



3rd Annual Meeting of AtomDeC

23rd-25th May, 2023

IPPT PAN, Warsaw, Poland

**AtomDeC: Atomic Design of Carbon-Based Materials for
New Normal Society**



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POLISH ACADEMY OF SCIENCES**

3rd Annual Meeting of AtomDeC
Atomic Design of Carbon-Based Materials for New Normal Society

BOOK OF ABSTRACTS

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3RD ANNUAL MEETING - ATOMDEC WARSAW POLAND

Date: 23rd May 2023

Time: 9:00 to 17:00

Venue: Wacław Olszak Auditorium, Floor II, IPPT PAN

Time	Title of the talk	Speaker
9:00-9:30	<i>Registration</i>	
9:30-9:45	<i>Opening and Introduction</i>	Amrita Jain
9:45-10:45	Progress in atomic-level analysis and synthesis of sp ² -carbon materials	Hiroto Nishihara
10:45-11:15	<i>Coffee Break</i>	
11:15-12:15	Carbon as catalyst, catalyst support and catalyst promoter for oxygen reduction reaction	Diego Cazorla-Amorós
12:15-13:30	<i>Lunch</i>	
13:30-14:00	TMO nanorods for supercapacitor application	Amrita Jain
14:00-14:30	Influence of temperature and atmosphere conditions on synthesis of g-C ₃ N ₄ compounds – properties and photocatalytic applications	Monika Michalska
14:30-15:00	<i>Coffee break</i>	
15:00-15:30	Adsorption properties of carbon-based materials studied by the DFT method	Eva Scholtzova
15:30-16:00	Swellable multi-layered graphene oxide structures: comparing solvation of the their powders vs. thin-film structures	Tamas Szabo
16:00-17:00	<i>Free discussion</i>	

3RD ANNUAL MEETING – ATOMDEC WARSAW POLAND

Date: 24th May 2023

Time: 9:00 to 17:00

Venue: Waclaw Olszak Auditorium, Floor II, IPPT PAN

Time	Title of the talk	Speaker
9:45-10:00	<i>Session Information</i>	
10:00-10:15	The calcination temperature effect on properties of g-C ₃ N ₄ /TiO ₂ composites	Vlastimil Matejka
10:15-10:30	Processing and mechanical properties of bulk GMS/AlSi composite via hot-pressing	Kamil Bochenek
10:30-10:45	Thermal treatment of melamine precursor for preparing graphitic carbon nitride materials – theoretical study	Peter Škorňa
10:45-11:15	<i>Coffee break</i>	
11:15-12:15	Examples of Intercalated 2D Materials	Siegfried Eigler
12:15-13:30	<i>Lunch</i>	
13:30-13:45	Colloidal synthesis of graphene composites for advanced Li-S batteries	Peter Nagy
13:45-14:00	A theoretical study of the corrugation of graphene oxide structure	Daniel Moreno Rodriguez
14:00-14:30	<i>Coffee Break</i>	
14:30-14:45	Multi-functional ordered carbonaceous frameworks synthesized from octaethynyl metalloporphyrin	Koki Chida
14:45-15:00	Interaction of graphene oxide with cationic biomolecules	Kadosa Sajdik
15:00-15:15	Cr ₂ O ₃ /ZnO composites – preparation, characterization and their potential utilization as photocatalysts	Jiří Pavlovský
15:15-15:30	Quantitative study on unpaired electrons in carbon edge sites	Keigo Wakabayashi
15:30-17:00	<i>Open discussion</i>	
18:00	<i>Conference dinner and short walk in city center</i>	
25th May 2023		
9:00-12:00	Open discussion, check out and lab tour	

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Progress in atomic-level analysis and synthesis of sp^2 -carbon materials

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Keywords: Temperature-programmed desorption, Single-layer graphene, Energy storage

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. Fig. 1 illustrates the outline of the AtomDeC project. Work Package 1 (WP1) led by Japan team synthesizes advanced carbon-based materials and has reported the progress in ordered carbonaceous frameworks[1, 2], molecular-based porous materials[3, 4], and graphene mesosponges[5, 6]. WP2 led by Czech team synthesizes composite materials and has reported Ag/TiO₂ composites[7] and gC₃N₄-based materials[8]. Hungary team leads WP3, oversees colloidal systems and analytics, and has reported water purification[9] and sustainable material synthesis[10]. Slovakia team leads WP4 with an external collaborator, Dr. Szilagyi, for modeling and theoretical calculations. Poland team leads WP5 for electrochemical applications and devices. Through the intimate collaborations among the five WPs, we have published many joint papers by the collaborations in WP1&4[11, 12], WP2&5[13], and WP1&2[14].



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

In this talk, the progress in atomic-level analysis and synthesis of sp^2 -carbon materials will be illustrated. Conventionally, many researchers have used X-ray diffraction (XRD) and Raman spectroscopy to evaluate the crystallinity and the number of defects in carbon material. However, the results obtained by XRD and Raman spectroscopy often cannot predict the performances of carbon materials. Why? As for XRD, the “crystallinity” means how the carbon structure is close to graphite or well-stacked turbostratic carbons. In other words, XRD is useful only for carbon materials with graphene-stacking structures. For example, single-walled carbon nanotubes and single-layer graphene cannot properly be evaluated by XRD: XRD predicts that these carbons are amorphous or poorly crystalline from the absence of carbon 002 peaks. However, these materials have good electric conductivity as well as chemical stability. As for Raman spectroscopy, many people know that D-band is derived from “defects” of sp^2 -carbon structure. However, what is the “defect”? There are actually two different types of defects: carbon edge site and basal defects, such as carbon pentagons and heptagons[12]. The latter is chemically more stable than the former. Raman spectroscopy cannot distinguish these different defect types. Thus, it has been difficult to precisely predict the conductivity

and chemical stability of carbon materials from XRD and Raman spectroscopy. To overcome this matter, we propose advanced temperature-programmed desorption (TPD) up to 1800 °C. By heating carbon samples up to 1800 °C, all edge sites terminated by oxygen-functional groups and hydrogen are decomposed into CO, CO₂, H₂O, and H₂ gases. From the total gas emission amount, we can obtain an important structural parameter, the total number of carbon edge sites (N_{edge} [mol/g]). N_{edge} is directly related to the chemical stability of carbon materials [15, 16]. Moreover, the average graphene-domain size (L_{TPD}) can be calculated from N_{edge} . L_{TPD} is directly related to electrical conductivity. Thus, the advanced TPD can complement the carbon characterization. Moreover, we have developed a new TPD system that enables qualitative and quantitative analysis of nitrogen species embedded in carbon materials with extremely high sensitivity (10-ppm-level detection is possible).

