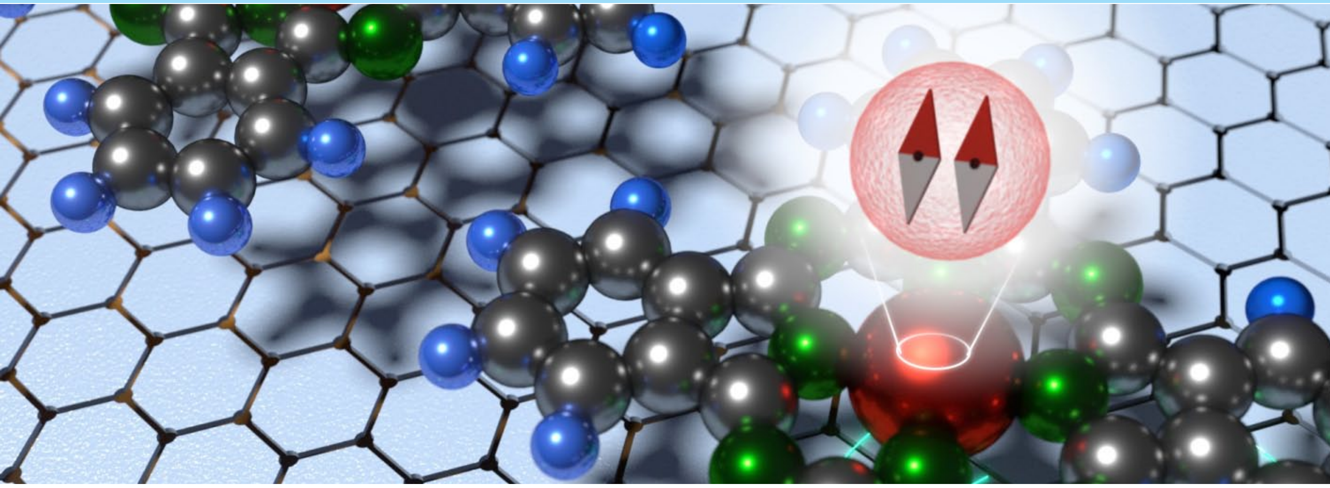
RCPTM NEWSLETTER
3/2018

REGIONAL CENTRE OF ADVANCED TECHNOLOGIES AND MATERIALS
Regionální centrum pokročilých technologií a materiálů

Palacký University Olomouc



Czech scientists have discovered a new way to control molecules' magnetic and electronic properties

A new way to control the electronic and magnetic properties of molecules has been discovered by scientists from the Regional Centre of Advanced Technologies and Materials (RCPTM) at Palacký University, Olomouc, together with colleagues from the Institute of Physics (FZU) of the Czech Academy of Science (CAS) and Institute of Organic Chemistry and Biochemistry (IOCB) of the CAS. Changes in molecules' electronic configurations can be commonly induced by applying external stimuli, such as light, temperature, pressure, or a magnetic field. Now Czech scientists have developed a revolutionary way to use weak non-covalent interactions of molecules with the surface of chemically modified graphene. This achievement has been published in the prestigious journal *Nature Communications*.

The arrangement of electrons, which move around in orbitals, determine not only molecules' electrical, optical, and magnetic properties, but also their biological activities. Molecules with orbitals containing just one unpaired electron have magnetic properties, while molecules containing two paired electrons in each orbital are non-magnetic. The possibility of modifying the electronic structure of single molecules and their magnetic properties has been of interest to researchers for several decades because of its great application potential. Switching from one magnetic state to another is, with respect to the small size of molecules, an important step towards developing molecular computers. Molecular switches also offer applications in nanoelectronics, biology, and medicine.

