Dear TWINFUSYON friends,

with this Newsletter we would like to say goodbye to the year 2017 and welcome the year 2018. You will find out about the TWINFUSYON school on layered materials serving biosensing organised in the Czech Republic this autumn and other TWINFUSYON activities of 2017, as well as our plans for 2018. And the plans are ambitious! Three TWINFUSYON schools are coming soon.

We also continue with the topic of Women in Science and would like to offer you our Calendar for 2018 which is a combination of a convenient weekly agenda and personal stories and interesting facts about women in science.

The scientific theme of this Newsletter is graphene. We offer you articles on graphene-based biosensors, graphene-gold nanocomposites, and graphene-based hybrids for biosensing. We also present a discussion of novel (bio) sensing techniques in connection with energy harvesting problems.

TWINFUSYON team
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Bye Bye 2017 and Welcome 2018: A Year of Graphene, 2D-materials and Biosensing!

During the first years of its exciting life, graphene was mostly a game for physicists. The most interesting discoveries and amazing results on graphene (including which eventually lead to the Nobel prize) were all obtained on mechanically exfoliated, perfect monolayers of graphene. Although such an approach was sufficient to render graphene a scientific breakthrough, it could hardly be up-scalable, thereby hampering any technological applications.

Later on, chemistry started playing a fundamental role in the development of chemical methods to produce graphene on large scale by chemical vapor deposition and chemical liquid exfoliation. The chemistry of graphene has played an ever increasing role in the large-scale production, chemical functionalization and processing as well as in numerous applications of such material, and it has been expanded to various new 2D inorganic and organic materials. The chemical approach offers absolute control over the structure of 2D materials at the atomic- or molecular-level and will thus serve as enabling strategy to develop unprecedented multifunctional systems, of different complexity.

During the last years, bio-sensing and bio-interfacing graphene with a large variety of biomolecules spanning from DNA, enzymes, proteins, antigens, antibodies, and human cells. Graphene and biosensors are a natural combination, as graphene’s large surface-to-volume ratio, unique optical properties, excellent electrical conductivity, high carrier mobility and density, high thermal conductivity and many other attributes can be greatly beneficial for biosensor functions. The large surface area of graphene is able to enhance the surface loading of desired biomolecules, and excellent conductivity and small band gap can be beneficial for conducting electrons between biomolecules and the electrode surface. Therefore, several biosensing schemes based on graphene have been under investigation, as shown in Figure 1.

A collection of the developed graphene biosensors is given in Table 1.

Still many obvious questions if we think of a perfect graphene-based biosensor need to be discussed:

What makes graphene a sensitive detector for biological molecules? Does the method of production and assembly of graphene affect its biosensing performance? Is graphene actually selective to differentiate molecules embedded on it? Is it possible to precisely control and detect how many molecules have been spontaneously captured by it? Can graphene be considered as a reliable material to be used in future lab-on-chip and implantable medical devices for real-time health monitoring? What are the other factors that can contribute to the successful commercialization of graphene for in vivo and in vitro biosensing applications?

Figure 1: Schematic illustration of the sensing tactics involved in a graphene-based biosensor for in vitro and in vivo applications [from: N. Chauhan et al. J. Mat. Res. 32, 2860 (2017)]
The upcoming 2018 will give an answer to those question and will see novel 2D materials further developed and tailored for specificity of bioreceptors. These materials will be employed and integrated in different sensor and biosensor platforms giving an ultra-high sensitivity and may provide a solution to some challenges, such as early stage cancer detection.

Although graphene-based materials are considered to have no significant toxicity in many biomedical applications, however, more elaborative studies are still needed before considering it as a reliable material for implantable devices. This would include monitoring the interaction of graphene with genetic molecules, acute toxicity studies (long term toxicity), intracellular metabolic pathway, and excretion studies from biological systems. These experimental studies are essential to design graphene based biosensors that will help us better understand the metastatic cancer, molecular basis underlying the brain function.

We look forward to more fundamental and detailed research which is required to resolve many clinical hurdles in order to bring graphene-based flexible and implantable biosensors in the market by next decade!

