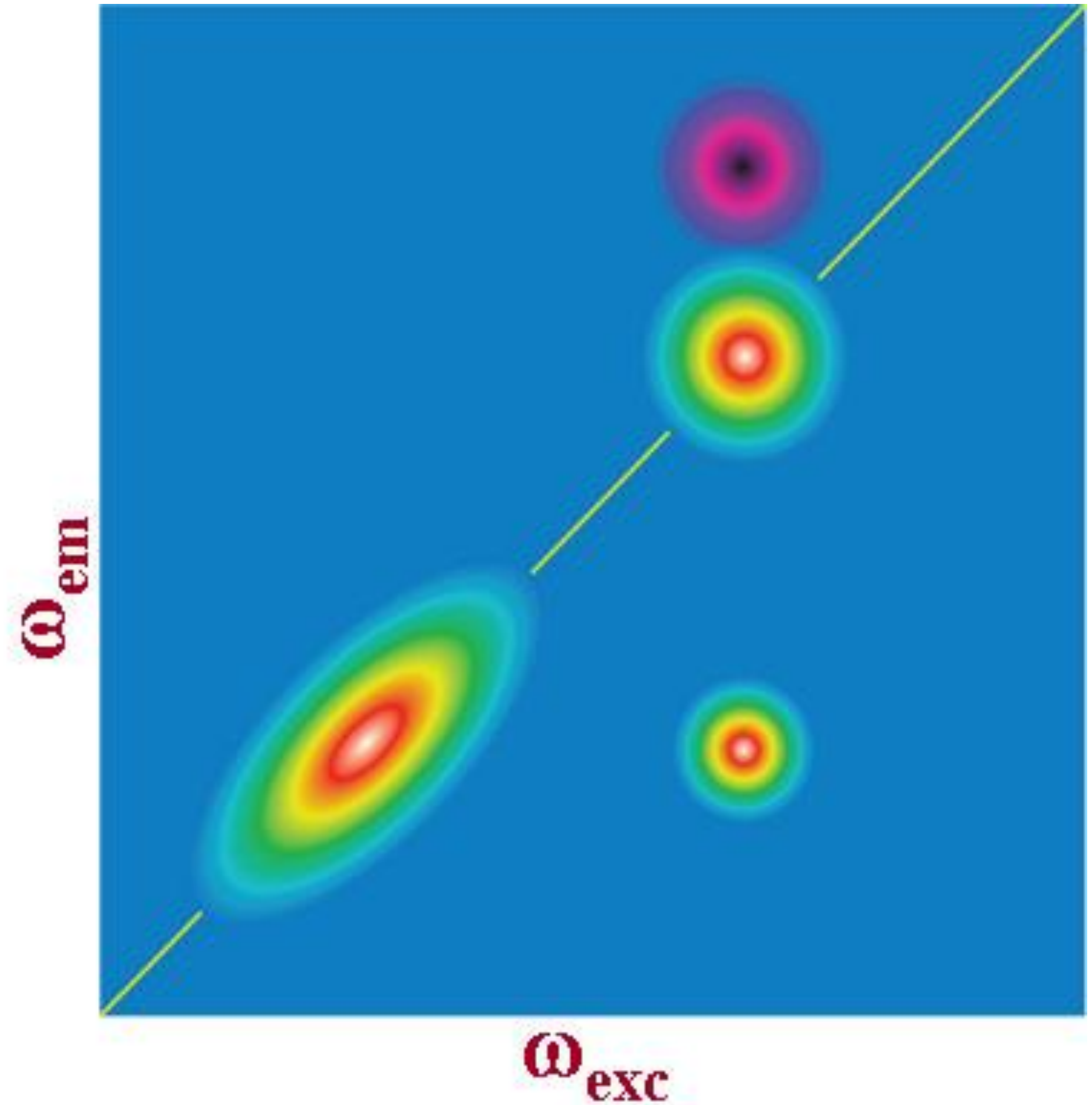
Chemical technologies:
Visoriai/ north part of Vilnius

Sunrise Valley Technology and Innovation Centre:
west part of Vilnius/ Savanoriai

FTMC: **National Institute of Metrology**:
Goštauto/Lukiškių str.
Central part of the city

Theoretical investgations

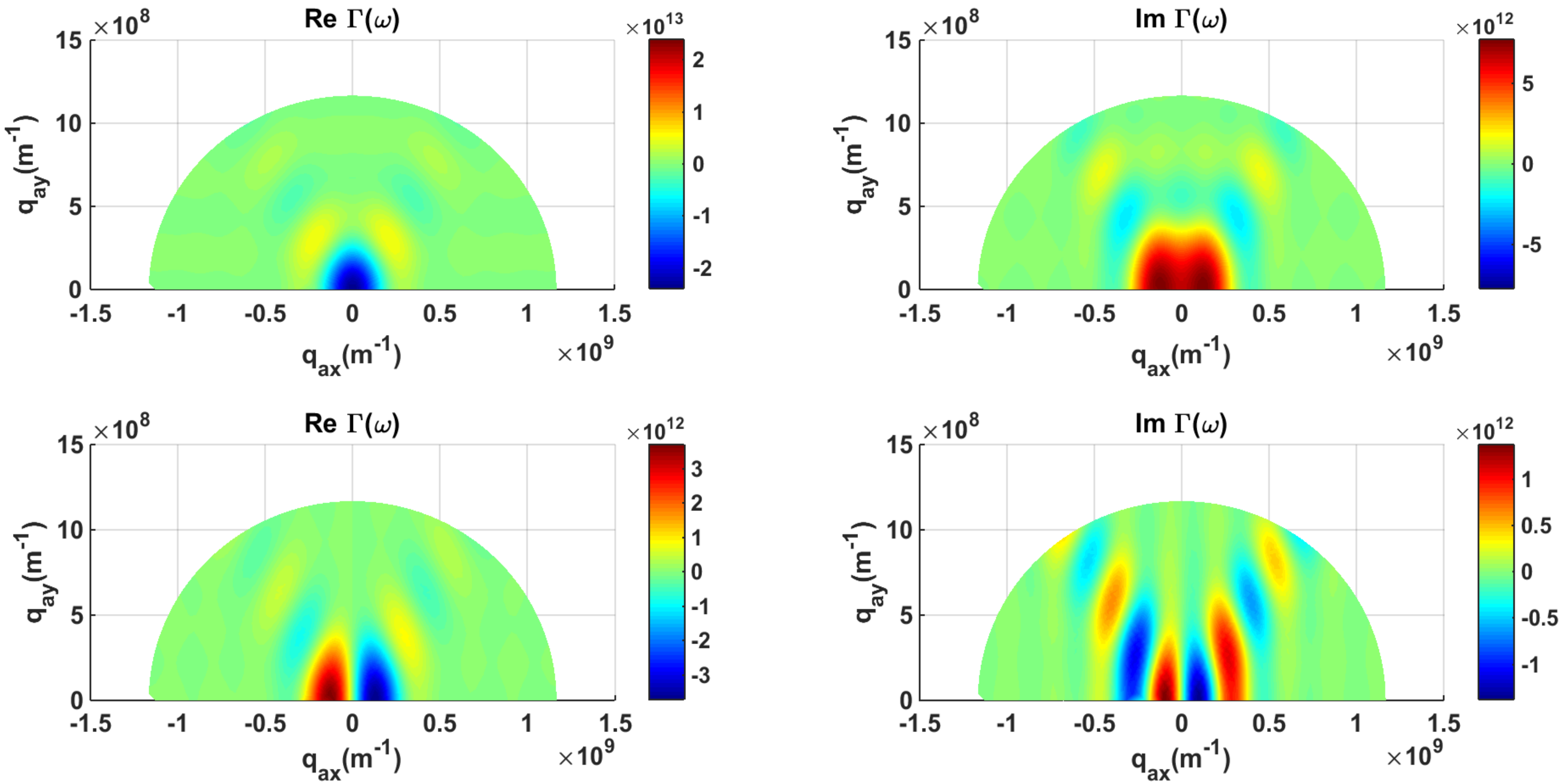
Investigations of electron interaction in graphene



Hipotetic 2D spectrum. ω_{em} is the emission frequeny, ω_{exc} – the excitation frequency. The round peaks and diagonale depict absorbance. Ovale part on the diagonale shows inhomogeneous spreading. The area far from the diagonale shows electrn trasfer beween orbital levels. Dark area above the diagonale depicts absorption to higher level.
http://www.chemphys.lu.se/research/techniques/2Dspec/

E. Pileckis. Masther thesis,2016
Department of Molecular Compound Physics

Investigations of electron interaction in graphene



Influence of (as)symetrization. Upper part: Cut of the bloc of the symetric scatter matrix ($q_c = 0$).
Lower part: Cut of the bloc of the assymetric scatter matrix ($q_c \approx 0$).

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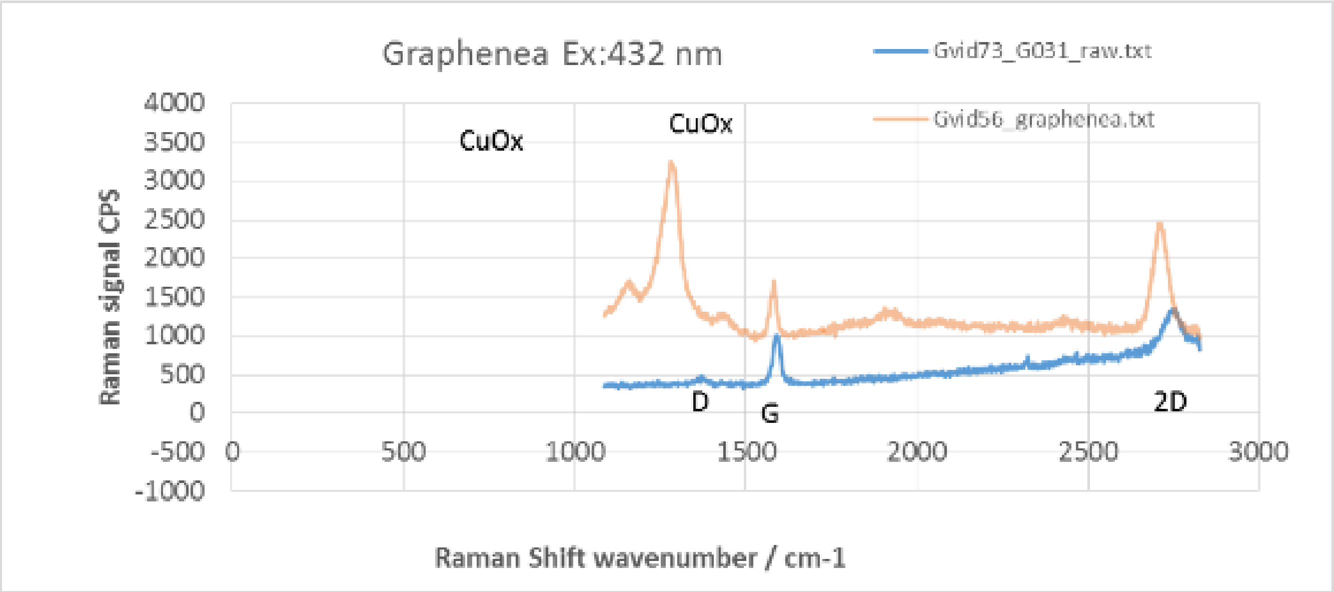
Department of Molecular Compound Physics

