V4-Japan joint research project

Atomic Design of Carbon-Based Materials for New Normal Society

AtomDeC 4th International Symposium

https://atomdec.info/

AtomDeC project:
the renaissance of carbon-material research

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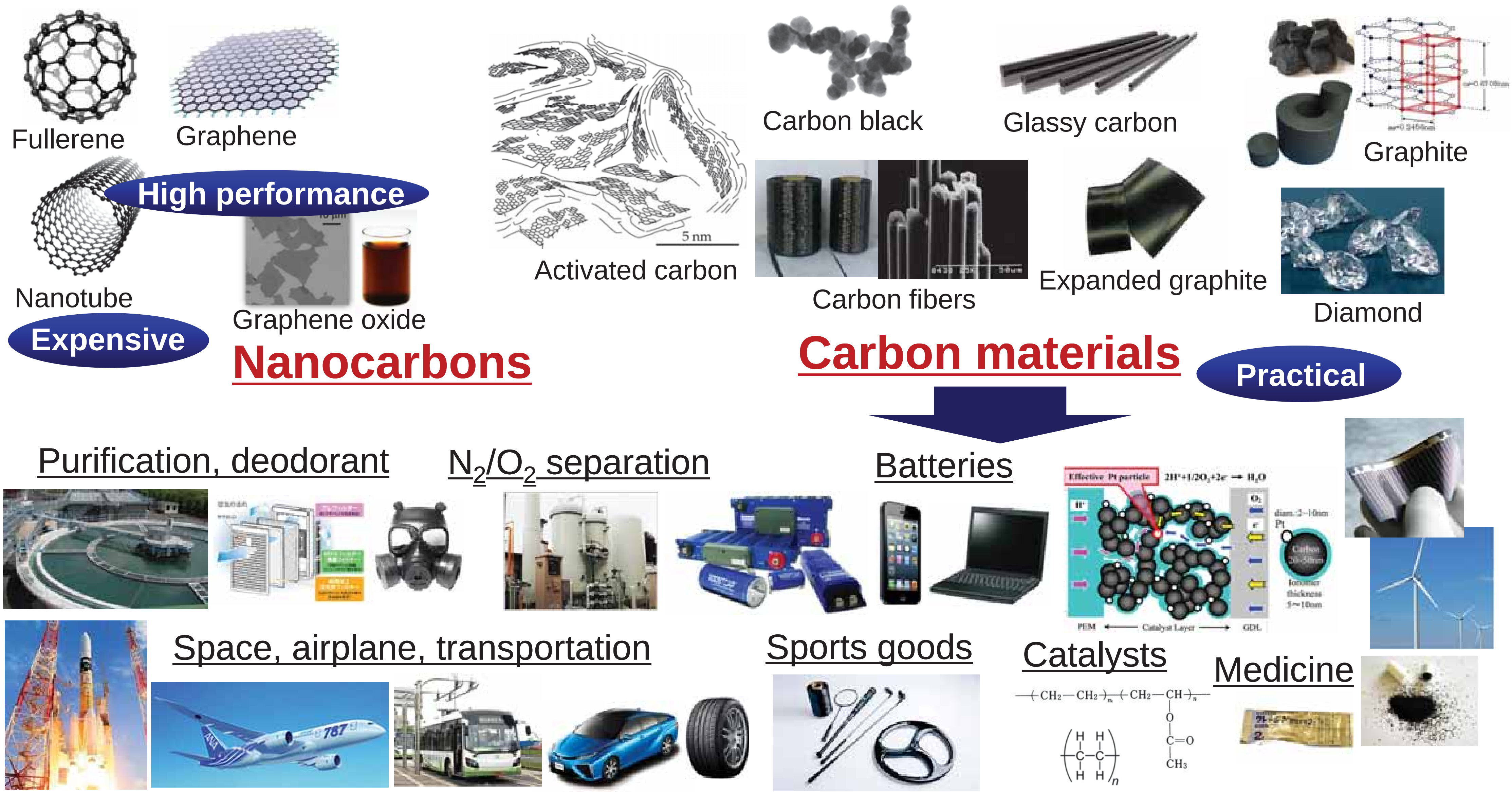
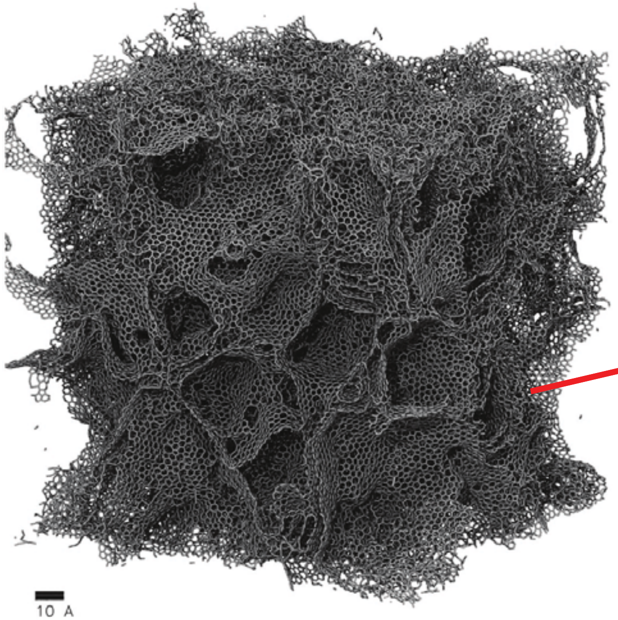
Advanced Institute for Materials Research, Tohoku University

Carbon materials



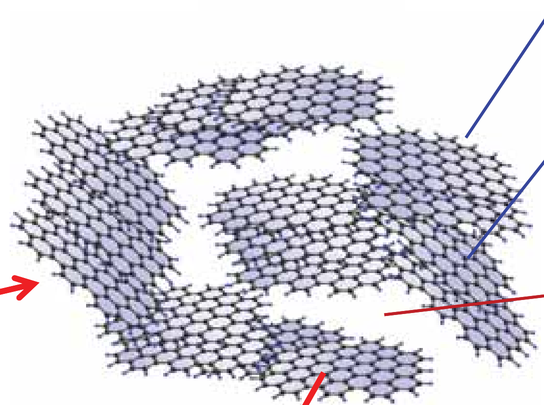
Carbon materials are widely used for various applications.
But, a poor structure controllability hampers further development.

Objective of the project



Cheng *et al.*, *Adv. Sci.* **4** (2017) 1700059.

Very complex structure



Edge plane

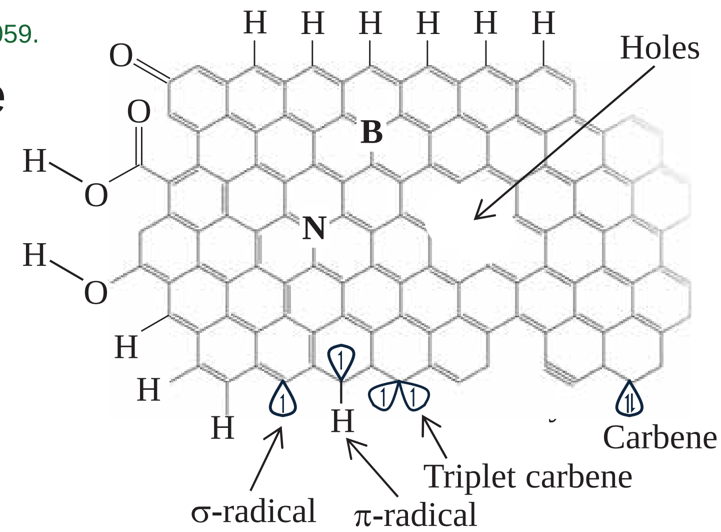
Catalysis, chemical stability, corrosion

Basal plane

Conductivity, chemical stability, mechanical strength and elasticity

Nanopores

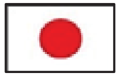
Adsorption, molecular sieve, mass transfer



The development of new science & technologies which allow atomic design of carbon-based materials is demanded.

"Atomic Design of Carbon-Based Materials for New Normal Society"

Team

Japan

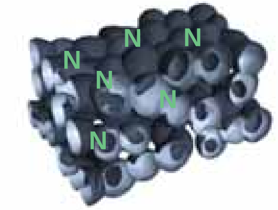
Work Package 1

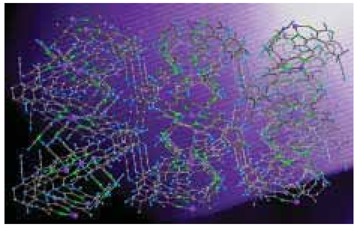
Synthesis of atomically designed carbon-based materials

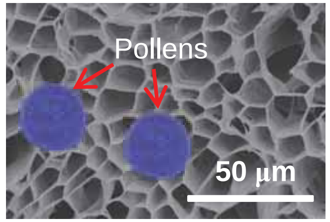
Nanoporous graphene, B,N,S,P-doping, MOF-like carbon alloys, honeycomb monoliths

PL: Dr. Hirotomo Nishihara

WP1, WP2 Synthesis



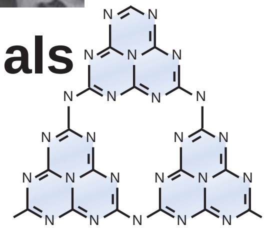





Czech

Work Package 2

Synthesis of atomically designed carbon-based composite materials



g-CN materials, inorganic materials

Dr. Monica Michalska

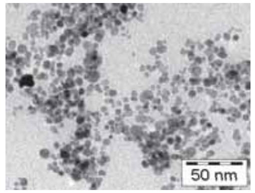

Hungary

Work Package 3

WP3 Analytics

Comprehensive characterization at the atomic/molecular/colloidal scale

2D carbon nanosheets, analysis of colloidal systems, nano-ESCA



Dr. Tamás Szabó


Slovakia

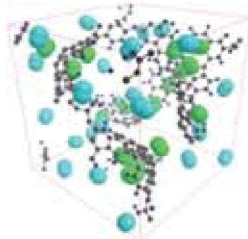

Canada

Work Package 4

WP4 Modeling

Modelling of atomically designed carbon-based materials

Theoretical calculations, synchrotron analysis



Dr. Eva Scholtzová **Dr. Robert K. Szilagyi**


Poland

Work Package 5

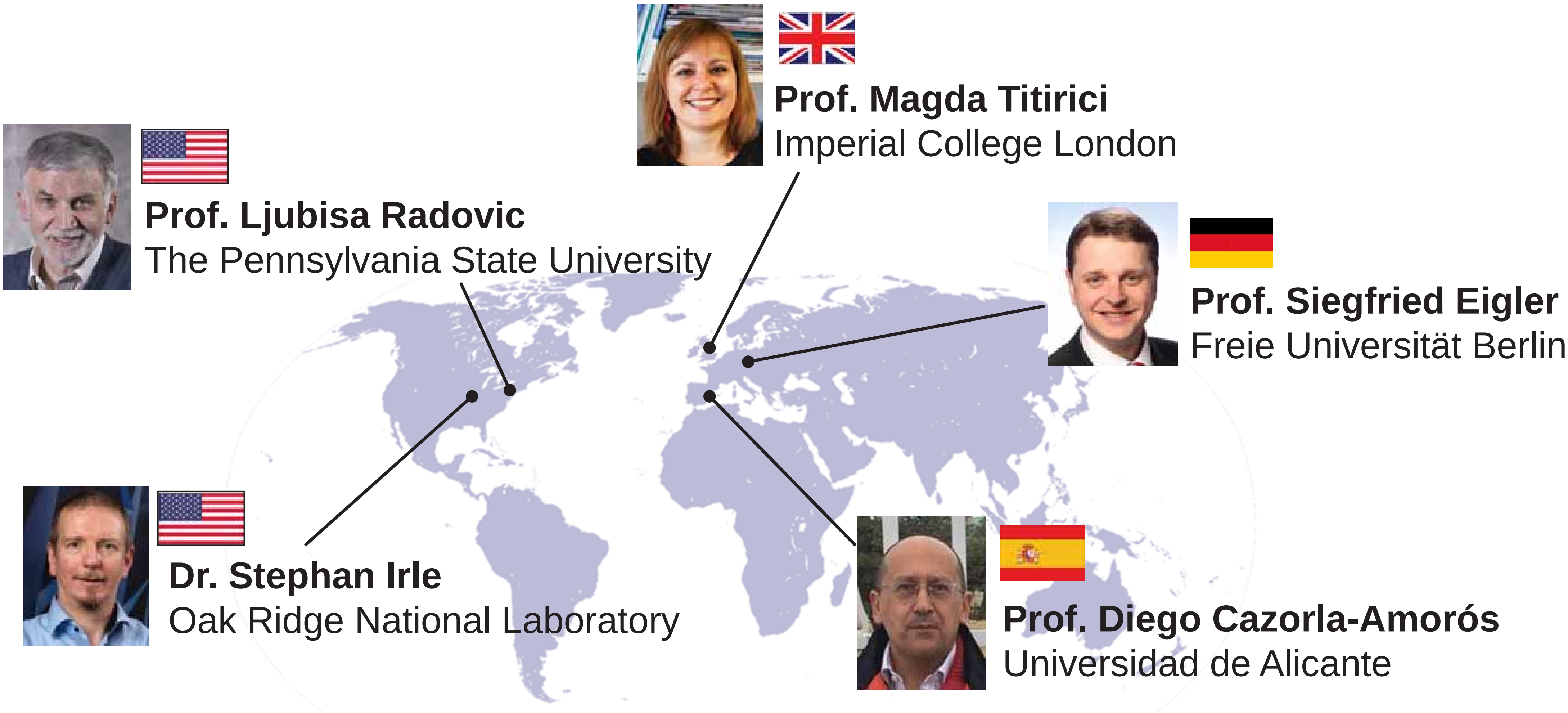
WP5 Devices

Emerging applications and technological implications

Polymer electrolytes, flexible devices, supercapacitors

SPL: Dr. Amrita Jain

International advisory board members



World top scientists support the AtomDeC project!