"Common practice is to induce the switching process by employing environmental stimuli, which is technologically demanding. Instead, we employed an atomically thin layer of graphite, known as graphene, and intentionally replaced some of the carbons in the structure with nitrogen atoms. By changing lateral positions of molecules on the surface using a scanning probe, we were able to reversibly switch from one magnetic state on pure graphene to non-magnetic states in the area of nitrogen atoms. Moreover, we observed changes in arrangements of electrons in the molecules by atomic force microscopy. This offers considerable possibilities to increase the resolution of scanning probe microscopy," said Pavel Jelínek.

Generally, the properties of molecules can be tuned by covalent chemical modification, leading to alteration of the molecular constitution, i.e. termination of old and formation of new chemical bonds within them. These strong interactions involve sharing of electrons that participate in the chemical bonds. However, this approach is not applicable for developing molecular switches as the chemical modification usually induces irreversible alteration. Therefore, Czech scientists have attempted to employ weak non-covalent interactions, although no such strategy has been contemplated before.

"It has been shown that use of cyclic planar molecules based on porphyrin with an iron atom in the centre leads to rearrangement of the electrons when the molecule is located in the vicinity of a nitrogen defect in graphene. Using a combination of theoretical calculations and experimental measurements, we confirmed that the non-covalent interaction between the iron and nitrogen atoms is strong enough to disturb the magnetic state of the molecule, but too weak to allow transition of the molecule back to the magnetic state as soon as the molecule is returned to a pristine graphene surface," said Pavel Hobza, a world-renowned expert on non-covalent interactions from the RCPTM and IOCB.

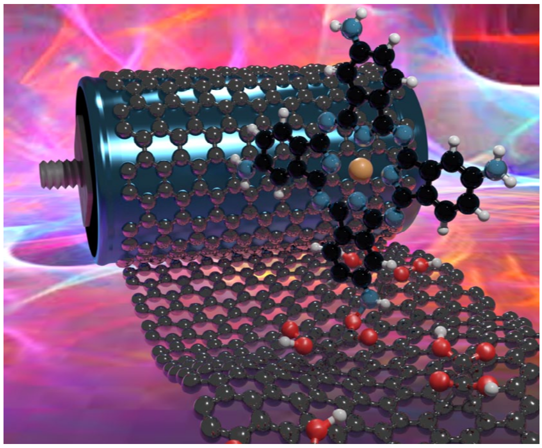
de la Torre B., Švec M., Hapala P., Redondo J., Krejčí O., Lo R., Manna D., Sarmah A., Nachtigallová D., Tuček J., Błoński P., Otyepka M., Zbořil R., Hobza P., Jelínek P.: Non-covalent control of spin-state in metal-organic complex by positioning on N-doped graphene, *Nature Communications* 2018, 9, 2831. IF = 12.353

Scientific Results

A new carbon-based material offers a promising way to store electrical energy

Fruits of two years' work on a prestigious European Research Council-sponsored project by Michal Otyepka and his team at RCPTM include a new carbon-based material that can be employed for constructing so-called supercapacitors used to store electrical energy. The material has been derived by chemically attaching phthalocyanine to a fluorographene-derived 2D skeleton, resulting in a 'zwitterionic' material with no net charge but containing both a positive and a negative electrical charge on each functional group. This has enabled preparation of a graphene surface with an organized network of electrical charges, providing a suitable environment for ion transmission and separation, as well as creation of an electrical double layer. The material has high capacity values and can be exploited as an electrode material in supercapacitors. Such a graphene derivative has high stability, good conductivity, and capacity that does not drop even after a vast number of charging cycles. Sodium sulphate serves as a safe electrolyte.