By utilizing the advanced TPD, we have developed highly porous and edge-site-free graphene mesosponge (GMS) materials [16]. GMS is synthesized by a hard-templating method using Al₂O₃ [16] or MgO [17] 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 m²/g) and a large pore volume (> 3 cm³/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 [18]. 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 (Et₃MeN/BF₄), which surpasses single-walled carbon nanotubes [19]. Also, GMS is useful for Pt support of polymer-electrolyte fuel cells [20] and as a cathode of lithium-oxygen batteries [12]. We have shared the GMS materials in the AtomDeC project and are trying to develop new applications, new composite materials, and new devices.

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Carbon as catalyst, catalyst support and catalyst promotor for oxygen reduction reaction

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Carbon materials exhibit unique properties that make them useful in an extraordinary large number of technological applications. The unique (and different) properties that can be found for carbon materials are due to their diversity in structure. From the structure point of view, and focusing only on sp² carbon materials, materials with long-range and short-range orders can be found what explains the large family of carbon materials. The second factor that determines the properties of the carbon materials is the surface chemistry, which is determined by the concentration of intrinsic defects and the presence of heteroatoms. Then, the combination of both structure and surface chemistry results in an enormous collection of materials with properties that can be tailored for many different applications. Among the different applications of carbon materials their use in industrial catalytic processes is very well known for more than 100 years. Recently, the development of electrochemical energy storage and production devices has impressively raised the interest in carbon materials. In this field, the role of carbon materials as catalyst or catalyst support is outstanding and strong research and technology development efforts are being done in order to optimize the performance of electrochemical technologies, which are still far from industrial requirements. In the specific application of energy generation through fuel cells or metal-air batteries, one important limitation is the oxygen reduction reaction (ORR) which occurs in the cathode due to the sluggish kinetics of the reaction. This requires the use of high amounts of precious metals that impede the deployment of the technology. In this sense, research on new catalysts either based on metal-free carbon materials or non-precious metal-based catalysts are subject of strong research trying to find catalysts that can substitute precious metals. Carbon materials, due to their unique properties, may have different roles in the ORR and they can be catalyst, catalyst support and promoter of catalytic activity. In this talk, we will present examples of the three mentioned functions of the carbon materials in ORR, that will show the great interest in designing at the nanoscale the structure and chemical composition of the material to boost the catalytic properties.

TMO nanorods for supercapacitor application

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Keywords: Supercapacitors; TMO material; Polymer gel electrolyte

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. 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].

Recently, transition metal oxides such as Co_3O_4 , MnO_2 , TiO_2 , Fe_3O_4 , WO_3 , NiO , V_2O_5 etc [3] have gained attention towards electrode materials in supercapacitors due to their high specific capacitance and energy density. Specially due to the high abundance, variable oxidation states and cost effectiveness, V_2O_5 is prone to be a promising electroactive redox material. Thanks to the high theoretical capacity (440 mAh g^{-1}) arising from multi-valence properties of V_2O_5 to form not only a multi-step faradaic process, but also different morphologies and crystal structures. Although researchers have focused on developing pseudocapacitive materials from their high specific capacitance obtained by faradaic reactions, their low electrical conductivity and cyclic stability are still the main challenges facing them.

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 the electrodes. It has been found out that vanadium oxide nanorods using ethylene glycol as a chelating agent gave best electrochemical results and hereon refers as VO@03. Fig. 1a shows the TEM image of VO@03. As can be seen from the figure nanorods has been created and also the morphology confirms the porous nature of material.

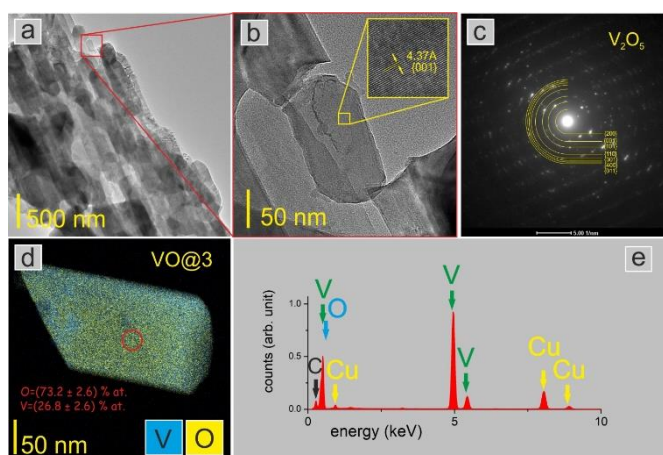


Fig 1. a) TEM image of VO@3, b) a single nanograin with an inset showing the crystalline structure of the grain. c) an electron diffraction pattern, analysis confirmed the orthorhombic structure for all samples. d) EDX map of a single VO@3 nanograin, e) EDX spectra collected from the area of the red circle marked on the grain in figure d). The presence of Cu and C is related to the substrate, a carbon film supported on a copper grid.

In order to check the material for supercapacitor application, galvanostatic charge-discharge was carried out and is shown in Fig 2 at a current density of 0.5 mA cm⁻². The non-linear pattern of the curves confirms the redox-nature of cell. The capacitance value is found to be of the order of ~137.6 F g⁻¹ with power density of ~ 2.3 kW kg⁻¹ and energy density of ~ 19.1 Wh kg⁻¹.

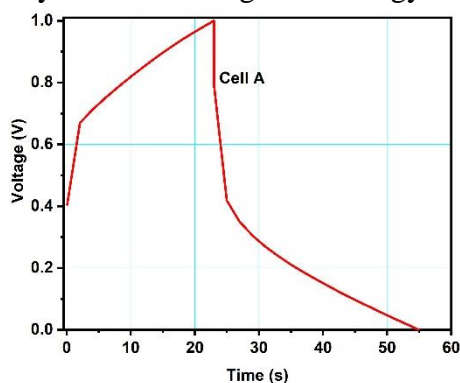


Figure 2: GCD curve of supercapacitor cell

Acknowledgment

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Influence of temperature and atmosphere conditions on synthesis of g-C₃N₄ compounds – properties and photocatalytic applications

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Keywords: melam; g-C₃N₄; photocatalysts

The purpose of this work is to obtain graphitic carbon nitrides compounds from melamine, which involves 30 min long thermal treatment of this g-C₃N₄ precursor in nitrogen or air flow at 400 – 550°C. The effect of the increasing temperature and atmosphere of the as-synthesized materials is examined for the degradation of the model acid orange 7 dye under UV (360 nm) or VIS (420 nm) light irradiation. The as-synthesized powders were characterized using pivotal techniques such as: elemental analysis, X-ray powder diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL), and UV-Vis diffuse reflection (UV-Vis DRS) spectroscopy. Additionally, the experimental part of the work was supported by the theoretical calculations such as Density Functional Theory (DFT) method.