Targets of the project

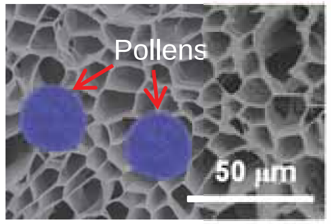
WP1, WP2 Synthesis

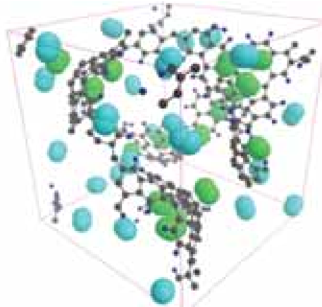
WP3 Analytics

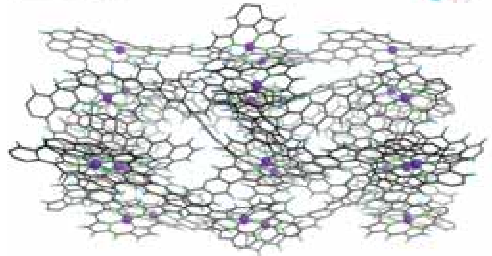
WP4 Modeling

WP5 Devices

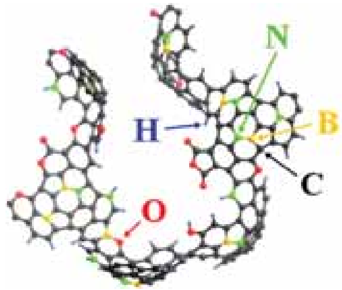
Expected achievements for new normal society

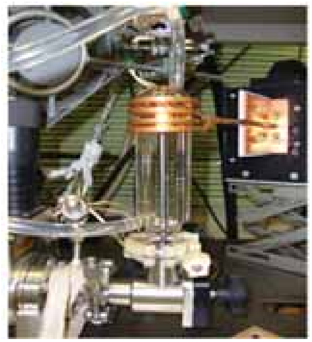




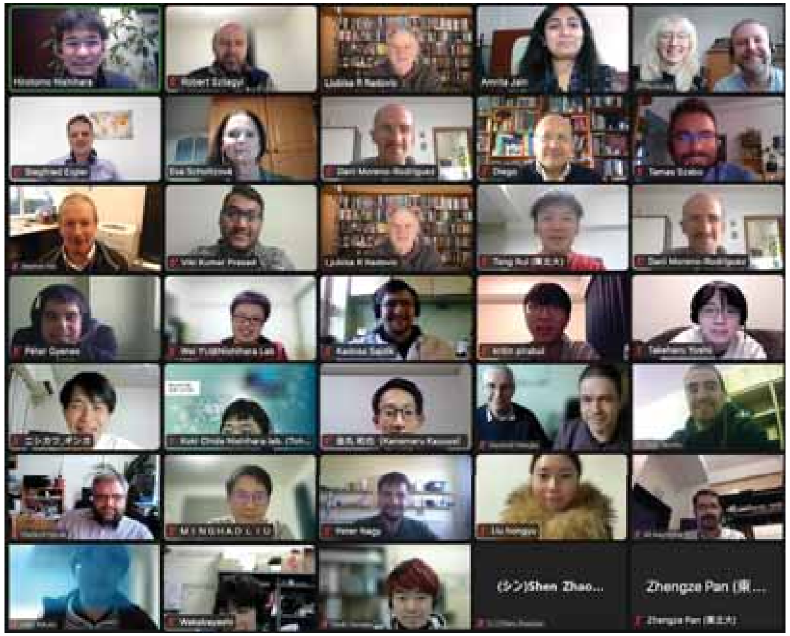


- **High throughput COVID-19 masks/filter**
- **Supercapacitors (double energy density)**
- **Flexible supercapacitors for extreme environments**
- **Ionic-liquid based green electrolytes**
- **H_2 storage (at least 20% increase)**
- **CO_2 fixation and conversion into C1 and C2 compounds**
- **Materials for environmental hazard mitigation**
- **New type power generation devices**
- **Heat-pumps using natural refrigerants**





1st symposium (online) *January 18-19, 2022*



2nd symposium (Smolenice) *November 2-4, 2022*

3rd symposium (Warsaw) *May 23-25, 2023*

4th symposium (Sendai) *August 1-3, 2024*

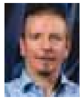
AtomDeC acknowledged original papers **2022'**

WP1 **Synthesis of microporous polymers with exposed C_{60} surface by polyesterification of fullerenol**
Chem. Commun., **58** (2022) 7086.

WP1 **Synthesis of hexa-aminated trinaphtho[3.3.3]propellane and its porous polymer solids with alkane adsorption properties**
Bull. Chem. Soc. Jpn. **95** (2022) 1296.

WP1 **Adsorption properties of templated nanoporous carbons consisting of 1-2 graphene layers**
Carbon Reports, **1** (2022) 123.

WP1 **Capacitance of Edge-Free Three-Dimensional Graphene: New Perspectives on the Design of Carbon Structures for Supercapacitor Applications**
Electrochim. Acta, **10** (2022) 141009.


WP1 WP4 **Mechanical Properties of Zeolite-Templated Carbons from Approximate Density Functional Theory Calculations**
Carbon Reports, **1** (2022) 231.

WP1 **The carbon chain growth during the onset of CVD graphene formation on γ-Al_2O_3 is promoted by unsaturated CH_2 ends**
Phys. Chem. Chem. Phys., **24** (2022) 23357.

WP1 **Pore-size control of soft mesoporous carbon by hot pressing**
Carbon Reports, **1** (2022) 214.

WP2 **The role of the g-C_3N_4 precursor on the P doping using HCCP as a source of phosphorus**
J. Mater. Res. Technol., **18** (2022) 3319.

WP2 **The effect of surface modification with Ag nanoparticles on 21 nm TiO_2: anatase/rutile material for application in photocatalysis**
Mater. Today Chem., **26** (2022) 101123.

WP2 **Structural studies and selected physical investigations of LiCoO2 obtained by combustion synthesis**
Beilstein J. Nanotech., **13** (2022) 1473.

WP2 WP5 **Surface modification of activated carbon with silver nanoparticles for electrochemical double layer capacitors**
J. Energy Storage, **54** (2022) 105367.

WP3 **Amino Acid Complexes of Zirconium in a Carbon Composite for the Efficient Removal of Fluoride Ions from Water**
Int. J. Environ. Res. Public Health, **19** (2022) 3640.

WP1 WP2 WP5 **Vanadium oxide nanorods as an electrode material for solid state supercapacitor**
Sci. Rep., **12** (2022) 21024.

WP2 **Synthesis of vacant graphitic carbon nitride in argon atmosphere and its utilization for photocatalytic hydrogen generation**
Sci. Rep., **12** (2022) 13622.

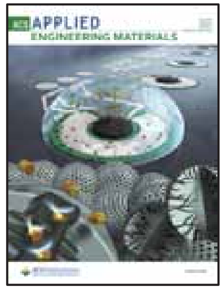
WP2 **Post-synthetic modification of graphitic carbon nitride with PCl3 and POCl3 for enhanced photocatalytic degradation of organic compounds**
Diamond Related Mater., **130** (2022) 109439.

AtomDeC acknowledged original papers 2023'

WP1 **Synthesis and electrocatalysis of ordered carbonaceous frameworks from Ni porphyrin with four ethynyl groups**
Catal. Today, **411-412** (2023) 113830.

WP1 WP4 **Edge-Site-Free and Topological-Defect-Rich Carbon Cathode for Li-O_2 Batteries**
Adv. Sci., **10** (2023) 2300268.

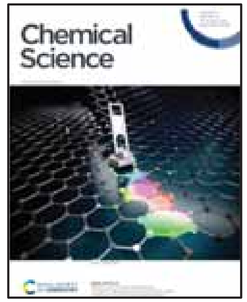
WP1 **Critical impact of nanocellulose on the synthesis of porous cellulose monolith with oriented microchannels: Structure control, mechanics, and mass transport**
Nano Res., **16** (2023) 8018.



WP1 **Quantitative study on catalysis of unpaired electrons in carbon edge sites**
Carbon, **210** (2023) 118069.

WP1 **Development of Microdrip Enzyme Device Using Carbon-Coated Porous Silica Spheres**
ACS Appl. Eng. Mater., **1** (2023) 1426.

WP1 **Bimetallic ordered carbonaceous frameworks from Co- and Cu-porphyrin bimolecular crystals**
Carbon, **201** (2023) 338.



WP1 **Nanoporous Membrane Electrodes with an Ordered Array of Hollow Giant Carbon Nanotubes**
Adv. Funct. Mater., **33** (2023) 2303730.

WP1 **Chemistry of zipping reactions in mesoporous carbon consisting of minimally stacked graphene layers**
Chem. Sci., **14** (2023) 8448.

WP2 WP5 **Utilization of compressible hydrogels as electrolyte materials for supercapacitor applications**
RSC Adv., **13** (2023) 11503.

WP2 **Effect of Ag modification on TiO2 and melem/g-C3N4 composite on photocatalytic performances**
Sci Rep., **13** (2023) 55270.

WP2 WP5 **Chemical synthesis of polyaniline and polythiophene electrodes with excellent performance in supercapacitors**
J. Energy Storage, **73** (2023) 108811.

WP2 WP5 **One-step synthesis of a sustainable carbon material for high performance supercapacitor and dye adsorption applications**
Mater. Sci. Eng. B, **297** (2023) 116766.

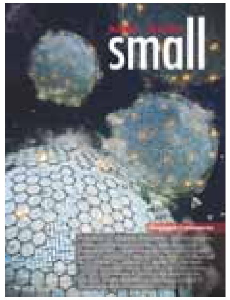
WP2 **Graphitic carbon nitride/xylene soot metal-free nanocomposites for photocatalytic degradation of organic compounds**
Diamond Related Mater., **139** (2023) 110434.

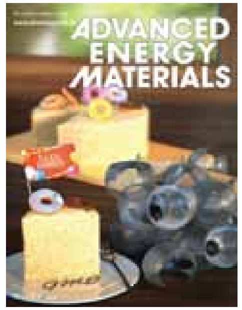
WP1 **Structural Engineering of Nanocarbons Comprising Graphene Frameworks via High-Temperature Annealing**
Bull. Chem. Soc. Jpn., **96** (2023) 510.

AtomDeC acknowledged original papers 2024’

WP1 **Hierarchically Porous and Minimally Stacked Graphene Cathodes for High-Performance Lithium–Oxygen Batteries**
Adv. Energy Mater., **14** (2024) 2303055.

WP1 **Silicon Radical-Induced CH4 Dissociation for Uniform Graphene Coating on Silica Surface**
Small, **20** (2024) 2306325.





WP1 **Highly Permeable and Regenerative Microhoneycomb Filters**
ACS Appl. Mater. Interfaces, **16** (2024) 29177.

WP1 **A thermodynamically favorable route to the synthesis of nanoporous graphene templated on CaO via chemical vapor deposition**
Green Chem., **26** (2024) 6051.

WP1 **Theoretical Insights into the Role of Defects in the Optimization of the Electrochemical Capacitance of Graphene**
Energy Mater. Devices, in press.

WP1 **Unlocking Chemical Environment of Nitrogen in Perovskite-Type Oxides**
Chem. Sci., **15** (2024) 10350.

WP1 WP4 **Quantitative and qualitative analysis of nitrogen species in carbon at the ppm level**
Chem, ***in press***

WP2 WP3 WP5 **Flexible, tough and high-performing ionogels for supercapacitor application**
J. Materiomics, ***in press***

WP2 WP5 **Carbon framework modification; an interesting strategy to improve the energy storage and dye adsorption**
Energy Adv., **3** (2024) 1354.

WP2 WP5 **Enhanced electrochemical properties of multiwalled carbon nanotubes modified with silver nanoparticles for energy storage application**
Mater. Chem. Phys., **317** (2024) 129200.

WP2 WP3 **Comparative study of photocatalysis with bulk and nanosheet graphitic carbon nitrides enhanced with silver**
Sci. Rep., **14** (2024) 11512.

WP3 **Aqueous heterocoagulation-driven assembly of graphene oxide and polycation-coated sulfur particles for nanocomposite Li-S battery cathodes**
J. Colloid. Interf. Sci., **655** (2024) 931.

WP2 **Graphitic C3N4 and Ti3C2 nanocomposites for the enhanced photocatalytic degradation of organic compounds and the evolution of hydrogen under visible irradiation**
J. Photobio. A Chem., **447** (2024) 115260.

