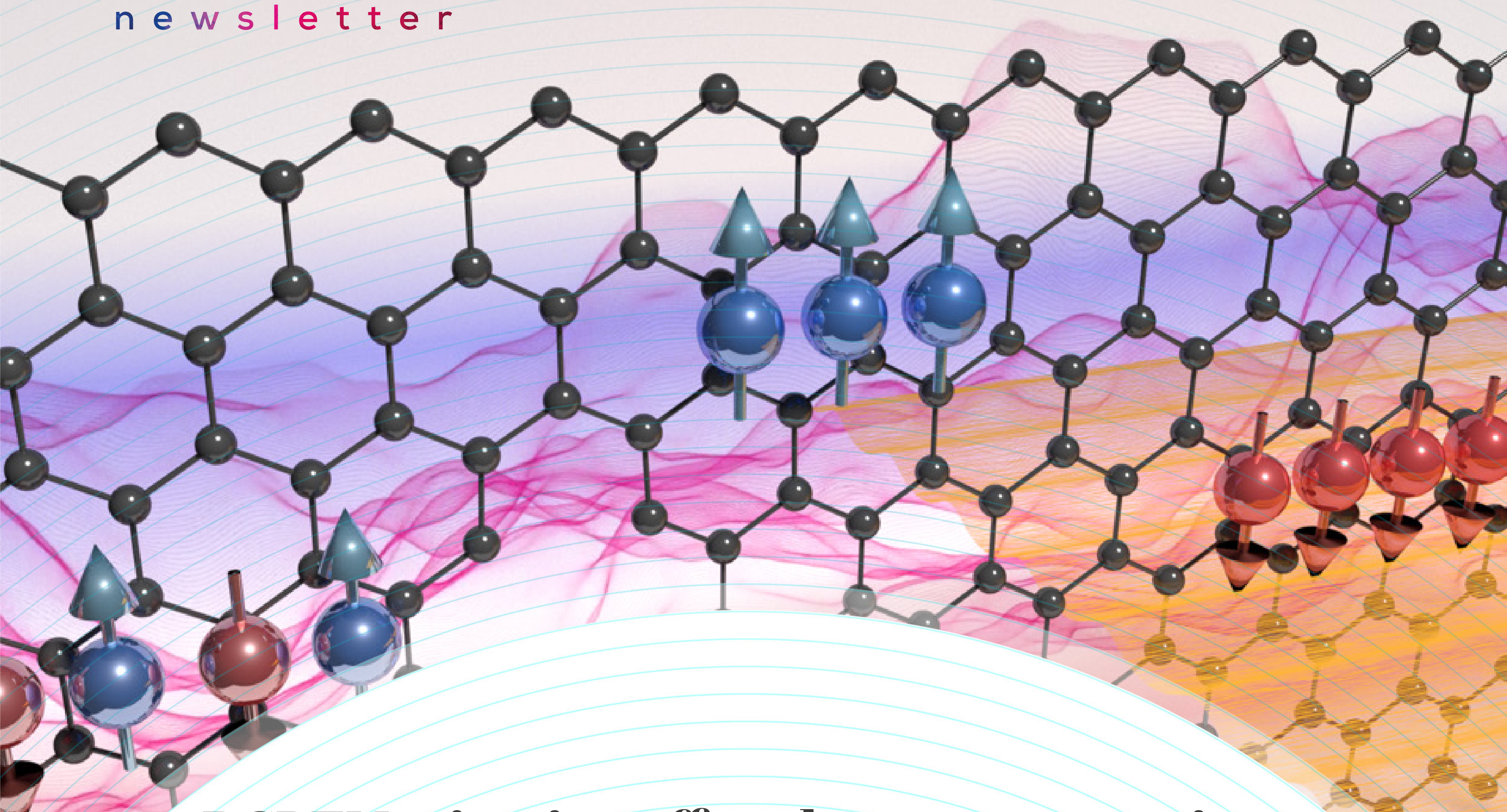
RCPTM newsletter 3 2019



RCPTM scientists offered a new perspective on the role of graphene in spintronics

Since its discovery in 2004, graphene has been considered to have major potential applications in modern electronics, mainly due to its extraordinary conductivity and transparency to passing light. Thus, it is being gradually used in a number of components including transistors and displays. However, graphene is also viewed as a material with promising potential future uses in so-called spintronics: a young electronics industry in which electron spins are used for storing, transferring and processing information. An electron's spin—the inner angular momentum—can have two orientations, 'up' or 'down', so it offers two new logical states in addition to the electron charge used in conventional electronics. Hence, through exploitation of spin-polarized currents, future spintronic devices are expected to provide faster information processing, lower energy consumption and higher density of information processing units.