During the presentation, it will be showed a novel approach to the development of g-C₃N₄-based materials, demonstrating that created organic composites with lower temperatures displayed the highest photocatalytic properties, allowing us to save time, energy, and money on the manufacturing of a high-quality photocatalyst.

Acknowledgement:

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Adsorption properties of carbon-based materials studied by the DFT method

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Keywords: carbon-based material, adsorption, DFT

Immobilisation and disabling of organic pollutants (P) from the environment have become the subject of study in recent years due to their detrimental effect on our health. In addition, the properties of advanced materials based on carbon materials - CBM (graphene, graphene oxide) are a hot topic due to the use of these materials in the newest technologies, e.g., in wastewater treatment or green technologies. For example, more than 600 drugs were identified in the waters of different world areas.

Graphene (G), 2D carbon layered structure with excellent mechanical properties and electronic conductivity, was used, e.g., for gas adsorption. Modifying G to the graphene oxide (GO) or by the presence of defects improves its adsorption ability of pollutants.

The complementary approaches involving computational simulations are essential for obtaining a better overview of the structure and properties of these materials and elucidating relations among the structure, composition and properties. Nowadays, the structural, physicochemical, or mechanical properties are intensively studied by the density functional theory (DFT) methods on the materials mentioned above.

Our workgroup within the AtomDeC Consortium also studies the adsorption ability of CBM synthesised experimentally in other workgroups. For example, the adsorption ability of graphene modified by 5- and 7-membered rings as defects for methylene blue was studied by periodic modelling to add complementary information for the Japanese, Czech and Polish co-workers. Further, the structural models for GO adsorption of benzethonium chloride were proposed for the Hungarian workgroup of our Consortium.

The adsorption energies as a measure of the structural stability of P-CBM complexes and their respective mutual interactions were studied in detail.

Acknowledgement:

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Swellable multi-layered graphene oxide structures: comparing solvation of the their powders vs. thin-film structures

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Keywords: graphite oxide; structural expansion; intercalation; solvation

Graphene oxide (GO) is the most prominent functionalized graphene derivative. A remarkable property of GO is easy hydration/solvation by vapours or liquids^[1], which results in expansion of interlayer distance. Intercalation of GO powders using liquid solvents is rather rapid and typically saturates within minutes. Likewise, the rate limiting process of solvent take-up upon imminent contact with vapours is the progressive saturation of the atmosphere with the vapour and not the insertion of its molecules into the interlayers of graphite oxide. The present structural study^[2] shows that the GO membranes are not always demonstrating the same hydration/solvation properties as precursor graphite oxides. Certain types of membranes exhibit unique hydration/ solvation properties, not found in precursor graphite oxide powders (Figure 1). In particular, both GO membranes and graphite oxides are hydrated very similarly in pure water, but insertion of ethanol and methanol into the GO membrane structure is hindered, being limited to one monolayer while in the graphite oxide powders up to 3–4 layers of these solvents can be inserted. Remarkable temperature and pressure dependent swellability features of these different microstructures will also be discussed. The tunable solvation/layer expansion properties of graphene-based membranes are relevant for various materials science applications including particle synthesis in the interlayers or membrane separation of solutes by size exclusion mechanisms.

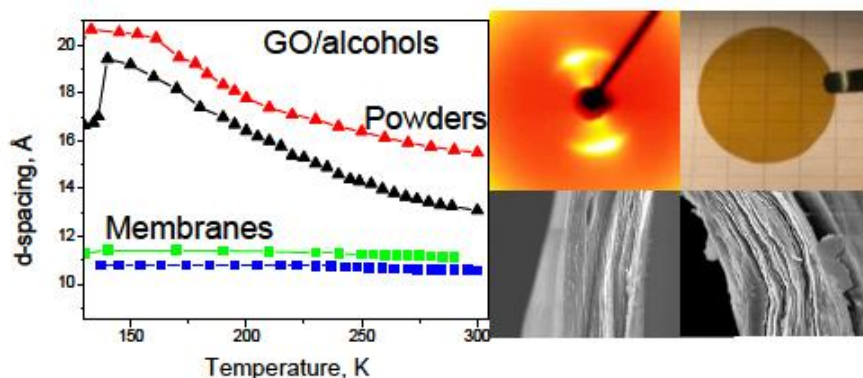


Figure 1 Left: The temperature-dependence of the basal spacings of powdered vs membrane samples of GO immersed in alcohols. Right: X-ray diffraction image and visual and electron microscopic appearance of a GO membrane.

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The calcination temperature effect on properties of g-C₃N₄/TiO₂ composites

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Keywords: g-C₃N₄/TiO₂ composite, characterization, photocatalysis

The composites g-C₃N₄/TiO₂ prepared using: i) co-calcination of TiO₂ + g-C₃N₄ mechanical mixture, and ii) thermal hydrolysis of TiOSO₄ in the presence of bulk g-C₃N₄ were subjected to calcination at selected temperatures. The loss on weight and TG analysis were used to evaluate the thermal stability of the composites. Obtained samples were further characterized using SEM technique, X-ray powder diffraction method and FTIR analysis. Specific surface area of the samples was measured using physisorption of nitrogen, optical band gap energies of the samples were evaluated using Tauc approach. Comparison of the effect of adopted procedures of g-C₃N₄/TiO₂ preparation on their photodegradation activity was performed using photodegradation of rhodamine B under VIS light. The photodegradation mechanism was evaluated based on the photodegradation experiment in the presence of scavengers.