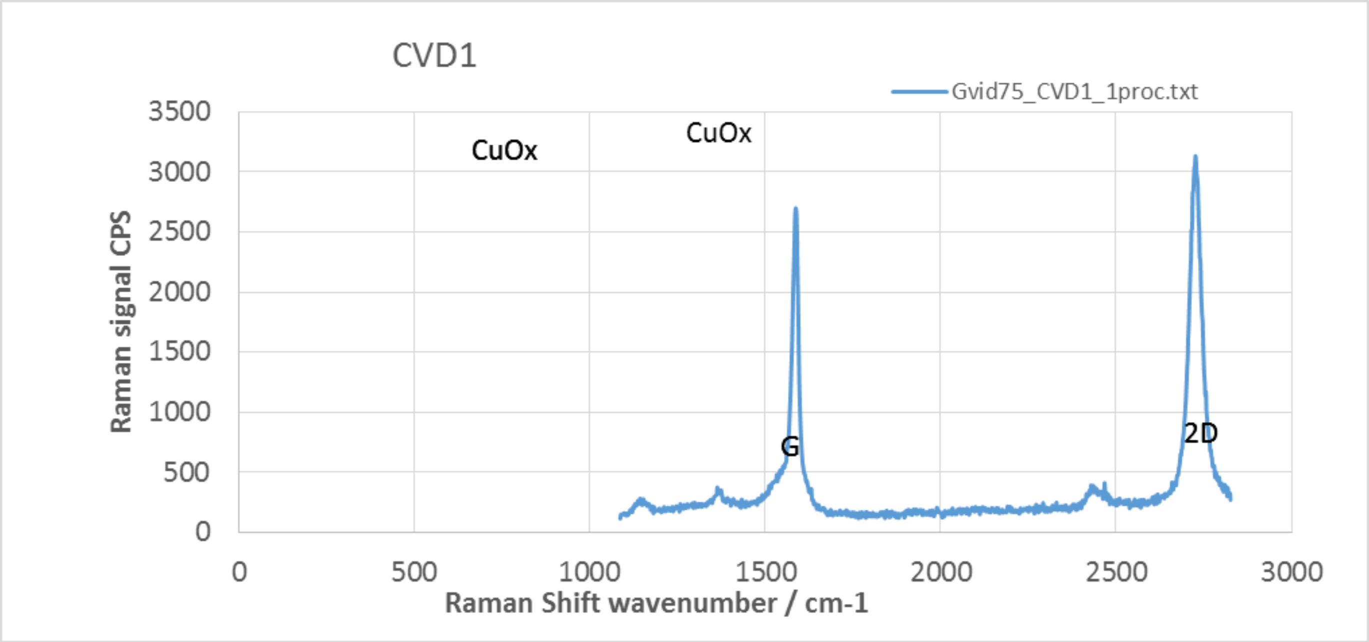
Synthesis

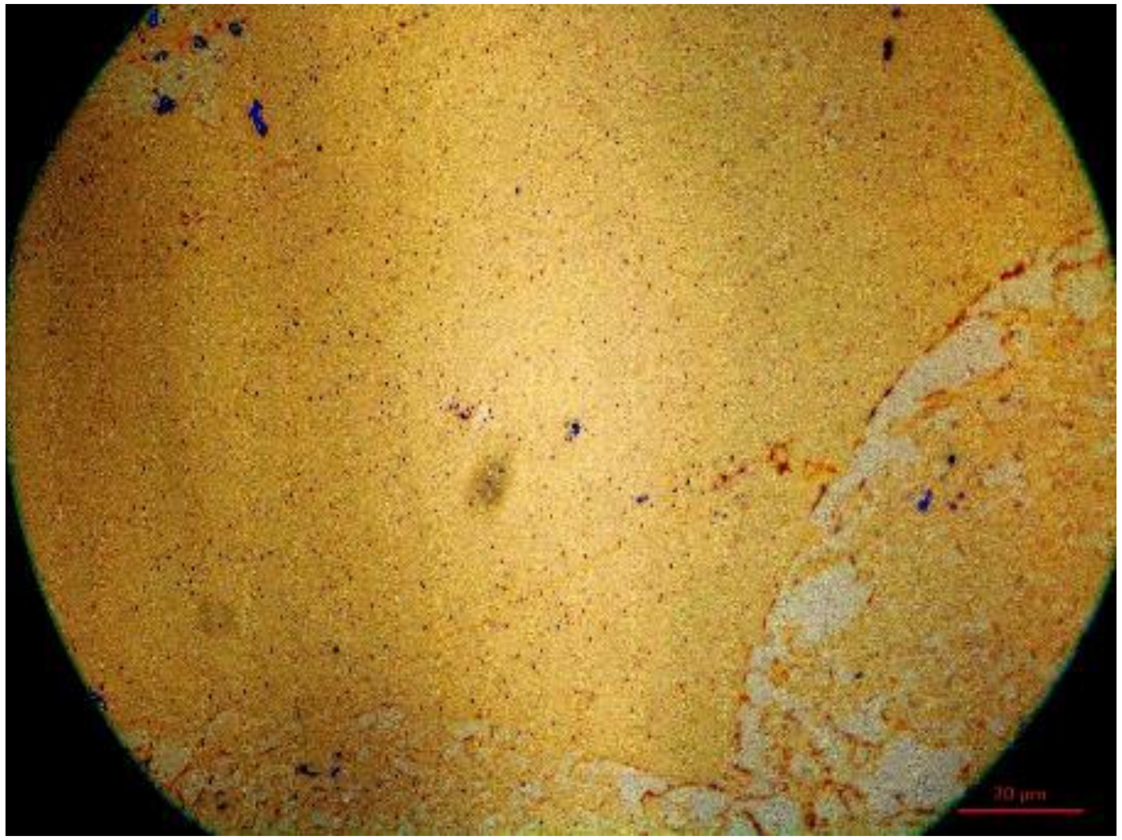
CVD growth

As grown - Cu



After transfer – SiO_2





Graphene transfer

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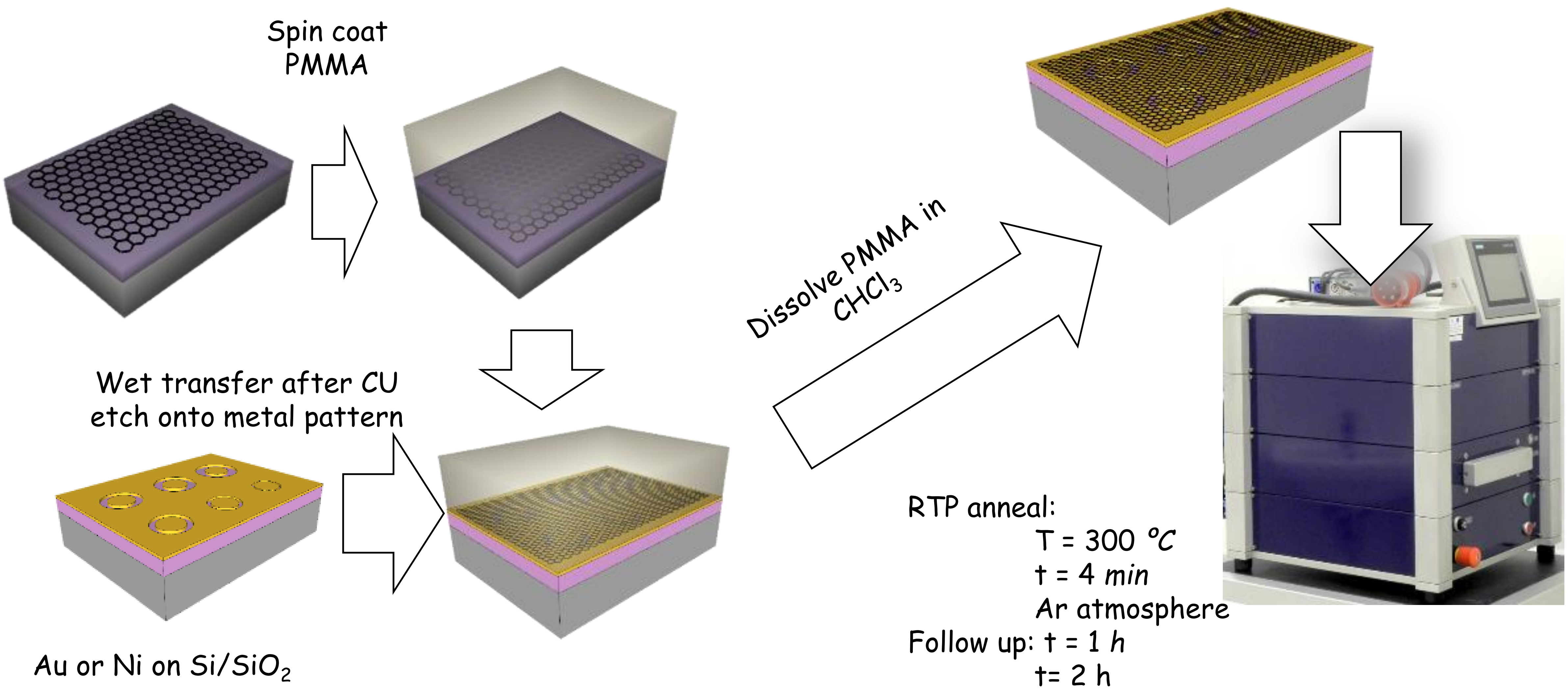
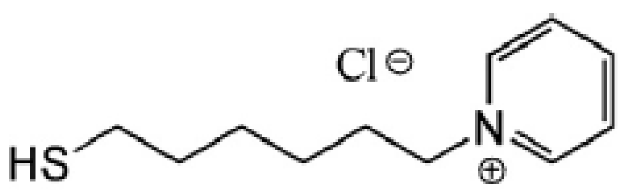
METAL FIRST
Contact fabrication scheme



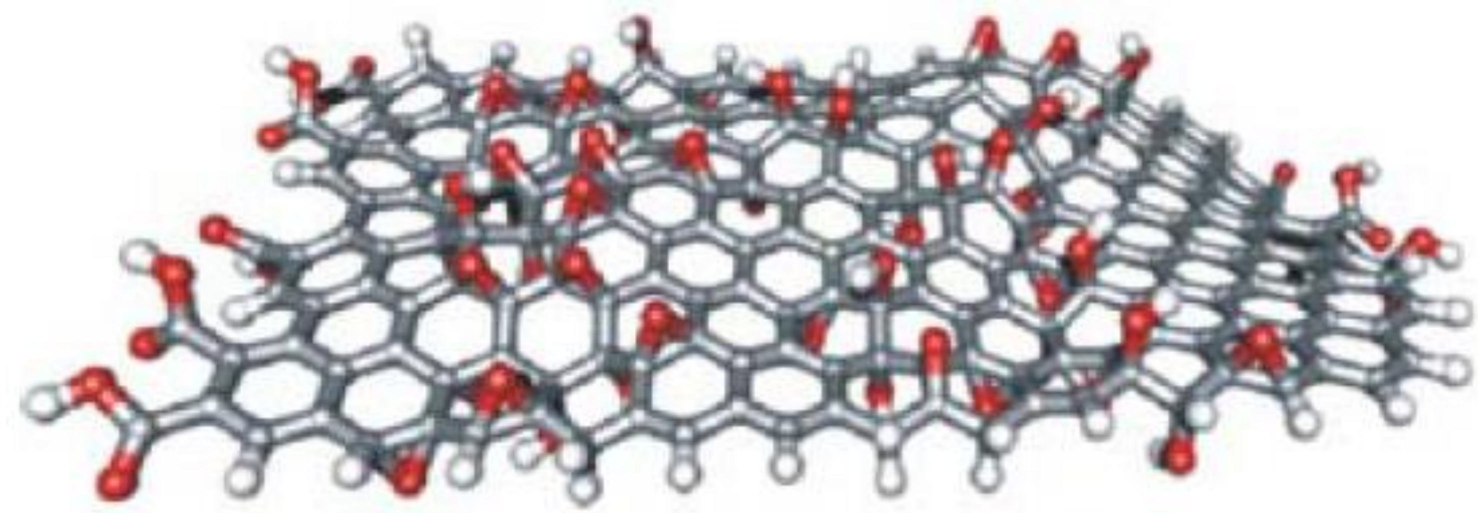
Characterisation

Ion-pairing at electrochemical interface: SERS study of GO adsorption



MHP

positively charged



Graphene oxide

negatively charged

GO adsorption on Au electrode modified by positive charge bearing SAM:ion-pairing mechanism

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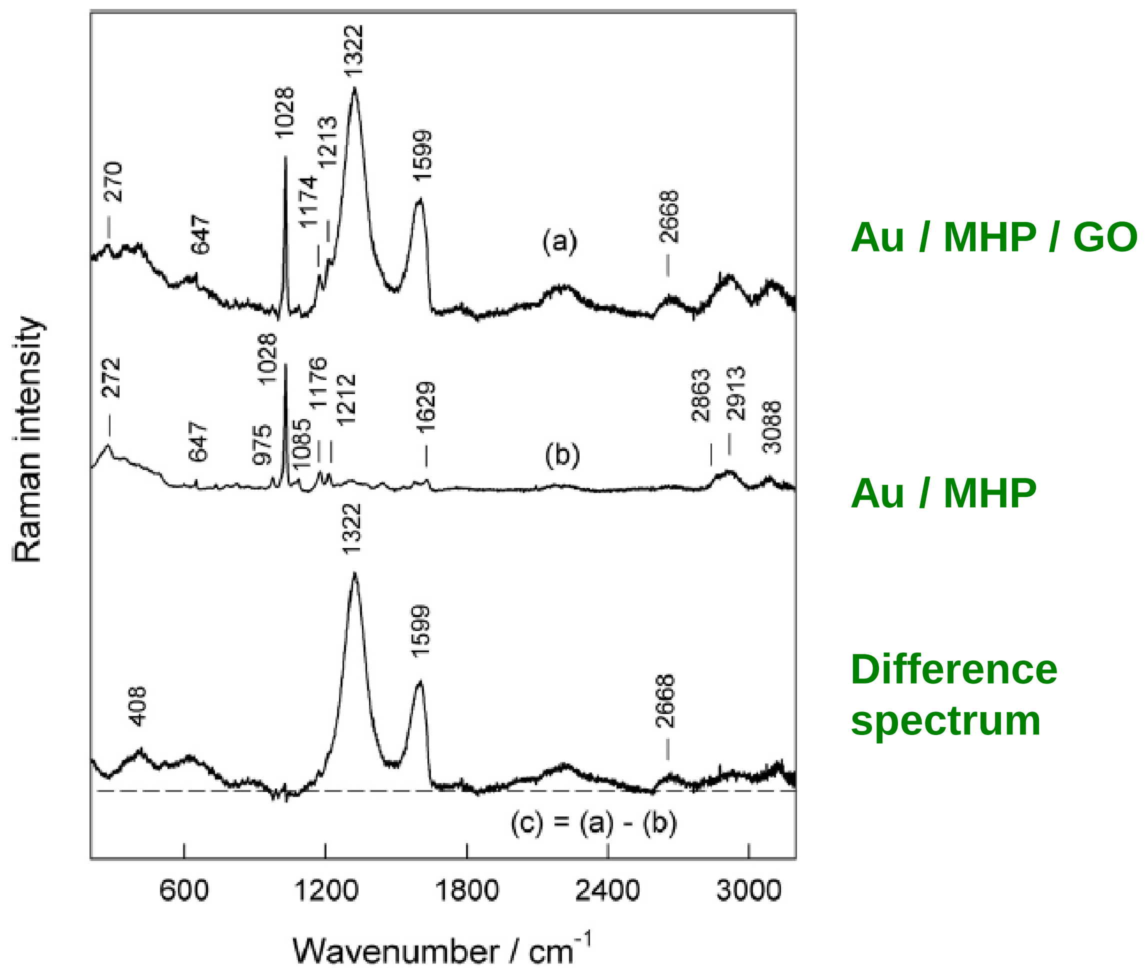
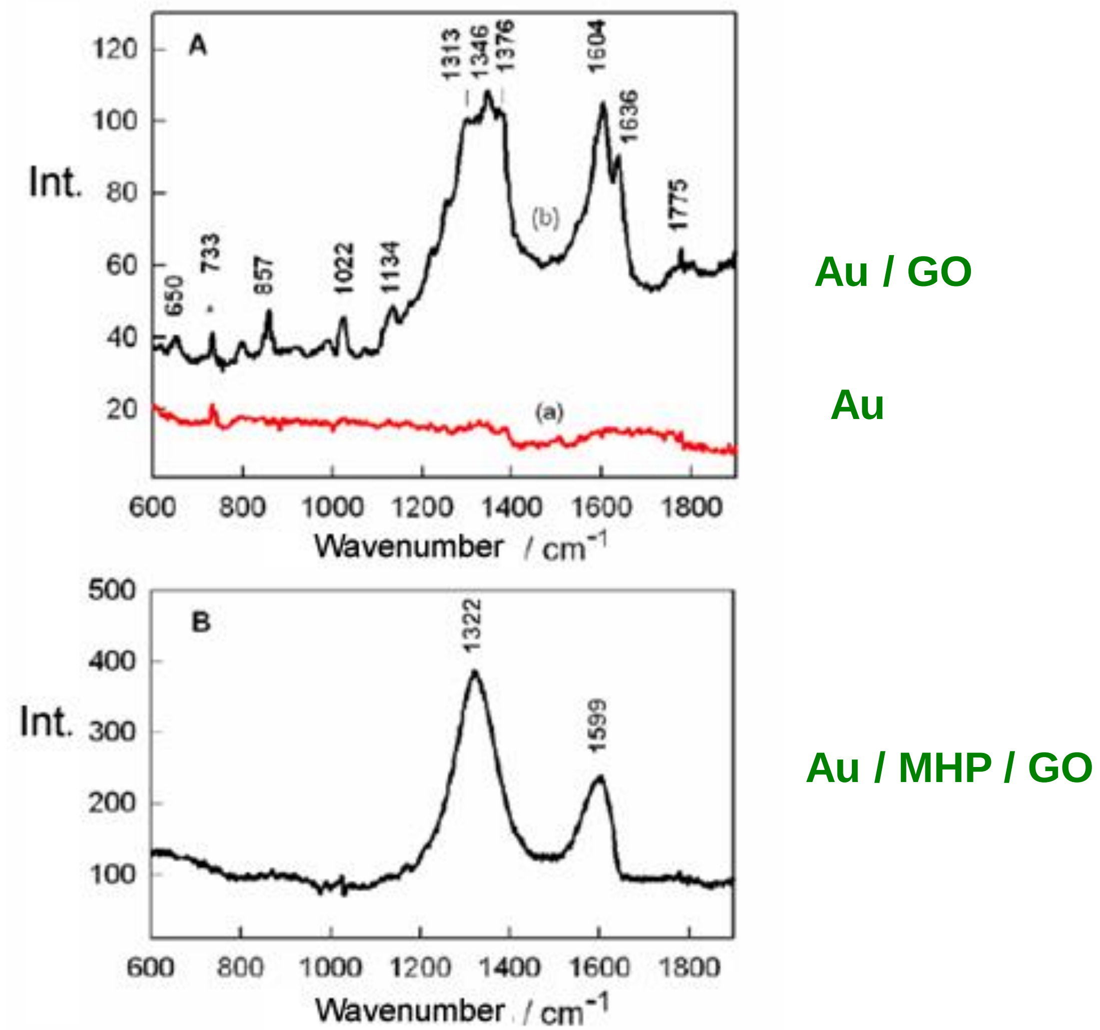
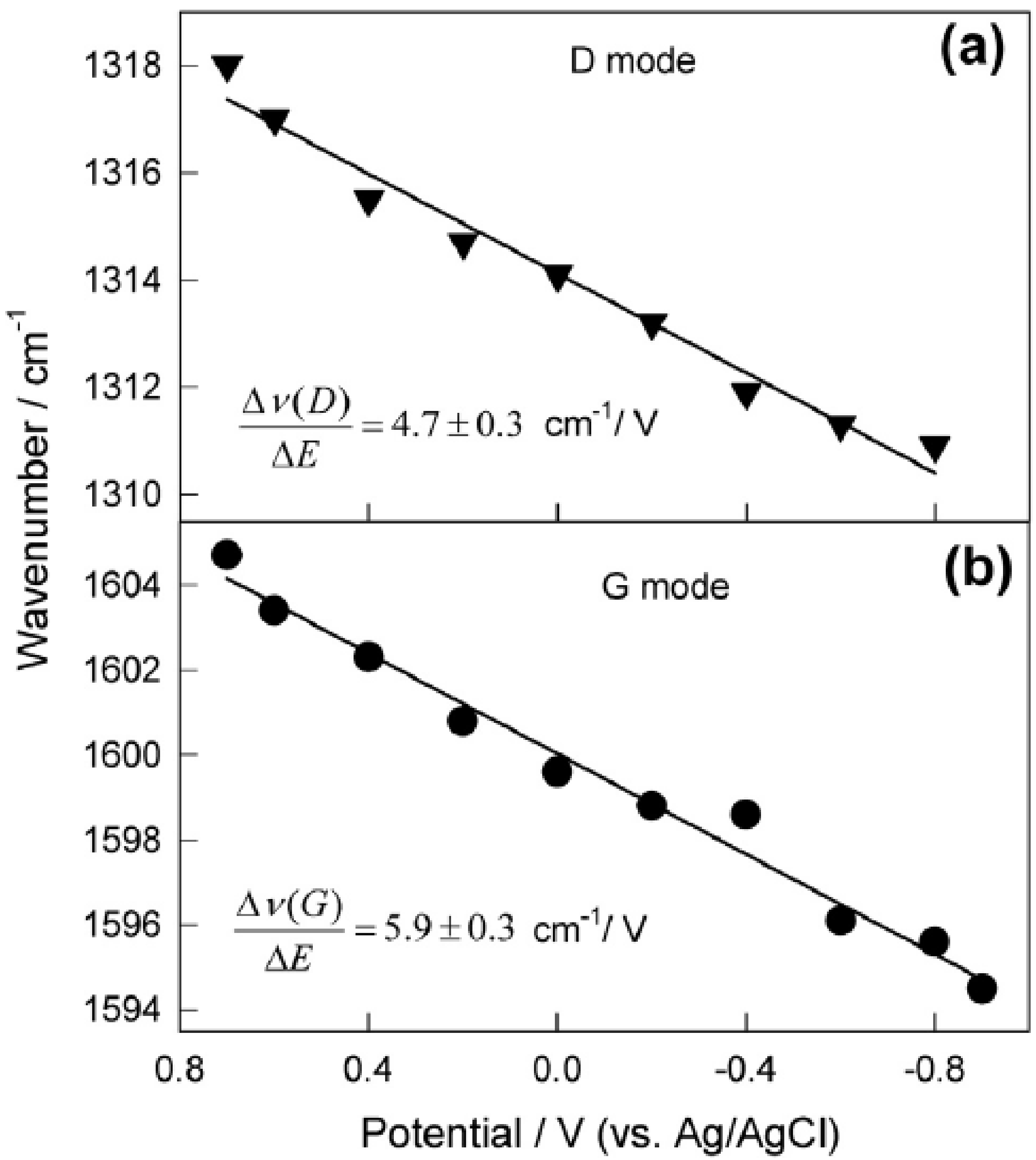