WP4 **Metal-free hybrid nanocomposites of graphitic carbon nitride and char: Synthesis, characterisation and photocatalysis under visible irradiation**
J. Taiwan Inst. Chem. Eng., **158** (2024) 104864.

WP5 **Could halide perovskites revolutionalise batteries and supercapacitors: A leap in energy storage**
J. Energy Storage, **88** (2024) 111468.

AtomDeC acknowledged review/book chapter

WP1 **Ordered carbonaceous frameworks: A new class of carbon materials with molecular-level design**
Chemical Communications, **58** (2022) 3578

WP1 **Aligned Macroporous Monoliths by Ice-Templating**
Bulletin of the Chemical Society of Japan, **95** (2022) 611

WP1 **Coordination chemistry for innovative carbon-related materials**
Coordination Chemistry Reviews, **466** (2022) 214577

WP1 **Progress in templated nanocarbons and related materials chemistry**
Carbon Reports, **3** (2024) 47

WP1 **Structural control of nanoporous frameworks consisting of minimally stacked graphene walls**
Frontiers in Materials, **10** (2024)

WP1 **Carbon-Coated Anodic Aluminum Oxide: Synthesis, Characterization, and Applications**
Appl. Phys. Rev., ***in press***

WP5 **Role of Dielectric Permittivity in Electrode Materials for Energy Storage Device Applications: A Fundamental and Brief Overview**
An Introduction to Permittivity, Nova Science Publishers, 2022, pp. 219-238.

WP5 **Porous Carbon Materials for Supercapacitor Application**
Handbook of Porous Carbon Materials, Springer Nature, Singapore, 2023, pp. 117-146.

WP3 **Recycling waste sources into nanocomposites of graphene materials: Overview from an energy-focused perspective**
Nanotech. Rev., 12 (2023)

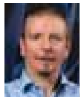
WP5 **Sustainable electrochemical energy storage devices using natural bast fibres**
Chem. Eng. J., 465 (2023) 142845

WP2 **Highly Carbonized, Porous Activated Carbon Derived from Ziziphus Jujuba for Energy Storage**
Advanced in Clean Energy and Sustainability, Springer, Singapore, 2023, pp. 549-559.

44 papers & 11 reviews/book chapters!

Collaborations of WP1

Published projects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WP1 WP4 **Quantitative and qualitative analysis of nitrogen species in carbon at the ppm level**
Chem, ***in press***


WP1 **Structural Model of Oxidatively Unzipped Narrow Single-Walled Carbon Nanotubes**
Carbon, ***in press***

On-going projects


WP1 **Electrocatalytic glycerol oxidation with OCF**
On going


WP1 **Analysis of hard carbons by TPD**
On going


WP1 **TPD analysis of N-doped carbons**
On going

WP1 WP3 **Sonication of mechanically soft carbon frameworks**
On going

WP1 WP4 **TPD for S-containing carbons**
On going

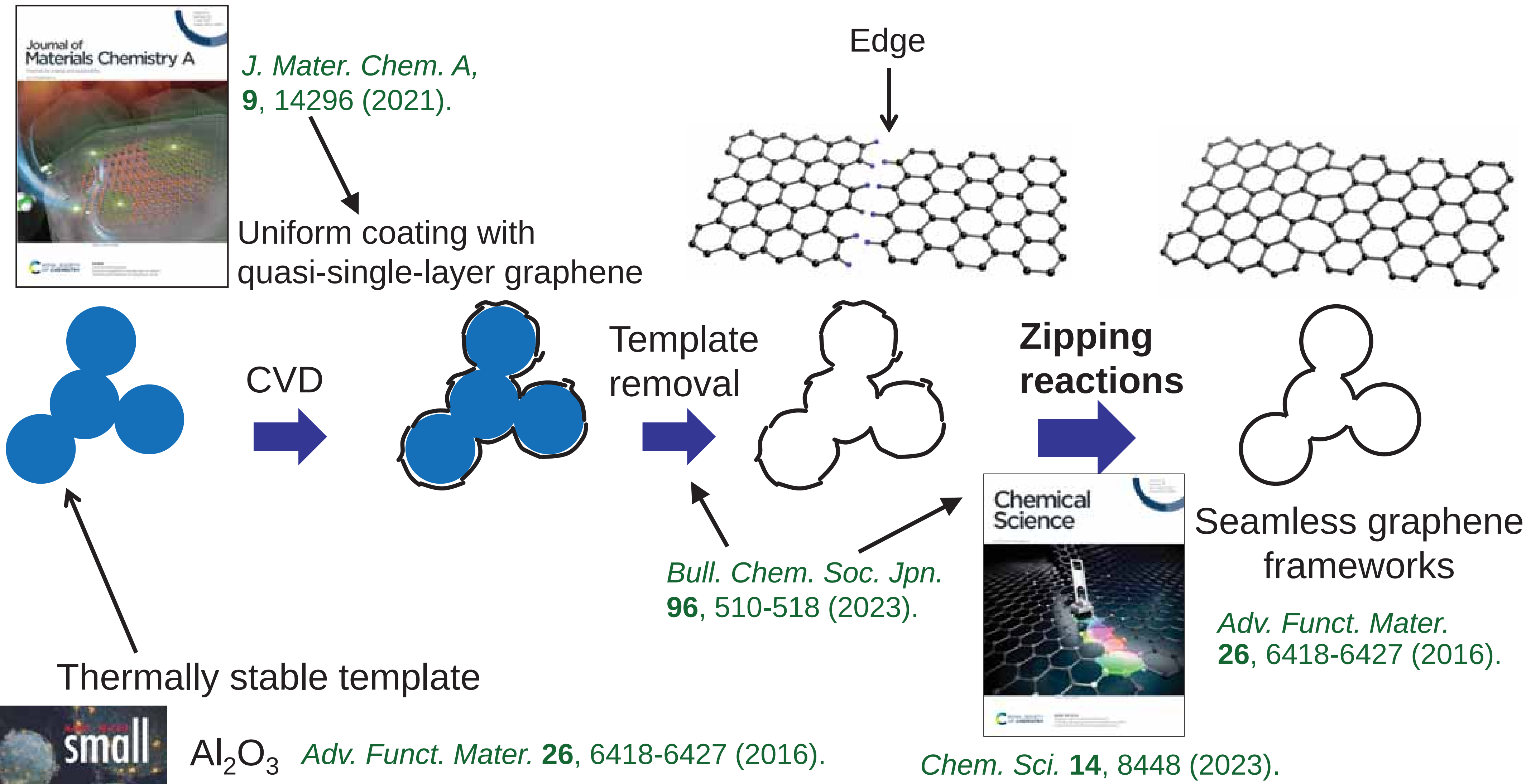
WP1 WP2 **TPD analysis of g-C_3N_4**
On going

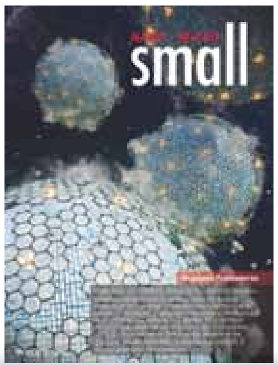
WP1 WP2 WP5 **Electrochemical properties of Ag/GMS**
On going

WP1 WP4 WP5 **GMS for liquid phase adsorption**
On going

WP1 WP4 WP5 **GMS/gel electrolyte supercapacitors**
On going

A strategy for seamless graphene frameworks





Al_2O_3 *Adv. Funct. Mater.* **26**, 6418-6427 (2016).

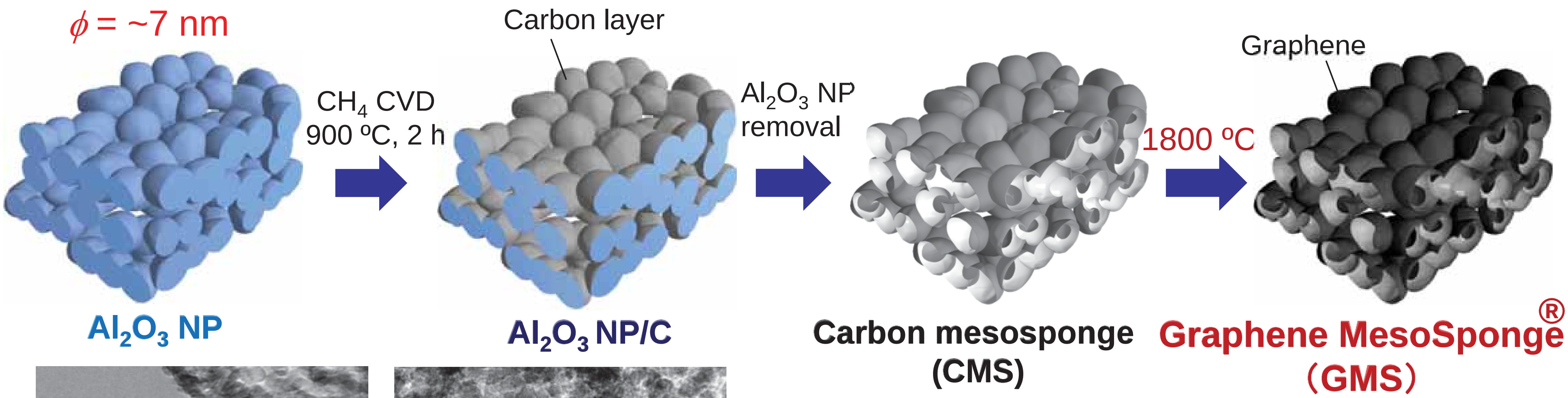
MgO *J. Mater. Chem. A*, **9**, 14296 (2021).

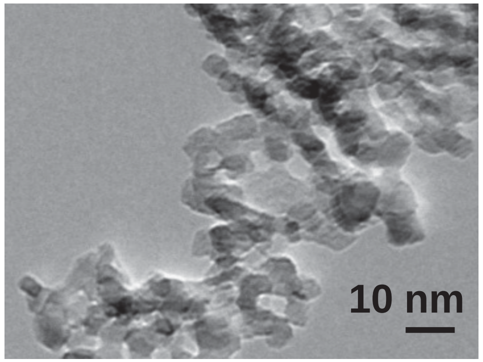
CaO *Green Chem.*, **26**, 6051 (2024); *Catal. Today*, **437**, 114763 (2024).

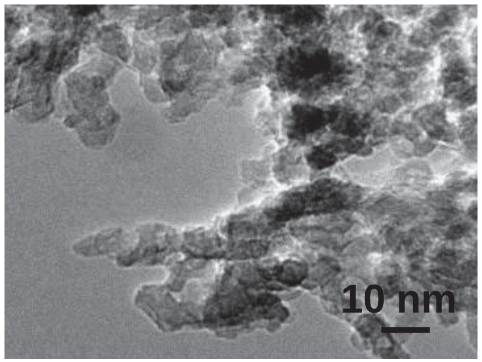
SiO_2 *Small*, 20, 2306325 (2024).

Graphene MesoSponge® (GMS)

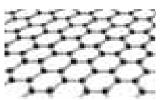
Adv. Funct. Mater. **26**, 6418-6427 (2016).







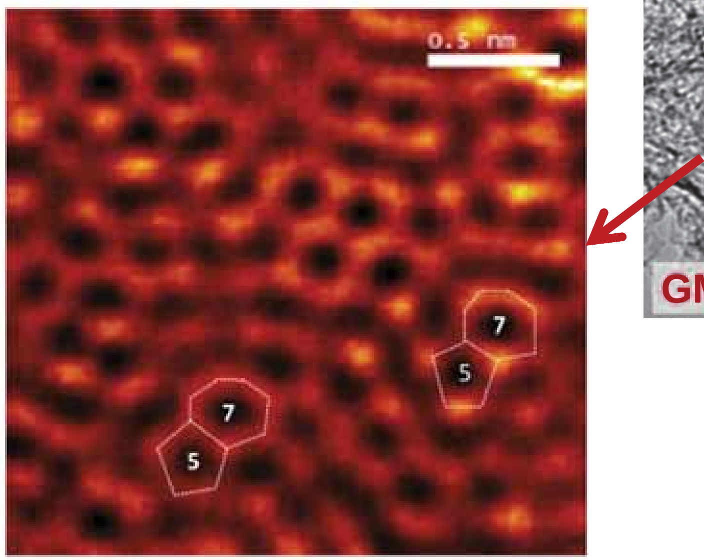
S_{BET} = 220 m^2/g C: 16 wt% (0.19 g/g)

