

# 2<sup>nd</sup> ATOMDEC ANNUAL MEETING

Atomic Design of Carbon-Based Materials for New Normal Society

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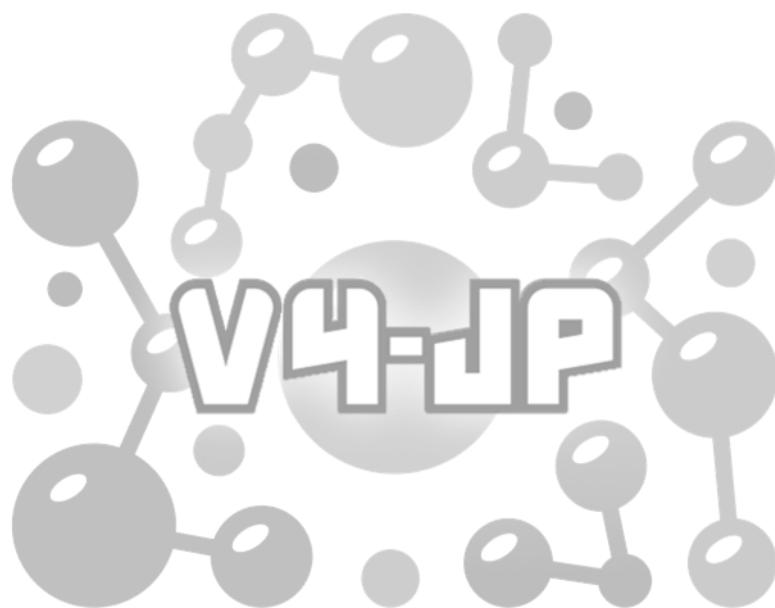


## BOOK OF ABSTRACTS

November 2 – 4, 2022

Smolenice, Slovakia



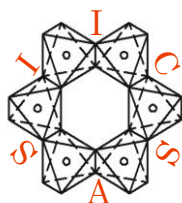


**AtomDeC**

2<sup>nd</sup> annual meeting, 2.11.-4.11.2022

Smolenice, SLOVAKIA

# BOOK OF ABSTRACTS



Publisher: Institute of Inorganic chemistry  
Slovak Academy of Sciences  
Dúbravská cesta 9  
845 36 Bratislava

Edited by: Eva Scholtzová

ISBN 978-80-973578-3-2

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## **Sustainable Batteries and Electrocatalysis for Clean Energy Technologies**

M. Titirici<sup>1\*</sup>

<sup>1</sup> *Imperial College London, Department of Chemical Engineering*

(\*) [m.titirici@imperial.ac.uk](mailto:m.titirici@imperial.ac.uk)

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It is imperative we mitigate and then reverse carbon emissions. COPS 26 just happened with the goal of global commitment to keep 1.5 C within reach by 2050. A green industrial revolution powered by many of sustainable innovations evolving in parallel is essential. Yet we need to make sure that this new revolution happens sustainably and does not create more damage. We must learn from past mistakes and learn how to see the bigger picture rather than immediate goals. Batteries and catalytic processes are key for delivering the green industrial revolution by storing the intermittent renewable energy and releasing it when is needed most to decarbonize our economy across various sectors. Yet, battery materials and catalysts for various sustainable technologies are facing real challenges as they are based on critical and expensive metals. In this talk, I will present recent research advances from my research team in the area of sustainable batteries with focus on Na and Al as well as the production of green H<sub>2</sub> and sustainable plastics via electrocatalysis.

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## From oxo-functionalized graphene to porous graphene

S. Eigler<sup>1\*</sup>

<sup>1</sup>*Institute of Chemistry and Biochemistry, Freie Universität Berlin, Altensteinstraße 23a, 14195 Berlin, Germany*

(\*) [siegfried.eigler@fu-berlin.de](mailto:siegfried.eigler@fu-berlin.de)

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*Keywords: graphene; porous graphene; chemical modification*

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Rims or edges of flakes of graphene are more active compared to the bare plane. Thus, energy applications or applications such as filtering of molecular species, or formation of composite materials, benefit from porosity in carbon materials.[1] However, up to now, there remains a lack of knowledge, in particular, in predicting the properties of porous carbon materials. The first rational step towards gaining precise insights into structure property relations requires reproducible synthetic protocols towards porous carbon-based materials.

Along these lines, we present our recent advances in preparing porous graphene from oxo-functionalized graphene. We demonstrated already in 2012/2013 that the surface of graphene layers, stacked as graphite, can be oxidatively functionalized by oxo-addends, to allow dispersion of flakes of oxo-graphene (oxo-G) in water.[2] Interestingly, flakes do not contain wrinkles, while the larger flakes of graphite bear wrinkles. That observation indicates the higher reactivity of any non-ordered structure. From the point of molecular chemistry, this point is clear, e.g. the reactivity of naphthalene (6,6-rings) is completely different to azulene (5,7 rings). Finally, we proved the higher reactivity of graphene close to defect-sites and regiochemically formed C-C bonds.[3]

The rationalization of those insights and observations motivated us to investigate the processing of oxo-G, which bears an almost intact hexagonal carbon framework, in addition to some defects, which are present on the few-nm scale, as proved with atomic precisions using transmission electron microscopy.[4]

Here, we present the formation of pores in graphene, on surface and in dispersion, respectively. Thereby the pore size can be adjusted between few nm and up to several hundreds of nm. Both approaches are based on etching protocols. In the first approach, flakes of oxo-G, deposited on substrates, had to be thoroughly washed after immersion in potassium permanganate to allow controlled thermal etching at 400 °C, forming pores.[5] In the second approach oxo-G was dispersed in water and hydroxyl radicals were photochemically generated to etch pores into oxo-G.[6] Both approaches require an almost intact hexagonal carbon framework, otherwise flakes with diameters of 20 µm disintegrate to undefined carbon materials.

In addition, we show how the electrochemical oxidative functionalization close to defect sites in graphene improves the catalytic activity towards the reduction of oxygen to hydrogen peroxide.[7] Thereby, we also present how tape-cleavage of carbon layers from electrodes can help quantifying experimental results.

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## **Preparation of porous carbons: design of porosity for sustainable engineering applications**

D. Cazorla-Amorós<sup>1\*</sup>

<sup>1</sup> *Department of Inorganic Chemistry and Materials Institute (IUMA), University of Alicante, Ap. 99, 03080, Alicante, Spain;*

(\*) [cazorla@ua.es](mailto:cazorla@ua.es)

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*Keywords: porous carbons; porosity; energy storage*

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Carbon materials provide a combination of unique physicochemical properties that make them suitable for many applications. These materials may display relatively large electrical conductivity, high porosity development with a high apparent surface area and surface chemistry that can be adapted to the desired application. Moreover, their low cost is a very important parameter for industrial application. Therefore, they are used in large quantities in potable water treatment plants and are key components of different electrochemical devices like supercapacitors, Li-ion batteries and fuel cells. They can be found in a large variety of morphologies (powder, fibre, cloths, monoliths, etc.), that make possible to adequate them to the appropriate characteristics in different applications.

In this talk, we will review the preparation methods of porous carbons from the most conventional processes used in the industry to some of the most recent developments that provide examples of carbon materials that can be synthesized with different morphologies and structures. These methodologies allow us to obtain materials with porosities that can be adapted to specific applications. In this sense, three examples of results obtained by our research group (volatile organic compounds removal, hydrogen storage and micro-supercapacitors) will be presented to show the relevance of the porosity design to optimize the performance of the porous carbon materials.

## AtomDeC project: the renaissance of carbon-material research

H. Nishihara<sup>1\*</sup>

<sup>1</sup>Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai, 980-8577, Japan

(\*) [hirotomo.nishihara.b1@tohoku.ac.jp](mailto:hirotomo.nishihara.b1@tohoku.ac.jp)

*Keywords: amorphous carbon; disordered carbon; modeling*

The expression “New Normal” is often used for emerging lifestyles after the COVID19 pandemic. Our project, Atomic Design of Carbon-Based Materials for New Normal Society (AtomDeC), aims to contribute to the creation of an upgraded, human-centred society, where new technologies serve sustainable developments, mitigate the threat of future pandemics, and are devoted to human welfare. To achieve these targets, we focus on the development of advanced carbon-based materials which are key in everyday applications and devices: batteries, power generators, energy converters, mobile devices, structural materials, environmental filters, health care, and medical products. Carbon-based materials have been widely used in industry and our surroundings, however, most practical materials have disordered structures and amorphous portions, and it hampers the further improvement of their performances. In the AtomDeC project, we stick to the structure control and analysis at the “atomic level”. We will develop atomically designed and drawable materials like zeolite-templated carbon[1], graphene meso-sponge[2], and ordered carbonaceous framework[3]. Not only pure carbon materials but also carbon-based composite materials[4, 5] are the target of this project. Also, we will use advanced analytical techniques including temperature-programmed desorption up to 2300 °C, which can provide deep insight into the atomic-level structural properties of graphene sheets [6, 7].