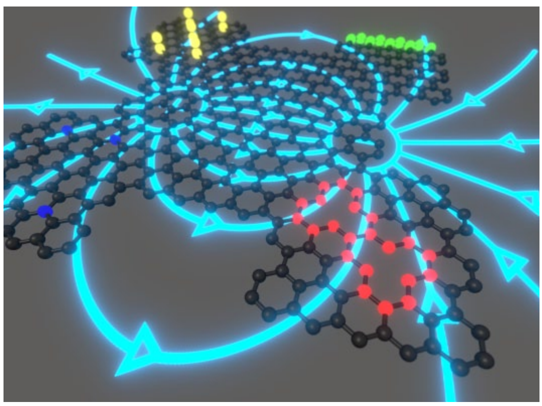
RCPTM scientists have only recently begun to focus on electrode materials for supercapacitors. The next goal is to obtain a material with even higher energy density, more specifically a material enabling storage of larger amounts of energy. In the following step, the scientists will focus on creating a supercapacitor prototype that will exploit the prepared materials.



Bakandritsos A., Chronopoulos D. D., Jakubec P., Pykal M., Čépe K., Steriotis T., Kalytchuk S., Petr M., Zbořil R., Otyepka M.: High-Performance Supercapacitors Based on a Zwitterionic Network of Covalently Functionalized Graphene with Iron Tetraaminophthalocyanine, *Advanced Functional Materials* 2018, 28 (29), 1801111. IF = 13.325

A review has highlighted dramatic progress in research on magnetism in graphene and its derivatives

Graphene, a single two-dimensional sheet of carbon atoms, has captured immense interest from the scientific community since its isolation in 2004. Despite the different noteworthy properties it possesses, a number of applications require graphene to be made magnetic. Therefore, scientists have proposed different ways to achieve it. This dramatic progress achieved in this area has been summarized by RCPTM scientists in a review paper on chemical strategies for imprinting magnetism into graphene and related 2D materials, which has been published in the journal *Chemical Society Reviews*. The review presents a systematic classification of the methods used for equipping graphene with magnetic properties, evaluation of the effectiveness of various approaches for imprinting magnetism into graphene, and discussion of possible uses of the methods for challenging future applications, especially in spintronics and biomedicine. It also covers emergence of magnetism in graphene analogues and other selected 2D materials. In particular, it addresses transition metal dichalcogenides, metal dihalides, metal dinitrides, MXenes, hexagonal boron nitride, and other relevant 2D compounds/molecules. Finally, the review highlights several challenges that have not yet been addressed, such as: experimental difficulties hindering synthesis of graphene-based systems with controlled introduction of defects; experimental engineering of sizes and edges in spatially confined graphene representatives; combinations of defects of various natures; competition among various types of interactions towards self-sustainable magnetism in graphene and related 2D materials up to room temperature; strengthening the magnetic anisotropy in graphene; and connection of 'magnetic' graphenes and other 2D materials to other functional components in devices.

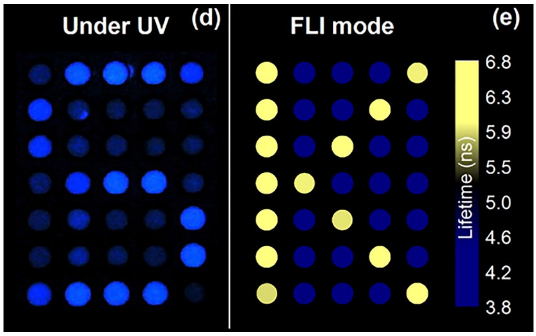


Tuček J., Błoński P., Ugolotti J., Swain A.K., Enoki T., Zbořil R.: Emerging chemical strategies for imprinting magnetism in graphene and related 2D materials for spintronic and biomedical applications, *Chemical Society Reviews* 2018, 47 (11), 3899–3990. IF = 40.182