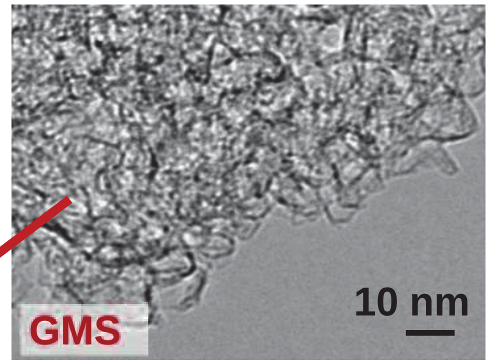


Areal density of carbon: 8.60 × 10^{-4} g/m^2

*Areal density of graphene: 7.61 × 10^{-4} g/m^2

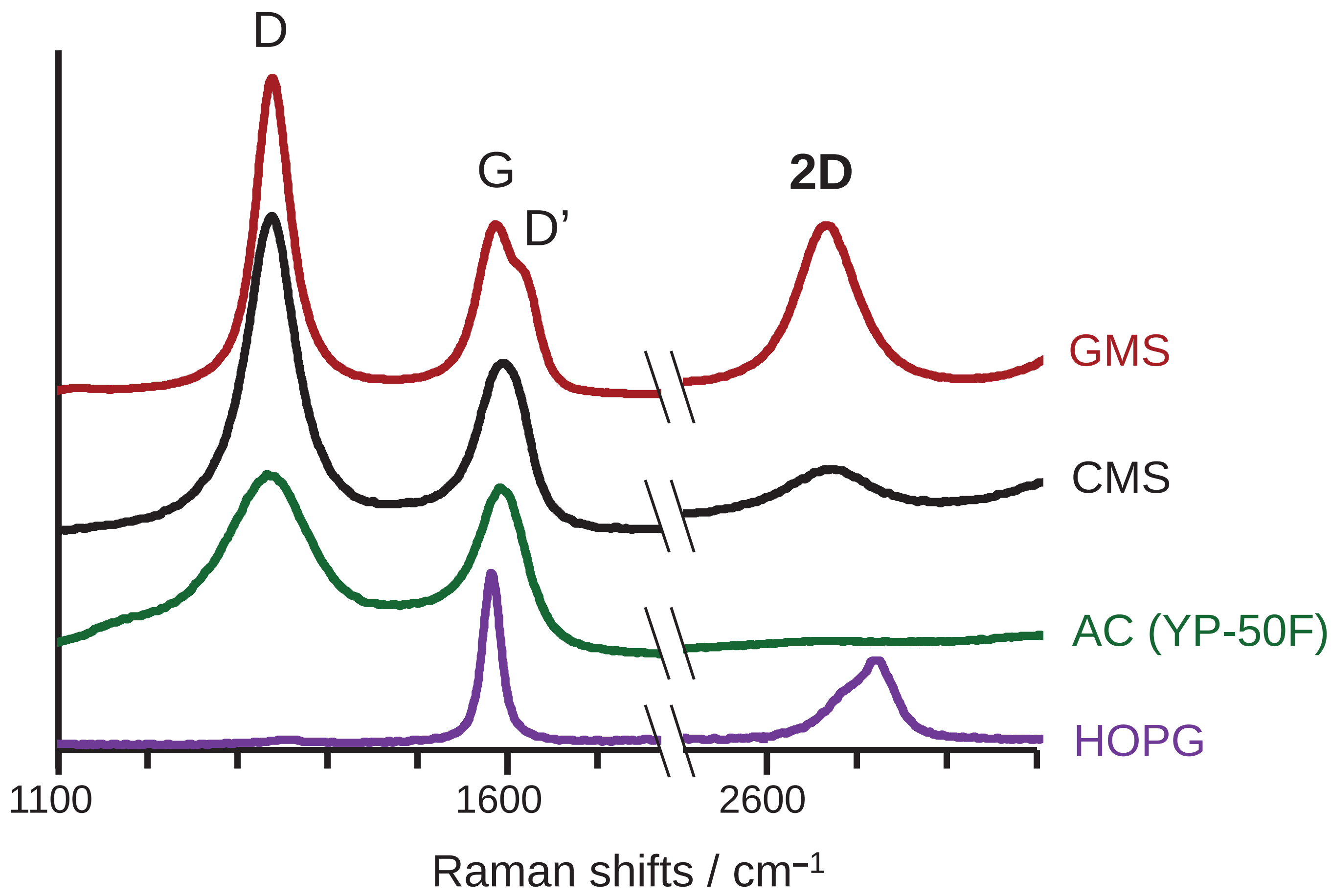
Average stacking number ≒ 1.1





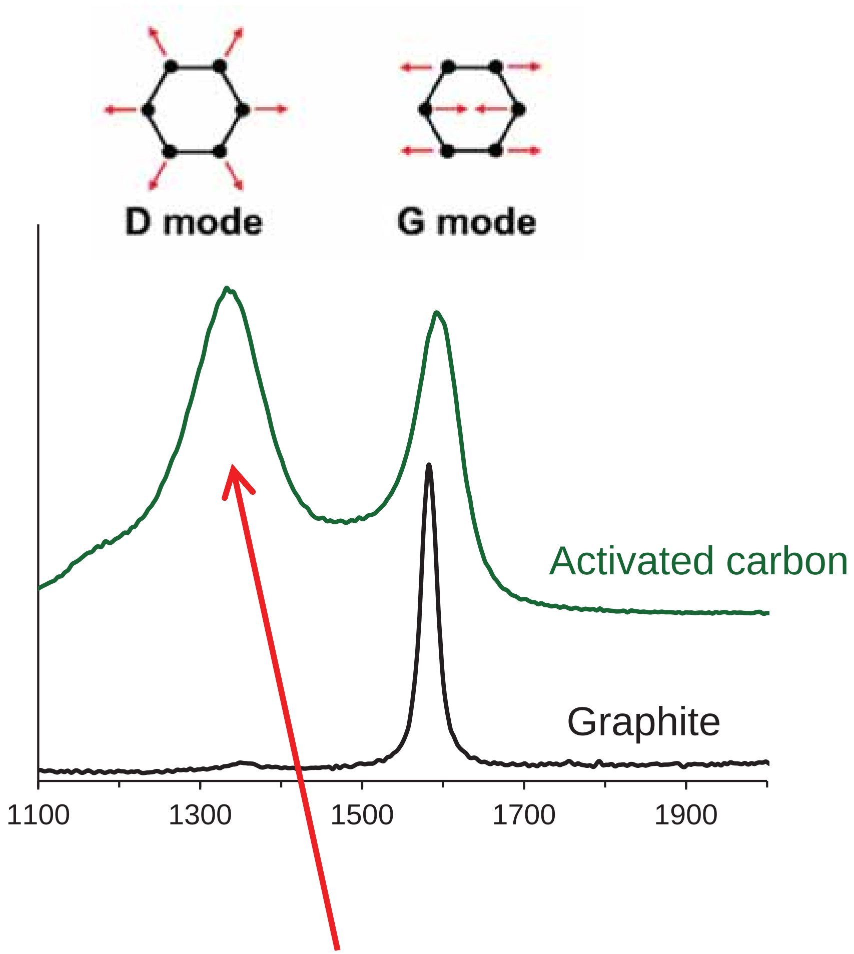
Adv. Sci., **10** (2023) 2300268.

Raman spectrum of GMS

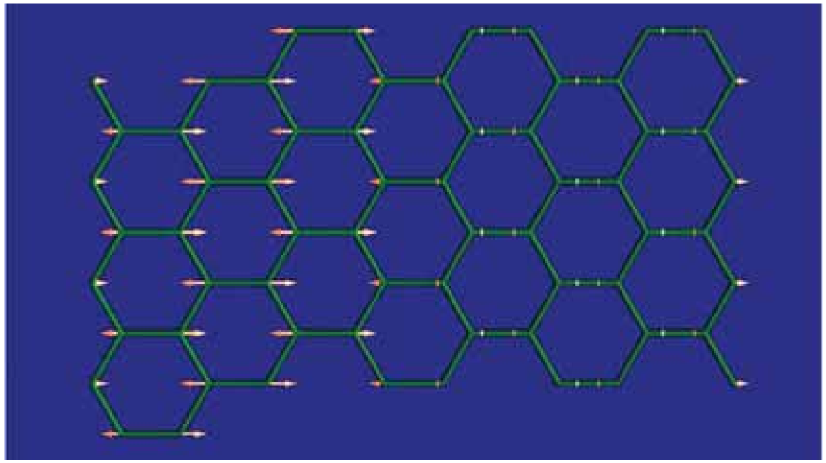


GMS shows intense D and D' peaks derived from 'defects,' although GMS has a few number of edge sites.
Why??

Origins of Raman G and D peaks



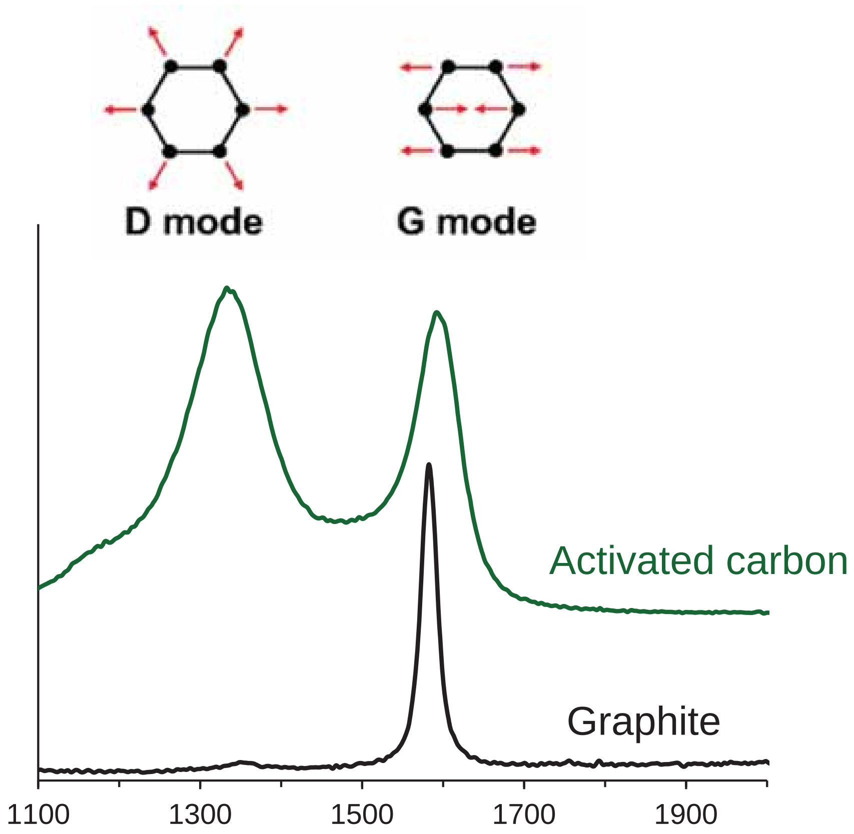
Calculated by Dr. Eva Scholtzová

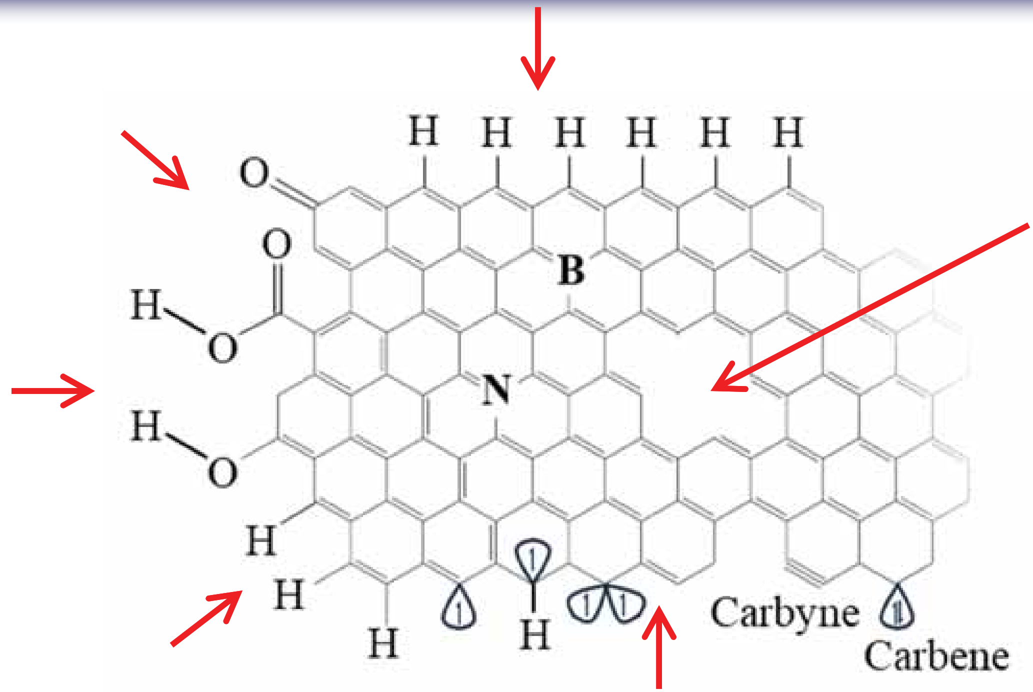


D band is originated from “defects” of graphene.