The outline of the AtomDeC project is shown in Fig. 1. Work Package 1 (WP1) led by Japan team synthesizes advanced carbon-based materials. WP2 led by Czech team synthesizes composite materials. WP1 and WP2 are cooperatively in charge of the “Synthesis” role. Hungary team leads WP3 “Analytics”. Slovakia team leads WP4 “Modelling” together with an external collaborator, Dr. Szilagyi. WP5 “Devices” is led by Poland team. Through the intimate collaborations among the five WPs, we will develop high-performance carbon-based materials and their composites which are atomically designed and controlled.

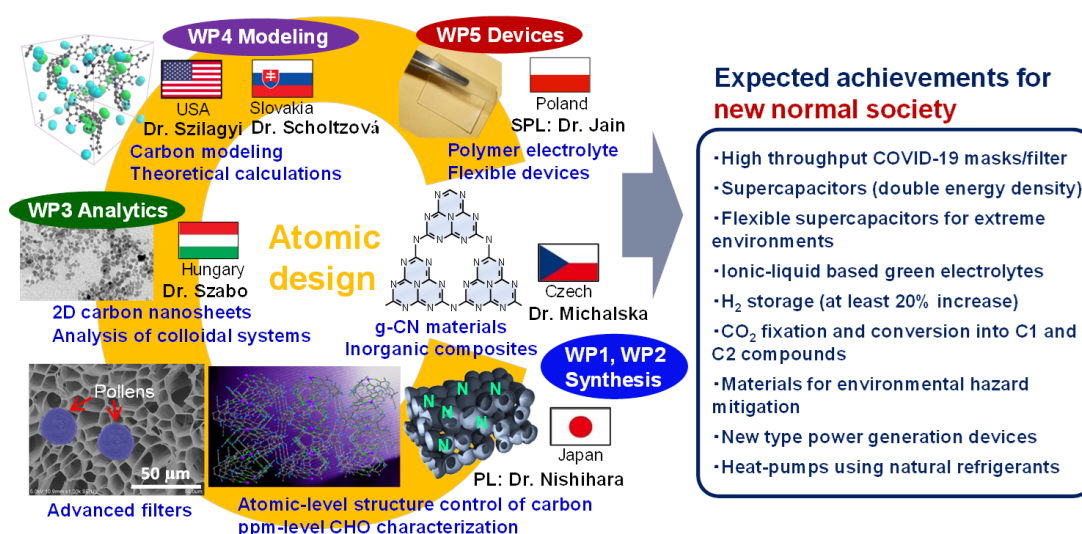


Fig. 1 Organization of the international team and expected achievements for new normal society.

In this talk, the progress of the AtomDeC project especially related to WP1 is reported.

The first topic is graphene mesosponge (GMS)[2]. GMS is synthesized by a hard-templating method using Al<sub>2</sub>O<sub>3</sub> [2] or MgO [8] nanoparticles via precisely controlled chemical-vapor deposition in which the average stacking number of graphene sheets is adjusted to 1 (one-atom-thick). After template removal, the resulting mesoporous carbon is annealed at 1800 °C to form GMS. By such a high-temperature treatment, most carbon edge sites that cause corrosion of batteries can be removed, and GMS exhibits ultra-high stability against chemical oxidation as well as electrochemical oxidation. Despite such durability, GMS possesses a high surface area (ca. 2000 m<sup>2</sup>/g) and a large pore volume (> 3 cm<sup>3</sup>/g). Moreover, GMS has a high electric conductivity which is superior to carbon blacks. Furthermore, GMS is mechanically flexible and tough. GMS shows reversible deformation and recovery upon applying mechanical force and its removal [9]. Such unique properties of GMS enable its use as next-generation durable and high-performance carbon material for battery applications. As an electrode material for electric double-layer capacitors, GMS exhibits ultra-high voltage stability up to 4.4 V even in a conventional organic electrolyte (Et<sub>3</sub>MeN/BF<sub>4</sub>), which surpasses single-walled carbon nanotubes [10]. Also, GMS is useful for Pt support of polymer-electrolyte fuel cells [11] and as a cathode of all-solid Li-S batteries. We have shared the GMS materials in the AtomDeC project, and are trying to develop new applications, new composite materials, and new devices.

The second topic is advanced temperature-programmed desorption (TPD) up to 2300 °C. We are adopting this technique for visualizing low-crystalline porous carbon materials, by coupling it with other advanced analytical techniques and theoretical calculations. Moreover, we extend the TPD method to analyze heteroatoms embedded in carbon materials.

Also, some other topics and collaboration achievements will be mentioned in this talk.

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## Silver modified TiO<sub>2</sub> and melem/g-C<sub>3</sub>N<sub>4</sub>: preparation, characterization, and photodegradation activity against model dye acid orange 7

M. Michalska<sup>1\*</sup>, V. Matejka<sup>1</sup>, J. Pavlovsky<sup>1</sup>, J. Serencisova<sup>2</sup>, L. Gembalová<sup>3</sup>,  
G. Simha Martynková<sup>4</sup>

<sup>1</sup> Department of Chemistry and Physico-Chemical Processes, Faculty of Materials Science and Technology, VŠB-Technical University of Ostrava, 17. listopadu 2172/15, 708 00 Ostrava-Poruba, Czech Republic

<sup>2</sup> Energy Research Centre, CEET, VŠB-Technical University of Ostrava, 17. listopadu 2172/15, 708 00 Ostrava-Poruba, Czech Republic

<sup>3</sup> Department of Physics, Faculty of Electrical Engineering and Computer Science, VŠB-Technical University of Ostrava, 708 00 Ostrava, Czech Republic

<sup>4</sup> Nanotechnology Centre, CEET, VŠB-Technical University of Ostrava, 17. listopadu 2172/15, 708 00 Ostrava-Poruba, Czech Republic

(\*) [monika.kinga.michalska@gmail.com](mailto:monika.kinga.michalska@gmail.com)

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**Keywords:** silver nanoparticles; TiO<sub>2</sub>, melem/g-C<sub>3</sub>N<sub>4</sub>, photocatalyst

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In this work, we paid our attention to presenting the results of the two interesting semiconductor materials: TiO<sub>2</sub>, and melem/g-C<sub>3</sub>N<sub>4</sub>, and tested their performances as photocatalysts for the degradation of the model acid orange dye (AO7). A wet, easy chemical, and low-temperature approach for creating ca. 5 nm-sized Ag NPs spheres (Ag content: 0.5, 1.0, and 2.5 wt.%) were developed. Various complementary techniques along with: X-ray powder diffraction (XRD), scanning (SEM) and transmission (TEM) electron microscopy, X-ray energy dispersive spectroscopy (EDS), photoluminescence (PL), and UV-Vis diffuse reflection (UV-Vis DRS) spectroscopy were used to thoroughly characterize the synthesized powder materials. All materials were examined as potential photocatalysts using the AO7 photodegradation methodology. To compare the photodegradation tests, two separate lamps with wavelengths of 368 nm (UV light) and 420 nm (VIS light) were used. The surface modification of both TiO<sub>2</sub> and melem/g-C<sub>3</sub>N<sub>4</sub> materials with 0.5 wt% Ag revealed the best photocatalytic performances under UV and VIS light. For samples: TiO<sub>2</sub> and melem/g-C<sub>3</sub>N<sub>4</sub> containing 0.5 wt% Ag, photodegradation activities using a UV lamp (3 h, 368 nm irradiation) exceeded 95 and 94%, respectively. After 3 hours of irradiation, the materials showing the highest photoactivities were melem/g-C<sub>3</sub>N<sub>4</sub> with 0.5 and 1 wt. Ag, which displayed 98% activity under the irradiation with VIS light. Our research provides a unique, environmentally friendly, and cost-effective chemical method for producing photocatalysts suited for the degradation of organic pollutants in wastewater treatment.

### Acknowledgement:

This work was financially supported by the Ministry of Education, Youth and Sports, Czech Republic (contract no. 8F21007) through the research project cooperation between the AtomDeC Consortium (V4-Japan/JRP/2021/96/AtomDeC) by funding received from the Visegrad group(V4)-Japan 2021 2nd Joint Call on “Advanced Materials”.