Carbon dot fluorescence lifetime-encoded anti-counterfeiting

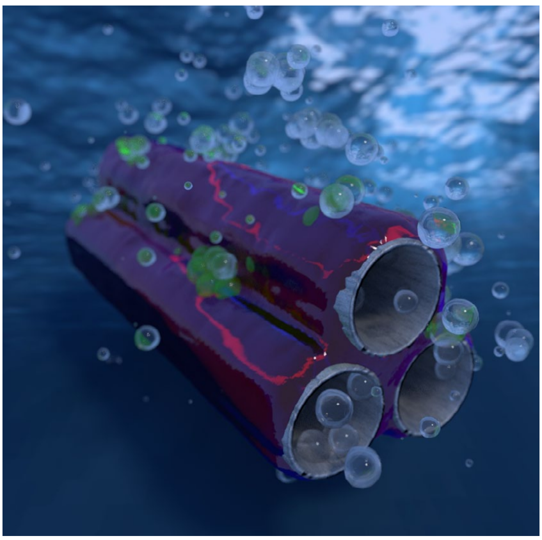
Counterfeiting of valuable documents, currency, and branded products is a global threat. Thus, there are urgent needs for effective high-tech solutions to combat and prevent it. Use of luminescent nanomaterials as anti-counterfeiting inks is highly promising, and many types of such security inks based on various materials have been recently developed. In particular, carbon dots (CDs) are attracting increasing interest in many fields because of intrinsic advantages such as broad-band optical absorption, strong luminescence, strong resistance to photobleaching, high chemical stability, low toxicity, and good biocompatibility.

RCPTM scientists demonstrated the first application of CDs for fluorescence lifetime-encoded anti-counterfeiting in work published in *ACS Applied Materials & Interfaces*. The emission colours of such luminescent inks are identical, but intrinsic fluorescence lifetimes are distinctive and well-separated, allowing authentication of security tags exclusively by fluorescence lifetime imaging. The researchers demonstrated that the fluorescence lifetime response of CD-inks was stable during continuous photoexcitation and remained stable even after long-term storage. Furthermore, they proved the applicability of this method for the first anti-counterfeiting luminescent tagging. Due to the combined advantages of fluorescence lifetime-encoded technique; high fluorescence quantum yield; high authentication security and accuracy; robust stability; and low cost, CDs could be of prime interest for protection of high-value merchandise; government documents; and banknotes.



Kalytchuk S., Wang Y., Poláková K., Zbořil R.: Carbon Dot Fluorescence-Lifetime-Encoded Anti-Counterfeiting, *ACS Applied Materials & Interfaces* 2018, 10 (35), 29902–29908. IF = 8.097

Scientists have developed a new co-catalyst for more effective solar water splitting



Titanium dioxide (TiO_2) is still one of the most promising materials for producing hydrogen via photocatalytic water splitting. However, the overall efficiency of the process is impaired by rapid recombination of photogenerated charge carriers (electrons and positively charged vacancies) due to the slow kinetics of the oxidation reactions on TiO_2 surfaces. Decorating TiO_2 with co-catalyst nanoparticles can effectively overcome this drawback, but noble metals such as platinum or palladium, which are frequently used as co-catalysts, are not cost-effective options. In collaboration with colleagues from Friedrich-Alexander University Erlangen-Nürnberg, RCPTM researchers have developed a novel type of co-catalyst prepared by homogenously distributing nanoparticles of NiCu alloys on surfaces of TiO_2 nanotubes. Preparation of the NiCu co-catalyst involves sintering of ultrathin layers of nickel and copper deposited on the surfaces by magnetron sputtering. The researchers found that nickel-copper alloy nanoparticles in the ratio 0.5 Cu : 0.5 Ni can provide equal catalytic efficiency to platinum.