Acknowledgement:

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Consolidation of GMS powder with aluminium via hot-pressing – processing and mechanical properties

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Keywords: Scanning electron microscopy; Micro-mechanical testing

The GMS powder provided by Advanced Institute for Materials Research (AIMR), Tohoku University (TU), Sendai, Tohoku, Japan was a substrate to produce bulk AlSi-GMS composite through hot-pressing technique. The powder of AlSi (NewMetKoch, 99% purity) and GMS were manually mixed, as a trial batch, and consolidated via hot-pressing. The process was performed in the following parameters: temperature of 600°C, pressure of 30MPa, and heating speed of 10°C/min. The process was conducted under a vacuum atmosphere. The material was examined via SEM (Fig. 1) and compressed on Zwick Z050 Universal Testing Machine (SEM images after compression Fig. 2).

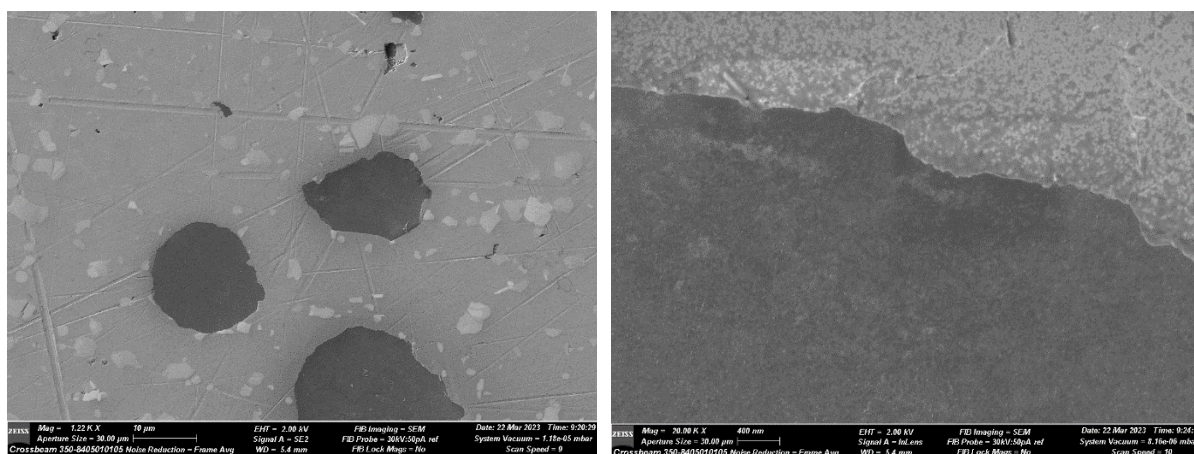


Fig 1 . SEM images of AlSi-GMS sintered via hot-pressing

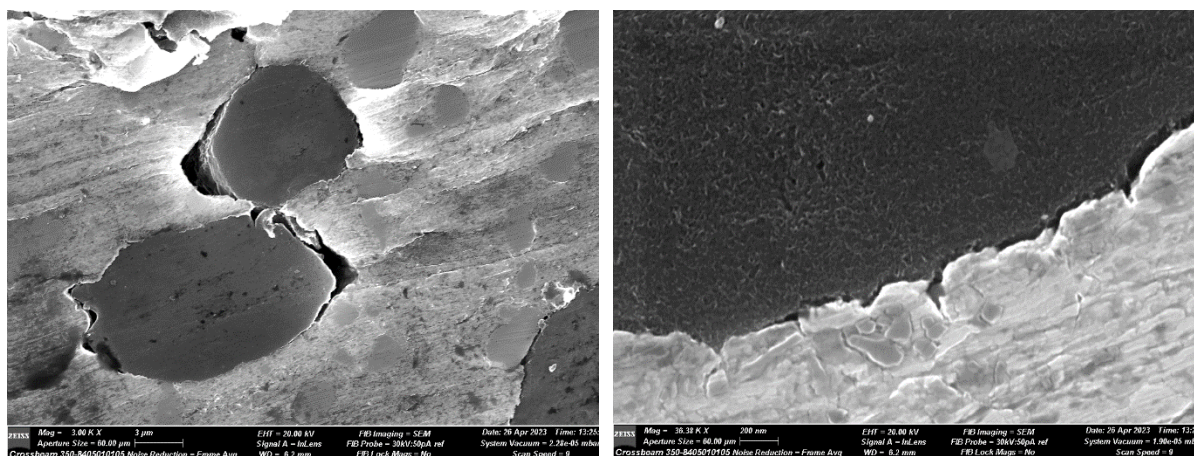


Fig 2. SEM images of AlSi_GMS composite after compression test.

The pressure during compression tests exceeds 900 MPa. The post-experiment SEM examination shows, that GMS powder sustain the high pressure during compression, even if the interface between AlSi matrix and GMS powder is damaged. This results encourage to use GMS powder as a reinforcement for different metal matrix composite produced through hot-pressing (ex. copper or silver based).

Acknowledgment:

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Thermal treatment of melamine precursor for preparing graphitic carbon nitride materials – theoretical study

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Keywords: hydrogen bond interactions, UV-Vis calculations, carbon materials

Graphitic carbon nitride (g-C₃N₄) stands for a remarkable class of materials. It has attracted tremendous attention because of its unique properties, metal-free nature, and facile synthesis from inexpensive nitrogen-rich organic precursors [1-3]. Moreover, it reveals photocatalytic activity, both as pristine powder and as a nanocrystalline film in a heterojunction photocathode [4–6]. Polymeric g-C₃N₄ consists of heptazine-based melon chains that are elegantly assembled in a zigzag fashion and tightly linked by hydrogen bonds to form a 2D planar array [7, 8].

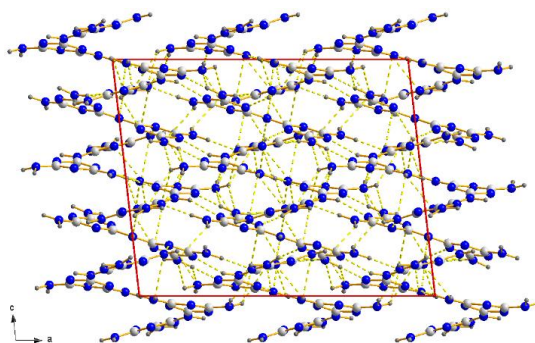


Figure 1 Hydrogen bond interactions in the crystal structure of melam.