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## Heterocoagulation: a versatile tool for carbon nanocomposite formulation

T. Szabo<sup>1\*</sup>

<sup>1</sup> University of Szeged, Department of Physical Chemistry and Materials Science, Rerrich Bela ter 1, H-6720 Szeged, Hungary

(\*) sztamas@chem.u-szeged.hu

Keywords: nanocomposites; heteroaggregation; colloidal particles

Graphite oxide is a multilayered assembly of individual nanosheets of graphene oxide. Both nanostructures can be considered as the primary sources of graphene materials, which have a principal role in materials science and nanotechnology. However, it might be less known that the nanocomposites of these carbonaceous materials may bear enormously versatile roles in catalysis, environmental technology and biomedical science as well. To highlight some of these promising functions, we aim to demonstrate the benefit of using graphene oxide in the following three areas: (1) settling enhancement of semiconductor nanocomposite photocatalysts for improved processability of treated wastewaters [1], (2) carbon-promoted photocatalytic hydrogen production using composite materials [2] and (3) magnetically modified carbon materials for anticancer magnetic hyperthermia [3]. Colloid chemistry plays a vital role in the synthesis of these nanomaterials: composite formulation in each of the above cases is based on heteroaggregation of particles dispersed in aqueous media (Figure 1), offering a mild route that preserves the chemistry and functionality of the graphene oxide counterpart.

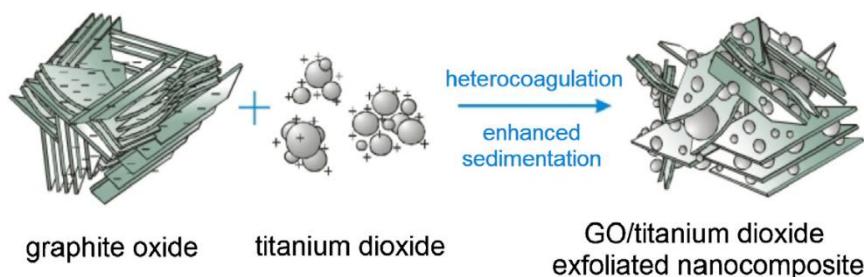


Figure 1: Scheme of the simplified synthesis pathway for formulation of graphene oxide nanocomposites.

### Acknowledgement:

The project no. 124851 has been implemented with the support provided from the National Research, Development, and Innovation Fund of Hungary (NKFIH), financed under the FK funding scheme. We also thank the support from the EU Horizon 2020 research and innovation programme and the NKFIH (project No. 2019-2.1.7-ERA-NET-2021-00029) for the Visegrad Group-Japan 2021 Joint programme. Support of the János Bolyai Research Scholarship from the Hungarian Academy of Sciences is also acknowledged.

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## Atomically designed carbon based materials studied by DFT method

E. Scholtzová<sup>1\*</sup>

<sup>1</sup> Institute of Inorganic Chemistry, Slovak Academy of Science, Dúbravská cesta 9, 84536 Bratislava, Slovakia

(\*) [eva.scholtzova@savba.sk](mailto:eva.scholtzova@savba.sk)

**Keywords:** DFT; modelling; carbon based materials

Carbon based materials (CBM) surround us in our everyday lives. Their favourable physical, chemical, electrical and mechanical properties resulted in their mass-scale production and broad utilisation. However, environmental compatibility, sustainability, and recyclability demand critical control of the quality of their manufacturing, such as controlled purity and structural homogeneity.

The next generation of activated carbons for hydrogen storage materials, batteries and fuel cell materials needs the atomic scale control of composition, structure, and properties. It can be achieved by employing complementary theoretical methodologies and realistic computational models. The *ab initio* Density Functional Theory (DFT) for the solid state can be used to reach the closest agreement with experimental results at a high level of theory. Using the DFT method, the additional structural, physicochemical and mechanical properties of new CBM materials prepared within the frame of the AtomDeC project can be elucidated and supply the experimental results.

For example, the DFT method was successfully applied to analyse the characteristic bands of the Raman spectra of the CBM (Fig. 1).

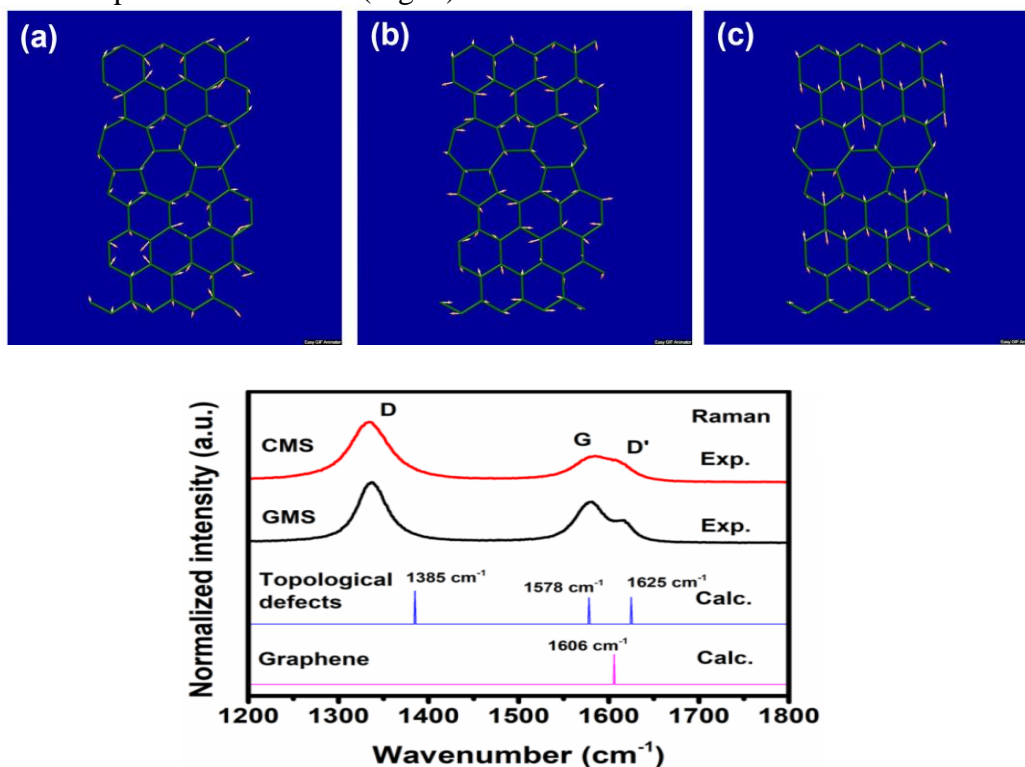


Figure 1| Calculated vibrational modes corresponding to the Raman bands of (a) 1384 cm<sup>-1</sup> (D band), (b) 1576 cm<sup>-1</sup> (G band), and (c) 1626 cm<sup>-1</sup> (D') in a model graphene structure including topological defects (5,7-membered carbon rings).



Further, the formation of N<sub>2</sub>, HCN, and NH<sub>3</sub> gases, as defined by the TPD measurements, was investigated employing DFT calculations. The energetics associated with a comprehensive set of fragmentation pathways initially leading to N-containing radicals or products was modelled. A direct correlation was established between the predicted product formation energies and the experimental desorption temperatures. This provides insights into the thermal desorption pathways and the plausible N-environments in porous carbon materials.

**Acknowledgement:**

The work is supported by the Visegrad Group-Japan 2021 2<sup>nd</sup> Joint Call on Advanced Materials in cooperation with the International Visegrad Fund funded by the Slovak Academy of Sciences, Slovakia (contract no. V4-Japan/JRP/2021/96/AtomDeC).

## Modified carbon materials for energy storage application

A. Jain<sup>1\*</sup> and M. Michalska<sup>2</sup>

*1Institute of Fundamental Technological Research, Polish Academy of Sciences, Pawińskiego 5B, 02-106 Warsaw, Poland*

*2 Department of Chemistry and Physico-Chemical Processes, Faculty of Materials Science and Technology, VŠB-Technical University of Ostrava, 17. listopadu 2172/15, 708 00 Ostrava-Poruba, Czech Republic*

(\*) [ajain@ippt.pan.pl](mailto:ajain@ippt.pan.pl)

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*Keywords: Supercapacitors; Activated carbon; Polymer gel electrolyte*

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Interest in the application that requires high energy density like consumer portable electronic devices, energy back-up systems, hybrid vehicles has led research towards low-cost, high-performance and environmentally friendly device called “Supercapacitors”. Supercapacitors can store and deliver energy by simply utilizing the charge separation at the electrode-electrolyte interface. The thin electrolyte film and high surface areas of electrode materials significantly contribute to the high capacitance of the device. Power densities of supercapacitors are thousand times higher than those of lithium ion batteries, along with much larger energy density values as compared to conventional capacitors. The construction of supercapacitor is same as that of traditional capacitors, the difference is that the metal electrodes are replaced by highly porous electrodes. Depending upon the charge storage mechanism and the active material used, supercapacitors are divided into two classes: electrical double layer capacitors (EDLCs) and pseudocapacitors [1-2]

Variety of carbon-derived materials have been intensively studied as electrode materials for supercapacitors because of their quality to transformed into various forms to facilitate high surface area, excellent electrical conductivity and high energy capacity. While choosing the materials, the most important factors affecting the performance of EDLCs are the specific surface area and pore size distribution of the material. The maximum capacitance is achieved when the pore size of the electrode material is close to the size of electrolyte ions so that ions of the electrolyte can access more area of the electroactive material. Activated carbon has been chosen in the present studies because of its cost effectiveness and good processability. It is inexpensive as compared to other competing materials [3]. In the present studies, activated carbon was modified with silver nanoparticles, the introduction of silver nanoparticles helps in improving the performance by decreasing the polarization.