Fundamental spintronics components include so-called spin valves. These devices apply giant magnetoresistance (discovery of which was acknowledged by Nobel Prize in Physics awarded in 2007). A spin valve consists of three basic units: a spin state generator (or 'spin injector', usually an inorganic ferromagnet), a non-magnetic conductive material for transfer of spin states, and a ferromagnetic spin detector. Graphene has promising potential to transfer spin orientation between two conductive magnetic materials because it can preserve the spin of electrons with a sufficiently long relaxation time (~ 10 ns). However, it has not been previously considered a possible candidate for generating spin-polarized states due to its diamagnetic behaviour and weak spin orbital bonding. Thus, modifying graphene in a manner that addresses these limitations but retains its current functionality as a spin state generator and high carrier mobility poses an enormous challenge in materials research.

In work published in the journal *Advanced Materials*, RCPTM researchers were able to develop nitrogen-doped graphene that met this challenge. "We managed to prepare graphene doped with nitrogen predominantly in the pyridinic configuration. Such chemical modification results in the creation of two different spin systems that coexist together within a single material. The new material contains localized spin centres operating as spin state generators, as well as areas with conductive electrons responsible for transmitting the spin information," says Aristeidis Bakandritsos of the Magnetic Nanostructures research group. Prof. Zbořil deems this result to be a significant step towards organic spintronics. "The dual role of graphene for spin injection and transport could lead to the replacement of existing inorganic ferromagnets. In addition, spintronic properties and spin state switching can be easily tuned by applying microwaves, which represents an interesting alternative to the commonly used external magnetic and electrical fields," concluded Zbořil.

The work follows previous studies by RCPTM scientists on the control of electronic and magnetic properties of graphene (Tuček J. et al. *Nat. Commun.* 8, 14525, 2017; Błoński P. et al. *J. Am. Chem. Soc.* 139, 3171–3180, 2017; Tuček J. et al. *Adv. Mater.* 28, 5045–5053, 2016; de la Torre B. et al. *Nat. Commun.* 9, 2831, 2018; Tuček J. et al. *Chem. Soc. Rev.* 47, 3899–3990, 2018).

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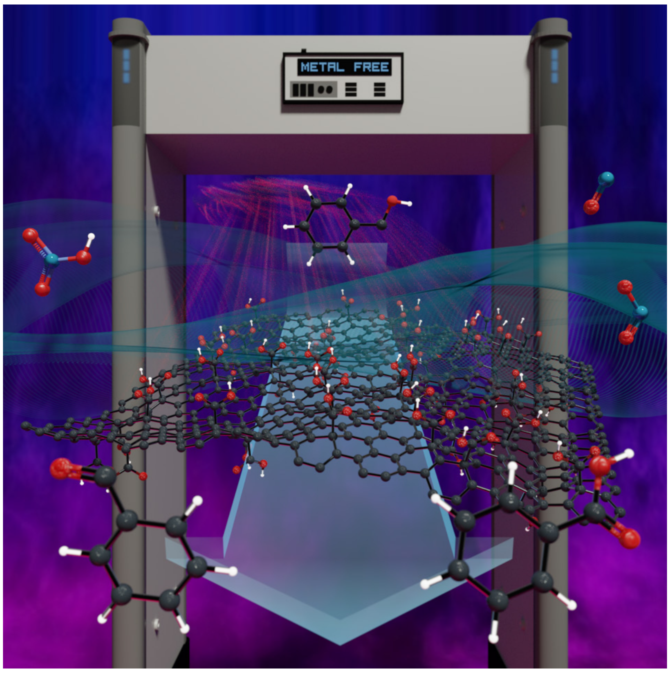
Graphene acid is pushing the boundaries in non-metallic catalysis