**Table 1: Current generation reports of graphene-based Biosensors**

[P. Suvarnaphaet et al. Sensors 2017, 17, 2161]
Quantification of charges and adsorbates at electrochemical solid-liquid interfaces with polarization optical methods

by Christoph Cobet, Miao-Hsuan Chien, Saul Vazquez Miranda, and Kurt Hingerl, Center for Surface- and Nanoanalytics (ZONA), Johannes Kepler University, Linz, Austria

Whether we discuss novel (bio-) sensing techniques, new efficient electro-catalytic reactions in connection with energy harvesting problems, or a daily problem like the corrosion protection - the key functionality is usually determined by atomic scale structural, chemical and physical properties at a solid-liquid interfaces. Research in this framework is thus seeking for respective analytical methods since a long time. Nevertheless, the knowledge about the nanoscopic appearance of solid-liquid interfaces lags far behind the knowledge obtained on surfaces in ultrahigh vacuum environment. Plenty of success in ultrahigh vacuum is related to electron spectroscopy techniques as e.g. Scanning Auger Electron Spectroscopy or X-ray Photoelectron Spectroscopy (XPS). These methods benefit from their extremely high surface sensitivity. The underlying short mean free path of electrons in matter, on the other hand, makes these techniques unsuitable for an in-situ application in electrolyte. Electrons don’t reach the solid-liquid interface and are absorbed either in the bulk electrode or in the electrolyte [1].

Astonishing results are recently gained by measuring either through ultrathin electrodes or through electrolyte films [2]. In particular we would mention the success with “almost ambient pressure XPS” which allows meanwhile photo emission experiments through stable surface water layers without further coverage. A drawback is the thickness impact on the physical and chemical properties. Less interfering are electrochemical scanning tunneling microscopy (EC-STM) [3] and X-ray diffraction/spectroscopy techniques which could provide structural information at the sub-nanometer scale [4].

Classical electrochemical methods, on the other hand, analyze macroscopic quantities like the con-
centration of ions in an electrolyte, the interfacial charge transfer i.e. Faraday currents in cyclic voltammetry or the capacity of the electrochemical double layer. But they cannot distinguish between surface modifications and near surface processes.

In our opinion, polarization optical methods like Spectroscopic Ellipsometry (SE) can contribute considerably by measuring in-situ and non-destructive in the spectral range of transparency of either the electrode or the electrolyte. First of all SE is selective regarding interfaces. While measuring the polarization change of light upon reflection or transmission, one can obtain, furthermore, an extremely high surface sensitivity, i.e. sub-monolayer sensitivity (Fig.1). The beneficial parameter is the phase shift D between two polarization components. Note, reflection or absorption methods, which measure intensities (amplitudes) are orders of magnitude less sensitive for weakly or non-absorbing materials [5, pp. 816]. This holds in particular for solid liquid interfaces where the refractive index difference between the two interface media is small.

In a recent work we could demonstrate in a proof of principle experiment at single crystal Cu electrode surfaces [6] that ellipsometry in fact can detect sub-monolayer coverages as well as the electron excess at the electrode surface. By using dedicated optical layer models for the electrochemical double layer region, we could further demonstrate that one can quantify very accurately e.g. the amount of absorbed ions and the electron excess by in-situ SE. As a test example we determined the amount of Cl- adsorbed at a Cu(111) surface in HCl-solution. From EC-STM it is known that the Cl ions adsorb in a structure (Fig.2). The latter corresponds to 5.9x10^14 ions per cm2. The obtained ellipsometric value calculated in a first rough approximation was deviating by less than a factor of two. The deviating smaller value is shown to be the result of a 1.8 times densified water layer at the Co surface. With the thereby proven model we could show finally that the Cu(111) surface is covered at cathodic potentials with 6.8x10^14 positively charged ions per cm2 - most likely hydronium ions. Contrary to the expectation, this surface protonation do not support the catalytic Hydrogen Evolution Reaction (HER) and is shown to suppress the respective Faraday currents as measured in CV. Finally we would mention that in-situ electrochemical SE is generally capable to determine the Point of Total Zero Charge (PTZC) by measuring the absolute electron density at the pristine electrode surface within a Drude electron model.