For electrolyte, gel polymer electrolyte (GPE) is attracting a lot of attention because of their flexibility, high ionic conductivity, leakage free and stable electrochemical performance. Generally, GPEs are composed of electrolyte salt which can provide electrolyte ions and polymeric material which act as a matrix and its designing helps to improve the electrochemical and capacitive performance of the devices [4]. In the present case, Poly(vinylidene fluoride-co-hexafluoropropylene) was used as a polymer, propylene carbonate as a plasticizer and magnesium perchlorate as a salt.

The supercapacitor cells were fabricated by using two-electrode system, in which electrolyte films were sandwiched in between activated carbon modified with silver nanoparticle electrodes. It has been found out that 3wt% of silver particle in activated carbon gave best electrochemical results and hereon refers as ACAg3

Fig. 1a shows the SEM image of ACAg3. As can be seen from the figure deposition of silver particles were confirmed and observed as a small balls and also the morphology confirms the porous nature of material. Fig 1b shows the nitrogen adsorption-desorption curve of ACAg3.

The surface area studies confirms the surface area of  $\sim 824 \text{ m}^2 \text{ g}^{-1}$ . The isotherm shows Type II pattern in which nitrogen gas was filled at low pressure. The material also shows the good balance of micropore and mesopore which is suitable for electrochemical studies. The pore size of the material was found to be of the order of  $\sim 0.5 \text{ nm}$ .

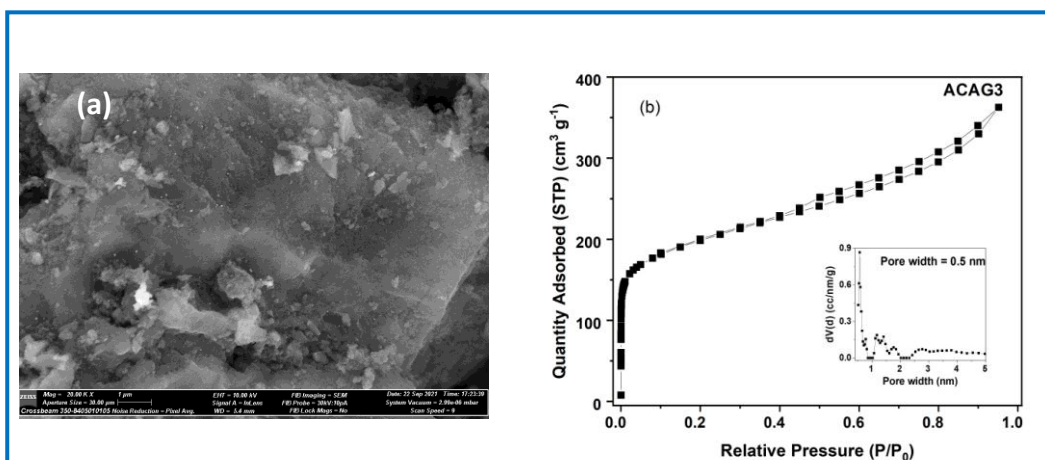


Fig 1 (a) SEM image of ACAG3 (b)  $\text{N}_2$  adsorption-desorption study of ACAG3

In order to check the material for supercapacitor application, galvanostatic charge-discharge was carried out. Fig 2 depicts the GCD curve of capacitor cell at a current density of  $1.0 \text{ mA cm}^{-2}$ . The non-linear pattern of the curves confirms the redox-nature of cell. The capacitance was calculated by using the discharge branch excluding the ohmic drop. The formula used is  $C_s = \frac{4(I \times \Delta t)}{(\Delta V \times m)}$ ,  $m$  is the mass of the electrode material,  $\Delta t$  is the discharge time and  $\Delta V$  is the potential difference. The capacitance value is found to be of the order of  $\sim 398 \text{ F g}^{-1}$ .

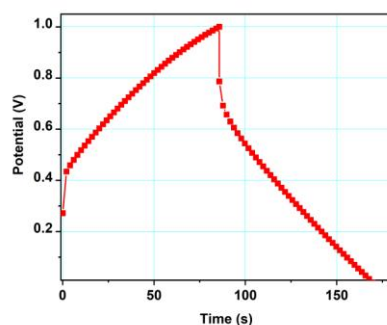


Figure 2: GCD curve of supercapacitor cell

Modified carbon was silver was carried out successfully and was investigated for supercapacitor application. The capacitance values was found to be of the order of  $\sim 398 \text{ F g}^{-1}$ .

#### Acknowledgment

This work was financially supported by the National Centre for Research and Development (NCBR, Poland); Project number: V4-Japan/2/17/AtomDeC/2022 and the Ministry of Education, Youth and Sports, Czech Republic (contract no. 8F21007) under the Visegrad Group-Japan 2021 Joint Call on Advanced Materials in cooperation with the International Visegrad Fund.

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## Advanced temperature-programmed desorption as a new characterization method for N-doped carbons

T. Yoshii<sup>1\*</sup>, G. Nishikawa<sup>1</sup>, R. Tang<sup>2</sup>, E. Scholtzová<sup>3</sup>, R. Szilagyí<sup>4</sup>, H. Nishihara<sup>2</sup>

<sup>1</sup>*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Miyagi, 980-8577, Japan*

<sup>2</sup>*Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, Sendai, Miyagi, 980-8577, Japan*

<sup>3</sup>*Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, 84536, Slovakia*

<sup>4</sup>*Department of Chemistry, UBC Okanagan, Kelowna, BC, V1V 1V7, Canada*

(\*) [takeharu.yoshii.b3@tohoku.ac.jp](mailto:takeharu.yoshii.b3@tohoku.ac.jp)

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*Keywords: Temperature-programmed desorption (TPD), N-doped carbons, High-sensitivity analysis*

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### Introduction

Nitrogen-doped (N-doped) carbon materials are attracting attention in various fields, such as catalysis for oxygen reduction reaction [1]. N-doping can be achieved in various processes and from diverse set of precursors (Fig. 1a) [2]. CHN elemental analysis and XPS were conventionally used for analysis of N species, but their measurement accuracy is about 0.1 wt% [3]. Thus, a technique for detailed qualitative and quantitative analysis of N species is desired. Herein, we propose high-temperature vacuum temperature-programmed desorption (TPD) as a new high-sensitivity characterization method for N-doped carbons.

### Methods

Prior to the TPD measurement, N-containing mesoporous carbons were obtained by chemical vapor deposition (CVD) of CH<sub>3</sub>CN on the Al<sub>2</sub>O<sub>3</sub> nanoparticle templates, followed by a removal of the template using hydrofluoric acid. Since the mesopore wall is composed of about one layer of graphene sheets, the TPD results are consistent with the surface sensitive XPS analysis. TPD measurements were carried out from room temperature up to 2100 °C under high vacuum. XPS and CHN elemental analysis were performed on samples heat-treated at designated temperatures for comparison with TPD measurements. Density functional theory (DFT)-based fragmentation simulations were employed for molecular cluster and periodic boundary models to support the assignment of thermal decomposition processes.

### Results and Discussion

In TPD result, thermal fragmentation followed by desorption of N-containing gases, NH<sub>3</sub>, HCN, and N<sub>2</sub>, was observed in a wide temperature range of 300-1800 °C (Fig. 1b). The nitrogen content calculated from the total amount of desorbed gas was 7.9 wt%, which is in close agreement to the CHN analysis (8.0 wt%) and XPS analysis (8.5 wt%).