Carbon nanomaterials, which are capable of accelerating chemical reactions in the absence of metals, carbon catalysts, are receiving considerable research attention. This is because they may replace classic heterogeneous catalysts, which often contain heavy-metal atoms, are more expensive, and less environmentally friendly. However, in the literature there are objections that some carbon catalysts, such as graphene oxide, are not proper catalysts, but participate in chemical reactions as reactants. It is often reported that the catalysis is not prompted by the carbon nanomaterial *per se*, but by metallic impurities present in its structure or reaction mixture. In collaboration with colleagues at the University of Padua, RCPTM researchers have tested whether graphene acid prepared from fluorographene in their labs can serve as a carbon catalyst for controlled oxidative conversion of alcohols to corresponding aldehydes or carboxylic acids. Using nitric acid as a cocatalyst, they managed to achieve high degrees of conversion and selectivity. The catalyst did not lose its activity even after 10-fold use, and detailed chemical analyses ruled out the potential participation of metal impurities. The combination of experiments with quantum-chemical calculations has resulted in the design of a catalysis mechanism in which the conductivity of graphene acid plays an important role. Graphene acid thus significantly pushes the boundaries of non-metallic catalysis.



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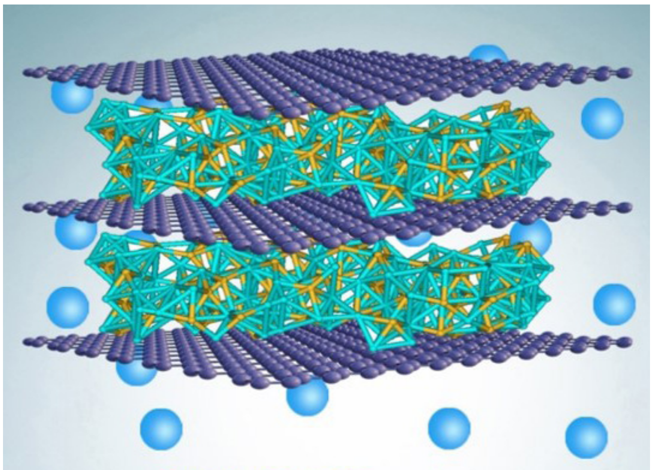
A new route to highly efficient and stable lithium-ion batteries

Lithium-ion batteries (LIBs) are the most commonly used type of rechargeable batteries. Work on the design of these batteries earned John B. Goodenough, Stanley Whittingham and Akira Yoshino the Nobel Prize in Chemistry this year. Due to the high density of the stored energy with respect to their size, these batteries are widely used in consumer electronics including mobile phones and laptops. The main components of a LIB are a cathode, usually composed of metal oxides, a carbon-based anode, and a lithium salt in an organic solvent. However, a weak point of currently used LIBs is their low stability after a series of charge cycles. Therefore, a number of laboratories in the world are developing and looking for new types of constituents, especially anodic materials. RCPTM scientists, in collaboration with colleagues from the Technical University of Munich and Queensland University of Technology in Australia, have developed and described (in the journal *Advanced Functional Materials*) a new composite anodic material with huge reversible capacity (1010 mAh g^{-1} at 0.12 A g^{-1}). The layered composite, composed of Ni_7S_6 nanolayers and graphene sheets, was prepared by sulfiding a two-dimensional metal–organic net containing nickel. Such an anode shows excellent stability and retains 95 percent of its original capacity even after 2,000 charge cycles. Scientists ascribe these extraordinary properties to the synergistic effect of nickel sulphide and graphene sheets. The specific porous nanoarchitecture with lots of channels enables faster charge transfer, excellent contact with electrolyte, and easy diffusion of lithium ions. The work follows previous and successful collaboration of these teams in the development of new energy storage materials. (Jayaramulu K. et al. *Adv. Sci.* 5, 1801029, 2018; Jayaramulu K. et al. *Adv. Mater.* 30, 1705789, 2018; Jayaramulu K. et al. *Adv. Funct. Mater.* 27, 1700451, 2017; Dubal D.P. et al. *Adv. Funct. Mater.* 29, 1900532, 2019).



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2D materials can act as lethal blades, but algae can resist them after some time

Researchers from RCPTM in collaboration with colleagues from the Institute of Botany of the Czech Academy of Sciences have shed light on the potential negative impact of carbon nanomaterials on microorganisms in aqueous environments. They confirmed that under certain conditions chemically modified graphene can change into "nano-blades" that damage unicellular algae in water. However, it was found that over time these organisms can construct effective defences against such mechanical attacks.