Spanu D., Recchia S., Mohajernia S., Tomanec O., Kment Š., Zboril R., Schmuki P., Altomare M.: Templated Dewetting–Alloying of NiCu Bilayers on TiO_2 Nanotubes Enables Efficient Noble-Metal-Free Photocatalytic H_2 Evolution, *ACS Catalysis* 2018, 8 (6), 5298–5305. IF = 11.384

Other publications from RCPTM

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Nguyen N.T., Ozkan S., Tomanec O., Zhou X., Zboril R., Schmuki P.: Nanoporous AuPt and AuPtAg alloy co-catalysts formed by dewetting–dealloying on an ordered TiO_2 nanotube surface lead to significantly enhanced photocatalytic H_2 generation, *Journal of Materials Chemistry A* 2018, 6 (28), 13599–13606. IF = 9.931

Nandan D., Zoppellaro G., Medřík I., Aparicio C., Kumar P., Petr M., Tomanec O., Gawande M.B., Varma R.S., Zbořil R.: Cobalt-entrenched N-, O-, and S-tridoped carbons as efficient multifunctional sustainable catalysts for base-free selective oxidative esterification of alcohols, *Green Chemistry* 2018, 20 (15), 3542–3556. IF = 8.586

Stetsovych O., Mutombo P., Švec M., Šámal M., Nejedlý J., Císařová I., Vázquez H., Moro-Lagares M., Berger J., Vacek J., Stará I.G., Starý I., Jelínek P.: Large Converse Piezoelectric Effect Measured on a Single Molecule on a Metallic Surface, *Journal of the American Chemical Society* 2018, 140 (3), 940–946. IF = 14.357

Lerch M.M., Di Donato M., Laurent A.D., Medved' M., Iagatti A., Bussotti L., Lapini A., Buma W.J., Foggi P., Szymański W., Feringa B.L.: Solvent Effects on the Actinic Step of Donor-Acceptor Stenhouse Adduct Photoswitching, *Angewandte Chemie International Edition* 2018, 57 (27), 8063–8068. IF = 12.102

Interview

"International collaboration plays a key role in research"

The world-renowned researcher Patrick Schmuki, based at Friedrich-Alexander University Erlangen-Nürnberg, has been collaborating with RCPTM for a long time. Since 2017 he has been directing the 'Advanced Hybrid Nanostructures for Renewable Energy Applications' project. He has been awarded a prestigious European Research Council grant, and is repeatedly one of the highly cited researchers listed in InCites database provided by Clarivate Analytics (formerly part of Thomson Reuters). He also participated in the *Rudolf Zahradník Lecture Series* in Olomouc.

At RCPTM, you lead the *Photoelectrochemistry group*, which is currently working on the development of novel hybrid materials and technologies enabling production of hydrogen as an energy resource via solar water splitting. About a year and a half ago you expressed your hope that the new laboratory with excellent workers and state-of-the-art equipment would lead to stimulating the research in this important area. How do you view and evaluate the first year and achievements of the group?

In my view, we have achieved very good progress in our research field. That is demonstrated by a good number of papers published (and more to come!). The setting-up phase is still not fully completed but particularly in collaboration with our sister lab in Erlangen we are steadily making the RCPTM lab a globally recognized group.

How do you evaluate the collaboration with the researchers from Olomouc?

Very good: we have experienced an open attitude and collaborative spirit—this is fostered by regular exchange with mutual visits of researchers between Erlangen and RCPTM.

Which area have you made the greatest progress in? Which results achieved so far would you highlight in particular?

We have established first class PVD sputtering facilities to grow functional thin films that we increasingly use to explore both photocatalytic features of surfaces and photoelectrochemical hydrogen generation. First results, particularly on the use of earth-abundant photocatalysts, have been very promising and accordingly resulted in publications.

What tasks are you going to focus on in the immediate future?

My immediate goal is to take even more advantage of the excellent infrastructure of Olomouc, by linking the photoelectrochemistry group with other top groups at RCPTM to exploit more synergy with mutual beneficial outcome.

The grant from the Operational Programme 'Research, Development and Education' amounting to 130 million Czech crowns has enabled purchase of state-of-the-art equipment. What do you think of the technical infrastructure at RCPTM? Which equipment is vital for your work?