The presented work continuously follows recent research on synthesising and preparing g-C₃N₄ by thermal treatment of the melamine precursor. The main aim of this work is to study the mutual interactions of the intermediates (melamine, melam, melem and melon) by applying the Density functional theory (DFT) method involving the dispersion corrections according to the D3 scheme implemented in the Vienna ab initio simulation package (VASP). Further, the calculated UV-Vis spectra of the respective intermediates were analyzed and compared with experimental measurements.

One of the essential parameters for studying of this carbon material are hydrogen bond (HB) interactions (Figure 1) among its intermediates [9]. The corresponding results are summarized in Table 1 and show the minimal, median and maximal distances of analysed HB interactions. The strongest interactions were identified in the crystal structure of melon, with a median value of 2.28 Å, followed by melamine (2.52 Å). The median values of melam (2.60 Å) and melem (2.59 Å) are very close despite the significant difference in the crystal structure of both systems as well as the number of hydrogen interactions.

The UV-Vis spectra (Figure 2) of the studied cluster models of respective intermediates were studied by B3LYP/6-311++G(d,p) approach implemented in the Gaussian 16 program package (G16). The UV-Vis spectra clearly show remarkable red shifts to higher energy values of bands for the primary melamine to the melon structure, similarly as in the study of Liu N. et al. [9].

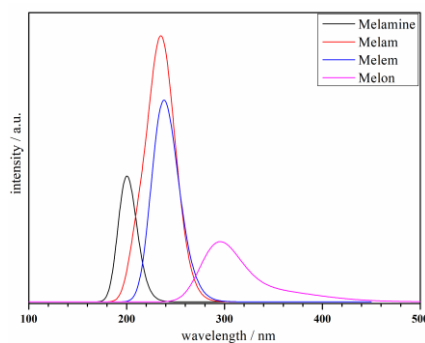


Figure 2 Uv-Vis spectra of studied cluster models.

The maximum absorption in UV-Vis bands is observed for melamine at 201 nm, melam at 235 nm, melem at 238 nm and melon at 296 nm (see Figure 2) and is in a good agreement with the results of other experimental and theoretical works [9-12].

Table 1 The minimal, median and maximal hydrogen bond interaction distances and n represents the number of HBs in crystal structure of studied systems

Model	H...A/Å			n
	min	medián	max	
Melamine	1.96	2.52	2.90	10
Melam	1.87	2.60	2.89	203
Melem	1.82	2.59	2.97	35
Melon	1.88	2.28	2.65	32

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Examples of Intercalated 2D Materials

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Keywords: intercalation, bilayer 2D-Material

Two-dimensional materials (2DM) science is advancing, and in this context van der Waals heterostructures are artificially assembled from individual 2DM flakes. Flake-to-flake transfer by stamping techniques is the method of choice, and polydimethylsiloxane (PDMS) pads are used for stamping.^[1] In general, intercalation of layered materials was established in the last century and led, for example, to our modern battery technology.^[2] The scientific basis for this was recognized with the Nobel Prize, awarded in 2019 to John B. Goodenough, M. Stanley Whittingham and Akira Yoshino.^[3] During intercalation, small atoms or molecules penetrate the layered structure, stretching the layers and forming the intercalation compound known for graphite.

The next step is the direct intercalation of bilayer 2DMs, and only a few examples are yet known. In a recent review article,^[4] we address the chemistry and physics of intercalated 2D layered materials, focusing on intercalated bilayer and few-layer systems. While intercalated few-layer systems of graphene and transition metal dicalcogenides are the focus, other intercalated 2DMs also exhibit interesting properties when thinned. The article begins with a brief introduction to the historical background of intercalation and highlights relevant concepts associated with few-layer intercalation. Synthetic methods for fabricating intercalated 2DMs, followed by an examination of current research directions, including superconductivity, bandgap tuning, magnetism, optical properties, energy storage, and chemical reactions are presented. The article highlights significant breakthroughs in each of these areas and provides an outlook on this emerging field of research.

Here, we further present a recent study of artificially assembled chemically functionalized bilayer materials, relevant for optoelectronic applications, such as molecular sensors.^[5] It is highly desirable to tune the optoelectronic properties of monolayer MoS₂ (1L- MoS₂). To achieve this, stable structures that can be reproducibly fabricated are essential, allowing for a better understanding of the mechanism leading to the optical properties. We demonstrate that the photoluminescence (PL) of 1L- MoS₂ can be modulated by photochemically functionalized graphene (F-G), which has been covalently modified by phenyl-groups. The heterostructure consists of graphene, phenyl-groups, and 1L- MoS₂. We show that the layer-sequence results in a significant difference in PL enhancement. MoS₂ supported by F-G (F-G/ MoS₂) has a 5-fold PL enhancement. However, MoS₂ shows only a 1.8 times PL enhancement if stacked underneath F-G (MoS₂/F-G).

The results indicate that the interaction between the graphene basal plane and MoS₂ interface are dramatically weakened with the enlarged interlayer distance in F-G/ MoS₂. Consequently, the PL enhancement becomes reduced with the thermal de-functionalization of F-G. We conclude that the phenyl-groups must be considered as a separate molecular component, given the different PL properties induced by layer sequence. Thus, the F-G/ MoS₂ heterostructures bring new ideas and have potential applications in optoelectronic devices.

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Colloidal synthesis of graphene composites for advanced Li-S batteries

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Keywords: Lithium-Sulfur Battery, graphene composite, heterocoagulation

In the past decade Li-S batteries were one of the focused scopes of advanced battery research due to their exceptional theoretical energy density. One group of materials which considered to be interesting is the reduced graphene oxide (rGO) containing sulphur composites owing to their chemical structure making them suitable candidate to overcome on the technological drawbacks of this energy storage device (e.g. insulating nature of sulphur, polysulfide shuttling effect causing fast capacity loss, etc.). To this day, unique materials science solutions are emerging that are capable to outperform and take over the market of the Li-ion batteries of today. Nevertheless, it is also visible that there is no well-established technique capable to systematically study these composites in terms of the nanostructure and its effect for the electrochemical performance.

Heterocoagulation is a method based on destabilisation and aggregation of dissimilar (or dissimilarly charged) particles leading to composites with self-assembling nanostructure based on their surface charges. In this work we prepared stable dispersions of colloidal sulphur and streaming potential measurement has been applied to follow the surface charge properties of the dispersions during the overcharging using cationic polyelectrolyte and subsequent heterocoagulation with graphene oxide (GO) dispersion by adding the sulphur dispersion in increments like a titration. This approach showed high repeatability of isoelectric point - where the fast coagulation expected to occur - when the equilibration times between adding the increments were optimised. For reducing the GO to rGO in the as prepared composite low temperature thermal treatment has been applied and an extensive thermoanalytical investigation where carried out to set optimal reduction temperature. Furthermore, based on the scopious structural characterisation it was clearly seen that a turbostratic carbon with relatively high amount of oxygen containing functional groups (as rGO) enveloped with polymer and amorphous sulphur phase has been synthesised.