The researchers prepared three chemical forms of nanomaterials with different levels of oxidation. This proved to be important. The graphene with the lowest number of functional groups on its surface could physically damage microorganisms, acting like a relatively large but very thin blade or razor that disrupted the cell membranes. By contrast, graphene materials with a higher number of bounded functional groups did not have this ability. Moreover, the researchers demonstrated that the materials were most damaging to a selected group of microorganisms (unicellular algae) in the first hours of the interaction. The algae then began to produce proteins and hydrocarbons that coated the graphene oxide, thus averting the danger. The work follows long-term research by RCPTM on interactions of nanomaterials with biosystems and microorganisms. Previously, for example, RCPTM scientists have developed a method for overcoming bacterial resistance to silver nanoparticles (Panáček A. et al. *Nat. Nanotechnol.* 13, 65–71, 2018), measuring temperature in living cells using carbon nanoparticles (Kalytchuk S. et al. *ACS Nano* 11, 1432–1442, 2017) and diagnosing significant biomolecules using magnetic nanomaterials (Ranc V. et al. *Anal. Chem.* 86, 2939–2946, 2014).

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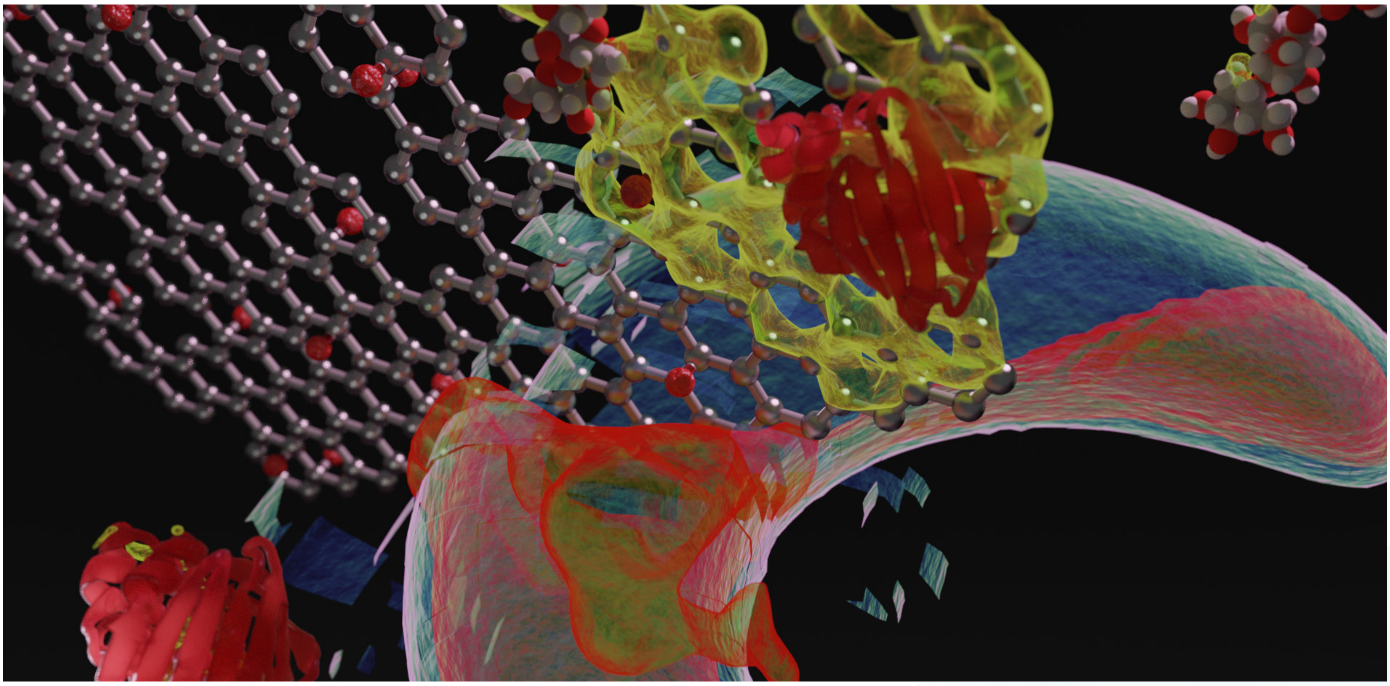

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Michal Otyepka:

“The ERC project has entered the second half, now we are going to focus on applications of our derivatives”

In 2016, the RCPTM managing director Michal Otyepka won the first ever European Research Council (ERC) grant for Palacký University, for a project called Two-Dimensional Chemistry towards New Graphene Derivatives. The project is now at the half-way point, an appropriate stage to evaluate results obtained so far.