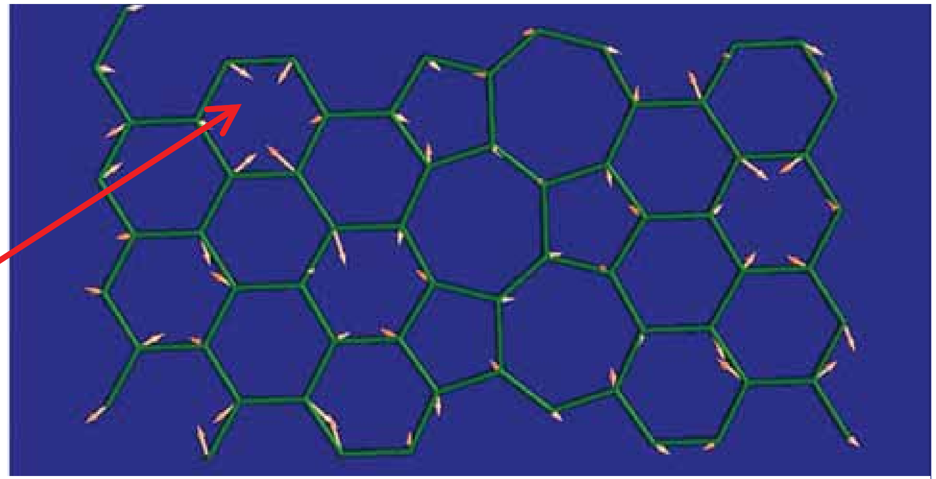
However, what is “defects”?

Topological defects





Edge sites are generally recognized as 'defects'.

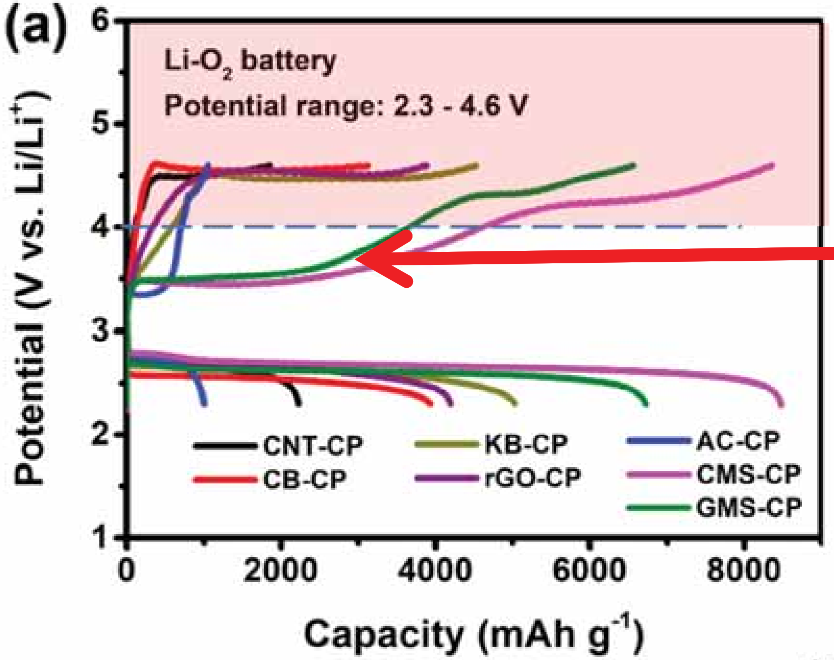


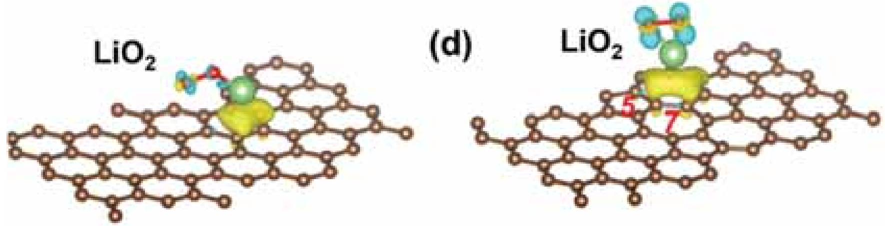
D mode becomes active also near 5,7-membered rings (topological defects).

Function of Topological defects: catalysis

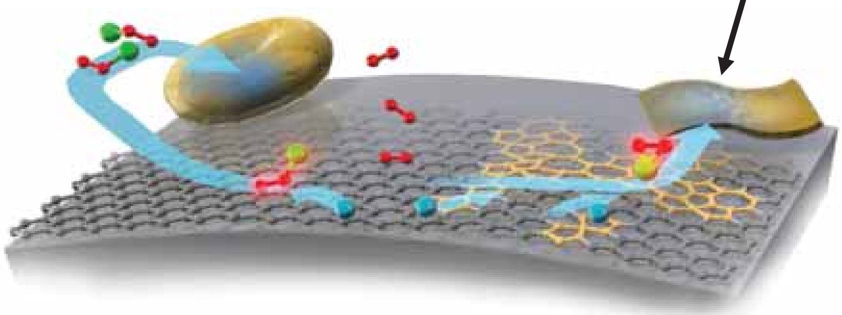


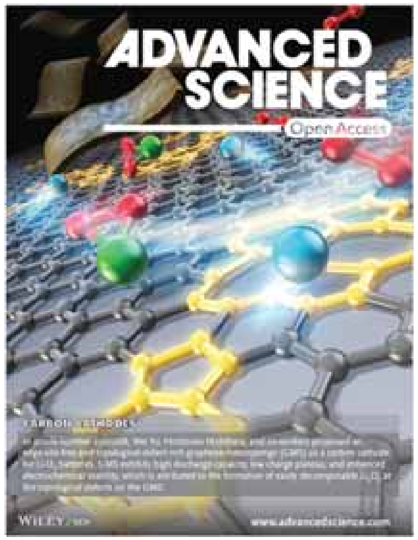
0.5 M LiTFSI/TEGDME

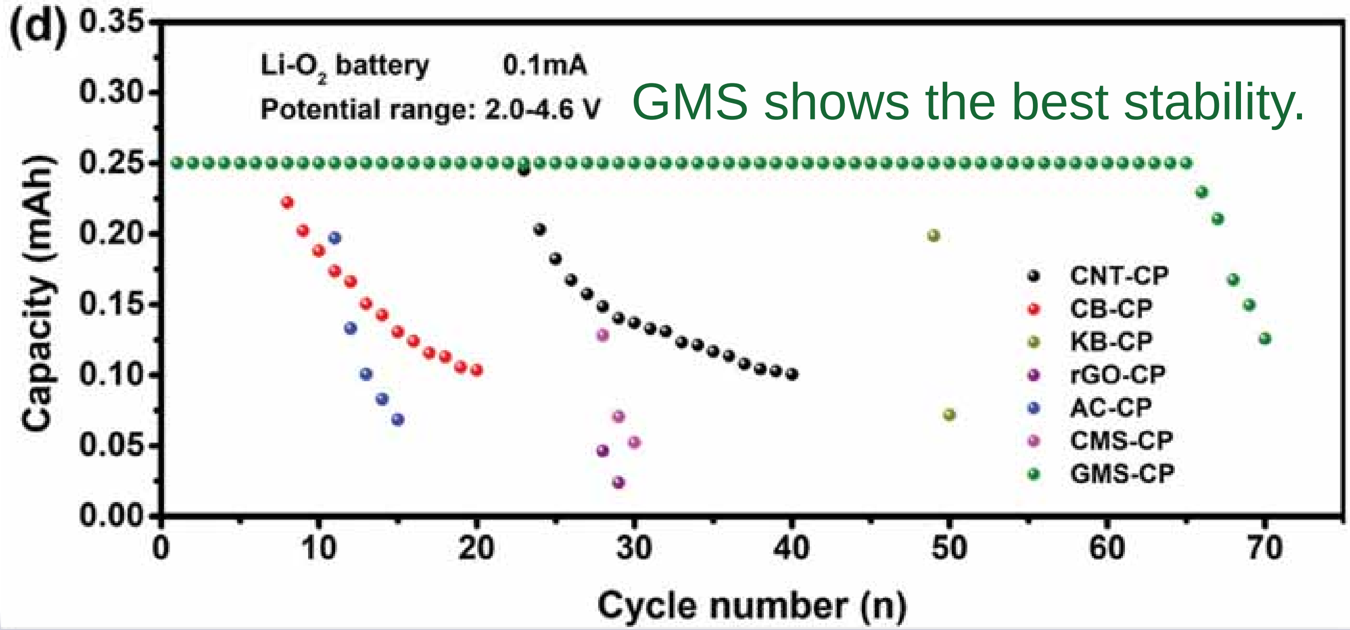




Unique catalysis for the formation of amorphous Li_2O_2







GMS shows the best stability.

Adv. Sci., **10**, 2300268 (2023).

HT-TPD (up to 1800 °C)

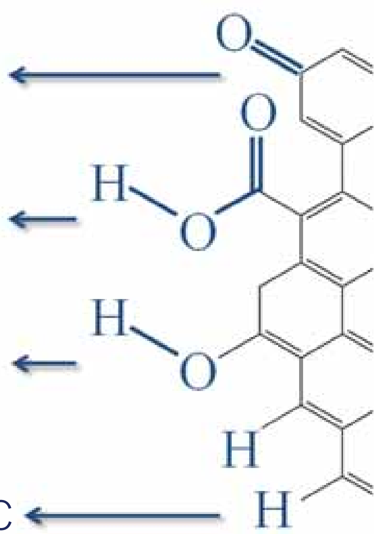
Carbon, **80**, 135 (2014)