Reduced graphene oxide possesses a special kind of layered, disordered microstructure providing more interlayer space, serving as a perfect host material and can enable the facile intercalation of active sulphur particles enabling faster reaction kinetics. Employing rGO/sulphur composite cathode can realize the highly efficient intercalation/anchoring of sulphur within the rGO host and precise microstructure regulation of S/C composite cathodes

for Li-S batteries. This ultimately helps diminish the shuttle effect of lithium polysulphides, thereby enhancing the electrochemical stability in Li-S batteries.

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A theoretical study of the corrugation of graphene oxide structure

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Keywords: graphene oxide; density functional theory; corrugation

Graphene oxide (GO) is a heterogeneous material which consists of a graphitic sheet decorated with oxygenated functional groups: epoxy (–O–) and hydroxyl (–OH) groups on the basal plane and carboxyl (–COOH) groups located at the edges, for example.

The GO properties are based on the structure and composition at different scales, which depend on the level of oxidation, defects, ratio, and arrangement of the functional groups, oxygenated and non-oxygen groups [1]. Thus, the corrugation behaviour of the GO is related to its composition and distribution of functional groups and defects, which may affect the properties, e.g., adsorption and mechanical properties, catalysis, conductivity, etc.

This study aims to investigate the effect of the different functional groups on corrugation, using their minimal unit as a preliminary step to understand the mechanism on large scales and its properties.

The density functional theory method (DFT) in the solid state, with the PBE functional and the D3 scheme for dispersion corrections (DFT-D3), was used to optimise the structures. In addition, the density-derived electrostatic and chemical (DDEC6) method [2] was performed for partial charges and the bond order (BO). The electron localisation function (ELF) [3] and Laplacian electron density [4] were suitable for studying the topology of the electron density (ρ).

A few models were proposed: firstly, the pristine graphene (G) from where the GO models were generated by adding the functional groups like epoxy (GO_{ep}), hydroxyl (GO_{hy}) and carboxyl (GO_{ca}).

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Multi-functional ordered carbonaceous frameworks synthesized from octaethynyl metalloporphyrin

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Keywords: Ordered carbonaceous frameworks, Single-atomic metal, Electrocatalyst

Carbon materials have been widely utilized as catalyst supports and electrode materials from their developed porosity and electrical conductivity. Recently, organic crystals, metal-organic frameworks (MOF) and covalent organic frameworks (COF) have attracted significant attention as precursors on nanoporous carbon materials. However, the chemically defined ordered framework structures of MOFs and COFs are generally lost during the carbonization, resulting in amorphous carbon materials. Thus, the carbonaceous materials with the molecular-level controlled structure have been challenging. In this regard, we have discovered that carbon materials with an ordered structure, called ordered carbonaceous frameworks (OCFs), can be yielded from simple heat treatment of a Ni porphyrin cyclic dimer ($\text{Ni}_2\text{CPD}_{\text{py}}$, **1**).^[1] The OCFs also retained Ni- N_4 coordination units originating from the precursor porphyrin molecules, and these single-atomic Ni species in OCFs electrochemically catalyzed CO_2 conversion into CO with high Faraday efficiency. In addition, precursors for OCFs have been extended to Ni- or Fe-porphyrin monomers with ethynyl moieties, which can be readily synthesized with a much simpler process than $\text{Ni}_2\text{CPD}_{\text{py}}$.^[2-4] OCFs possess both advantages of MOFs and carbon materials, such as well-defined ordered structure, thermal/chemical stability, and electrical conductivity, towards electrocatalysis and gas separation/storage application.^[5] Herein, we focus on a new type of precursor, metalloporphyrin possessing eight ethynyl moieties (**6**) and producing a variety of functional OCFs.

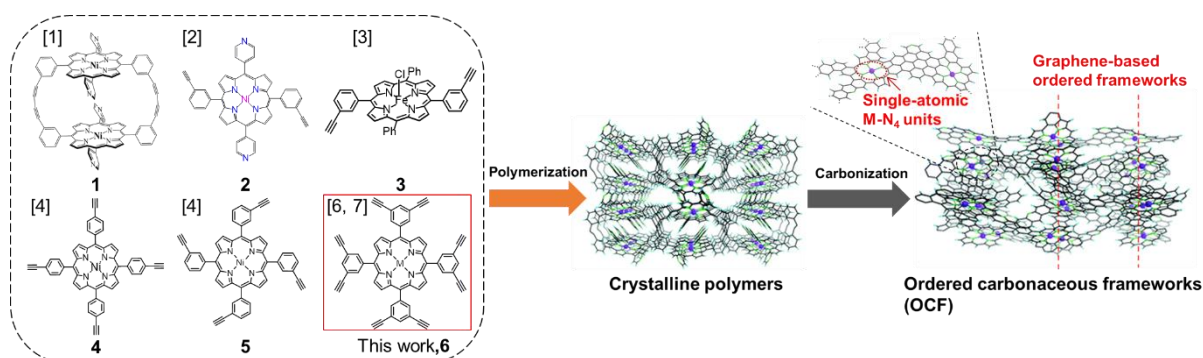


Fig. 1 Synthetic scheme of OCFs by the carbonization of metalloporphyrins (**1-6**).

Ni-porphyrin with eight ethynyl moieties (**6**) has been employed as the precursor. Microporosity was developed during the carbonization process, and the resulting OCF shows the largest recorded S_{BET} of $673 \text{ m}^2 \text{ g}^{-1}$ in OCFs thus far (Fig. 2a). In addition, Fig. 2b indicates the OCF with well-developed porosity demonstrates a unique mechanical flexibility that

enables force-driven reversible transition due to the structure composed of a non-stacked graphene sheet.[6]

Furthermore, the extension of metal species in OCFs to Co, Cu and Fe has been succeeded using the same metalloporphyrin frameworks (**6**). XAFS analysis reveals the retention of M-N₄ coordination units without metal aggregation in the resulting M-OCFs (M; Ni, Co, Cu, and Fe) prepared at 600°C. A series of catalysts with four types of single-atomic metal species allow the systematic screen of the catalytic performance. Therefore, we have applied these M-OCFs to the glycerol electrolytic oxidation reaction (GEOR). Despite the similar activity for oxygen evolution reaction, differences in activity dependent on the type of metal were observed for GEOR. Single-atomic Cu species were found to be most effective in the reaction with the lowest overpotentials of the reported transition catalyst.