What stage of investigation are you at now? Does the ERC grant help to open the door to collaboration, as you anticipated?

Using football jargon, I could say we're playing the second half. In the first half, I tried to put together the project team and create good conditions for their work, which I managed to a considerable extent. The team is stable now, besides me, it includes another three scientists and three PhD students, and another support will join us in October. The collaboration within RCPTM is flawless, and I'm also fostering our collaboration with foreign colleagues. While engaged in the project, I've managed to establish contacts with a number of internationally recognised laboratories, e.g. in Italy and Spain. I believe it will bear fruit soon. However, I am not entirely happy with the laboratory facilities for synthetic chemistry, a problem that is also troubling other colleagues at RCPTM. We have to rent facilities outside the centre. Although we are doing well, I cannot imagine extending the scope of our research activities in the existing premises.

The aim of the grant is to prepare super-functional 2D graphene-derived materials. What has been accomplished so far in this area?

We have understood very well the chemistry of fluorographene, which allows us to prepare a full range of graphene derivatives in a targeted and controlled way. We can prepare hydrophilic and hydrophobic, conductive or semiconductive, and magnetic and luminescent graphene derivatives. We can attach selective chemical groups to the graphene surface that can bind various other substances, ranging from metal ions to proteins. We have created a nice and diverse chemical kit from which graphene derivatives with the desired properties can be constructed, and used in other nanocomposites.

When you were beginning the project, you said you would focus on answering the question of whether there are specific rules for "2D chemistry", that is, what takes place on the graphene surface and other two-dimensional materials. How successful have you been so far?

Pursuing this goal has been very stimulating since we started. In principal, chemical bonds between elements with similar chemical surroundings have similar properties. There is a C-F bond in fluorographene, which by the way is one of the strongest simple covalent bonds in chemistry. It could be assumed therefore that it would be stable, and all other C-F bonds would behave similarly. Conversely, once a C-F bond is broken, the surrounding bonds will start to behave differently. If more bonds are broken in the vicinity, a mixture of differently fixed bonds is formed, the binding energy of which can vary up to five-fold. But even in this chaos, firm rules can be found, which will be then reflected in the chemistry and properties of graphene derivatives. For example, it turns out that when C-F bonds are broken, a particular direction is favoured in the structure of fluorographene, and in a controlled chemical reaction this can be used to prepare materials which show magnetic arrangement up to room temperature. I can compare it to worn-out socks, where the fibres fall out of the fabric in one direction first, and all that remains is the regular structure of the warp and weft.

If you initially focused on understanding the chemistry of fluorographene and revealing its possibilities, what will be the next stage?

In the second stage, I want to focus more on applying our derivatives. We're trying to use them as catalysts, sorption materials, for sensor and energy storage. In the latter, in particular, we have progressed dramatically and managed to prepare new derivatives that can be deployed as electrode materials for supercapacitors. I recently applied for a project that could help us to get closer to manufacturing our electrode material on an industrial scale and testing it in existing parts.

You have been in charge of RCPTM since July. What condition was the centre in when you took over?

Professor Zbořil has managed, over the past nine years, to create a top internationally recognized workplace. Thanks to his visions, world-renowned scientists applying cutting-edge experimental techniques with funding for intensive research are gathered under one roof. What lies behind this success is hard work of all the employees, for which they deserve warm praise. But we must get ready for changes coming in the near future. The H2020 research programme period is ending, the volume and structure of the structural funds is changing, and new challenges and projects are on the way.

So how do you view RCPTM's future?

We are at a major crossroads. I strongly prefer the road that leads to establishment of the proposed new institute at Palacký University. I see huge potential in integration and collaboration with other experts from CRH, IMTM, IOCB and the University Hospital Olomouc. It will enable us not only to enrich each other by intertwining our research activities and strengthening international bonds, but also to respond more effectively to future scientific challenges, which by their nature will be broadly multidisciplinary. After all, integration trends are nothing new. We can see this trend abroad, where a number of similar institutes have been and are being established around the world. I believe that integration will eventually succeed, despite the difficulties, and that Palacký University will benefit from it, getting closer to renowned foreign universities and enhancing its social status, which will definitely attract motivated students.