Next, the results of the TPD analysis were compared with those of the XPS analysis (Fig. 1c). The XPS spectrum of the sample before the heat treatment was fit using three components: graphitic-N, pyrrolic-N, and pyridinic-N. In the sample heat-treated at 1000 °C, the amount of graphitic-N was almost unchanged, while the amount of pyridinic-N, and pyrrolic-N decreased. Further heat treatment at 1400 °C resulted in an overall decrease in N content and the disappearance of pyrrolic-N. Since NH<sub>3</sub> completely desorbed at around 1400 °C in the TPD measurement, it was suggested that NH<sub>3</sub> was caused by the desorption of pyrrolic-N in the sample. On the other hand, N<sub>2</sub> desorbed at high temperatures above 1400 °C was attributed to graphitic-N. From the detailed analysis, it was concluded that the pyrrolic-N was desorbed as NH<sub>3</sub> and HCN in a temperature range of 300-1200 °C and pyridinic-N was desorbed as HCN and N<sub>2</sub> at around 1000 °C. The thermally stable graphitic-N was desorbed as N<sub>2</sub> in the high temperature region above 1200 °C. DFT-based fragmentation simulations employing molecular cluster and periodic boun-

dary models explains well the experimental TPD results and support the assignment of thermal decomposition processes. These results indicate that the amount of each N-environment can be quantitatively determined from TPD measurements.

Furthermore, TPD analysis was performed on a sample with a very small amount of N content and showed a high quantitative accuracy of the order of 10 ppm (0.001 wt%). On the other hand, 0.1 wt% was the lower limit of detection using XPS and CHN elemental analysis, indicating that TPD analysis can analyze nitrogen with higher sensitivity than conventional methods.

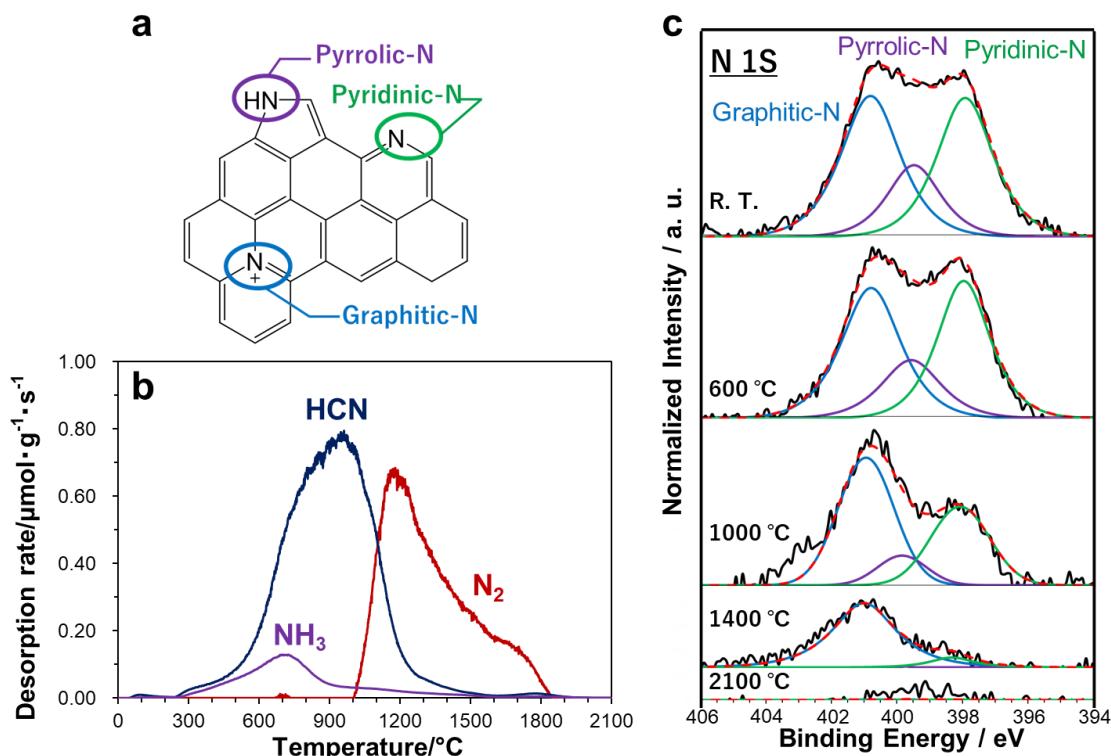


Fig. 1 (a) Nitrogen species in carbon materials. (b) TPD profile up to 2100 °C of N-containing mesoporous carbon. (c) XPS spectra of heat-treated N-doped carbon samples.

## Conclusion

In this study, a high-temperature vacuum TPD measurement method was developed to characterize N species in carbon materials. Three N-containing gases,  $\text{NH}_3$ ,  $\text{HCN}$  and  $\text{N}_2$ , desorbed in the temperature range of 300–1800 °C, and all N species in the material could be determined by this method. Combined with the results of XPS and DFT calculations, the thermal decomposition process to each desorbed gas species was suggested. These results demonstrate that TPD analysis is a promising new method for chemical speciation and quantitative analysis of N species in carbon materials with high sensitivity.

## Acknowledgement:

The AtomDec Consortium is supported by the Visegrad Group-Japan 2021 2<sup>nd</sup> Joint Call on Advanced Materials in cooperation with the International Visegrad Fund. It is funded by the Japan Science and Technology Agency (JST SICORP Grant No. JPMJSC2112 (Japan) and Slovak Academy of Sciences, Slovakia (V4-Japan/JRP/2021/96/AtomDeC). This work is also supported by JSPS KAKENHI Grant no. 20K22459.

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## Monitoring the effect of different conditions on interaction and intercalation between Bovine Serum Albumin and Graphene Oxide system

K. Sajdik<sup>1</sup>, T. Szabó<sup>1\*</sup>

<sup>1</sup> University of Szeged, Department of Physical Chemistry and Materials Science, 6720 Szeged, Rerrich Béla sq. 1.,

\*[sztamas@chem.u-szeged.hu](mailto:sztamas@chem.u-szeged.hu)

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*Keywords: BSA, graphene-oxide, intercalation*

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Recently, the scientific interest of graphene-based materials has been impressive, especially in the medical and pharmaceutical fields. This is no coincidence, as these materials, such as graphene oxide, are promising for medical applications due to their physicochemical properties, such as large specific surface area. Because of this it has huge importance to understand fundamentally the interaction between graphene oxide (GO) and the biomolecules, such as serum albumins.

To our surprise, only a few articles [1][2] are available in the literature that specifically explore the exact types of interactions between bovine serum albumin and graphene oxide in detail including the quantitative characterization. Therefore, at the basic research level, we would like to provide a comprehensive explanation of the interaction effects between BSA and GO. The most common methods employed previously were UV-Vis spectrophotometry in the UV range, Circular Dichroism, Scanning Electron Microscopy, Fluorescence Quenching. These techniques such as CD provide useful information but some other approaches may reveal additional structural characteristics. For example, we also used UV-Vis spectrometry, but using the less misleading Biuret test in the Vis range. We also performed XRD measurements for the analysis of the intercalation of BSA molecules between the GO lamellae, a method we have not seen yet in the literature we reviewed so far. We also measured the zeta potential of the BSA/GO composite.

These measurements were carried out at several pH-s and ionic strength, so we monitored the adsorption properties of GO, the desorption processes of BSA from GO, the size of this composite and the occurring intercalation in different conditions. If we understand this interaction well, and are able to exploit it for the formulation of creams or ointments that exhibit prolonged release of the drug e.g. pain-relieving molecules on GO carriers.

### Acknowledgement:

The project no. 124851 has been implemented with the support provided from the National Research, Development, and Innovation Fund of Hungary (NKFIH), financed under the FK funding scheme. We also thank the support from the ERA-NET COFUND /EJP COFUND Programme with co-funding from the EU Horizon 2020 programme and the NKFIH (project No. 2019-2.1.7-ERA-NET-2021-00029) in the frame of supporting the AtomDec Consortium by the Visegrad Group-Japan 2021 Joint Call on Advanced Materials. Support of the János Bolyai Research Scholarship from the Hungarian Academy of Sciences is also acknowledged.

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## DFT study of defects in graphene

D. Moreno-Rodríguez<sup>1\*</sup>, E. Scholtzová<sup>1</sup>, H. Nishihara<sup>2, 3</sup>

<sup>1</sup> Institute of Inorganic Chemistry, Slovak Academy of Science, Dúbravská cesta 9, 84536 Bratislava, Slovakia

<sup>2</sup> Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai, 980-8577, Japan

<sup>3</sup> Advanced Institute for Materials Research, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai, 980-8577, Japan

(\*) [daniel.moreno@savba.sk](mailto:daniel.moreno@savba.sk)

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*Keywords: defects; DFT; pentagonal, heptagonal and octagonal rings.*

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Graphene is a two-dimensional (2D) material formed by a one-atom-thick planar sheet of carbon atoms packed in a honeycomb-like lattice. Defects in the structure impact the topology, destroying the geometric symmetry and the thermal, mechanical, magnetic, and electrical properties [1]. In addition, some intrinsic defects, like adjacent pairs of heptagonal and pentagonal rings, may appear by rotating a single pair of carbon atoms, known as the Stone-Wales defect (SW) [1]. The present work characterizes modified graphene structures with the SW defect (MG7) and octagonal rings (MG8). It compares them to the pristine graphene (G) structure as the first step for further understanding the implication for properties.