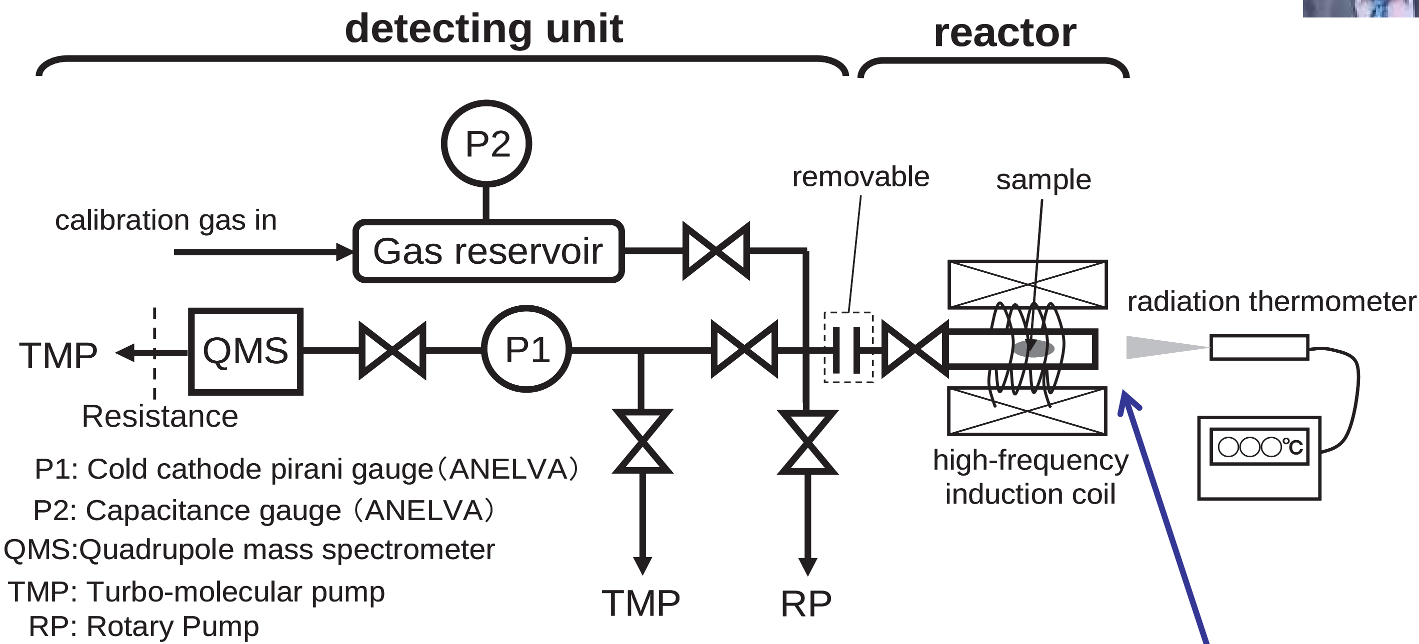
CO :
700 ～ 980 °C

CO_2, H_2O :
100 ～ 400 °C

CO, H_2O :
600 ～ 700 °C

H_2 :
700 ～ 1600 °C

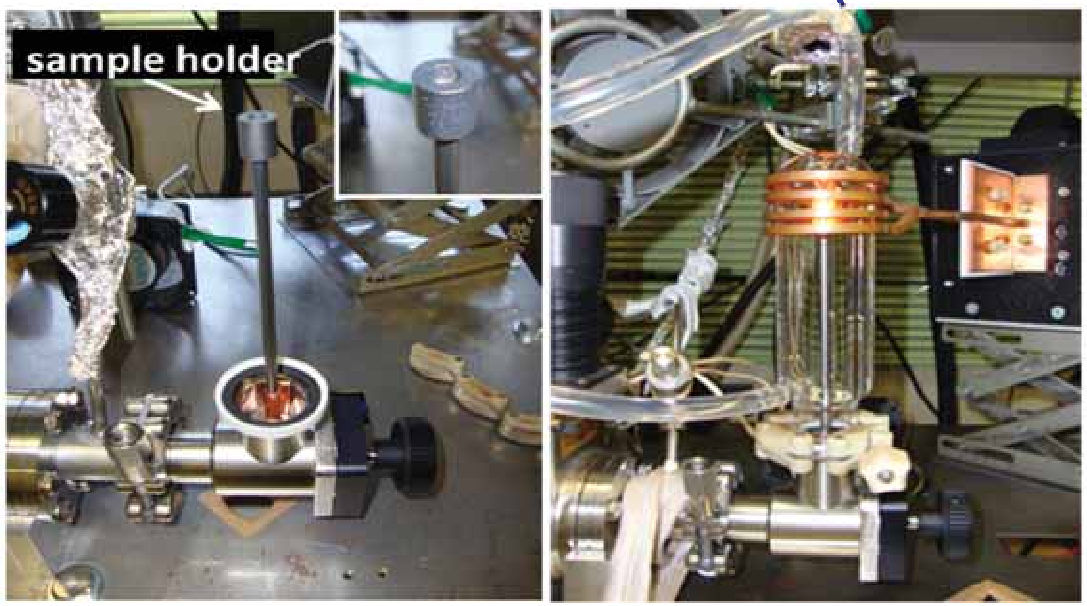




<High-temperature vacuum TPD>

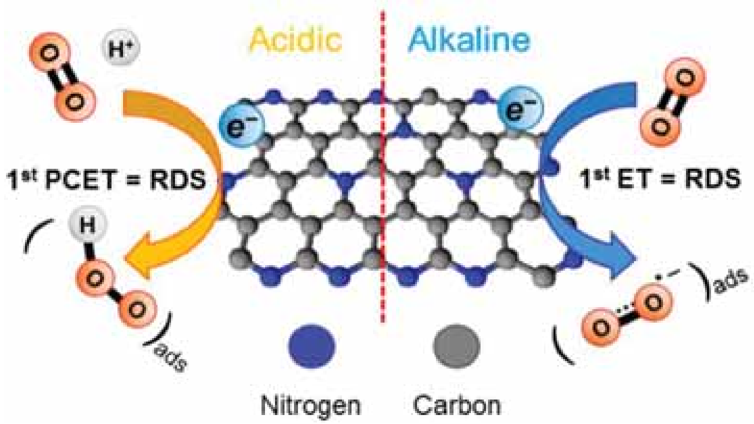
Sensitivity:
100 times higher than commercial TPD

Maximum temperature: **1800 °C**



Quantitative estimation of carbon edge sites is possible.

Application of HT-TPD to N-doped carbons

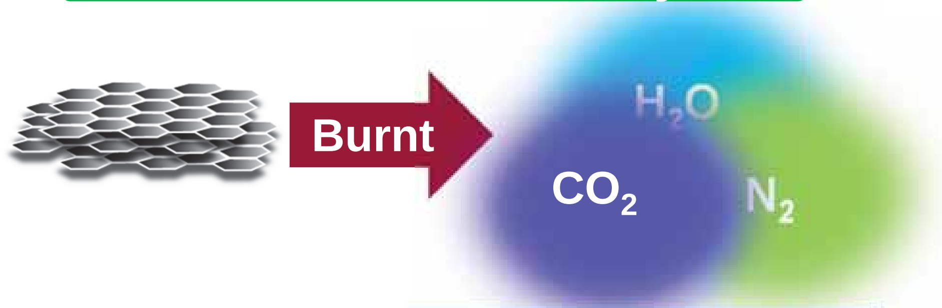


N-doped carbons

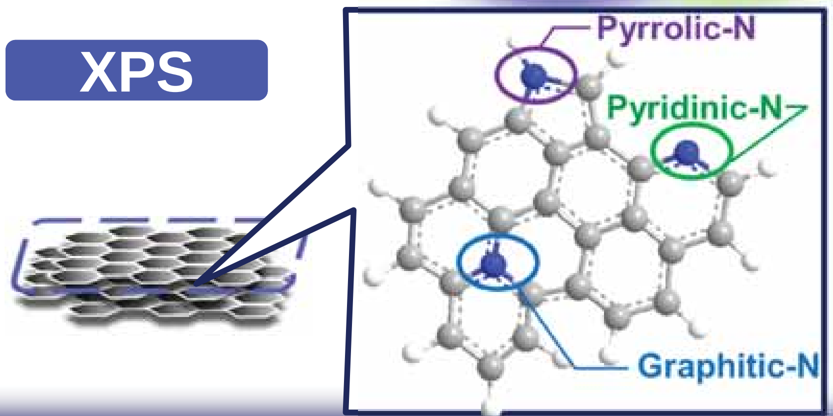
- Promising materials for many applications including fuel cells, supercapacitors, and batteries.

Conventional analysis methods

CHN Elemental Analysis



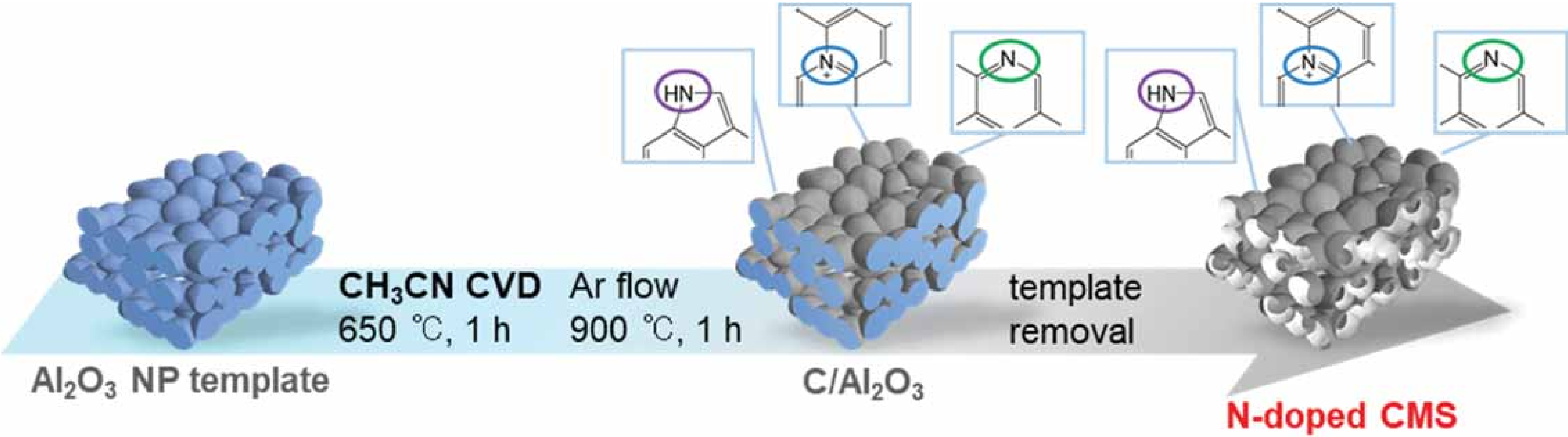
XPS



	Bulk analysis	Identification of N species	High-sensitivity (< 0.1 wt%)
CHN	○	✕	✕
XPS	✕	○	✕
HT-TPD	○	○	○

We propose HT-TPD as a new method.

N-doped CMS as a model material

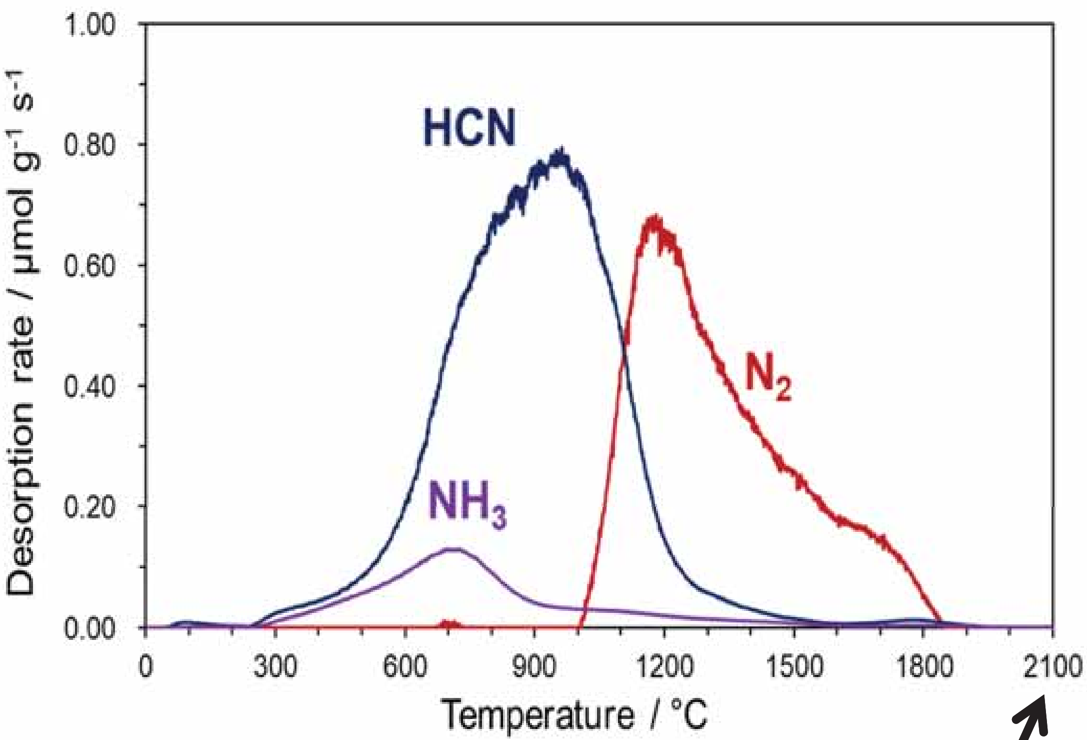


Surface = Bulk

We can compare the three methods: CHN, XPS, and HT-TPD.

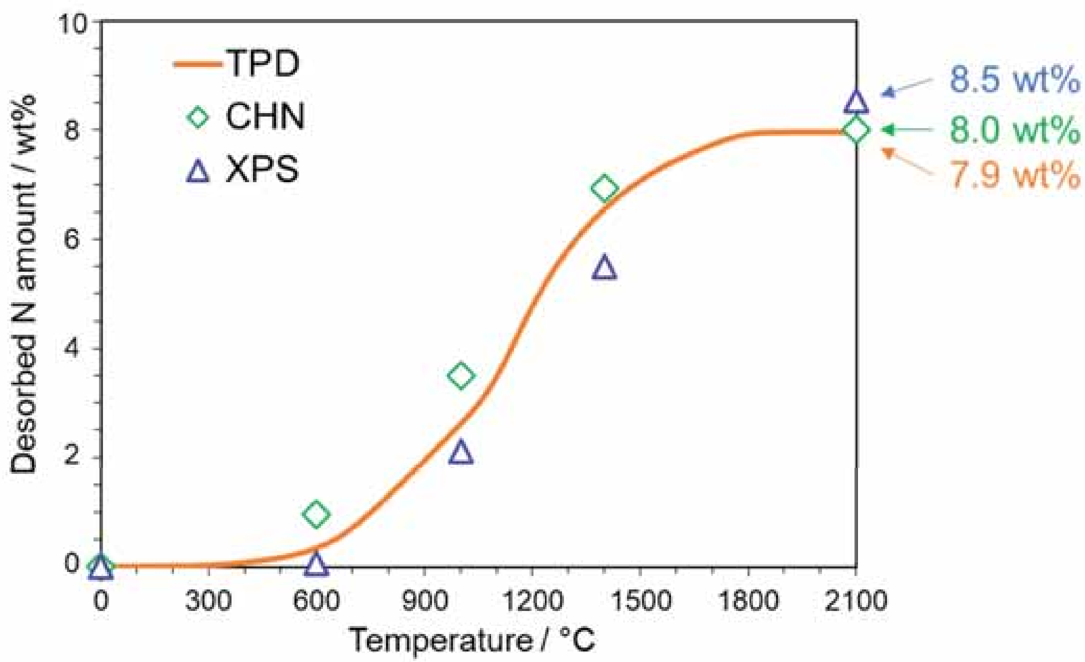
HT-TPD results

N species are desorbed as NH_3, HCN, and N_2.