NANOBIOWAT presented its research results

Chief representatives of the NANOBIOWAT research project, funded by the Technology Agency of the Czech Republic (TAČR), presented major results of the project to consortium members, as well as industrial partners, relevant authorities, students, etc. The latest trends in environmentally friendly nano- and bio-technologies were introduced through a series of lectures and an on-site demonstration.

"I regard this project as one of the best I've encountered in my professional career. Such fruitful collaboration between academics and industrial partners is not common," said Ladislav Lehký, a TAČR consultant, who attended the event together with members of the partner institutions, TAČR, the Ministry of the Environment of the Czech Republic, the Czech Environmental Inspectorate, the Administration Office of the Morava River Basin, and other governmental bodies. "Representatives of these institutions decide about any groundwater and soil remediation. Therefore, we found it vital to familiarize them with nano- and bio-technologies, or their combinations. The practical demonstrations also served as parts of the evaluation procedure and official scrutiny that the project would have faced anyway," said Jan Filip, scientific coordinator of the project from RCPTM.

Since 2012, in collaboration with the largest domestic remediation companies, three academic partners have developed new eco-friendly technologies within the Competence Centre that are capable of removing organic, inorganic, and microbial pollutants from contaminated waters and soils. The most important results include six patents, 29 proven technologies, two utility models, one functional sample, and over 90 publications. A book entitled *Advanced Nano-Bio Technologies for Water and Soil Treatment* will come out in December 2019, published by Springer.

The primary investigator, Radek Zbořil, values the application potential of the results achieved in the project. "A number of technologies have already been applied to existing remediation sites in the Czech Republic and abroad. A combination of biotechnology and nanotechnology has proved to be the most effective and economically attractive approach for treating contaminated groundwater. This has been confirmed by concrete results at a number of sites," Prof. Zbořil concluded.

RCPTM research activities aroused interest at a conference in Salerno

Aristeides Bakandritsos of the RCPTM Magnetic Nanostructures research group spoke about carbon nanostructures and their uses in biomedical, magnetic and environmental technologies at the conference "Chemistry Meets Industry and Society (CIS 2019)" in Salerno, in August 2019. The conference aimed to bring academics and industrialists together and streamline the transfer of scientific results into practice.

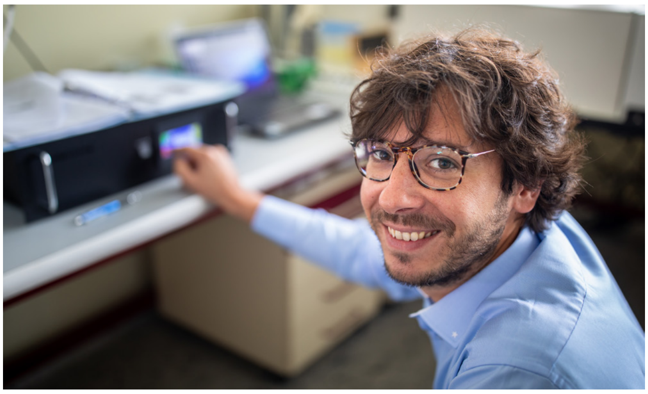
Prof. Bakandritsos presented, as part of a plenary lecture, RCPTM research results primarily regarding fluorographene chemistry, which could be used in spintronic, energy storage or catalytic applications. The topics also included quantum dots and their applications in biomedicine, where they can be used as tracers for *in vivo* imaging and *in vitro* temperature reporters in cells. "Both the conference organisers and the audience were very positive about the quality of RCPTM research and its collaboration with the private sector. Further, we had fruitful discussions with Profs. Paolo Fornasiero, Michele Melchionna and Silvia Marchesan from the University of Trieste regarding future collaboration in work on catalysis, and organic materials for charge transport-related applications," said Prof. Bakandritsos.

An ERC CZ grant will support development of a new class of catalysts

An expert on nanomaterials for energy and environmental applications, Alberto Naldoni of the RCPTM Photoelectrochemistry research group, has successfully submitted an application in response to the 4th tender of the ERC CZ programme. Moreover, Alberto's project was ranked joint first of seven applications. Winning a META-CAT grant with a budget of around 16 million Czech Crowns is another notable achievement of this newest but dynamically developing research group, following a research grant from the OP RDE call Excellent Research Teams.

"The support from the Ministry of Education is a recognition of the excellent research carried out at RCPTM. It marks the starting point for the development of an internationally recognised research programme for the direct conversion of solar energy into fuels and the development of sustainable chemistry. The *ERC CZ* grant will give me greater independence in research and raise my chance of winning an *ERC* grant in the *Consolidator* category," said Naldoni, who previously worked at the Institute of Molecular Science and Technologies (ISTM) in Milan.