References:

The demand for nanocomposites of graphene decorated with metallic nanoparticles (NPs) is increasing on account of their applications in science and technology. Graphene layers decorated with plasmonic metal nanoparticles provide a new way to develop enhanced catalytic, magnetic, optoelectronic, energy storage, and biosensing materials. The combination of the unique graphene conductivity properties and the high reactivity of metal NPs results in the ability to control phenomena such as the spatial localization of the surface plasmon resonance of the metallic particles [1], the enhancement of light absorption of graphene sheets, the bio-conjugation with a variety of molecules to produce biosensors [2], and the improvement of the catalytic activity of the nanoparticles [3].

Although most of the approaches present in literature produces graphene-oxide flakes decorated with metal nanoparticles, TWINFUSYON consortium aims at developing reproducible large area and clean graphene-gold nanocomposites.

Therefore, Graphene was grown by Chemical Vapor Deposition (CVD) technique and subsequently transferred on a standard Si/SiO2 substrate and sprayed by nanoparticles of various shape (spheres, stars, pyramides) dispersed in ethanol. The series of fabricated samples was characterized by SEM microscopy, allowing us to evaluate their spatial distribution on graphene, as shown in Figure 1.

Raman scattering provided us with a single-peak 2D line in the spectra of all samples, with a weak disorder-induced D line, indicating that the present nanoparticles do not damage the graphene structure.

We have used infrared magneto-spectroscopy (cyclotron resonance and Faraday rotation) to perform a complete optical readout of the level and type of doping in our samples. This is possible due to specific cyclotron mass of massless charge carriers, which is directly proportional to the Fermi energy, EF=mv². This is in contrast to conventional materials with parabolic bands, in which the cyclotron mass is strictly independent of EF. The type of doping was obtained from the sign of Faraday rotation related to cyclotron resonance signal.

We observed fairly weak variation of the Fermi energy among different graphene/gold-nanoparticle samples.

In all cases, the Fermi energy was found close to EF=-250 meV, similar to the reference sample without any decoration. The decoration by gold nanoparticles had thus surprisingly minor effect on the doping of graphene.

References:
Graphene-based Hybrids For Biosensing

by Maria Michela Giangregorio and Maria Losurdo
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Carbon-based materials (nanocrystalline diamonds, carbon nanotubes and graphene) are widely tested for biosensing applications. Specifically, in contrast with carbon nanotubes that can also show cytotoxic effects due to their degree of dispersion, level of functionalization, length and low purity, and nanocrystalline diamonds that have nano-roughness and an uncontrolled surface hydrophilic/hydrophobic character, graphene has a simple topography and can be synthetized in a pure form with large flakes which is vital for biological tests. This is why the research on biomedical applications of graphene has seen dramatic progress and yet mostly in its beginning stage [1].

Since 2008, researchers have started investigating the potential biomedical applications of graphene [2] and interesting works have been carried out to explore the use of graphene and its derivatives such as graphene oxide in biomedical applications [3]. These applications include drug/gene delivery, biosensors, cancer therapies and biocompatibility to antibacterial effects [4,5,6].

Within TWINFUSYON we are exploring the interaction of graphene with human cells.

The osteoblastic cell attachment and proliferation on graphene strongly depend on the substrate on which graphene is transferred, and the different cell adhesion on graphene transferred on silicon, SiO2, SS and glass is summarized in Figure 1.

We found that there is no significant difference in the number of attached cells between graphene coated and uncoated glass and SS substrates demonstrating that cell growth was not affected by the presence of graphene on glass and SS substrates, while higher number of cells was attached to the graphene coated layer in comparison with silicon and SiO2 on Si. So, osteoblasts clearly preferred graphene coated substrate than silicon and SiO2/Si wafers. We have also investigated graphene on plastic substrates like PET that resulted to have lower toxic effects on osteoblasts and to improve more strongly the cell adhesion with respect the other substrates, as shown in Figure 1.