Twofold function of monolayer:
1. Prevention from direct GO interaction with surface;
2. Electrostatic attraction

Mechanism of dependence of GO spectral parameters on electrode potential



$$\Delta r_{(C-C)} = 0.157\sigma_C + 0.146|\sigma_C|^{3/2} + 0.236\sigma_C^2,$$

$\sigma_C = 0.013\ e^-$ **Charge transfer per C atom**

$k = \Delta E_F/\Delta E,$

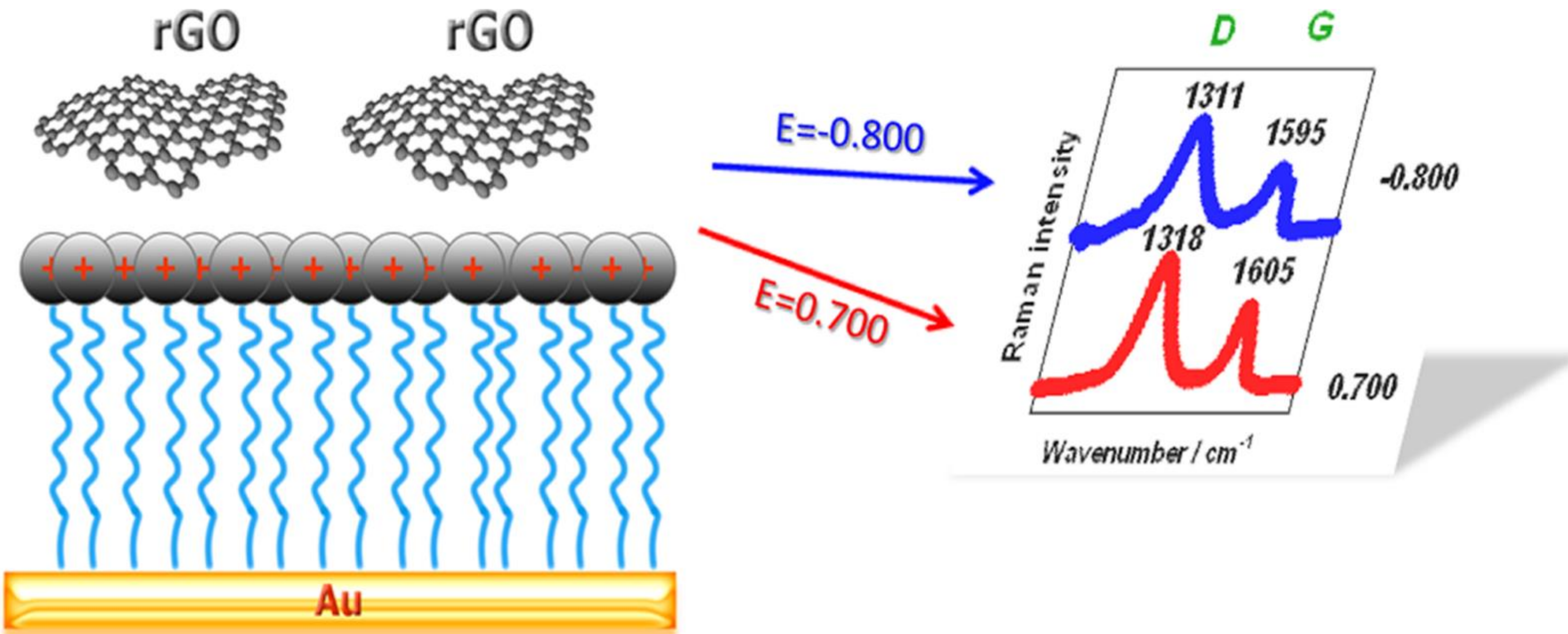
$k = 0.83.$

k=0.5 – 0.7 in the case of SWCNs [J. Phys. Chem. 2009, p. 1340]

Adsorbed GO might be used for sensing the potential at interfaces

Changes in length of C–C take place !

Electrochemical SERS of GO adsorbed on Au modified by positively charged SAM



The reduced GO was prepared at Au modified by positive charge bearing SAM. ν(D) and ν(G) linearly depend on *E* with slopes 4.7 ± 0.3 and 5.9 ± 0.3 cm^{-1}/V, respectively. The effect was explained in terms of changes in the C–C bond length induced by the electrochemical doping. This phenomenon might be explored in analysis of the *E* in diverse environments.

Enhanced microwave-to-terahertz absorption in graphene

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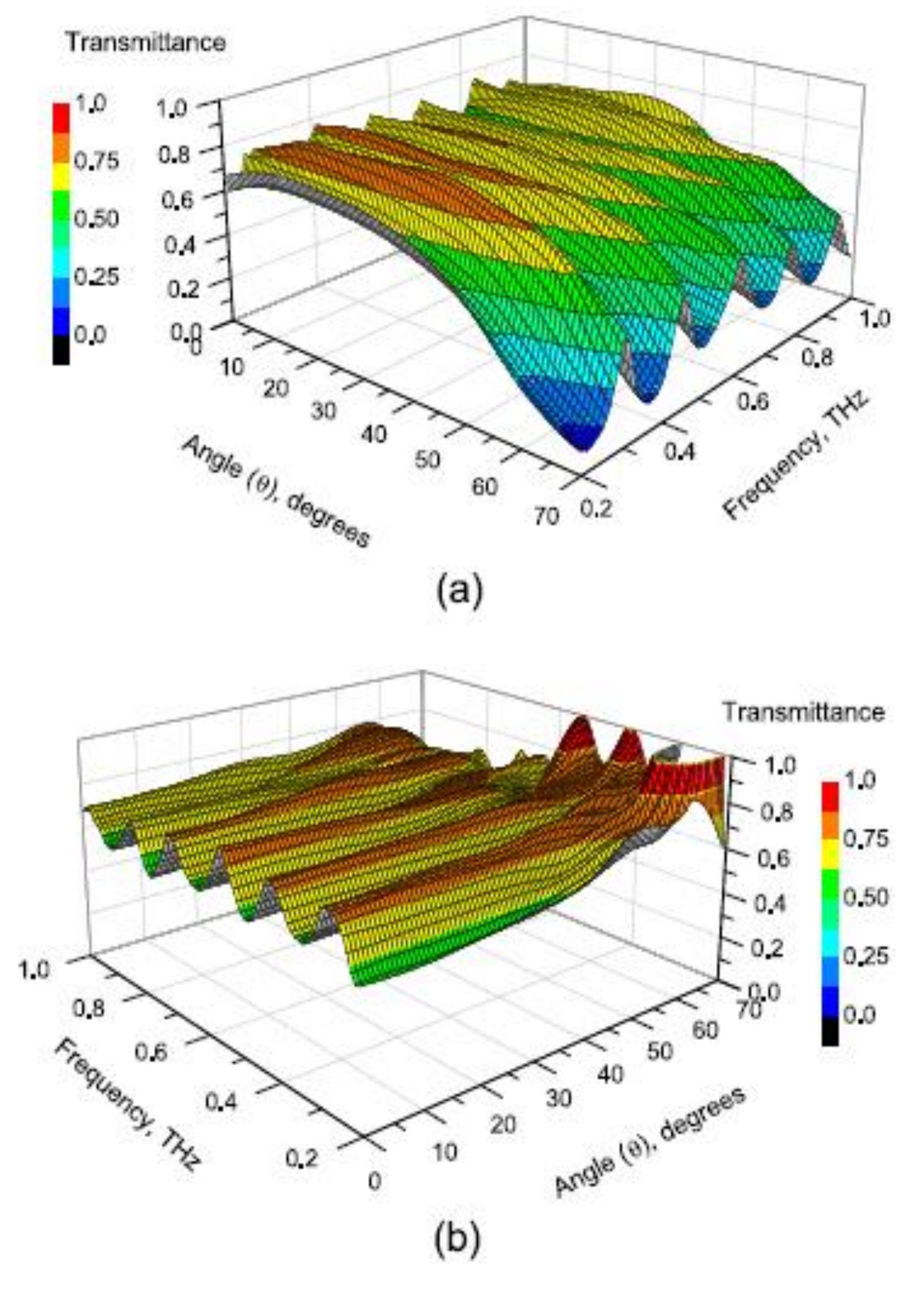

Measured data. Dependence of (a) s-wave and (b) p-wave transmittance through graphene on substrate on frequency and angle of incidence for one graphene layer film.