The aim of the project, called *Light-driven biorefinery using metacatalysts,* is to develop a new class of catalysts with high selectivity, efficiency and properties that can be managed and optimized during the course of chemical reactions. Metacatalysts will allow the emergence of ultra-compact portable fuel synthesis devices in biorefineries powered by light radiation.



Results of the two-year project will serve to further develop the scientific field of photochemistry. Dr Naldoni focuses on use of sunlight for applications in photochemistry, plasma and catalysis and his research has already resulted in a number of prestigious publications (Naldoni A. et al. *Science* 356, 908–909, 2017; Naldoni A. et al. *ACS Catal.* 9, 345–364, 2019; Mascaretti L. et al. *Adv. Mater.* 31, 1805513, 2019).

The *ERC CZ* programme aims to promote excellent research in the Czech Republic by implementing projects submitted in response to calls of the European Research Council which successfully passed both rounds of evaluation by the Council's expert panels with grades A or B, but did not receive financial support from the European body. The *ERC CZ's* 4th tender elicited nine applications, seven of which met the criteria.

National Sustainability Programme ended, with results exceeding original commitments

In September, RCPTM ended implementation of the Advanced Technology and Materials Centre project, which was supported by the National Sustainability Programme (NPU) with grants worth 285 million Czech Crowns over the preceding five years for developing its research infrastructure. 34.5 million of the total sum was spent on equipment, for example an advanced scanning tunneling microscope, which is used at RCPTM to image molecules and monitor their interactions with surfaces, and a transmission electron microscope for materials research. The programme was approved in 2012 by the Czech government as one of the tools for increasing the competitiveness of Czech science.

RCPTM staff managed to meet all the objectives, exceeding expectations in some cases. For example, the project's outputs included more than 25 patents, while only five were projected in the original plan. Publication activity also exceeded expectations: RCPTM originally committed to generating 500 publications in high-impact journals, but over 1400 were generated in the project. Two of the most remarkable outputs are the discovery of the first non-metallic magnets (Tuček J. et al. *Nat. Commun.* 8, 14525, 2017) and previously mentioned method for overcoming bacterial resistance to silver nanoparticles (Panáček A. et al. *Nat. Nanotechnol.* 13, 65–71, 2018).

Through the project, the centre's instrumental facilities have been significantly enriched with, for example, a scanning electron microscopy operating in ultra-high vacuum mode, a spin resonance spectrometer, a supercritical fluidic chromatograph, a supercomputer for solving computational chemistry tasks, and other materials research and optical instruments.

We welcome a new member of the RCPTM Managing Board

Julius Lukeš, Director of the Institute of Parasitology, Biological Centre CAS, has been a new member of the RCPTM Managing Board since October 1. He has replaced Professor Jan Řídký, who resigned from the board with thanks from the RCPTM management for his job in this supervisory body. Professor Lukeš ranks among the most prominent domestic scientists, and enjoys an excellent reputation abroad. Last year he was the only Czech to win an award from the American Association for the Advancement of Science (AAAS). The Association elected him as one of its elite members (so-called Fellows) in the biological section for his long-term contribution to evolutionary studies in protistology and molecular parasitology, focusing on kinetoplastida and apicomplexa. Since 2004 he has been a member of the Learned Society of the Czech Republic. In 2009 he became the first recipient working outside Prague of a Praemium Academiae award. In 2014 he became a member of the American Academy of Microbiology, and in 2015 member of the European Academy of Microbiology.

11th annual Nanocon conference

The Nanocon annual international conference on nanomaterials, the largest event of its kind in the Czech Republic and one of the most important European expert meetings in the field, is starting its second decade. The 11th will take place at the Voroněž Hotel in Brno on October 16–18. The expert guarantor of the nanomaterials research and application programme is, as previously, Radek Zbořil from RCPTM.