Figure 2 shows the evolution of the cells area on graphene on PET also as a function of culture time.

We demonstrated that the cells coverage/adhesion on graphene on plastic substrates further improves as a function of the culture time compared with the PET substrate and a PSCC (cell...
culture polystyrene) reference material. Moreover, we found that there is not cells detachment at long culture time. Our study also demonstrated that the cell adhesion and growth on graphene on PET can be also improved at shorter culture time absorbing fibronectin to graphene, allowing to work with smaller cells concentration.

Our next step is to integrate graphene with metal nanoparticles as support for cell growth to realize hybrid heterojunctions that are compatible with live cells and can be used to monitor/quantify in real time during the cell growth using the SPR imaging without stopping their growth or killing them.

References:

CEITEC NANO RESEARCH INFRASTRUCTURE

The CEITEC Nano Research Infrastructure is the largest cleanroom nanocentre in the Czech Republic. It provides complex equipment, expertise, and methods for nanotechnology and advanced materials research. The facility includes:

- Nanofabrication laboratory, which provides equipment and expertise for nanolithography, etching & deposition, and packaging;
- Nanocharacterisation laboratory used for electrical, magnetic and optical measurements, microscopy and nanomanipulation, and UHV Technologies;
- Structural analysis laboratory providing services for electron microscopy, X-ray diffraction, and sample preparation;
- Micro & Nano X-ray CT laboratory
- Laser Spectroscopy laboratory with equipment for the implementation of qualitative and quantitative analyses in single-pulse, double-pulse (with increased spatial resolution and detection limits), LIBS + LIFS (Laser Induced Fluorescence Spectroscopy) modes.

The CEITEC Nano Research Infrastructure is a single-sited, multi-material, multipurpose user facility providing services for internal and external academic and commercial users. The thematic focus is physics, electronics, and material science research (mainly), but also bio-related and medical research.

The Infrastructure is situated in CEITEC BUT campus in Purkyňova 123, Brno, the Czech Republic. The users can access infrastructure via self-service open access model. The facility is also able to provide complete services, including nanofabrication, nanocharacterization or data analysis to a limited extend. The facility also provides general and equipment training.

Detailed information is available at the facility website.

CEITEC also has other Core Facilities, including Nanobiotechnology, NMR or X-ray diffraction situated at Masaryk University campus Bohunice in Brno. These facilities mainly focus on life sciences. The full list of the facilities with relevant information is available on the CEITEC website.
TWINFUSYON NEWS

TWINFUSYON School FROM Structures to Optical functions: LAYERED Materials serving biosensing

The school “FROM Structures to Optical functions: LAYERED Materials serving biosensing” focused on fundamentals of optical response of bulk materials and layered systems. The school took place on October 21st to 25th, 2017 at CEITEC, Brno, the Czech Republic and was the third school organised within the TWINFUSYON project.

The school consisted of two parts:

- The introductory lectures were devoted to the optical properties from THz range to ultraviolet; information obtainable from the grazing-incidence reflectivity of X-rays were also be discussed.
- Advanced lectures covered important aspects of the optical spectroscopy of layered structures exhibiting plasmon resonances, exploitable in biosensing. Furthermore, experimental procedures using transmittance, reflection and ellipsometry were covered during the school.

Besides lectures on various topics, the school also included practical sessions and a laboratory tour at CEITEC BUT.

Cooperation with CZECH METROLOGY INSTITUTE (CMI)

by Josef Humlíček, CEITEC MU, Brno, the Czech Republic

Metrological approach to measurements is based on the requirements of traceability and knowledge of measurement errors. While the latter is nowadays typical of most of well-conducted experimental work, the traceability to etalons is by no means obvious. We have performed a study in measurements of thin film systems, which are at the heart of the biosensing with optical tools.

The chosen system was a single layer of an inert material grown on single—crystalline silicon. The Si substrate is very popular, owing to its extremely high quality of device—grade wafers and low cost. At CEITEC, we have carefully measured film thickness and refractive index in near—infrared and visible ranges, and determined the film thickness. The uncertainties of our results depend mostly on calibrations of the photon energy scale, and linearity of detection, typically fairly good even in the absence of appropriate standards. Consequently, we have etched off a part of the film, and asked our colleagues at the CMI to use their specialized large—area scanning probe microscope to confirm or reject our results.