The research infrastructure is becoming increasingly excellent. For our work, the state-of-the-art transmission electron microscope

is extremely valuable. I believe the upcoming FIB TEM sample preparation facility will further strengthen the infrastructure and be of utmost benefit, particularly for analysing multilayer-based photoactive surfaces. EPR expertise is excellent and we are still only on the brink of realizing this technique's importance for advanced catalyst design.

The project also aims to foster collaboration of researchers from several countries. You can be a shining example of such partnership. Have you managed to build up contacts with other specialists from abroad?

In general, I and my group operate highly internationally; we have contacts with leading researchers in the field in Europe, the USA, Japan, and South Korea. International collaboration is the key to success in high-level research, and certainly research carried out at any prestigious institute should be internationally competitive. Creating a strong group, which in turn gives access to other strong groups, is vital.

What are the key challenges in the field of renewable energy in your opinion? Which of them would you like to address in collaboration with the RCPTM team?

Our team focuses on generation of hydrogen as a fuel of the future (and related aspects such as storage, etc.). While a main consideration in photocatalysis is efficiency vs. cost, the long-term stability of catalysts (or their regeneration) is also of utmost importance. All these points, in my view, need to be tackled from a fundamental understanding of the designed catalysts, and I feel that at RCPTM we have excellent tools for defined 'experimental modelling and assembly' towards a next generation of non-classic photoactive materials.

Awards

The physical chemist Aleš Panáček has won a 'President's Prize' of the Czech Science Foundation (GACR)

This researcher from Olomouc received his prize for outstanding results he obtained while carrying out a project called 'Study of bacterial resistance elimination using combination of antibiotics with silver compounds or with silver nanoparticles using *in vitro*, *in vivo* or *in silico* methods'.

"This prize is recognition for work not only by me but also my colleagues from Palacký University's Faculty of Science and Faculty of Medicine and Dentistry. I regard it as evidence that our efforts have been worthwhile, as also reflected, of course, in the excellent research results. However, winning such a prize also provides a spur to continue pushing the limits of the research rather than resting on your laurels," said Aleš Panáček.

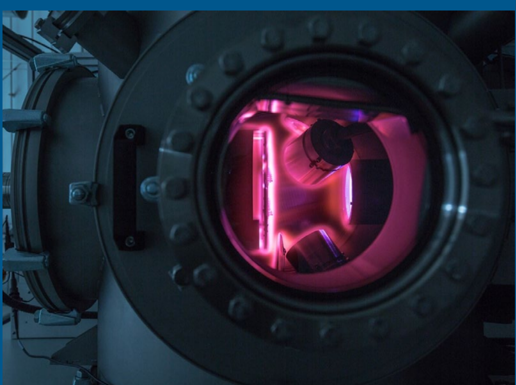
Results of the research have already been published in the prestigious journal *Nature Nanotechnology*, and he is convinced that this made a significant contribution to his selection for the award. The aforementioned project was conducted by a joint teach of researchers from RCPTM, the Faculty of Medicine and Dentistry, and the Centre of the Region Haná for Biotechnological and Agricultural Research. The study describes a unique resistance mechanism to silver nanoparticles the bacteria possess and the way this can be overcome by pomegranate extract. Such findings could significantly contribute towards resolving the global antibiotics resistance crisis.

Aleš Panáček has been focusing on biological effects of nanosilver for approximately 16 years, since his doctoral studies. In 2006 he was one of the authors of a pioneering study published in the *Journal of Physical Chemistry B* in which the scientists explored the activity of silver nanoparticles against a wide range of bacteria including high resistant strains. This paper is considered a pioneering study in the area of describing antibacterial effect of silver nanoparticles, receiving an outstanding number of citations (over 1300; Scopus October 2018).