K. Batrakov,et al. Appl. Phys. Lett. 108, 123101 (2016)
Department of Optoelectronics

Enhanced microwave-to-terahertz absorption in graphene

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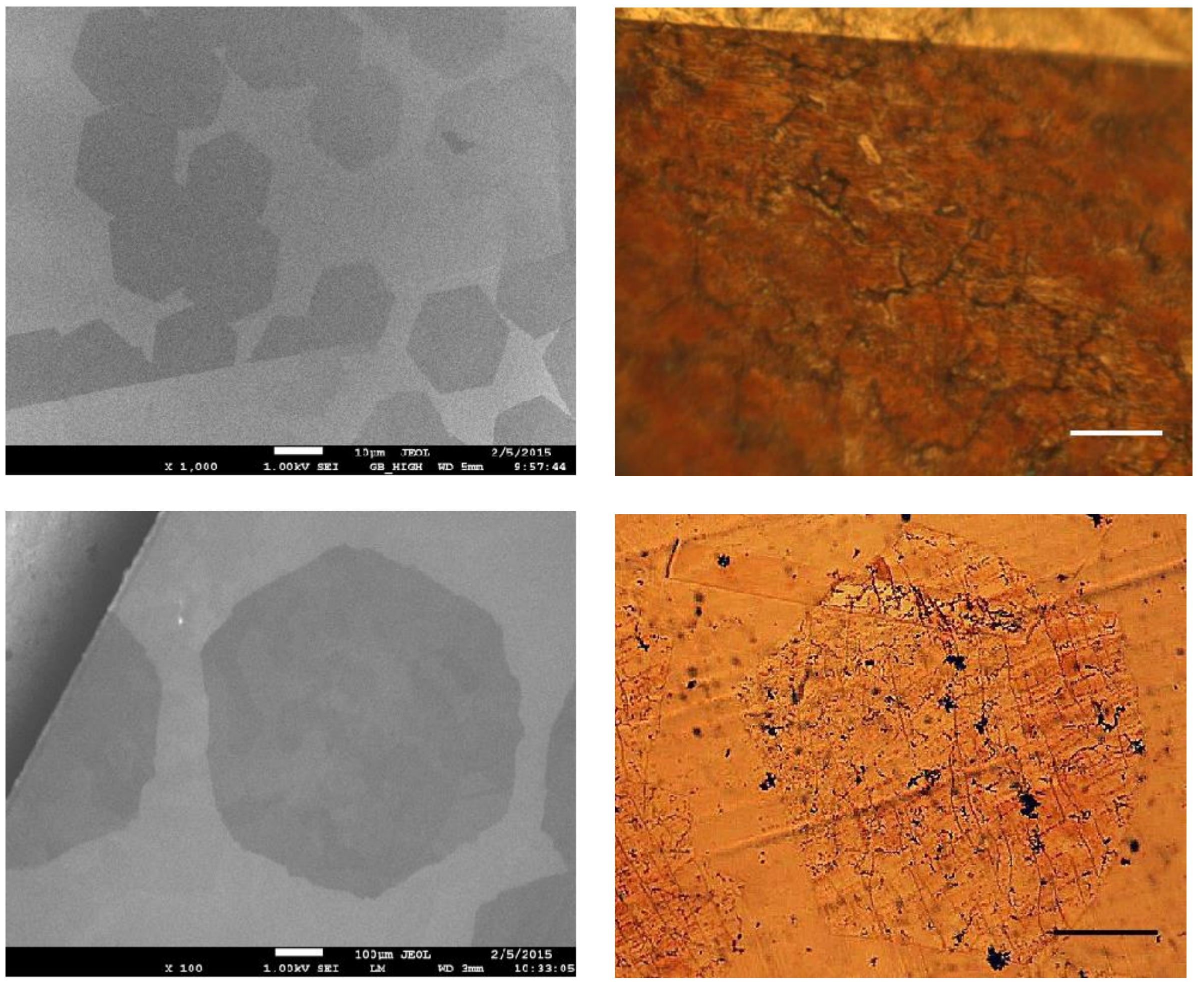

SEM images of graphene hexagonal domains corresponding to (a) 20 μm-GRA and (c) 400 μm-GRA samples, when the synthesis was stopped before graphene covered the whole copper substrate. (b), (d) optical images of graphene samples after chemical treatment obtained according to technique proposed in Ref. 28. The disks drawn with a thin dotted line in (b) and (d) indicate the graphene domains in case of small and large grain size samples, respectively.

P.P. Kuzhir,et al. J. Nanophotonics. 11, 032511 (2017)
Department of Optoelectronics

Modification

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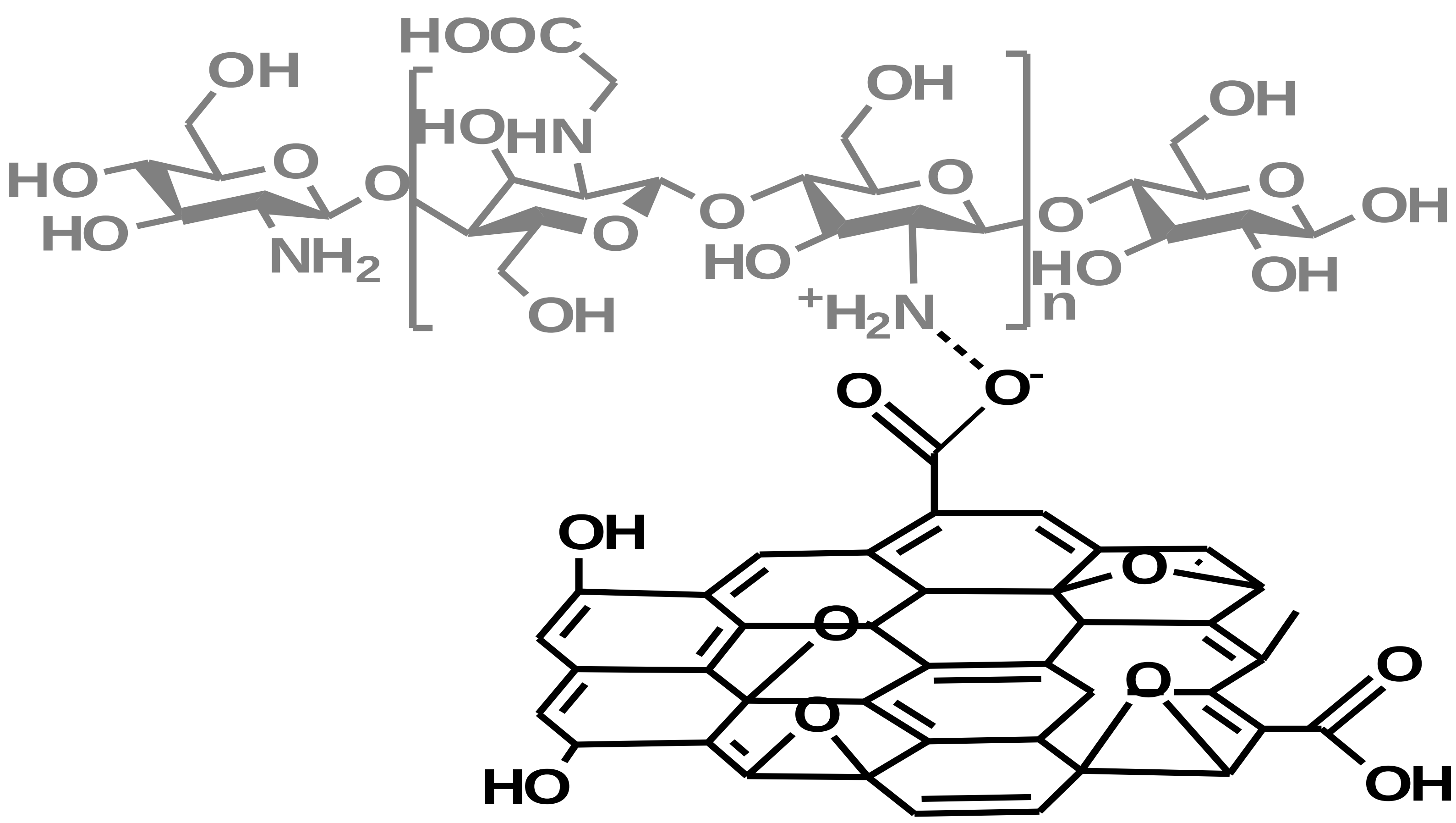
Graphene oxide modification with chitosan



R. Celiešiūtė, et al., *Chemija*, 24 (2013) 296
Deapartment of Nanoengineering

Graphene oxide reduction

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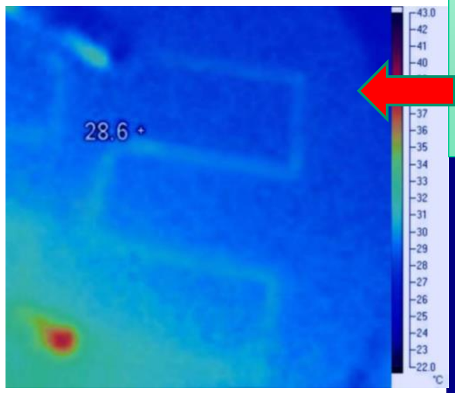
Graphite + Oxidation using strong oxidizing agents = Graphite oxide (GO)

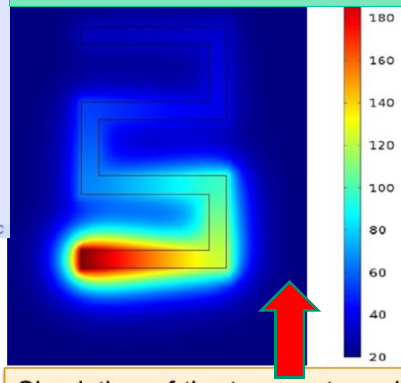
Multilayer

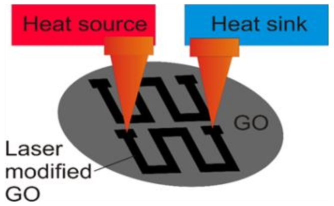
Laser induced GO reduction → Reduced GO – increase of thermal/electrical conductivity

- No need in complex heating systems (thermal GO reduction) or hazardous chemicals (chemical GO reduction);
- Controllable level of reduction;
- Precise focusing and beam guiding allows forming of complex patterns;
- Scalability.

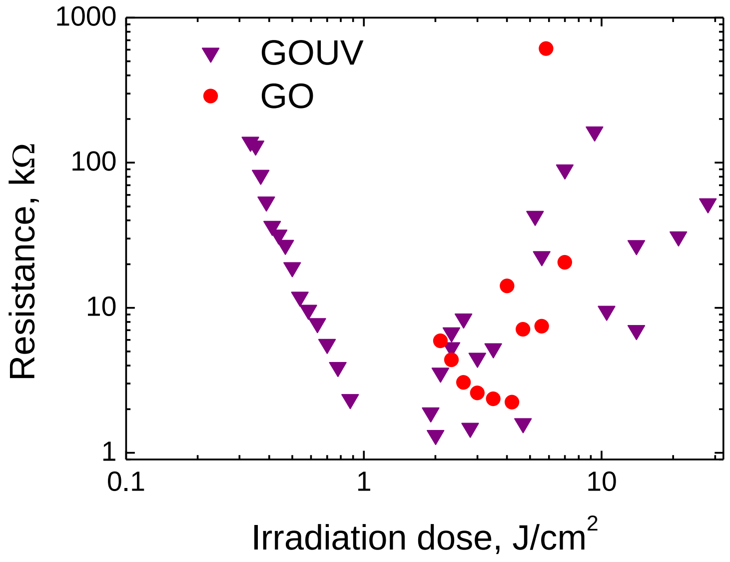


Temperature distribution in the double zigzag structure of graphite oxide coating formed by localized laser reduction method measured by thermo-visual camera.



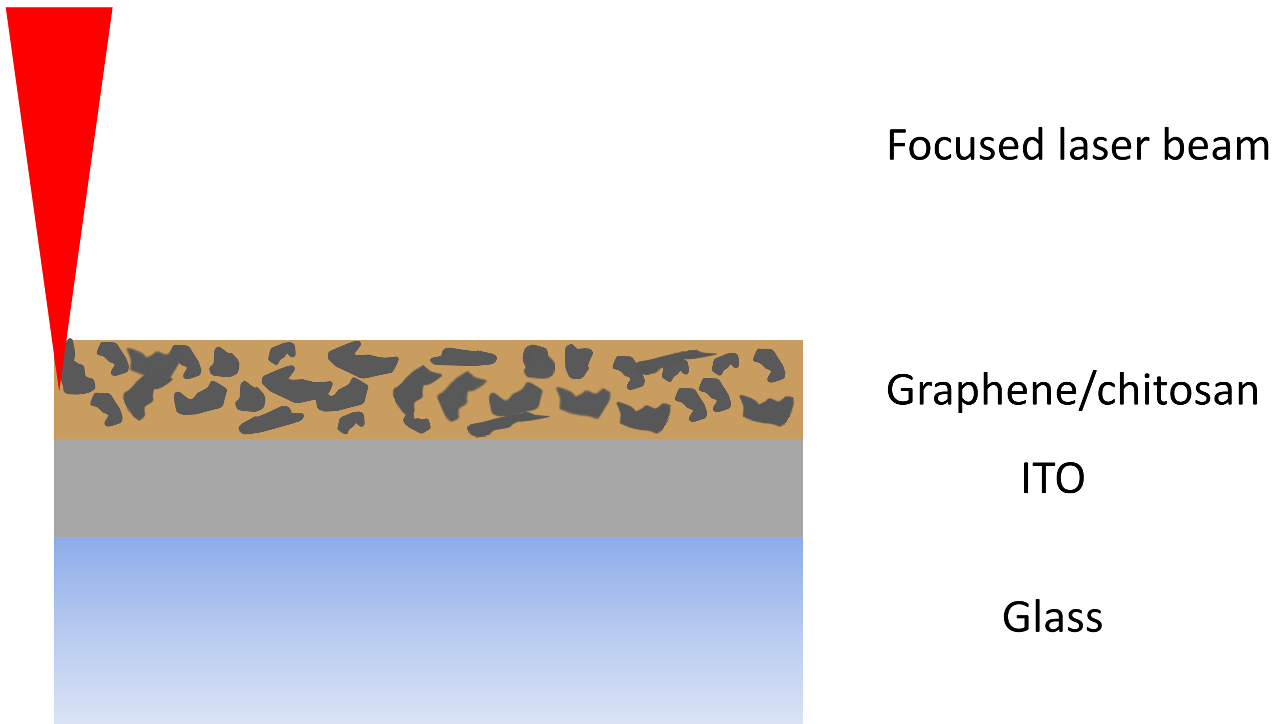


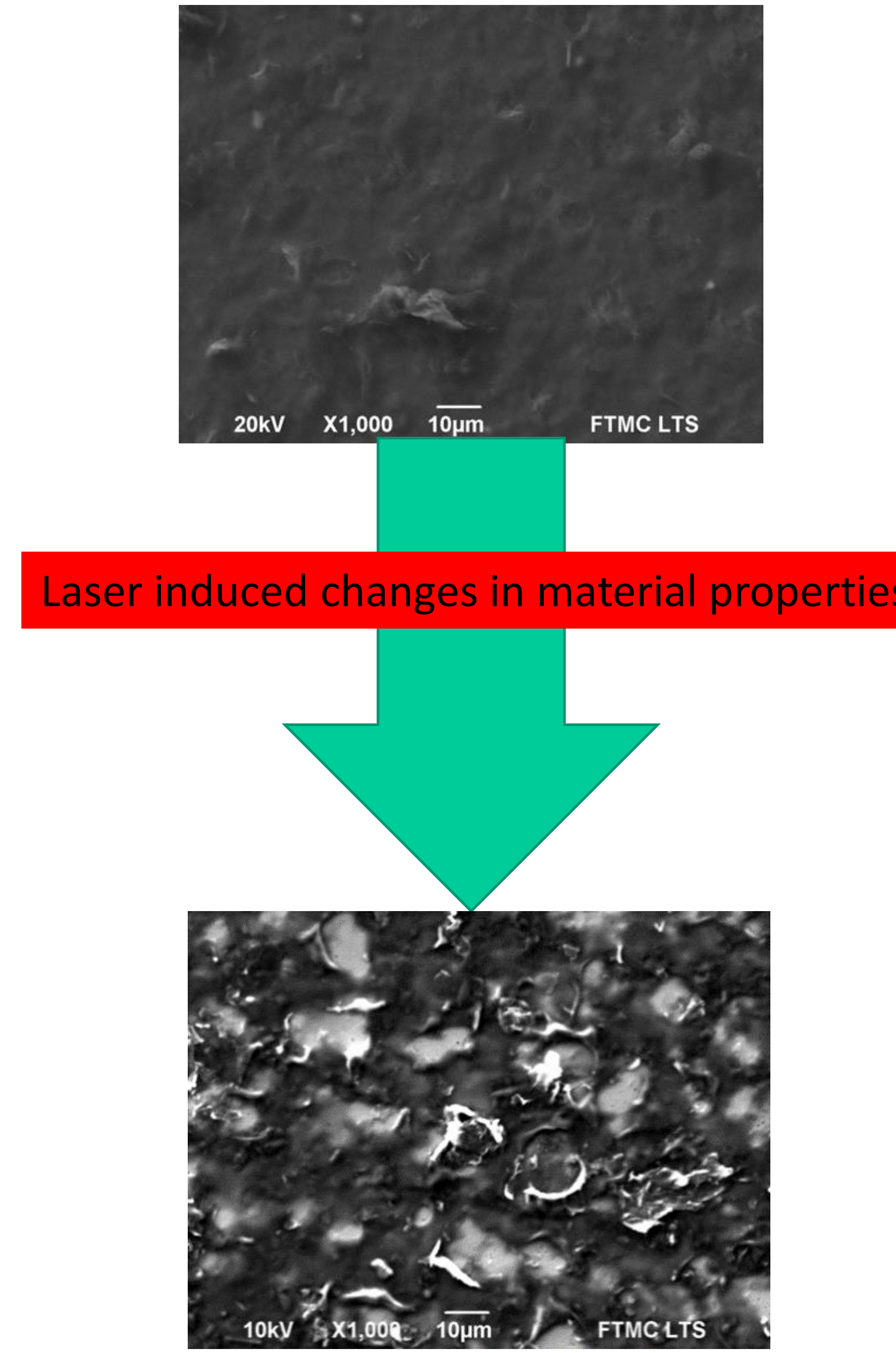
Simulation of the temperature distribution in graphene channel in graphite oxide layer in polycarbonate.