Very recently, we have found that the crystalline structures of precursor Ni-, Co-, and Cu-porphyrin (**6**) are the same each other. Thus, a bimolecular crystal can be yielded by simple mixing and recrystallization process to produce Co-Cu bimetallic OCFs. SEM-EDS and HAADF-STEM-EDS clearly indicate the homogeneous dispersion of single-site Co and Cu species without segregation in the resulting OCF (Fig. 3).[7]

In summary, a new type of OCF with mechanical flexibility has been synthesized by a simple carbonization of Ni porphyrin monomer with eight ethynyl moieties. Furthermore, we have succeeded in the extension of metal species in OCFs to Co and Cu, and the synthesis of bimetallic OCF. These findings will open up new applications, such as force-responsive electrocatalysis and switching materials.

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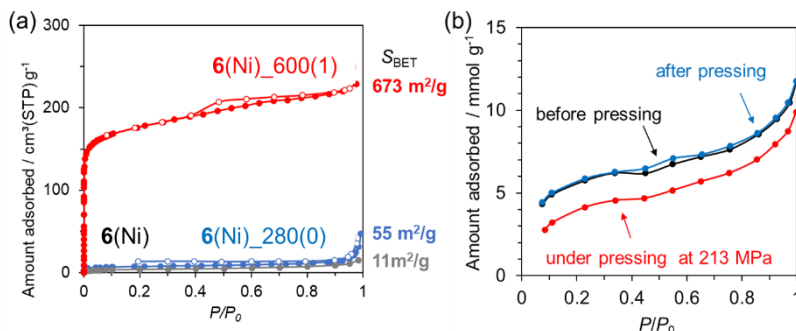


Fig. 2 (a) N₂ adsorption/desorption isotherms of **6**(Ni) and heat-treated samples. (b) Methanol adsorption isotherms (25°C) of **6**(Ni)₆₀₀₍₁₎ before (black), under (red) and after (blue) the application of a mechanical force (213 MPa).

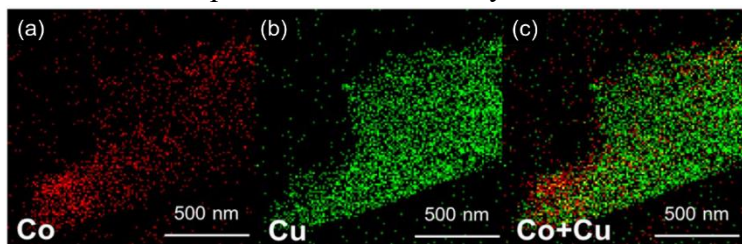


Fig. 3 (a-c) EDS elemental mapping images of **6**(Co/Cu)₅₀₀₍₀₎.

Interaction of graphene oxide with cationic biomolecules

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Keywords: 3 keywords; biomolecules; graphene oxide; adsorption

In order to continue the characterization of the binding of bovine serum albumin (BSA) on graphite oxide (GO) under given conditions (pH, I, T), we used new measurement techniques. At the previous meeting, I reported that BSA can bind not only to GO lamellae, but can also intercalate between two individual GO platelets, or even between stacks of multi-layered (unexfoliated) graphite oxide particles, which thereby forms a kind of layer-by-layer system.

Following the meeting in Smolenice, we decided to investigate the BSA/GO system also in the form of an ultrathin film structure obtained by the so-called layer-by-layer (LbL) deposition technique. [1] This includes the sequential deposition of monolayers of GO particles and BSA molecules on a proper solid support material, usually glass or quartz. Apart from XRD characterization which reveals the layered structure of this composite assembly, we aimed to perform additional structural characterization of the LbL BSA/GO films. This was performed in collaboration with the Colloid Chemistry group at the Jerzy Haber Institute in Kraków, Poland, where I have spent 3 weeks before the present meeting in the frame of an Erasmus scholarship. During my short-term scientific mission, we performed quartz crystal microbalance (QCM) and reflectometric studies to reveal the dry and wet mass of the BSA/GO films. The combined methods provided a deeper understanding into the structure and build-up of protein/graphene oxide thin films.

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Cr₂O₃/ZnO composites – preparation, characterization and their potential utilization as photocatalysts

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Keywords: Cr₂O₃/ZnO composites; chemical-structural characterization; photodegradation

Cr₂O₃/ZnO-based materials are interesting nanocomposites reminiscent of the so-called floral hierarchical heterostructures [1-5]. They are often prepared in two steps [1-5] and are used to detect formaldehyde [2].

These composites are usually obtained in the reaction of various concentrations of Zn(II) (aq) and Cr(III) (aq) with TEA (triethanolamine) at 80 °C during continuous stirring for 15 min at a pH of about 9. Washing and filtration processes are usually followed by calcination at 400 °C. If the ratio Zn/Cr is 0.5, ZnCr₂O₄ is formed directly. A relatively good photodegradation activity of phenol under UV irradiation was achieved [5].

In our work Cr₂O₃/ZnO composites were prepared according to the study [2]. The preparation of nanocomposites of different Cr₂O₃/ZnO ratios (4 samples), including the preparation of ZnO and Cr₂O₃ itself, was carried out. All prepared materials are characterized using various analytical- structural techniques: XRD, FTIR, PL spectroscopy, and DRS techniques, as well as SEM with EDS analysis for elemental mapping and morphology explanation. This is followed by photodegradation experiments for one type of dye (AO7) during UV irradiation.

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Quantitative study on unpaired electrons in carbon edge sites

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Introduction

Carbon catalysts have received considerable attention in recent years due to their potential to replace noble metal catalysts with earth-abundant elements. Unpaired electrons (radicals) are believed to be catalytically active species [1]. However, the origin of the unpaired electrons has not been fully understood. Thus, clarifying their position is crucial to provide straightforward guidelines for designing highly active carbon catalysts. Herein, we reveal the location of these unpaired electrons by advanced temperature-programmed desorption (TPD) coupled with magnetic susceptibility measurements using a superconducting quantum interference device (SQUID) magnetometer.