Introducing a Scientific Infrastructure

Pulsed reactive magnetron sputtering system

Installation of a magnetron sputtering system for preparing functional thin films and nanostructures with defined properties is providing exciting new opportunities to exploit advanced techniques at RCPTM. The principle of the deposition consists in reactive sputtering of metal, alloy, and dielectric targets in the plasma region with a high degree of ionization. In the plasma, the sputtered particles can then react with surrounding gases, such as O_2 or N_2, enabling the preparation of the target oxides, nitrides, and other compounds. The target nanostructure is formed on the substrate, which can be heated to a temperature of 1200 °C, rotated, and tilted. The whole process of the plasma deposition takes place in ultrahigh vacuum (the pressure before the deposition is ~10^{-5} Pa), which guarantees high chemical purity of the deposited materials. Plasma is generated by advanced high-voltage pulse generators, which are able to operate in different modes with a considerable level of controlling the properties of the deposition plasma and subsequently the parameters of the nanostructures. By optimizing plasma conditions, we can prepare materials that are thermodynamically difficult to obtain with other techniques. Further, diverse parameters such as the crystal phase, preferred orientations and the crystalline density, or stoichiometry, can be adjusted. The magnetron system is equipped with five magnetron sources that enable preparation of (multi)-doped and multi-layered thin-film systems. Currently, the plant is used mainly for preparing semiconductors with applications in photoelectrochemistry and photovoltaics.



Happened Recently...

Yury Gogotsi delivered the latest talk in the Rudolf Zahradník Lecture Series

A highly acclaimed scientist in the field of material chemistry, Yury Gogotsi from Drexel University, Philadelphia, has enriched the group of world's top chemists who have presented one of our series of *Rudolf Zahradník Lectures*. His lecture focused mainly on two-dimensional MXenes.

Professor Gogotsi has taken the research into two-dimensional systems far beyond the Nobel Prize material—graphene. He was a member of the team that discovered a new class of 2D carbides and nitrides—MXenes. These structures show great potential in sensory technologies, energy storage, water remediation, optoelectronics and medicine. "Currently we are collaborating in research on hybrid materials while exploiting the chemistry of fluorographene and the properties of some MXenes in order to develop high-efficiency supercapacitors," said Radek Zbořil, RCPTM Director, who is also convenor for the *Rudolf Zahradník Lectures*.

While RCPTM researchers are focusing on developing graphene derivatives, Prof. Gogotsi is concentrating on MXenes. According to him, the two materials will be combined in some applications, but used separately in others.

"The development of MXenes does not aim at replacing graphene in its applications. There is a large group of MXenes from which we are trying to pick the right one to reach the particular goal. Not only do the properties of the material but also the cost of its production represent a major issue when deciding about the specific use. With respect to it, graphene is ahead," said Prof. Gogotsi. In his lecture 'MXenes – Synthesis, Properties, and Applications of Two-Dimensional Carbides and Nitrides, the Largest Family of 2D Materials' he presented the history of MXenes research at Drexel University, the properties of these materials, and the potential for their use. The lecture is available on the RCPTM website.

Professor Gogotsi is the author or co-author of two books. He is a named inventor of more than 50 European or American patents, and author of more than 600 publications that have received 52 000 citations. His H-index has reached 102. He has been awarded various prestigious prizes and honorary degrees. This year he became a member of the International Scientific Board of the Neuron Fund.

RCPTM welcomed guests of a prestigious Times Higher Education summit

RCPTM actively participated in hosting the international summit *Times Higher Education* World University Rankings, which was held for the first time ever in Central Europe in April. Palacký University hosted the summit this time round. Some of the participants visited the research centres in Olomouc-Holice, which is part of the university premises. Radek Zbořil, RCPTM Director, escorted guests from diverse countries (*inter alia*, the Czech Republic, Kosovo, Turkey, and Indonesia) on a guided tour of the laboratories. He also introduced aspects of both fundamental and applied research covered by the centre, and highlighted some of the centre's most important findings.

"I had heard of the research centres in Olomouc before, but this was the first time I had visited them. They left a strong impression on me and the results they have obtained are outstanding. Of the 48 centres that have been established across the country, these are definitely among the most successful ones," said Prof. Karel Melzoch, Rector of the University of Chemistry and Technology, Prague.