Deapartment of Laser Technology

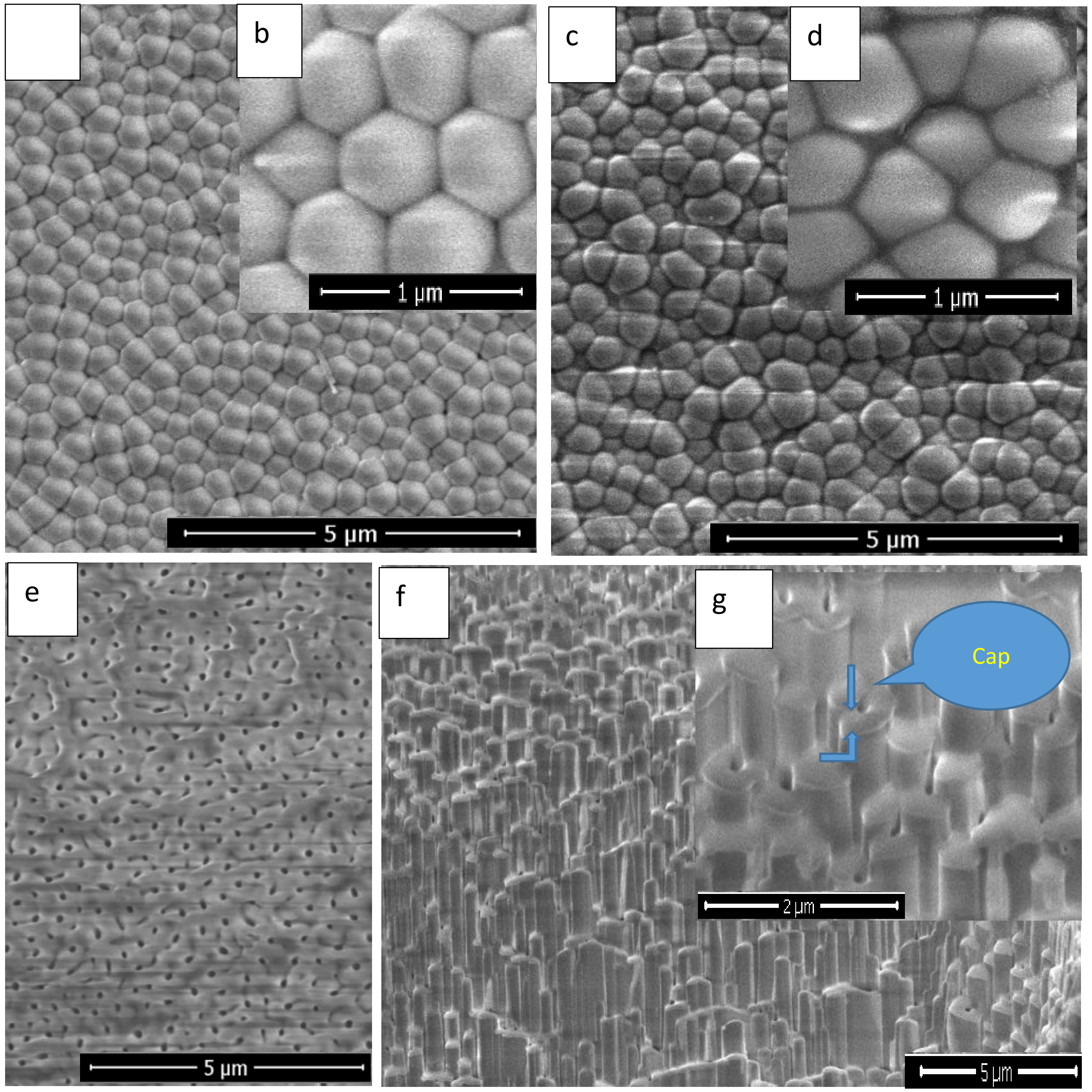
Laser induced modification of graphene/chitosan composites





Laser treatment improves electrochemical characteristics of graphene/chitosan composite films which are used as electrodes for bio-sensing applications.

Graphene-Alumina heterostructured films with nanotube morphology



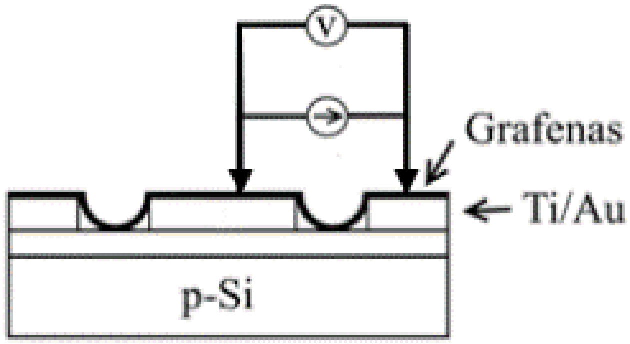
Porous alumina/graphene oxide film with non-typical nanotubed morphology and cell caps at the surface side were formed via anodizing of aluminium in the aqueous solutions of organic acid at the critical current densities.

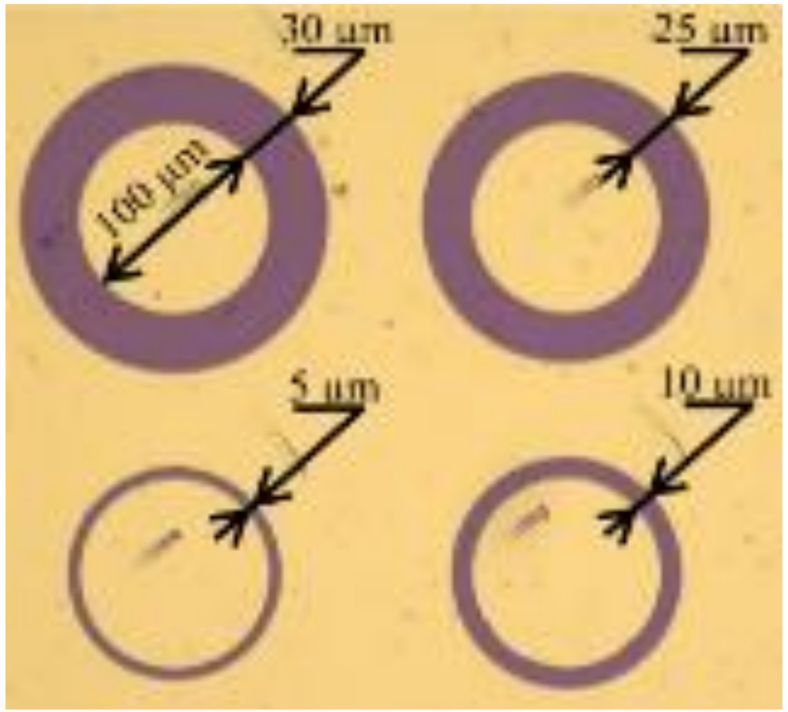
A. Jagminas, et. al.. J. Phys. Chem. C 120 (2016) 9490-9497.
Department of Electrochemical Materials Science