As in previous years, participants will be able to enjoy dozens of lectures by renowned scientists. The most important include a highly cited scientist in materials sciences, Niyazi Serdar Sariciftci (Johannes Kepler University, Linz) and one of the most highly cited chemists (Martin Pumera, UCT Prague). Prof. Sariciftci has provided highly valuable information on photo-induced, optical and magnetic resonance and descriptions of phenomena in semiconductors and metal-containing polymers. He is the inventor of solar cells operating on the principle of conjugated heterotransitions between polymers and fullerenes. He collaborates with RCPTM, and delivered a lecture in Olomouc last year as part of the *Rudolf Zahradník Lecture Series*. Martin Pumera focuses on chemical nanorobots, which may be deployed, for example, in biomedicine or environmental technologies. In collaboration with RCPTM he is developing 2D materials for catalysis, electrochemistry and biosensing.

The conference programme will be divided into five sections, with talks on uses of nanomaterials for electronic, magnetic, optical, environmental and medical applications. Scientists will also address the toxicity of nanomaterials and advanced methods for preparing and characterising nanosystems. A new feature of the conference programme this year will be a panel discussion on potential benefits of nanomaterials and nanotechnologies for the energy industry.

Science and Technology Week with RCPTM participation

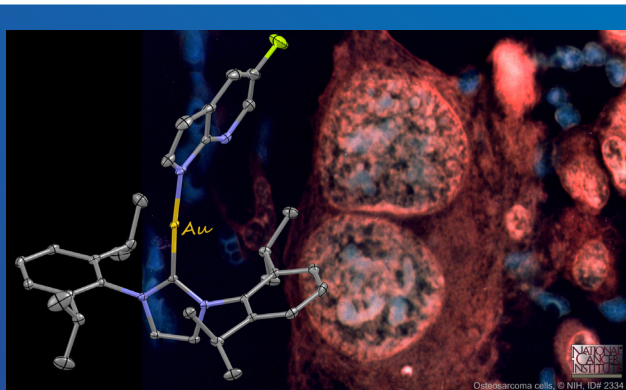
RCPTM will prepare an open day and lecture for high school students as part of the largest domestic science festival called the *Science and Technology Week*. The Academy of Sciences of the Czech Republic is organizing this event from November 11 to 17, coinciding with the 30th anniversary of the Velvet Revolution. The RCPTM programme is based on global threats (hot issues), which include shortage of drinking water. Hence, the head of the Environmental Nanotechnology research group, Jan Filip, has prepared a lecture for students called *Clean Water as a Gift and How Nanotechnology Can Help*. He will demonstrate how pollution from underground, surface, and wastewater can be removed using extremely small particles. He will also introduce other (nano) technologies that are environmentally friendly. Attendees will learn about the world of nanoparticles through excursions at RCPTM. For example, they will learn how nanotechnologies can contribute to improving human health and using renewable energy sources. Scientists will introduce participants to the main areas of chemical, material and optical research at RCPTM, taking them on a guided tour as well as showing different experiments.

Introduction into practice

The spectrum of anticancer agents has been extended by new gold complexes

Scientists from RCPTM's Biologically Active Complexes and Molecular Magnets research group have developed a new group of complex compounds with significant anticancer effects. After some years focusing on other approaches, they have started re-examining the potential of using gold to prepare organometallic anticancer compounds. New substances they have generated are significantly more effective than the most currently used complex drug cisplatin, and seem to have no significant negative effects on healthy human liver cells.

The use of highly effective organometallic gold complexes in anticancer therapy, specifically in the treatment of osteosarcoma (bone cancer) and ovarian cancer, including cisplatin-resistant ovarian tumours, has been protected since last July by a patent called N-heterocyclic carbene complexes of gold with bicyclic N-donor ligands and using these complexes to prepare anticancer therapy medicaments (CZ 307954 B6, originators: Trávníček, Z.; Vančo, J.; Dvořák, Z.). RCPTM scientists have been focusing on anti-tumour agents for many years. Prof. Zdeněk Trávníček's team have previously obtained patents for gold-, copper-, iron-, platinum- and tantalum-based compounds. They all have considerable anticancer effects, and some also have anti-inflammatory effects. However, the patent originators point out that the journey to using the prepared substances as pharmaceuticals is still long and complex, and many more experiments and collaborations with strong partners in both biomedical and pharmaceutical industries are needed.



RCPTM Regional Centre of Advanced Technologies and Materials

Palacký University Olomouc

Regional Centre of Advanced Technologies and Materials

Šlechtitelů 27
783 71 Olomouc
Czech Republic

Phone: (+420) 58 563 4973
Email: rcptm@upol.cz
Web: www.rcptm.com
Facebook: www.facebook.com/rcptmcz
Twitter: https://twitter.com/RCPTM1

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