The optimization was performed using density functional theory (DFT-D3) with the PBE functional. The density derived electrostatic and chemical (DDEC6) method [2] was performed for partial charges ( $\delta$ ) and the bond order (BO), the electron localization function (ELF) [3], and Laplacian electron density ( $\nabla^2\rho(r_b)$ ) [4] were suitable to study the topology of the electron density ( $\rho$ ), especially the bonding.

The  $\delta$ s have shown a homogeneity of the  $\rho$  in the G structure. Otherwise, the MG7 model presented a higher accumulation of the  $\rho$  (higher  $\delta^-$ ) in the frontier between the SW defect and the regular 6-rings. In contrast, the depletion of the  $\rho$  (higher  $\delta^+$ ) appeared on the 5- and 7-rings. The 8- and 5-rings in the MG8 model presented an atom with the highest  $\delta^-$  having a depletion of the  $\rho$  in the rest of the defect compared to the neighbours 6-rings. This agrees with the BO, where the bond strength is related to the  $\rho$  shared by the C atoms, as shown by the ELF.

The  $\nabla^2\rho(r_b)$  showed that the  $\rho$  is localized, the stronger the bond is. The 5- and 6-rings presented a more significant  $\rho$  delocalization than the 7- and 8-rings. Besides, between the 5- and 7-ring was the weakest bond, where the  $\rho$  is delocalized towards the inner part of the 5-ring, having a lack of  $\rho$  over the 7-ring area. Whereas, in the model MG8, the strongest bond corresponded to the armchair-bond between the 5-ring and a 6-ring (Fig.1).

The results have shown that the defects in MG7 and MG8 altered the  $\rho$  delocalization, affecting the bonding and likely the electron transfer, causing lower conductivity. However, the localized  $\rho$  in the structure caused by the defects can facilitate the interaction between graphene and other atoms/molecules.

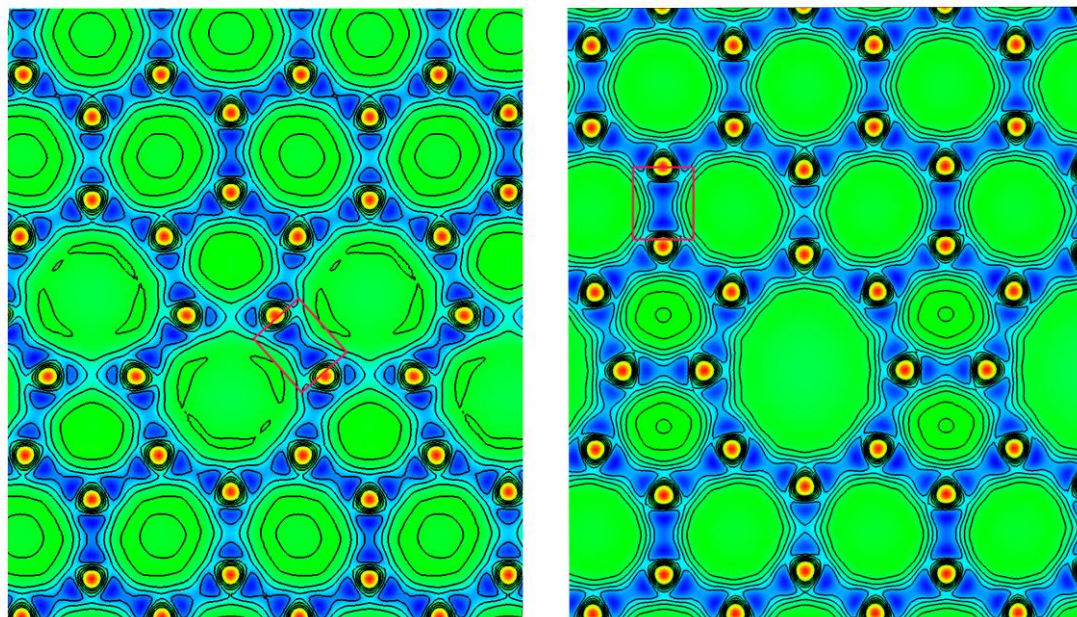


Figure 1. Laplacian of the electron density of the MG7 (left) and MG8 (right), being the electron charge concentrated when  $\nabla^2\rho(r_b) < 0$  (blue) and depleted in  $\nabla^2\rho(r_b) > 0$  (red). The red frame indicates the strongest bonds in the structure.

#### Acknowledgement:

The AtomDec Consortium is supported by the Visegrad Group-Japan 2021 2<sup>nd</sup> Joint Call on Advanced Materials in cooperation with the International Visegrad Fund. It is funded by the Japan Science and Technology Agency (JST SICORP Grant No. JPMJSC2112 (Japan) and Slovak Academy of Sciences, Slovakia (V4-Japan/JRP/2021/96/AtomDeC).

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## “Research capabilities of the IPPT laboratory – mechanical testing with in-situ observation”

K. Bochenek<sup>1\*</sup>, A Jain<sup>1</sup>, M Basista<sup>1</sup>

*Institute of Fundamental Technological Research Polish Academy of Sciences, Division of Advanced Composite Materials, ul. Pawińskiego 5B, 02-106 Warsaw, Poland*

(\*) [kboch@ippt.pan.pl](mailto:kboch@ippt.pan.pl)

*Keywords: Scanning electron microscopy; Micro-mechanical testing*

The Advance Composite Materials Division of Institute of Fundamental Technological Research of Polish Academy of Sciences in the frame of the AtomDeC Project is responsible for mechanical and electro-mechanical testing of manufactured materials. Main aim of this presentation is to show possible solution for mechanical testing of materials manufactured in the scope of AtomDeC Project.

One of the main tasks of our Division within the scope of the Project is to perform mechanical testing of thin carbon foil. In can be done in two different ways. First classical universal testing machine (Zwick/Roell ProLine Z050) can be employed to performed the tests. The observation of microstructure can be done by optical microscope with high speed camera (Keyence VW 9000 +VW-600C). This can be suitable for even small tensile tests specimens, however the maximum force should be at level of few hundreds of Newtons, which can be too high for thin carbon foils.

Second possible device to perform mechanical (and electro-mechanical) tests is Kammrath-Weiss Tensile-Compression Module that can be also fitted under SEM chamber, and the test can be performed under in-situ SEM observation. Here, two types of load cells are available - 50N and 5kN. Device can be also equipped with dedicated grippers for thin foils. Figure 1a presents device mounted inside SEM chamber, Fig. 1b shows the tensile test specimen under SEM (the nominal dimension of necking is 4 mm). Fig. 2 presents specimens – the thickness is approx. 100  $\mu\text{m}$ . The device can also work outside SEM chamber, and can be adopted to perform testing electro-mechanical properties.

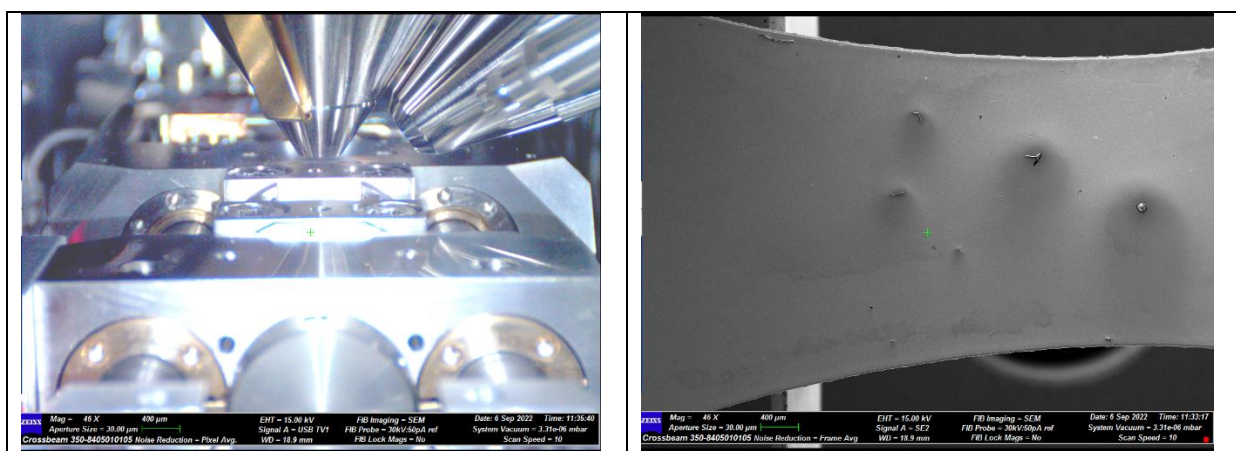


Fig.1. a) Testing device inside SEM chamber. b) SEM image of tensile test specimen.