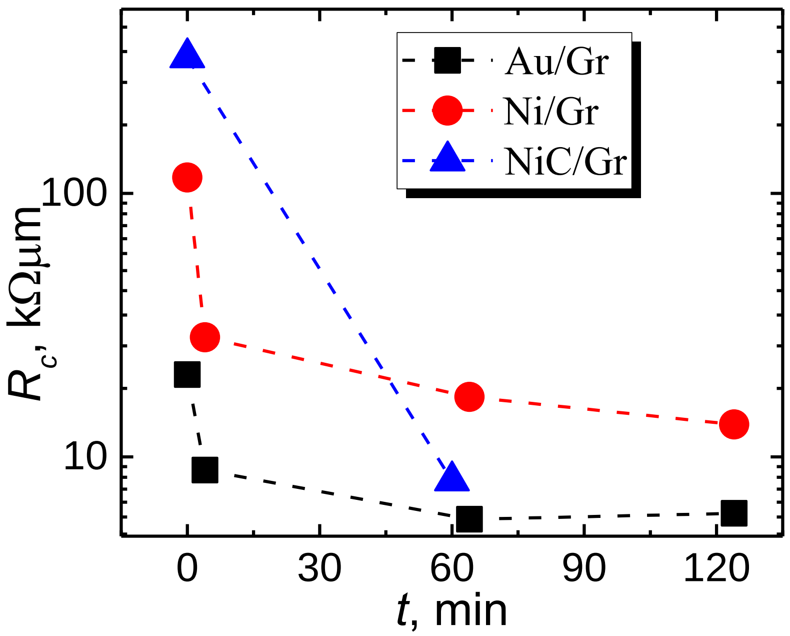
Applications

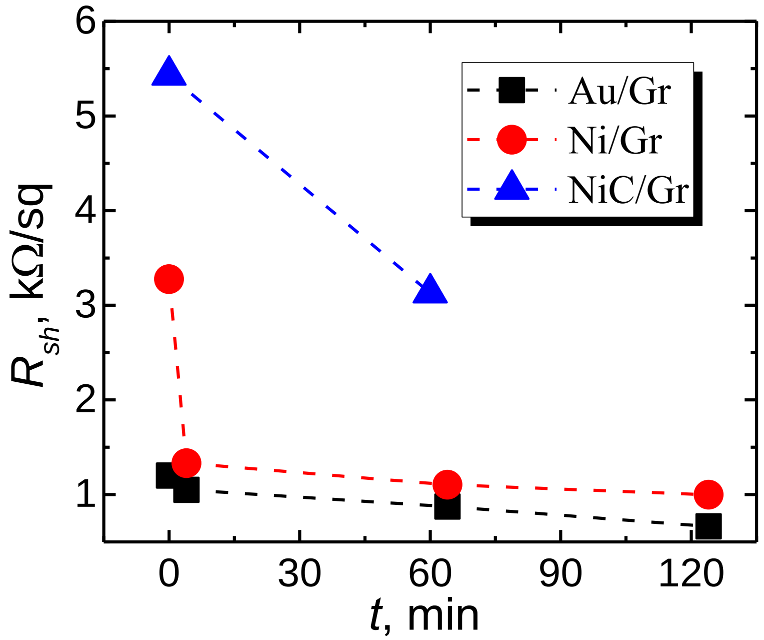
Graphene contacts

Graphene/gold and Graphene/nickel contacts









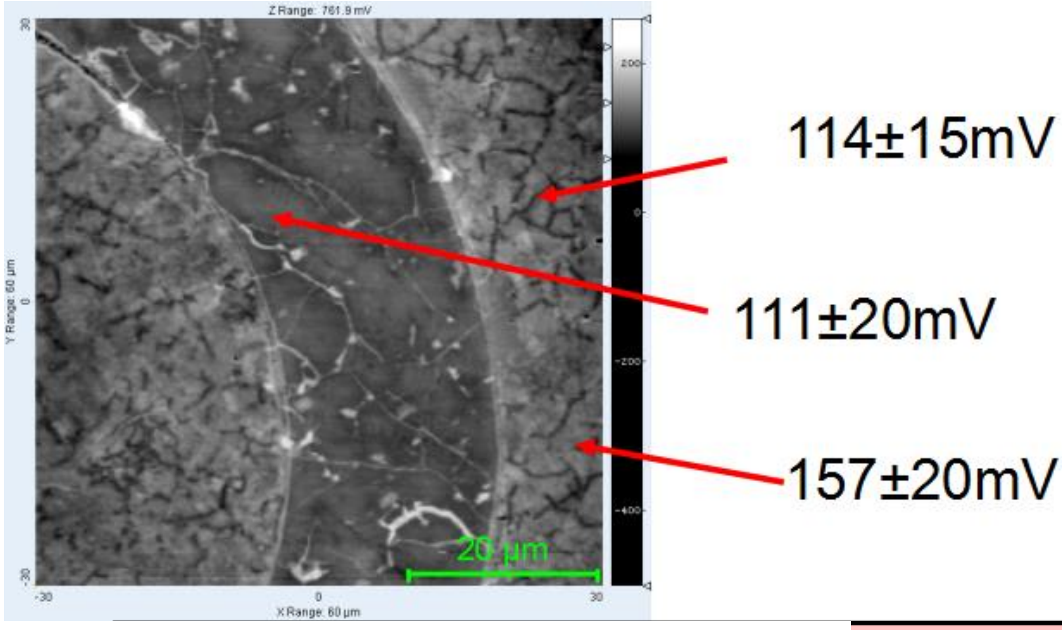
Deapartment of Physical Technologies

Graphene: Contact Annealing

Improvement of electrical contacts by annealing

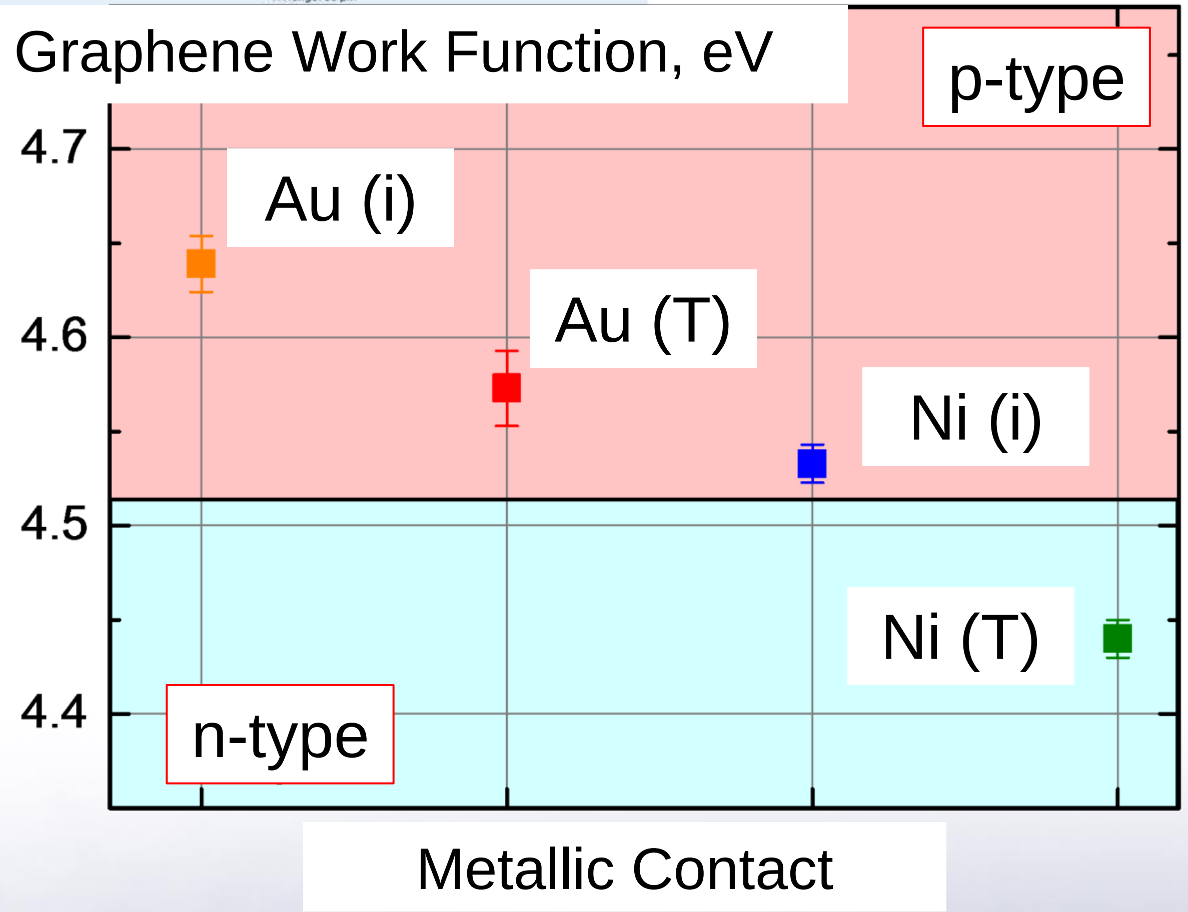
Testing & Analysis explain the changes due to annealing

Scanning Probe Microscopy
Tests by Kelvin Probe Force Micrsocopy (KPFM)



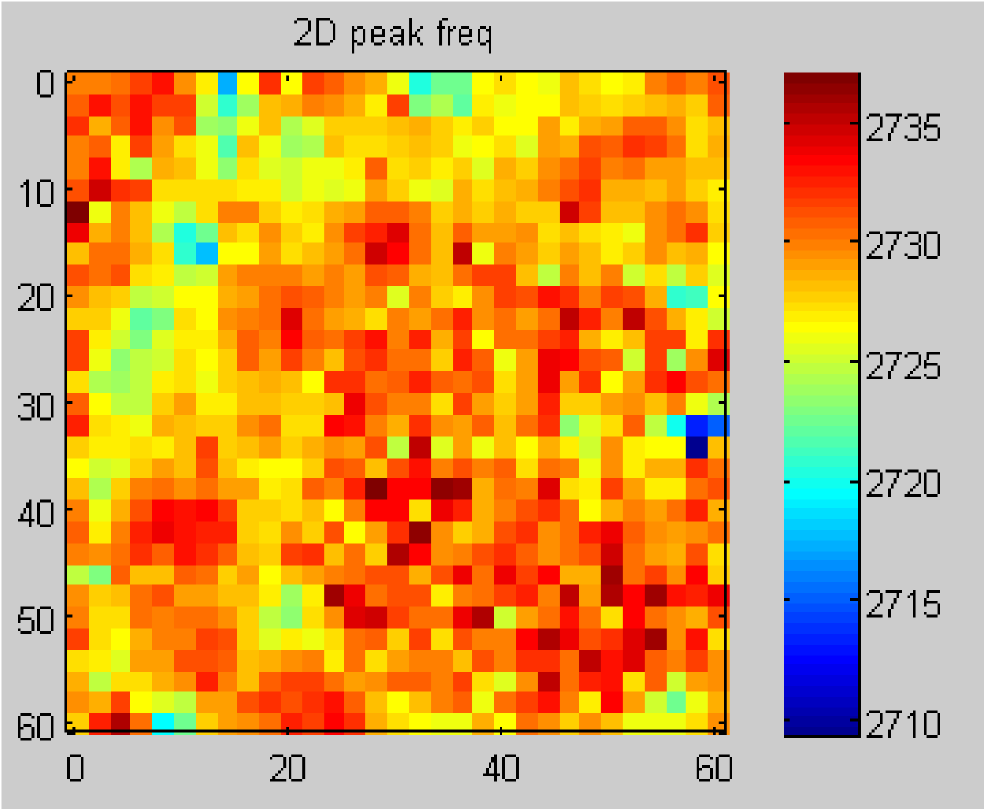
Measured characteristics:
1) maps of the contact potential differencs (CPD);

2) the work function of graphene on the contact.

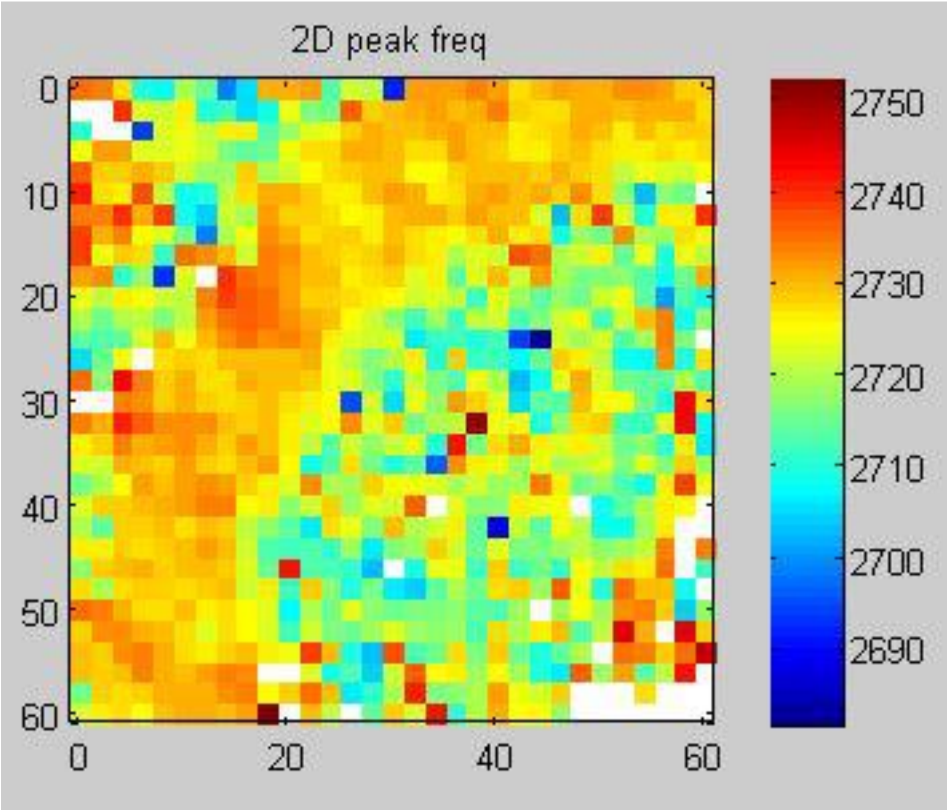


Graphene: Contact Annealing

Improvement of electrical contacts by annealing



Graphene on Au annealed



Graphene on Ni annealed

Raman spectra analysis: surface mapping for the 2G line:
the maps of the peak shift of the 2G line display the differences of

the interaction between metals and substrate.

Development of graphene supported catalysts

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FOR FUEL CELLS

- ❖Direct Borohydride Fuel Cells (DBFCs)
- ❖Direct Methanol Fuel Cells (DMFCs)
- ❖Direct Ethanol Fuel Cells (DEFCs)

FOR HYDROGEN GENERATION

Fabrication of graphene powder supported catalysts by means of microwave synthesis:

- ❖ **non-noble M/graphene catalysts (M = Co, Ni, Cu, Fe, etc.)**
- ❖ **Pt-M/graphene catalysts (M = Co, Ni, Cu, Fe, Mo, W, etc.)**
- ❖ **Au-M/graphene catalysts (M = Co, Ni, Cu)**

Development of graphene powder supported catalysts

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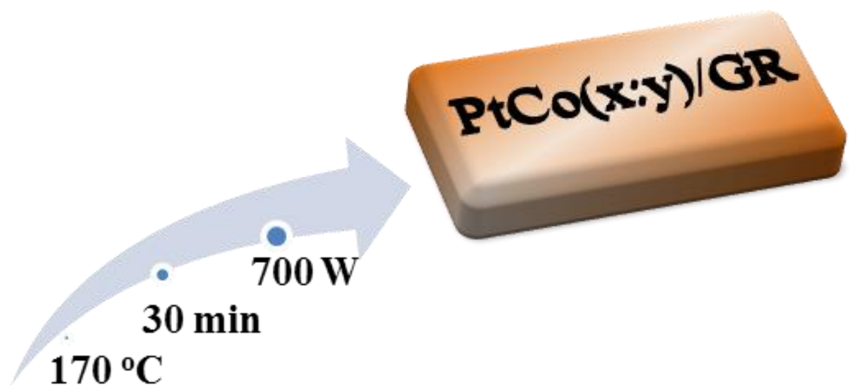
Fabrication of graphene supported Pt, Co and PtCo catalysts by microwave synthesis

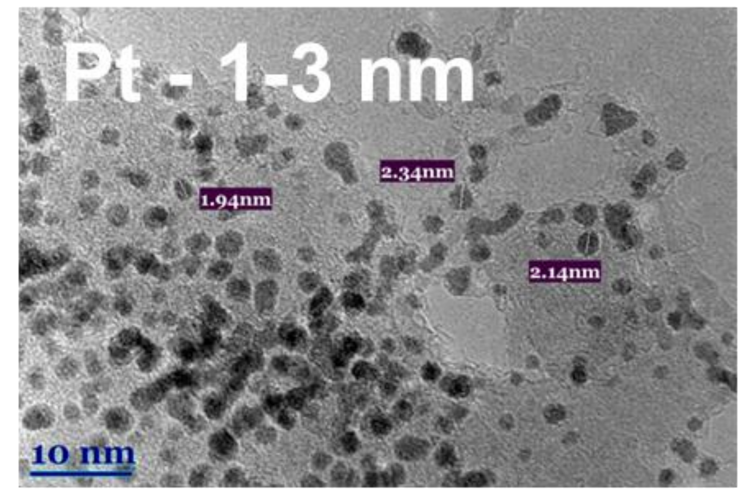
- Graphene powder (GR)
- H_2PtCl_6
- $CoCl_2$
- NaOH
- Ethylene glycol



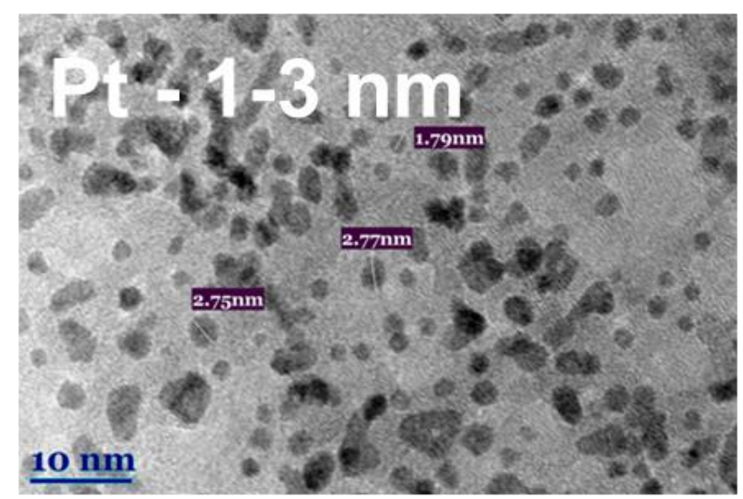
Microwave reactor Monowave 300 (Anton Paar).