Pavel Hobza, Radek Zbořil, and Michal Otyepka participated in the final panel discussion called *Science and Europe*. They considered options for raising Czech science's global profile, and all agreed that internationalization is crucial to ensure its competitiveness. "Internationalization is vital, yet Czech scientific environment is lacking it. What would be Czech science like if the number of foreign scientists expressed in percentage form was 40%, which is common at universities abroad, and not 6 –10%, which is the current situation. We will not progress if there is no healthy competition," said Radek Zbořil.

The scientists also appealed for stronger support and creation of optimal working conditions for researchers doing excellent work. "We are supporting mediocrity instead of excellence. We must rid the financial system of egalitarian principles. Doing first-class science should go hand-in-hand with clear financial benefits. Sadly, in our country, success is not valued," said Pavel Hobza.

Nanocon conference celebrated its 10th anniversary

The first conference in the Czech Republic to focus solely on nanomaterials was the Nanocon in 2008. Since then it has become an annual event, and one of the largest-scale conferences in this field in Central Europe. This year it was held (and its 10th anniversary celebrated) in the city of Brno, from the 17th to 19th of October, with the active participation of RCPTM, a co-founder of the event. Radek Zbořil (RCPTM's Director) was once again convenor, and two of the invited speakers were RCPTM representatives—Pavel Hobza and Aleš Panáček.

330 participants registered for the conference this year. RCPTM researchers arrived in large numbers, and participated in six sessions. Prof. Hobza gave a lecture entitled 'Electronic Structure of Fe(II) Phthalocyanine in the Isolated State and Adsorbed at Pristine Graphene and N-doped Graphene: Theoretical and Experimental Study'. Aleš Panáček, a distinguished physical chemist, focused on bacterial resistance to silver nanoparticles.

The conference hosted world-renowned scientists. One, Paras N. Prasad, Executive Director of the Institute for Laser, Photonics and Biophotonics, University at Buffalo, New York State, USA, is a multidisciplinary researcher in the field of photonics and nonlinear optics, who has achieved global success for his pioneering work on use of light-based technologies to address serious global health problems. Prof. Prasad presented a plenary lecture entitled 'Convergence of Science: Linking Nanotechnology with Photonics and Biology to Impact on Energy and Health Care.' Another, Antonio H. Castro Neto, Director of the Centre for Advanced 2D Materials, National University of Singapore, is a materials scientist and condensed matter theorist, who has achieved global recognition for his work on 2D materials. He delivered another plenary lecture entitled '2D Materials: Science and Technology'.

Coming Next...

Science and Technology Week at RCPTM: lecture and visits

Like last year, RCPTM is going to participate in the Czech Republic's most extensive annual science festival—the *Week of Science and Technology* of the CAS. The centre will open its doors for students and the general public between the 7th and 9th of November. There will be multiple programmes including, for instance, a lecture entitled 'Nanomaterials and Nanotechnology for Novel Energy Resources—a Way to a Sustainable World?' delivered by Štěpán Kment to high school students on Friday the 9th of November at 10 a.m., in Fort Science, Olomouc.

During this special event, RCPTM employees will introduce the visitors to various fields of the centre's chemical, materials, and optical research. The programme will also include displays of the centre's state-of-the-art equipment and performance of various experiments on the spot in the laboratories.

In Fort Science, the attendees will learn how scientists are responding to problems associated with increasing energy consumption, the need to identify and develop renewable resources, and the role nanotechnology could play in efforts to resolve the problems and meet the needs. Štěpán Kment, a highly esteemed scientist in the field of photoelectrochemistry, will address various topics ranging from alternative and sustainable energy resources such as photoelectrochemical and solar cells providing hydrogen and electrical energy, through new types of batteries, to supercapacitors.

Both events require registration in advance. Further information is available on the *Week of Science and Technology* webpage.

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

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