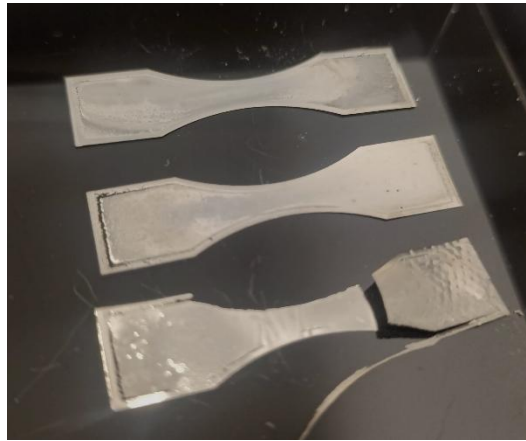


Fig. 2. Photo of specimens for tensile tests under SEM in-situ observation.

Besides the Project scope, our Division is specialized in sintering of composite materials and metal matrix composites by hot-pressing. For example chromium with aluminium oxide (material for valve seats) [1], nickel aluminide with rhenium admixture (high-temperature application) [2], FGM's based on AlSi and Al<sub>2</sub>O<sub>3</sub> for break discs [3]. Moreover, in our Department we are facing with modelling and calculation of mechanical properties of materials e.g. Young modulus [4], thermal properties [5] and determining the fracture mechanisms in composite materials [6].

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## Dispersibility of 3D graphene nanostructures in organic media

P. Nagy<sup>1</sup>, T. Szabó<sup>1\*</sup>

<sup>1</sup>Department of Physical Chemistry and Materials Science, University of Szeged, Aradi vértanúk tere 1, Szeged 6720, Hungary  
(\*)[sztamaz@chem.u-szeged.hu](mailto:sztamaz@chem.u-szeged.hu)

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*Keywords: graphene mesosponge, dispersion stability, organic media*

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In the past decades carbonaceous materials drawn a significant interest in materials science due to their outstanding electrochemical properties. This emerging field of research becomes more and more popular with the urgent need of high performance energy storage devices. One of the most relevant class of this materials is the graphene based materials because of their abundance, low cost and environmental effect. The graphene mesosponge (GMS), a new 3 dimensioned graphene based nanostructure has been considered as promising material for energy storage devices because of its huge surface area, oxidation resistance, and chemically pure graphene-like surface<sup>1,2,3</sup>. This material was chosen as a candidate for investigating of the dispersibility of hydrophobic carbons in non-aqueous media. Firstly, turbidity measurements were carried out, to determine the velocity of sedimentation. The polarity of the organic liquids wasn't related directly with the sedimentation rates and the majority of the settling rates in these dispersions followed the Stokes equation.

Afterwards, ultrasonic treatment was used to break down the particles to colloid size. To determine the average particle size, dynamic light scattering was used. Furthermore, in presence of electrolytes coagulation was observed, which confirms the assumption that electrostatic stabilization is also the main driving force of colloid stability in the studied organic solvents. For selected dispersions, the kinetics of the aggregation was measured as a function of electrolyte concentration. Based on the hydrodynamic size, critical coagulation concentrations and the dispersed weight fractions, we make recommendations for the most appropriate media towards stabilization of GMS particles for various applications.

### Acknowledgement:

The project no. 124851 has been implemented with the support provided from the National Research, Development, and Innovation Fund of Hungary (NKFIH), financed under the FK funding scheme. We also thank the support of the NKFIH (project No. 2019-2.1.7-ERA-NET-2021-00029) in the frame of supporting the AtomDec Consortium by the Visegrad Group-Japan 2021 Joint Call on Advanced Materials. Support of the János Bolyai Research Scholarship from the Hungarian Academy of Sciences is also acknowledged.

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# Underpinning Factors for Structural Evolution of Graphene-Based Nanocarbons up to 1800 °C

K. Pirabul<sup>1</sup>, Z.-Z. Pan<sup>2</sup>, and H. Nishihara<sup>1, 2</sup>

<sup>1</sup> Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi, 980-8577, Japan.

<sup>2</sup> Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi, 980-8577, Japan.

(\*) kritin.pirabul.p7@dc.tohoku.ac.jp

**Keywords:** Carbon; Stacking interactions; Thermal stability

High-temperature annealing (~1800 °C) is often used to modulate the structures and properties of graphene-based nanocarbon materials. It can enhance the crystallinity and eliminate the O- and H- terminal functional groups at the same time. However, most nanocarbons, including, fullerene (C<sub>60</sub>), carbon nanotubes (CNTs), and nanoporous carbon encounter severe structural change at such a high temperature [1-3]. In this work, we elucidated the crucial structural factors that determine the thermal stability of graphene-based nanocarbon materials.

We defined the structure retention degree (SRD) based on the change in the basal plane surface area of nanocarbons when they are subjected to heat treatment at 1800 °C. The larger the amount of graphene-stacking structure becomes, the lower the SRD becomes. SRD can be used as a measure of the thermal stability for very different graphene-based structures compared with traditional methods such as X-ray diffraction and Raman spectroscopy. Additionally, we differentiated two types of stacking structures, including, tight stacking and loose stacking. The tight stacking is formed by the bottom-up growth of graphene during the chemical vapor deposition process, whereas the loose stacking is generated by capillary shrinkage after template removal. As a result, we found that loosely stacked structures triggered extra stackings *via* the epitaxial effect at high temperatures (Figure 1). Moreover, we demonstrated that the threshold of the inner space size that triggers the thermal-induced structural change is about 4-7 nm.

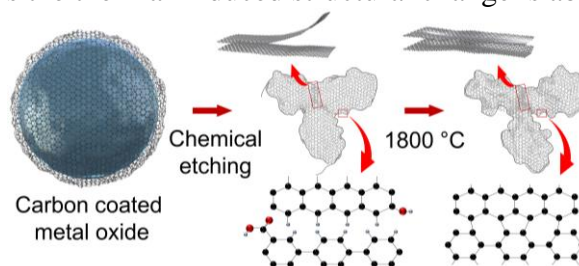


Figure 1 The structural change of templated nanocarbon. The red square shows loose stacking.

## Acknowledgment:

This work was supported by JSPS KAKENHI Grant no. 21K18862; the “Five-star Alliance” in “NJRC Mater. & Dev.”; Japan Association for Chemical Innovation; JST SICORP Grant no. JPMJSC2112. We thank Sasol Chemical Japan, Shiraishi Kogyo Kaisha, Ltd., and Kuraray Col, Ltd. for kindly providing SBa-200&MG70, SK-I, and YP-50F, respectively.

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## Preparation and properties of photocatalysts based on g-C<sub>3</sub>N<sub>4</sub> nano/AgIO<sub>3</sub>

J. Pavlovský<sup>1\*</sup>, P. Bančíková<sup>1</sup>, M. Michalska<sup>1</sup>, V. Matějka<sup>1</sup>, S. Vallová<sup>1</sup>, M. Ritz<sup>1</sup>, G. Simha Martynková<sup>2</sup>

<sup>1</sup> Department of Chemistry and Physico-Chemical Processes, Faculty of Materials Science and Technology, VŠB-Technical University of Ostrava, 17. listopadu 2172/15, 708 00 Ostrava-Poruba, Czech Republic

<sup>2</sup> Energy Research Centre, CEET, VŠB-Technical University of Ostrava, 17. listopadu 2172/15, 708 00 Ostrava-Poruba, Czech Republic

(\*) [jiri.pavlovsky@vsb.cz](mailto:jiri.pavlovsky@vsb.cz)

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*Keywords: AgIO<sub>3</sub>; g-C<sub>3</sub>N<sub>4</sub> nano; structural analysis and photodegradation*

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In this work, individual materials (g-C<sub>3</sub>N<sub>4</sub> bulk, g-C<sub>3</sub>N<sub>4</sub> nano, AgIO<sub>3</sub> and AgIO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> nano type composites with different percent of AgIO<sub>3</sub> (2.0 wt%; 3.9 wt%; 7.4 wt%; 10.7 wt% and 14.4 wt%) were prepared. AgIO<sub>3</sub> was prepared by precipitating KIO<sub>3</sub> and AgNO<sub>3</sub> solutions added to the g-C<sub>3</sub>N<sub>4</sub> nano followed by a sonification process. All these original composites were analyzed using several methods as photoluminescence spectroscopy (PL), UV-Vis diffuse reflection spectroscopy (DRS UV-Vis), infrared spectroscopy (IR), thermal gravimetric analysis (TGA) and X-ray powder diffraction (XRD). As a supplemented method, photodegradation experiments on model dye acid orange 7 (AO7) under UVA irradiation at 368 nm was used. The best composite of 10.7 wt% AgIO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> nano was found, while the highest efficiency in terms of photodegradation activity on AO7 dye (about 94 %) at 2 hours after UVA exposure (368 nm) was determined. This material exhibited interesting optical-electronic properties. The indirect band gap values of x wt% AgIO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> nanomaterials increased from 2.83 to 2.85 eV with increasing AgIO<sub>3</sub> content. A low intensity in the PL spectra is observed for composites with 2.0; 3.9 and 10.7 wt% AgIO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> nano. IR and XRD spectroscopy confirmed the presence of characteristic bands and diffraction lines. With the increasing amount of AgIO<sub>3</sub> in these composites, it was determined that a decrease in mass changes (TGA) in the temperature range of 425-630 °C and in the range up to 200 °C were observed. On the contrary, in the temperature range of 300-400 °C these mass changes increase slightly. These materials based on AgIO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> nano appear to be very interesting from the point of view of photodegradation activity on different types of dyes as pollutants in wastewater or their further use for the preparation of electrodes. The preparation of these photocatalyst materials was relatively simple and environmentally friendly and brings about other possibilities of use.