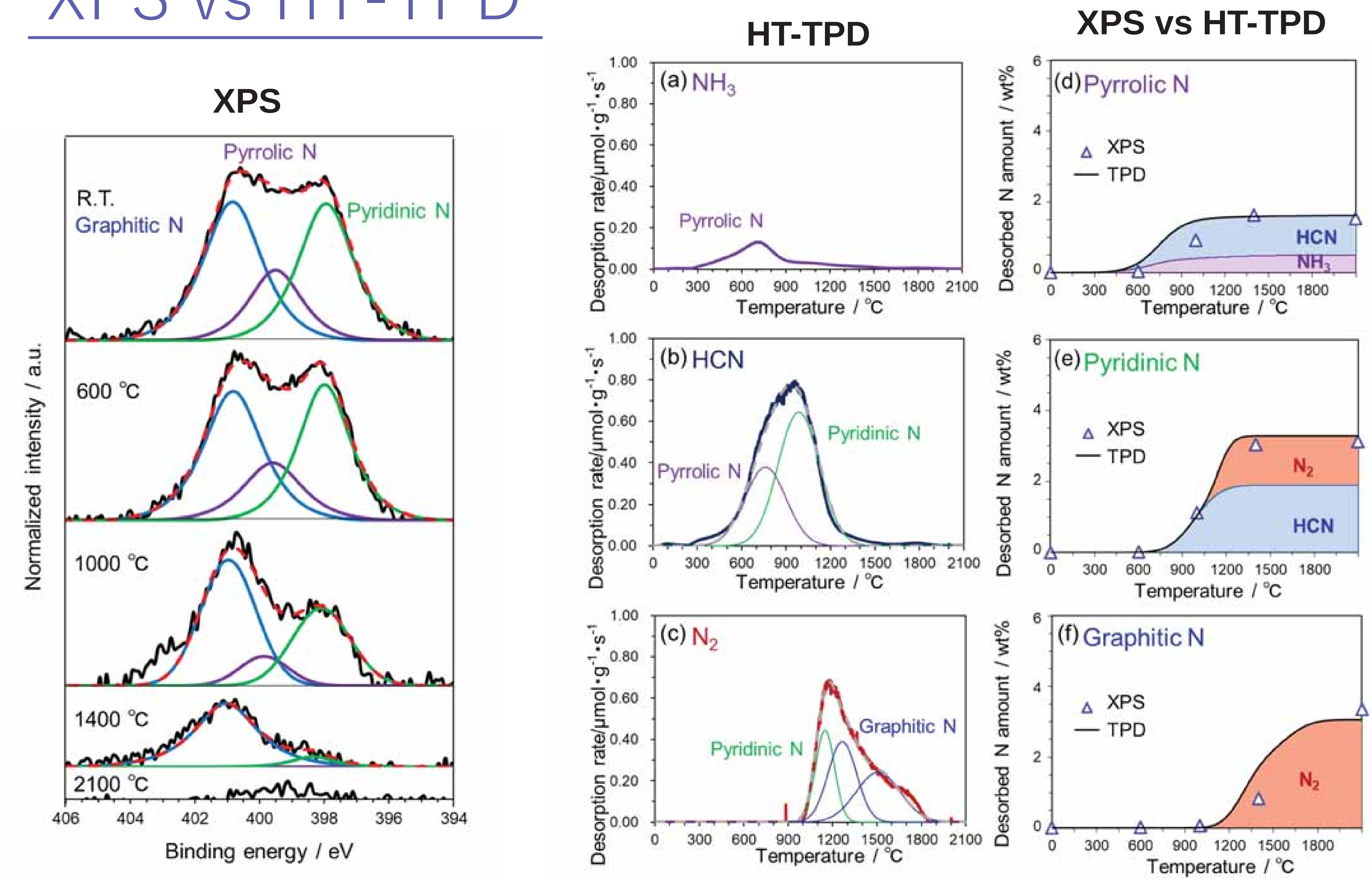
Maximum temperature was increased up to 2100 °C.

Comparison of CHN, XPS, and HT-TPD.



Quantification of HT-TPD is reasonable.
(The sum of NH_3, HCN, and N_2)

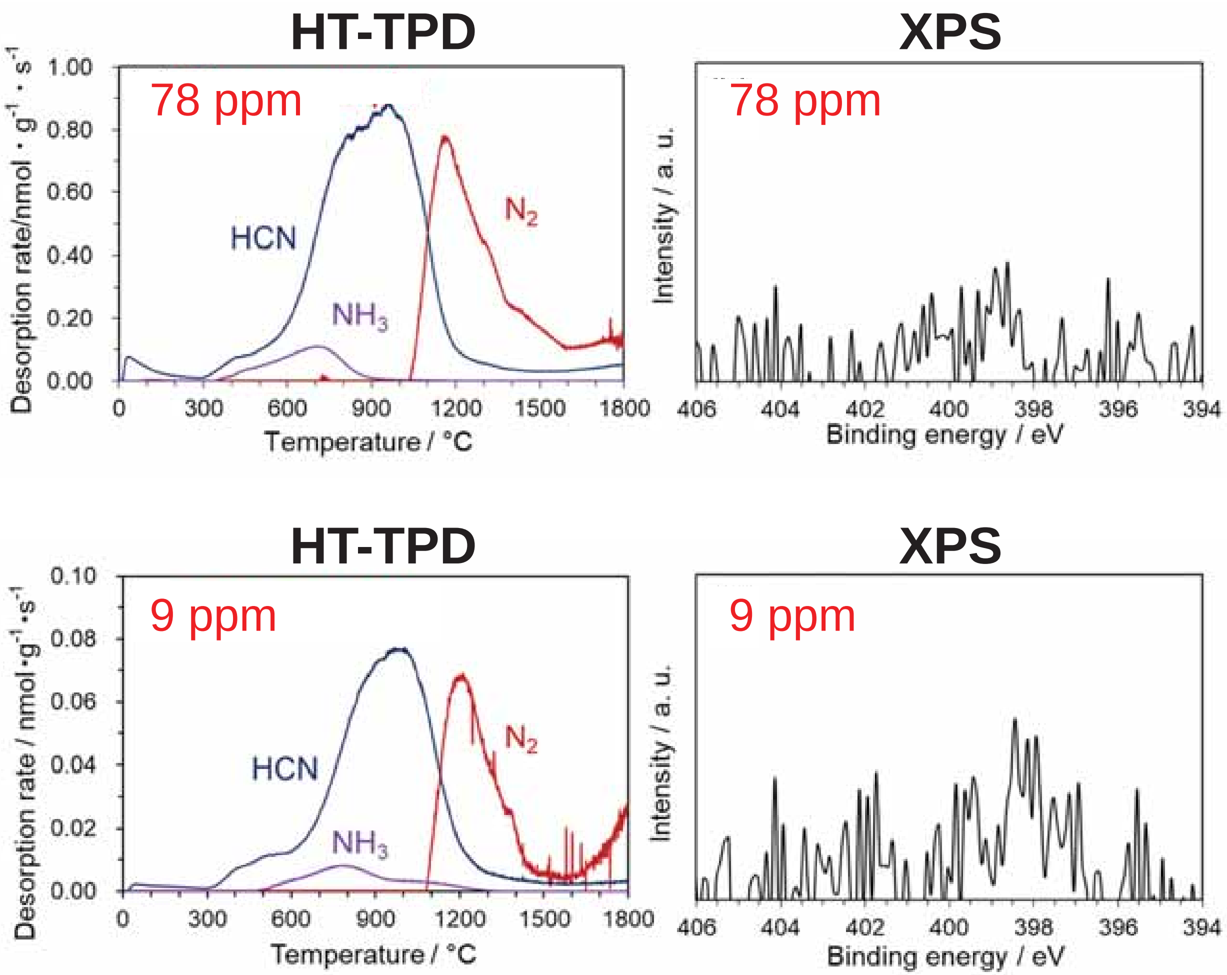
XPS vs HT-TPD

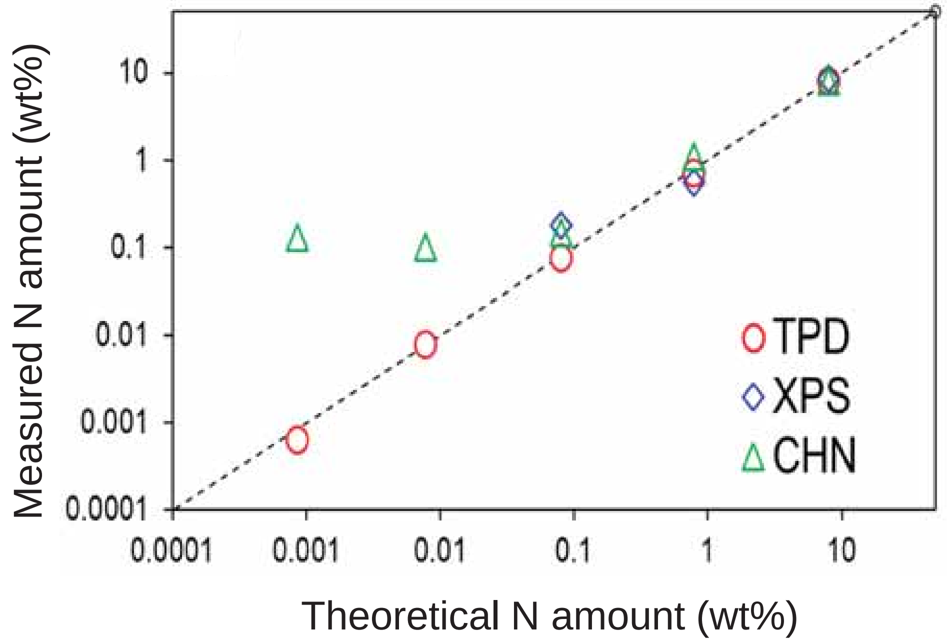


HT-TPD can quantify each amount of different N species.

Quantification of N at a ppm level

N-doped CMS + Graphite → Samples with small N content (~ 9 ppm)





HT-TPD can quantify N species at a ppm-level.

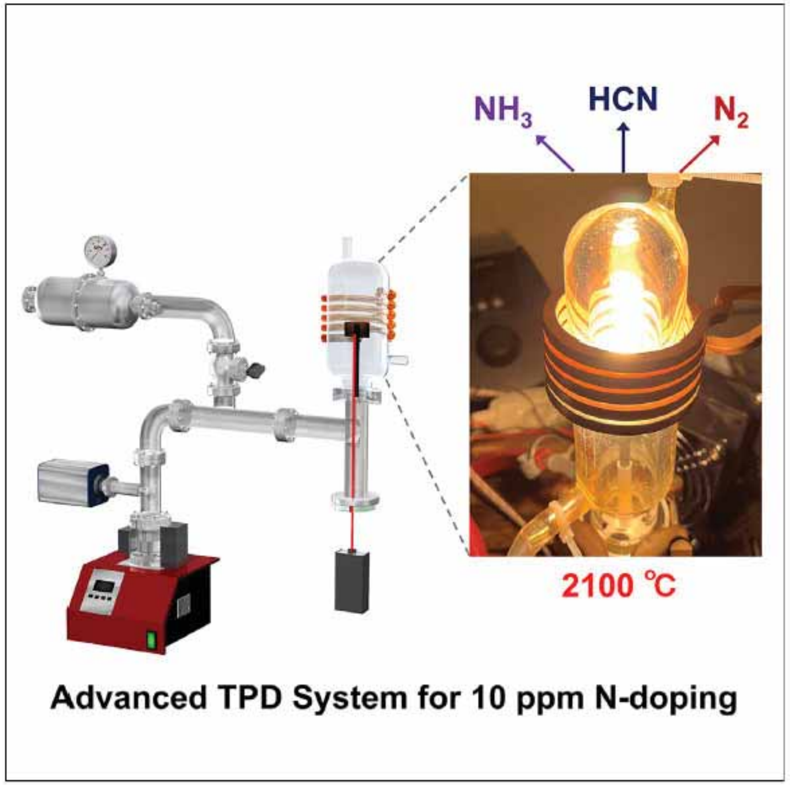
Chem,
DOI: 10.1016/j.chempr.2024.03.029.

Chem

CellPress
OPEN ACCESS

Article

Quantitative and qualitative analysis of nitrogen species in carbon at the ppm level



Takeharu Yoshii, Ginga Nishikawa, Viki Kumar Prasad, ..., Eva Scholtzová, Robert Karoly Szilagyi, Hirotomo Nishihara

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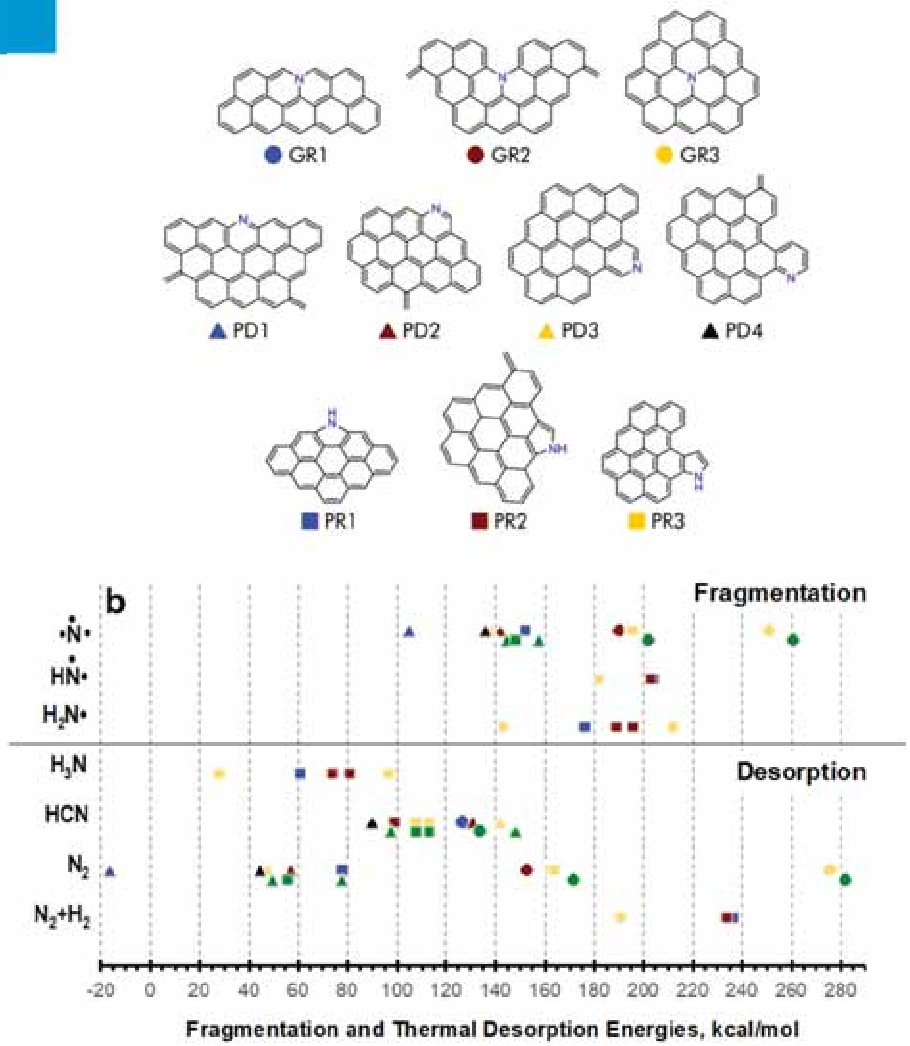
Highlights