- ❑ PtCo/GR with different Pt:Co molar ratios
- ❑ Pt nanoparticles in size of 1-3 nm in the prepared catalysts

PtCo(1:7)/GR



PtCo(1:44)/GR



L. Tamašauskaitė-Tamašiūnaitė, et. al. “Metal/graphene catalyst preparation method”. Lithuanian patent LT 6311 B (2016-09-12).
Deapartment of Catalysis

Development of graphene powder supported catalysts

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Electrocatalytic activity of PtCo(x:y)/GR catalysts towards

Borohydride oxidation **Methanol oxidation** **Ethanol oxidation**

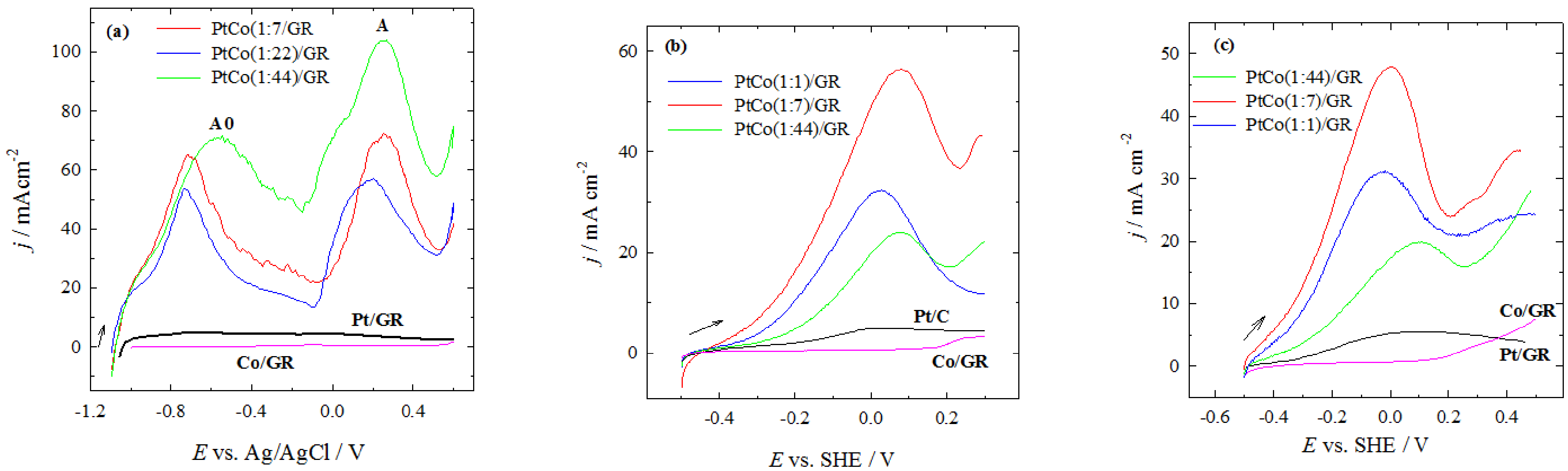
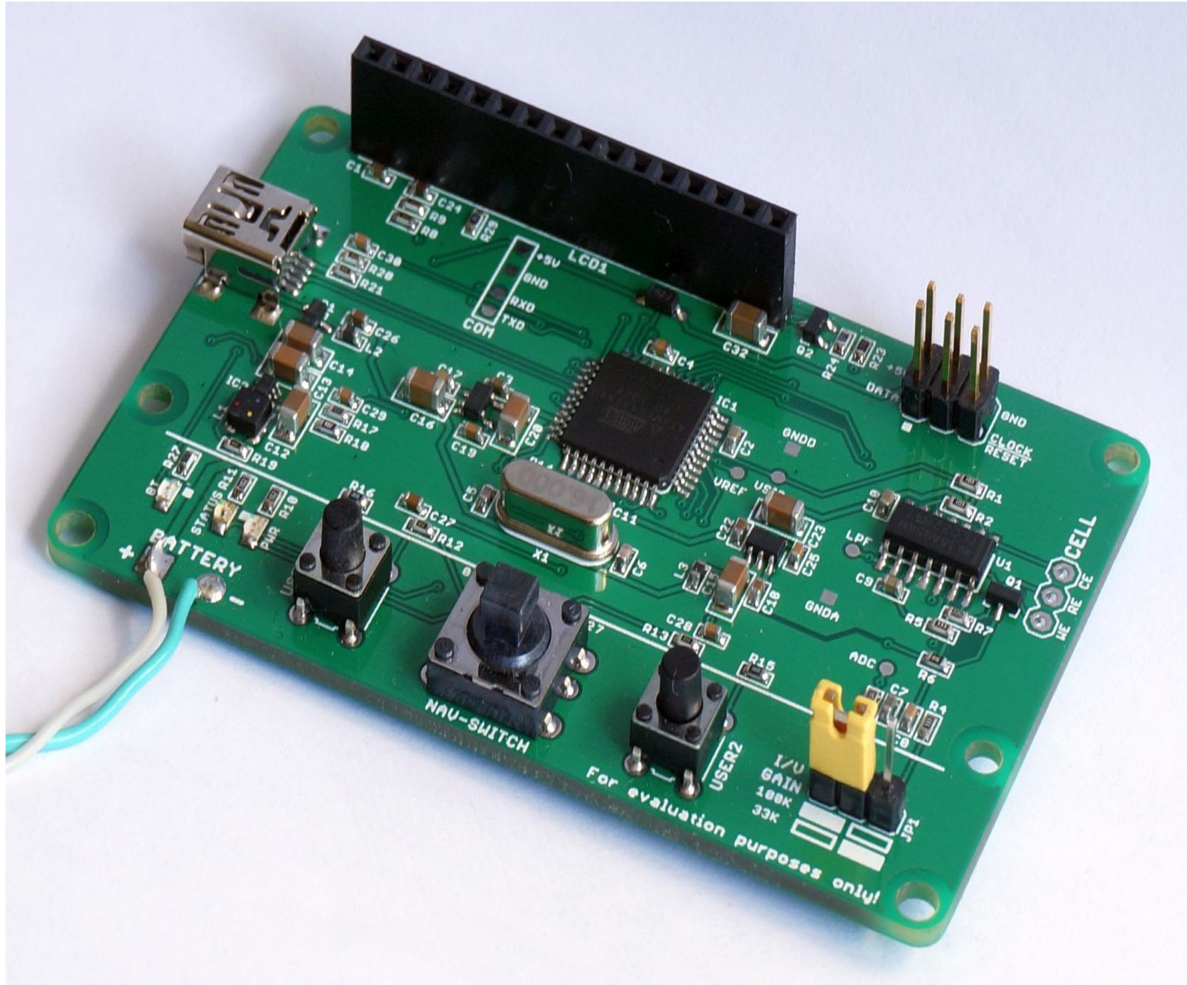


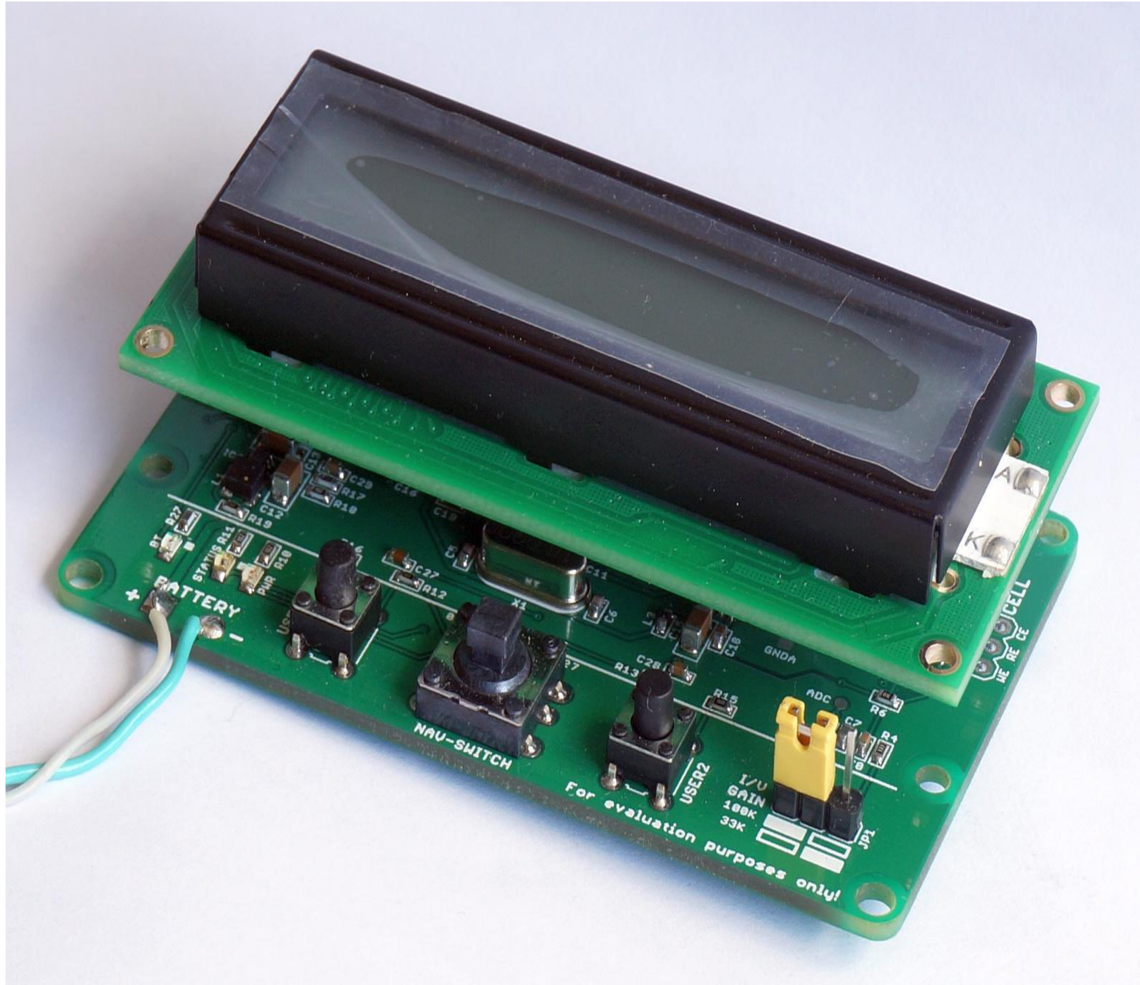
Fig. 2. Stabilized positive potential-going scans of Pt/GR, Co/GR and different PtCo/GR catalysts in 0.05 M $NaBH_4$ + 1 M NaOH at 10 mV s^{-1} (a), 1 M CH_3OH + 0.5 M NaOH at 50 mV s^{-1} (b) and 1 M C_2H_5OH + 0.5 M NaOH at 50 mV s^{-1} (c).

PtCo/GR catalysts show an enhanced electrocatalytic activity towards the oxidation of H_2 generated by catalytic hydrolysis of BH_4^- and direct oxidation of BH_4^- ions as well as methanol and ethanol oxidation comparing with the graphene supported bare Co or Pt catalysts

Development of biosensors

Chip biosensors: Hardware and chip





R. Celiešiūtė, et al., *Chemija*, 24 (2013) 296
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Sensor to ascorbate (vitamin C)

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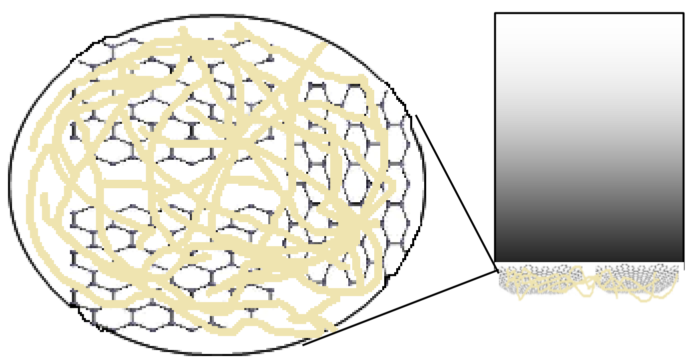
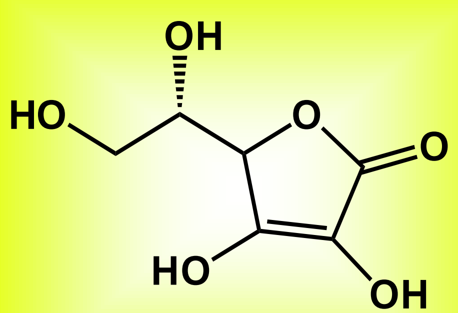
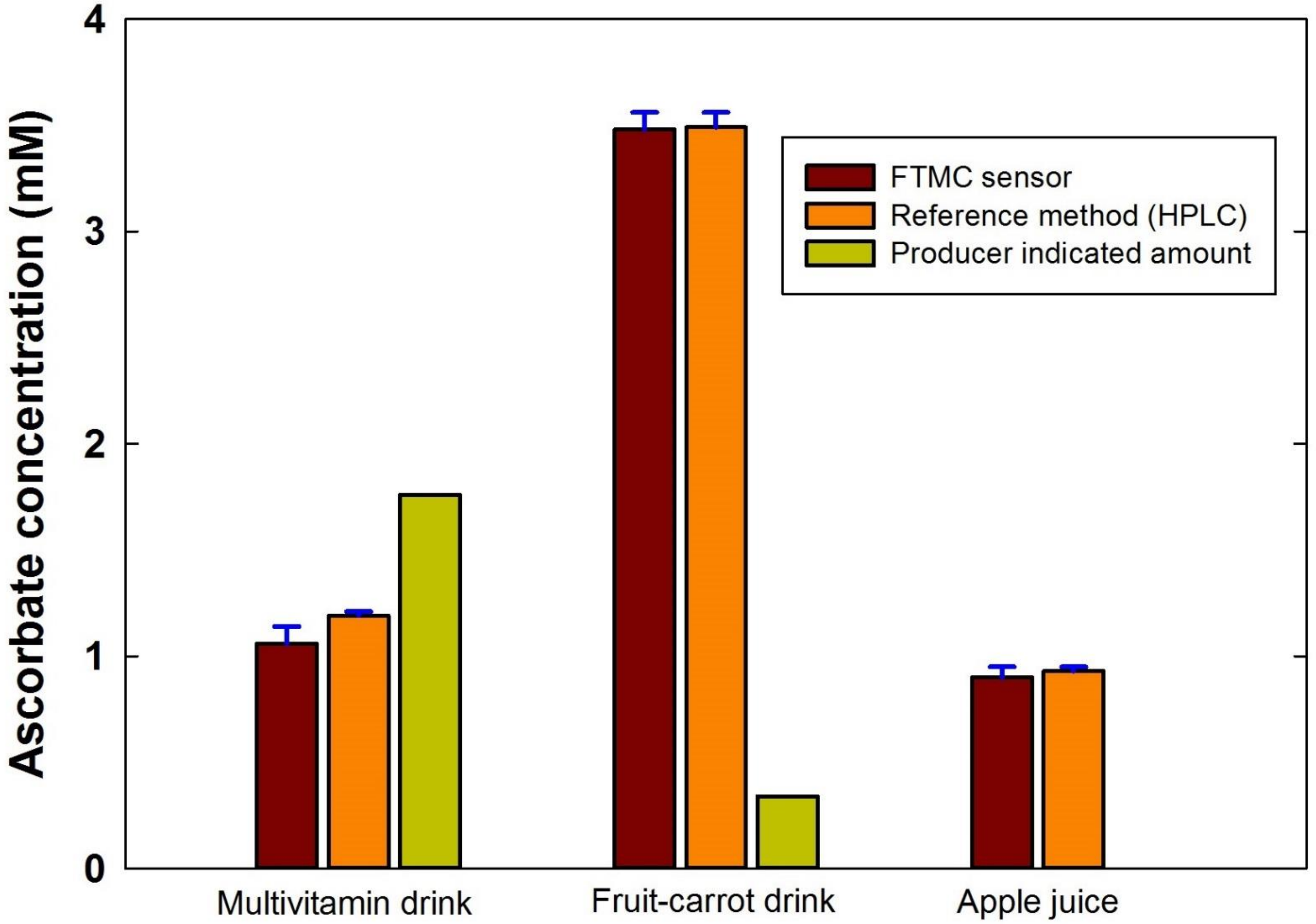
Sensor to ascorbate (vitamin C)



Graphene-chitosan composite film



Ascorbic acid (vit. C)