### Acknowledgement:

This work was financially supported by the Ministry of Education, Youth and Sports, Czech Republic (contract no. 8F21007) through the research project cooperation between the AtomDeC Consortium (V4-Japan/JRP/2021/96/AtomDeC) by funding received from the Visegrad group(V4)-Japan 2021 2nd Joint Call on "Advanced Materials".

## Thermal treatment processing of melamine precursor for preparing graphitic carbon nitride materials – theoretical calculations

P. Škorňa<sup>1\*</sup>, E. Scholtzová<sup>1</sup>, M. Michalska<sup>2</sup>

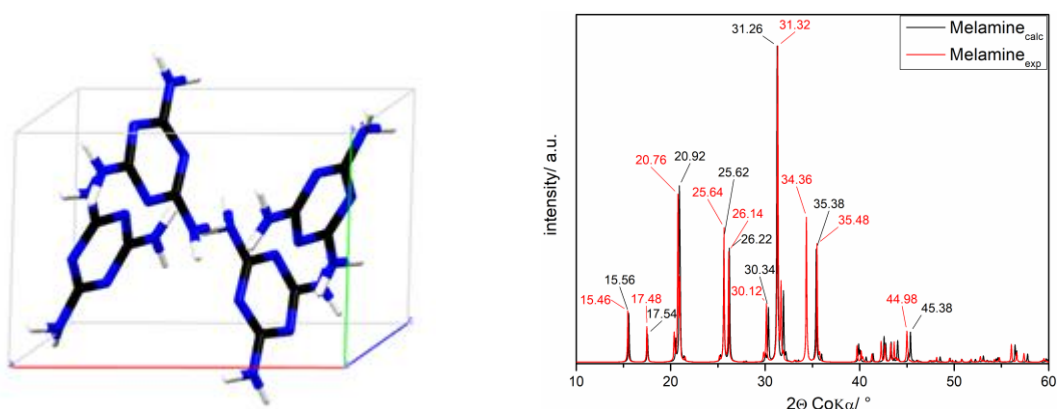
<sup>1</sup> Institute of Inorganic Chemistry of Slovak Academy of Sciences, Dúbravská cesta 9, Bratislava 84536, Slovakia

<sup>2</sup> Department of Chemistry and Physico-Chemical Processes, Faculty of Materials Science and Technology, VŠB-Technical University of Ostrava, 17. listopadu 2172/15, 708 00 Ostrava-Poruba, Czech Republic

(\*) [peter.skorna@savba.sk](mailto:peter.skorna@savba.sk)

**Keywords:** graphitic carbon nitride, DFT-D3 method, XRD pattern

Melamine (2,4,6-triamino-s-triazine) represents an important starting material for several industrial applications. It is used, for example, in the syntheses of melamine-formaldehyde resins or fireproof materials [1, 2], for the architecture of supramolecular structures, assemblies built up by cyanuric acid or melamine derivatives [3–5]. In the past few years, another interest arose in melamine and other compounds containing triazine rings because these are considered suitable molecular precursor compounds for synthesising graphitic forms of carbon nitride, g-C<sub>3</sub>N<sub>4</sub> [6]. In most of the postulated structures of g-C<sub>3</sub>N<sub>4</sub>, s-triazine ring systems are linked through trigonal N atoms forming extended 2D sheets. Another possible building block for g-C<sub>3</sub>N<sub>4</sub> was tri-s-triazine rings C<sub>6</sub>N<sub>7</sub>, which are cross-linked by trigonal N atoms [7–9].



**Fig. 1** DFT-D3 optimised structure (left), and calculated and experimental XRD pattern of melamine (right)

Among various analogues, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) constructed via tri-s-triazine units is considered the most stable allotrope in the environment. It is defined by various exciting properties such as reliable chemical and thermal endurance, super hardness, low density, wear resistance, water resistivity and biocompatibility [10]. Moreover, thermal gravimetric analysis and thermal gravimetric on g-C<sub>3</sub>N<sub>4</sub> indicate that the as-prepared g-C<sub>3</sub>N<sub>4</sub> is non-volatile up to as high as 600°C and will be almost completely decomposed until the temperature rises to 700°C [10].

The main aim of this work is to help analyse the experimental XRD patterns of the synthesised products in the g-C<sub>3</sub>N<sub>4</sub> preparation by applying the DFT method (Density functional theory) involving the dispersion corrections according to the D3 scheme.

**Acknowledgement:**

The AtomDec Consortium is supported by the Visegrad Group-Japan 2021 Joint Call on Advanced Materials in cooperation with the International Visegrad Fund. It is funded by Ministry of Education, Youth and Sports, Czech Republic (contract no. 8F21007) and Slovak Academy of Sciences, Slovakia (V4-Japan/JRP/2021/96/AtomDeC).

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## Preparation of composite g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> by thermal hydrolysis of titanyl sulphate in a presence of graphitic carbon nitride

V. Matejka<sup>1\*</sup>, J. Valousek<sup>1</sup>, M. Michalska<sup>1</sup>, J. Pavlovsky<sup>1</sup>, K. Foniok<sup>1</sup>

<sup>1</sup> Department of Chemistry and Physico-Chemical Processes, Faculty of Materials Science and Technology, VŠB-Technical University of Ostrava, 17. listopadu 2172/15, 708 00 Ostrava-Poruba, Czech Republic

(\*) [vlastimil.matejka@vsb.cz](mailto:vlastimil.matejka@vsb.cz)

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**Keywords:** g-C<sub>3</sub>N<sub>4</sub>; TiO<sub>2</sub>, Rhodamine B, photocatalyst

The thermal hydrolysis of titanyl sulphate (TiOSO<sub>4</sub>) in the presence of bulk graphitic carbon nitride was used for preparation of g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composites. Bulk graphitic carbon nitride was prepared by the thermal polymerization of melamine at 550°C. The amount of TiOSO<sub>4</sub> used for hydrolysis varied with the aim to progressively increased the TiO<sub>2</sub> content (10, 25 and 50 wt.%) in final composites. The samples prepared by the hydrolysis were further thermally treated at 400, 450, 475, 500 and 525°C in a muffle furnace. The prepared samples were characterized using scanning electron microscopy coupled with energy dispersive analysis, phase composition of the samples was revealed using X-ray diffraction method, specific surface area of the samples was measured using BET method. Other characterization techniques included Fourier transform infrared spectroscopy and thermal analysis. Optical band gap of the composites was evaluated using Tauc approach from registered and transformed UV-VIS DRS spectra. The photodegradation activity of prepared composites was tested by the degradation of Rhodamine B (RhB) under 2 h long irradiation with UV or VIS light of wavelengths 368 and 420 nm, respectively. The SEM images revealed the TiO<sub>2</sub> are present in a form of envelope around the g-C<sub>3</sub>N<sub>4</sub> particles. The elemental analysis revealed decreasing tendency of the carbon and nitrogen content and together with the values of yields of the calcination products confirm the decomposition of g-C<sub>3</sub>N<sub>4</sub> in the presence of TiO<sub>2</sub> if heated above the temperature 450°C. The prepared g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composites exhibit promising alternative to pure TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> photocatalysts.

### Acknowledgement:

This work was financially supported by the Ministry of Education, Youth and Sports, Czech Republic (contract no. 8F21007) through the research project cooperation between the AtomDeC Consortium (V4-Japan/JRP/2021/96/AtomDeC) by funding received from the Visegrad group(V4)-Japan 2021 2nd Joint Call on “Advanced Materials”.