Vacuum temperature-programmed desorption (TPD) up to 2,100°C is developed

TPD quantifies nitrogen content in carbon materials at 10 ppm levels

Gas emission profiles correlate with chemical environments of N-dopants

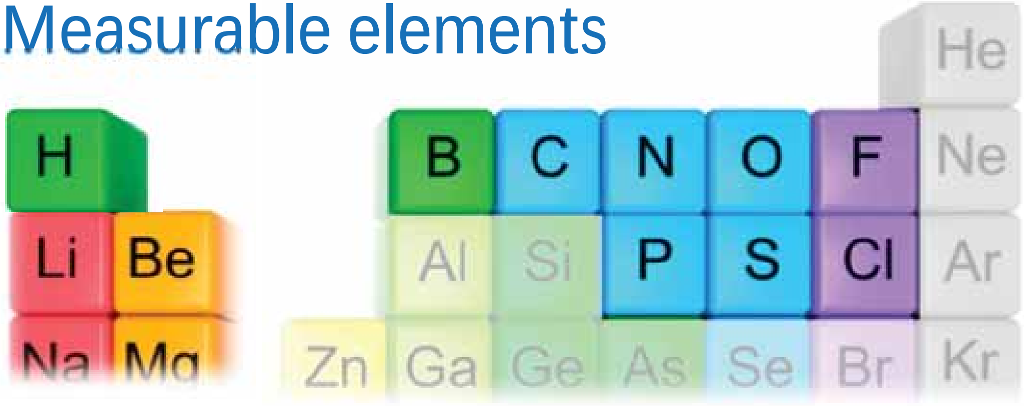


Prof. Robert K. Szilagyi
Dr. Eva Scholtzová

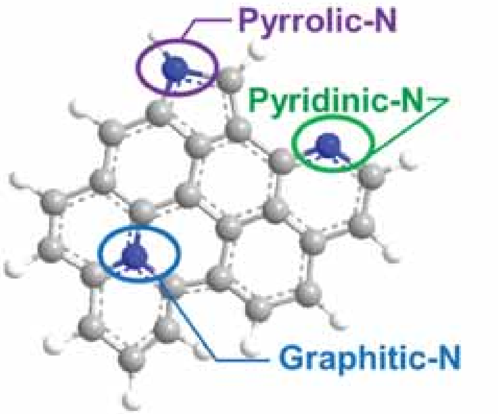
HT-TPD for various materials

Dr. Yoshii

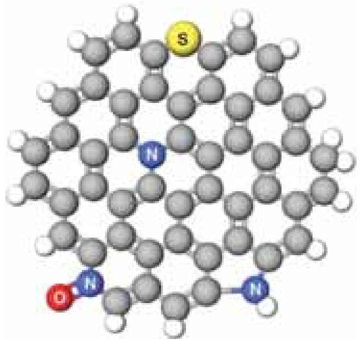
Measurable elements



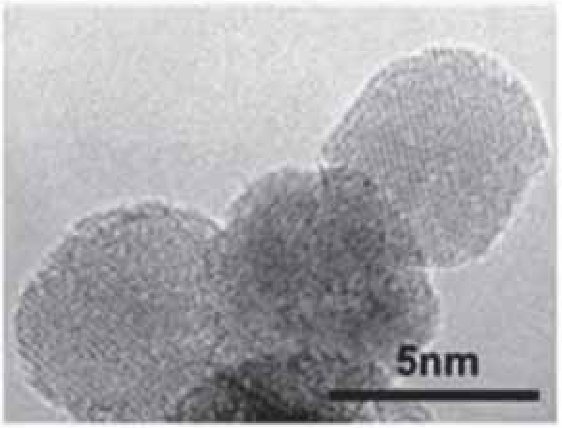
N-doped carbons

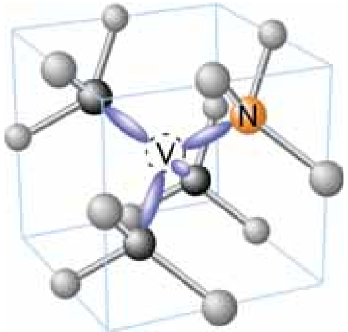


S-doped carbons



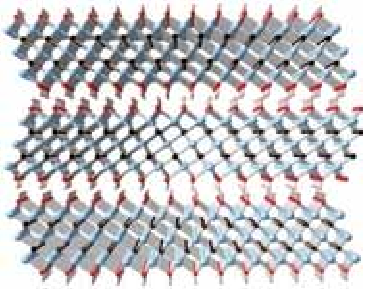
Nano diamonds





Inorganic materials

Oxides



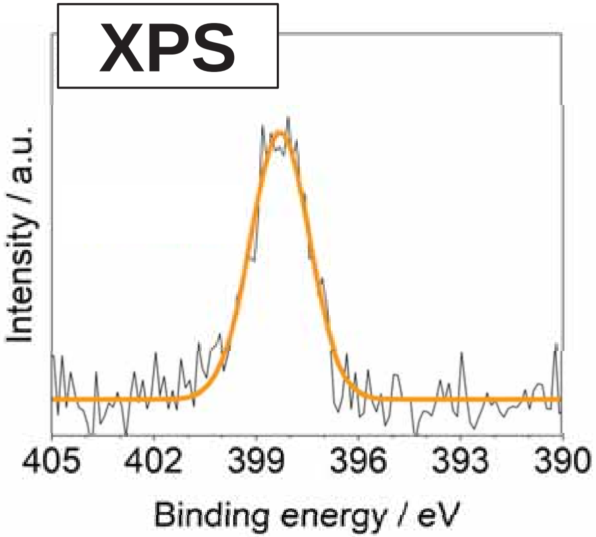
Carbides, nitrides

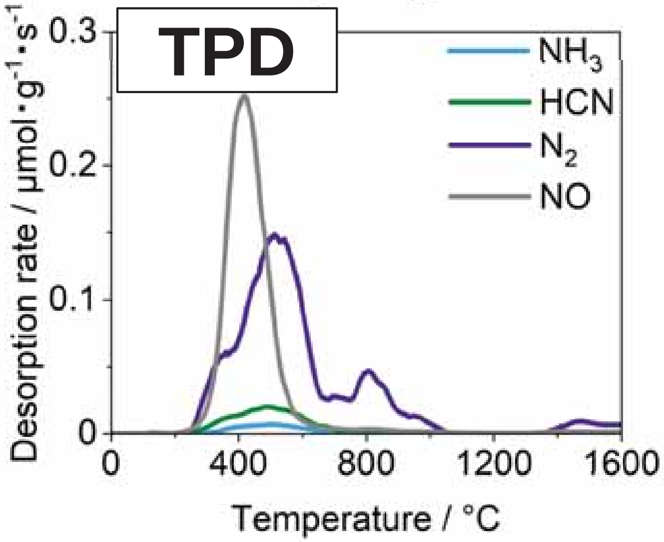
Analysis of N in perovskite-type oxides

Chem. Sci., **15** (2024) 10350.

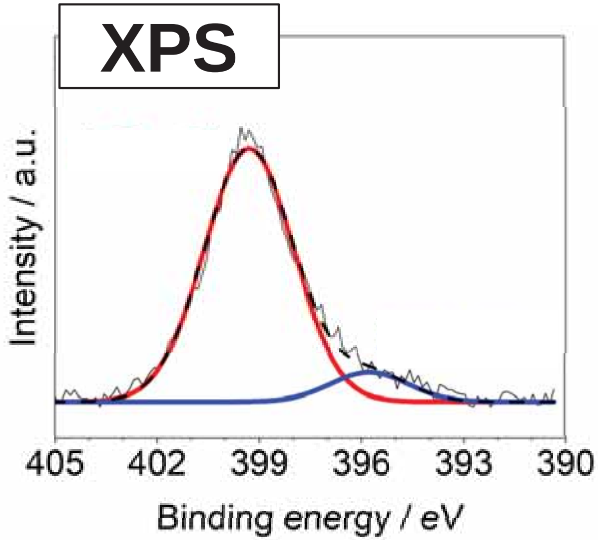
Dr. Yoshii

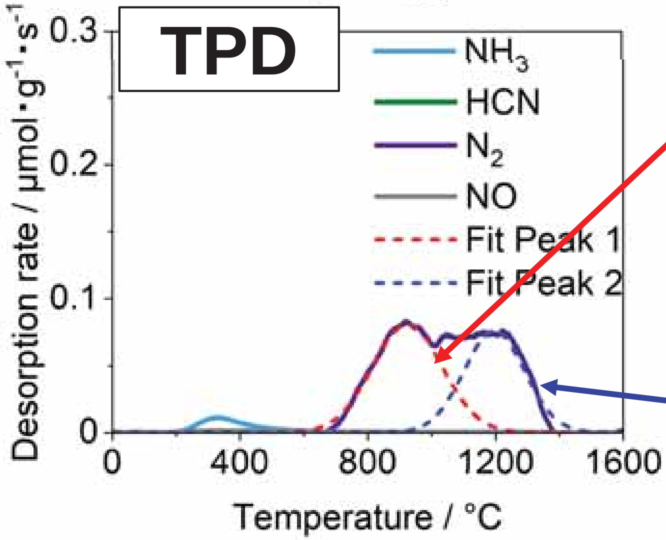
Photocatalysis △



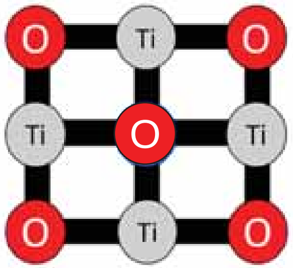


Photocatalysis ◎

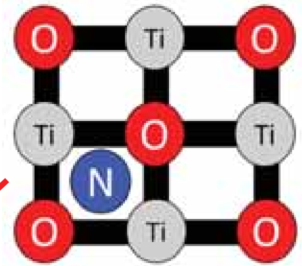


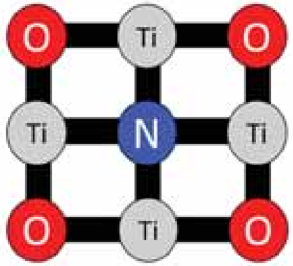


$C_xN_yH_z$



$La_2Ti_2O_7$





$La_2Ti_2O_7$

Summary

We have developed new science, materials, and technologies based on the concept of "Atomic Design of Carbon-Based Materials"

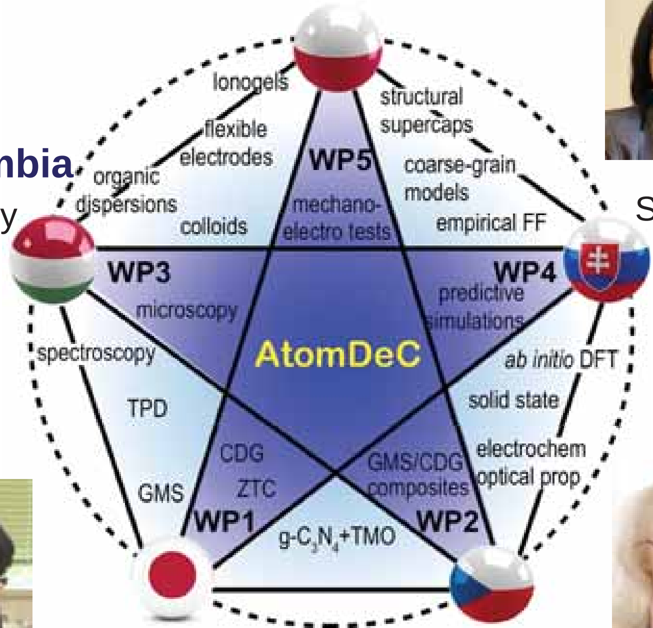
https://atomdec.info/

Canada

External collaborator

Dr. Robert K. Szilagyi

The University of British Columbia



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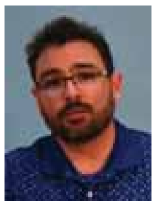

Dr. Eva Scholtzová

Slovak Academy of Science

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Dr. Monica Michalska

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Nishihara lab members