R. Celiešiūtė, et al., *Chemija*, 24 (2013) 296
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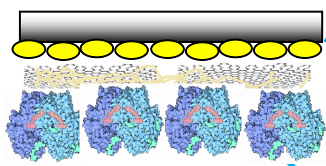
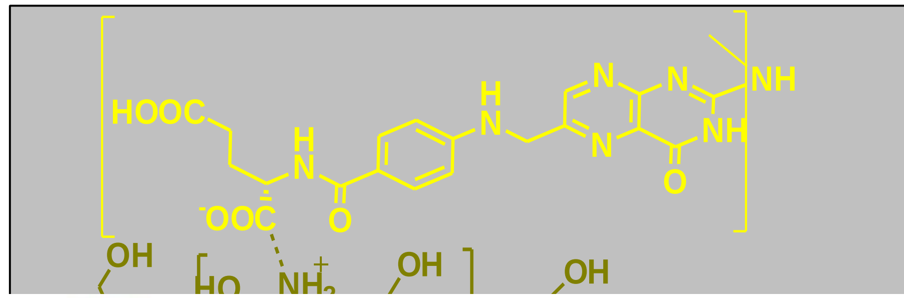
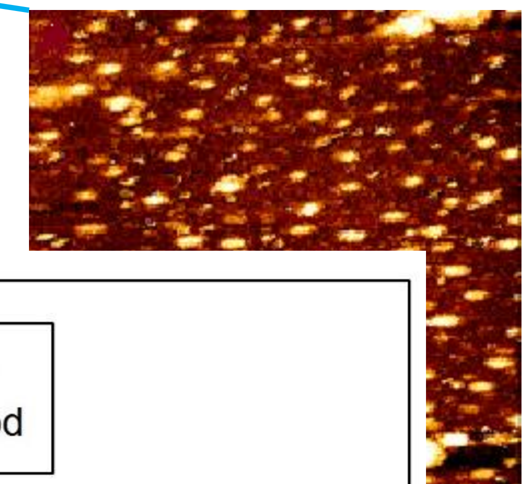
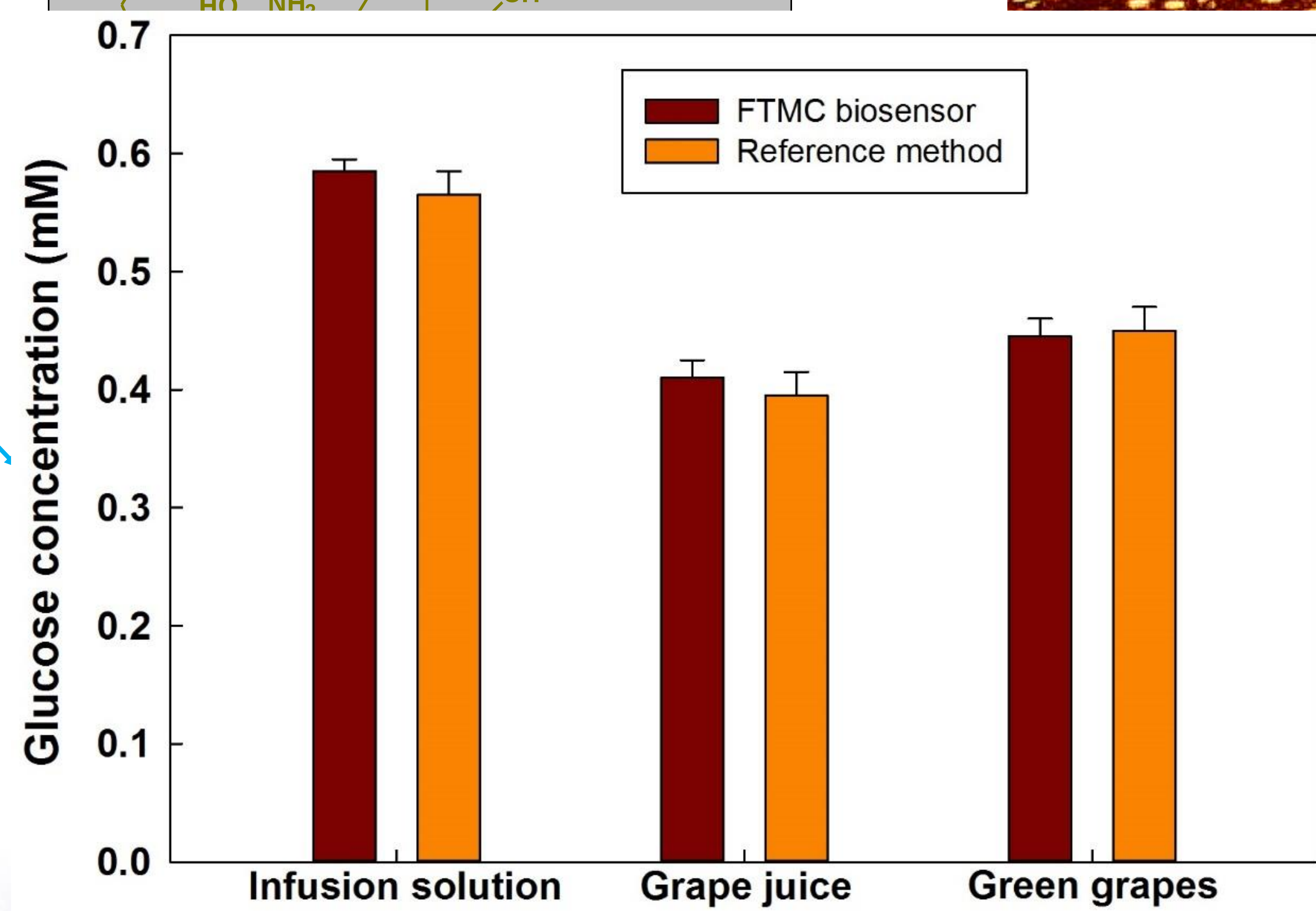
Biosensor for glucose





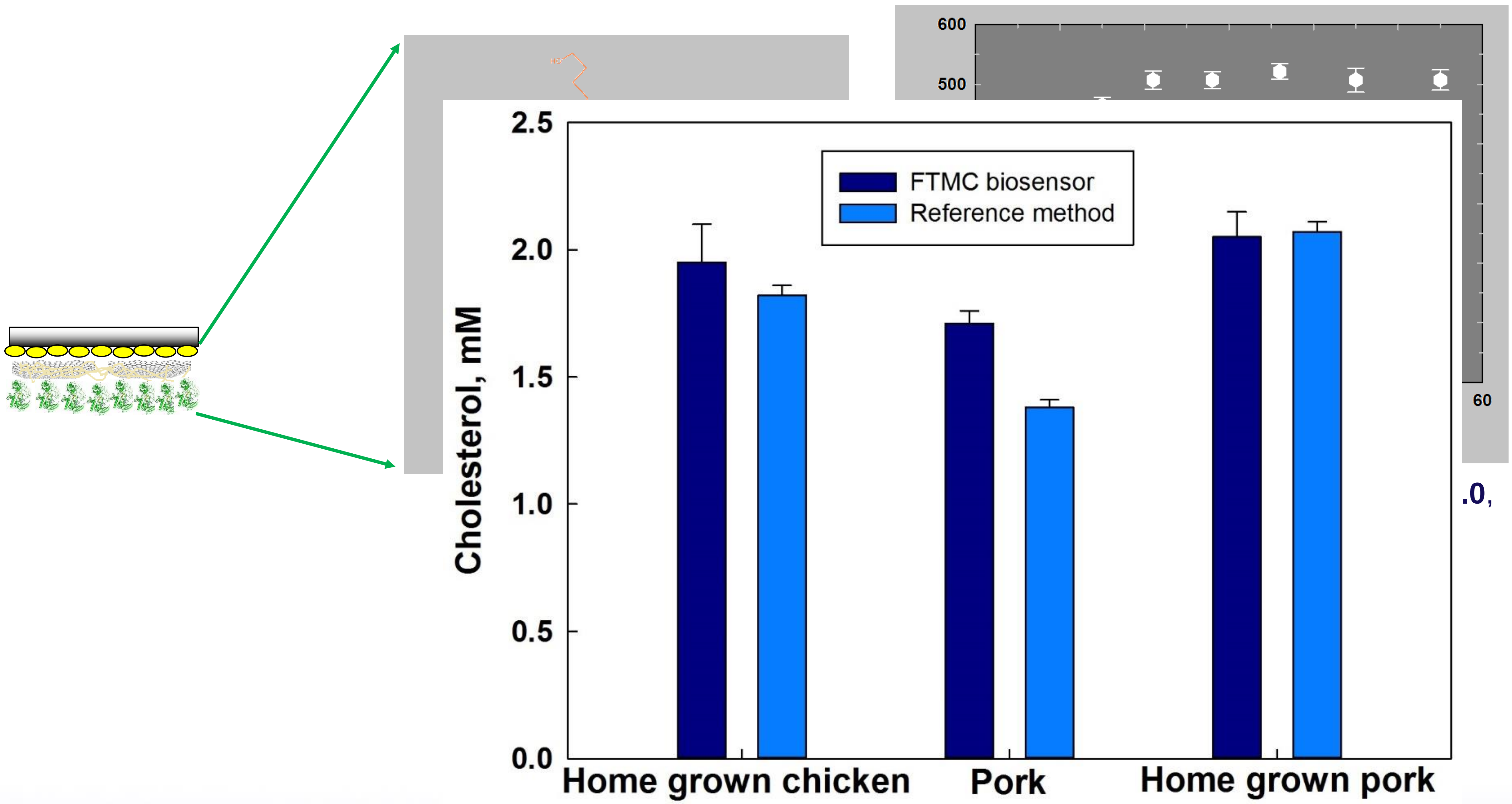




Venckus et al., Electroanalysis,26 (2014) 2273
Deapartment of Nanoengineering

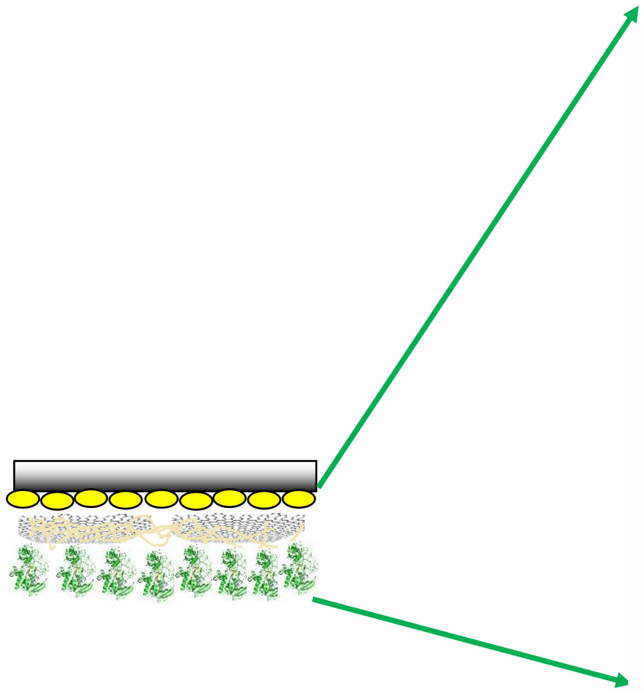
Testing of taster

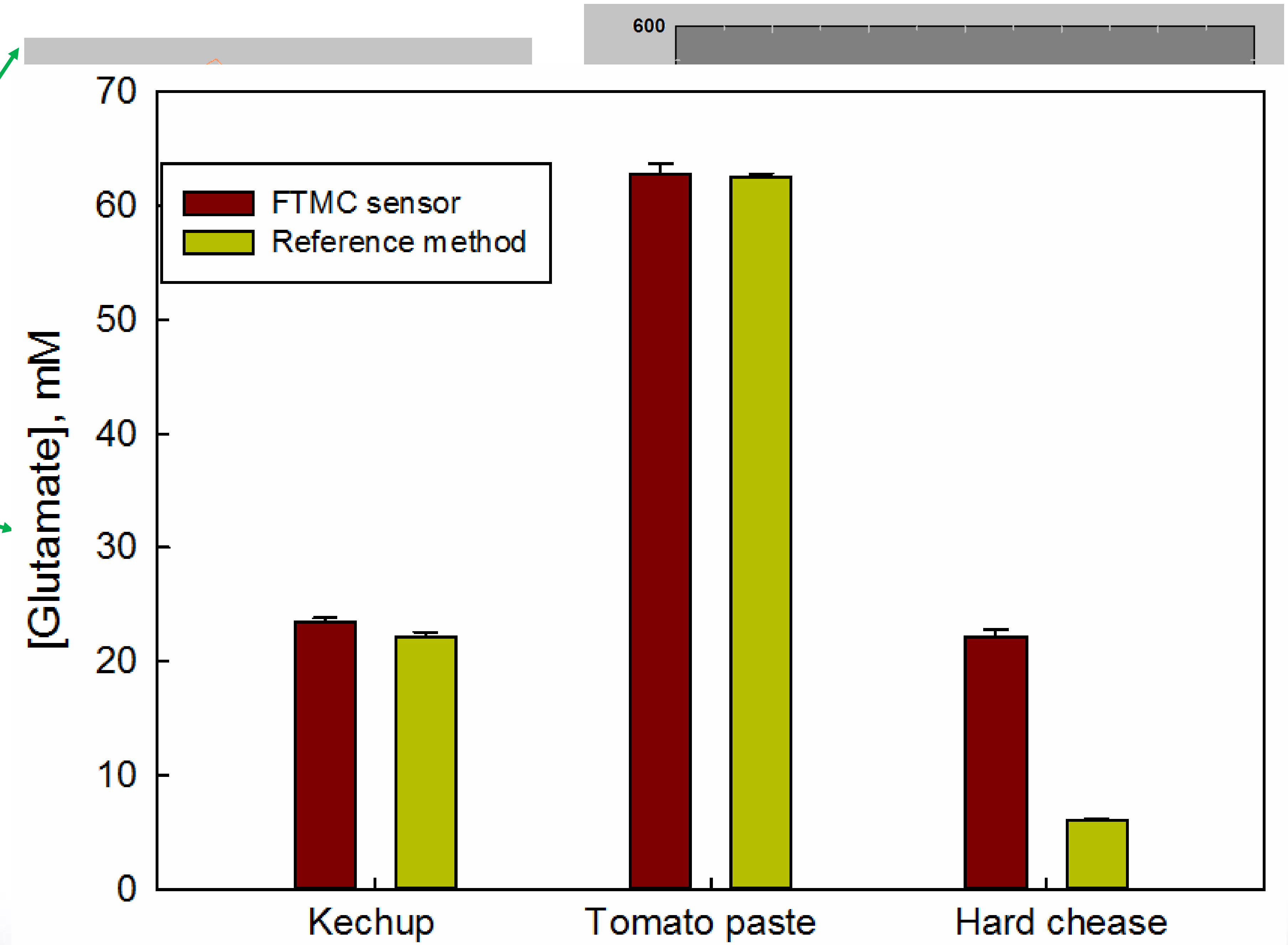
Biosensor for cholesterol



Testing of taster

Biosensor for glutamate





Celiešiūtė et al., Electroanalysis, in revision
Deapartment of Nanoengineering

Projects related to graphene research

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- ✓ European Social Fund project via Global Grant Measure, No. VP1-3.1-ŠMM-07-K-01-124,Nano- and lasertechnology application to the investigation and modification of graphene and to the development and miniaturisation of (bio)sensors for food quality control. 2011-2015, 359 k€
- ✓ Lithuanian Research Council project „Towards Future Technologies“, No. LAT 11/2016, Graphene supercapacitor powered FET all carbon circuit for sensing applications. 2016-2018, 299 k€

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