The conclusion was favourable, as the data from CMI and CEITEC agree within estimated error margins of both methods [1], see the figure below. Both measurements revealed important consequences of the inhomogeneity and roughness of the studied film.

The results from CMI are traceable to the national and international standards of length.

More information on metrological approaches can be found in [1].

[1] Petr Klapetek, Lecture at the TWINFUSYON school, Brno 2017. For more information contact pklapetek@cmi.cz
**UPCOMING EVENTS**

**XX Linz Winterworkshop Advances in Single-Molecule Research for Biology & Nanoscience**

**WHEN:** 2 — 5 February, 2018

**WHERE:** Linz, Austria

**TOPIC:** The school will focus on fundamentals of optical response of bulk materials and layered systems. The school/workshop will focus on biological single-molecule research and nanoscience, and include force and optical microscopy/spectroscopy techniques. This year, special sessions on nano-medicine and high-speed atomic force microscopy will be organized. It is the aim to provide a common platform for industry and academia.

*Do not miss it!*

More information is available on the [event website](#).
**20th International Winterschool on New Developments in Solid State Physics**

**WHEN:** 25 February — 2 March, 2018

**WHERE:** Mauterndorf, Austria

**TOPIC:** The Winterschool on New Developments in Solid State Physics has evolved over the last three decades from a rather small, thematically focused workshop back in 1980 to what it is today, a meeting with lectures and invited talks held by outstanding international speakers for an audience with a large percentage of graduate students and postdocs.

The school attempts to cover the most important developments of the last few years and to gain internationally leading experts as invited speakers. The educational aspect of the school will be strengthened by providing a set of tutorial lectures, again to be held by renowned speakers, to introduce the main topics of meeting in a concise way on a graduate/postdoc level.

- Solid-state-based quantum photonics and sensing
- 2D materials
- Electronic transport in low-dimensional systems and interfaces
- Topological phenomena and systems
- Nanomechanics

More information is available on the [school website](http://www.twinfusyon.eu).

**EPIOTICS-15 International School of Solid State Physics (co-organised)**

**WHEN:** 13 — 19 July 2018

**WHERE:** CNR, Rome, Italy

**TOPIC:** The school/workshop will bring together researchers from universities and research institutes who work in the fields of (semiconductor) surface science, epitaxial growth, materials deposition and optical diagnostics relevant to (semiconductor) materials and structures of interest for present and anticipated (spin) electronic devices. The school is aimed at assessing the capabilities of state-of-the-art optical techniques in elucidating the fundamental electronic and structural properties of semiconductor and metal surfaces, interfaces, thin layers, and layer structures, and assessing the usefulness of these techniques for optimization of high quality multilayer samples through feedback control during materials growth and processing. Materials of particular interest are silicene, Collective Excitations in Advanced Nanostructures semiconductor-metal interfaces, semiconductor and magnetic multilayers and III-V compound semiconductors.

More information will be available in the [Upcoming events](http://www.twinfusyon.eu).
Welcome 2018!

TWINFUSYON calendar for Promoting WOMEN in Science

The TWINFUSYON team has prepared a calendar “Women in Science” for 2018.

Let’s start with a fact. There are far fewer women than men working in scientific, mathematical, engineering, and technological careers (STEM). Diversity is essential in science: it recruits new ideas, different perspectives, and fresh approaches to problem-solving – the ingredients that fuel creativity required for innovation.

Underrepresentation of women in science cannot be solved in a day. Attitude and lab culture won’t change overnight.

With this agenda, we would like to attract your attention to gender-sensitive issues in science and encourage to keep them in mind during our daily duties. You can start small and promote gender inclusive culture in your lab/department, as well as be proactive in proposing long-term solutions for encouraging integration of women in the STEM workforce!

One person can make a difference and everyone should try.
(John F. Kennedy)

The calendar can be downloaded in PDF format HERE.