Methods

Four kinds of porous carbon materials with different amounts of edge sites were employed: zeolite templated carbon (ZTC) [2], activated carbon (AC, YP-50F), carbon black (CB, Ketjen Black EC-300J), and graphene mesosponge (GMS) [3]. The number of unpaired electron spins (N_{spin}) in each carbon was calculated from its magnetic susceptibility measured by SQUID (assuming the total spin quantum number of 1/2). TPD measurements were carried out up to 1800 °C under a high vacuum to calculate the number of edge sites (N_{edge}) for all materials. Edge-site surface area (S_{edge} [m² g⁻¹]) was calculated using N_{edge} [g⁻¹] as follows [4]:

$$S_{\text{edge}} = N_{\text{edge}} \times s_{\text{edge}} \quad (s_{\text{edge}}: \text{the area occupied by each edge site } (= 8.3 \times 10^{-20} \text{ m}^2))$$

Furthermore, the Brunauer-Emmett-Teller (BET) surface area (S_{BET}) was calculated from the N₂ adsorption data at -196 °C, and the basal-plane surface area (S_{basal} [m² g⁻¹]) was calculated by subtracting S_{edge} from S_{BET} . The catalytic activity of a series of carbons was evaluated from the dehydrogenative oxidation of 9,10-dihydroacridine.

Results and Discussion

To study the origin of unpaired electrons in each carbon material, N_{spin} was plotted against S_{BET} , S_{basal} , and S_{edge} . While no relationship can be seen between N_{spin} and S_{BET} or S_{basal} , a positive correlation was found between N_{spin} and S_{edge} (Fig. 1a), suggesting that carbon edge sites are the origin of unpaired electrons. Next, the relationship between N_{spin} and the edge site number (N_{edge}) is investigated in Fig. 1b. Since S_{edge} is proportional to N_{edge} , the relationship between N_{spin} and N_{edge} also shows a positive correlation. Notably, the ratio of N_{spin} to N_{edge} was found in a narrow range between 0.52 and 1.83% for all materials used in this study, even though the N_{edge} values of ZTC and GMS differ by nearly two orders of magnitude.

Secondly, to investigate the catalytic effect of unpaired electrons, dehydrogenative oxidation of 9,10-dihydroacridine was performed using carbon materials as catalysts. A positive correlation was found between N_{spin} and catalytic activity (Fig. 1c), suggesting that unpaired electrons present at carbon edge sites acted as catalytically active species in the oxidation

reaction. While previous studies on carbon catalysts lacked discussing reaction turnover numbers (TON), in this study TON can be quantitatively calculated. We find that the conversion of 9,10-dihydroacridine using ZTC was $4.06 \times 10^{-3} \text{ mol g}_{\text{cat}}^{-1}$, and N_{spin} was $1.66 \times 10^4 \text{ mol g}_{\text{cat}}^{-1}$, hence the TON was calculated to be 25, confirming a catalytic function of unpaired electrons.

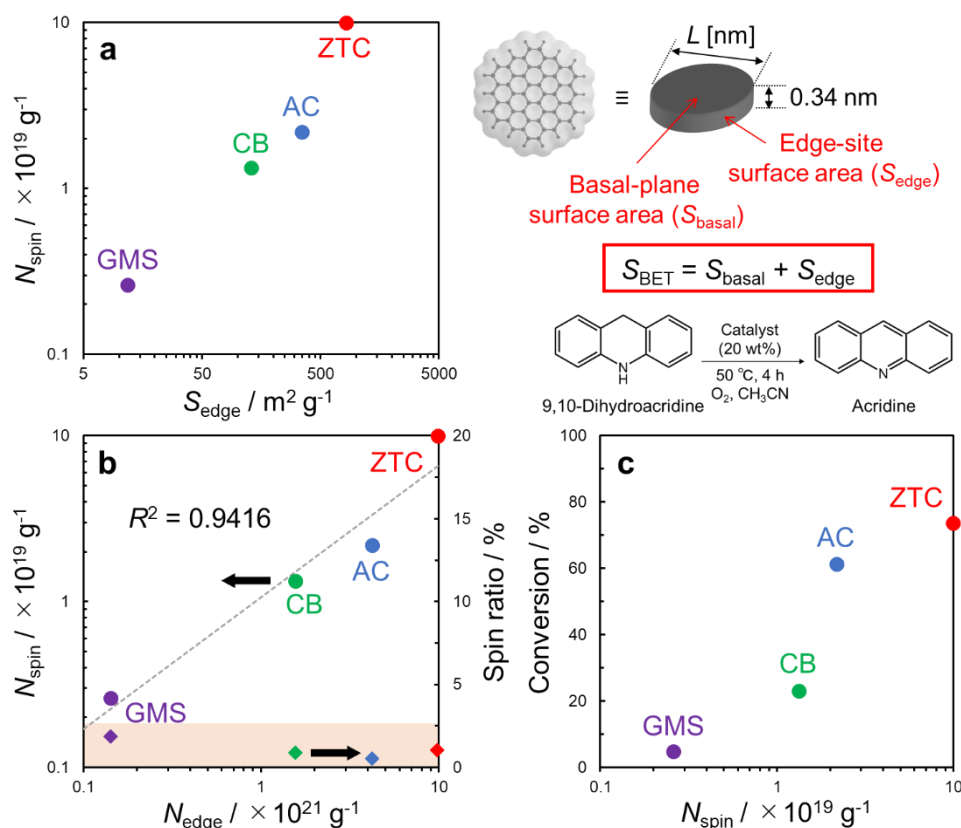


Fig. 1 (a) The plot of N_{spin} against S_{edge} (b) The plot of N_{spin} and spin ratio against N_{edge} . (c) The plot of conversion of 9,10-dihydroacridine against N_{spin} .

Conclusion

In this study, we have revealed that unpaired electrons in porous carbon materials predominantly originate from their edge sites by combining the high-sensitivity TPD technique and magnetic susceptibility measurements using SQUID. The ratio of N_{spin} to N_{edge} is constant at around 1%, regardless of the carbon structure. Furthermore, these unpaired electrons catalytically promote the dehydrogenative oxidation reaction. To summarize the above, carbon materials with a larger number of edge sites would be expected to have a larger number of unpaired electrons and thus exhibit higher catalytic performance. These findings offer the guideline for the design of highly active carbon catalysts.

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