INSTITUTE OF MATERIALS SCIENCE AND COMPUTING
THE UNIVERSITY OF IOANNINA

Layered and Nanoporous Materials Group

GROUP LNM @UoI

Ceramics and Composite Laboratory
Department of Materials Science and Engineering
University of Ioannina, Greece

D. Gournis

http://www.materials.uoi.gr/ccl/LNM-About.html

CERAMICS AND COMPOSITES LABORATORY

CCL

Department of Materials Science and Engineering
University of Ioannina

Hierarchically Porous and Hybrid Materials
Leader: M. A. Karakassides

Layered & Nanoporous Materials
Leader: D. Gournis

Biomaterials and Regenerative Medicine
Leader: S. Agathopoulos

X-ray Spectroscopy for Materials Characterization
Leader: D. Anagnostopoulos

Process Engineering for Materials
Leader: C. Salmas

High Temperature and Construction Materials
(Intredisciplinary Group)
Leader: Director of CCL

Layered and Nanoporous Materials (LNM) Group

- LNM is part of the **Ceramics & Composites Laboratory (CCL)** (establ. in 2001). Research covers *structural, chemistry and engineering aspects of materials*:
  - Carbon-nanostructured materials
  - Inorganic layered materials (clays, LDHs etc)
  - Nanoporous materials (micro- and meso-)
  - Organic-inorganic hybrid materials/nanocomposites
  - Nanoparticles / biocatalysts
- **Applications**: catalytic, energy, environmental, magnetic, electronic, optical, bio-related, medical, composites
- Work is extended through various collaborations with national and international research centers, other university departments and industrial partners.
- Several graduate students are currently pursuing their PhD and MSc degrees, while about 10 undergraduate students per year complete their Diploma Theses.

INSTITUTE OF MATERIALS SCIENCE AND COMPUTING

WHO WE ARE

LNM GROUP @UoI

accomplished

12 PhD (4 joint)
25 MSc
>130 Diploma

Dr. K. Spyrou *(Postdoc)*
Dr. P. Zygouri *(Postdoc)*
Dr. M. Subrati *(Postdoc)*

T. Gioussis *(PhD)*
E. Thomou *(PhD)*
N. Karouta *(PhD)*
N. Chalmpes *(PhD)*
V. Sikavitsi *(PhD)*

F. Evangelou *(MSc)*
D. Mpampatsoulis *(MSc)*

~10 Diploma studs.

Former:
L Jankovic *(Postdoc)*, A. Enotiadis *(PhD)*, T. Tsoufis *(PhD)*, A. Kouloumpis *(PhD)*, K. Litina *(MSc)*, G. Potsi *(PhD)*, E. Mpletsa *(MSc)*, E. Diamanti *(PhD)*, M. Katsiaflaka *(MSc)*, M. Antoniou *(Postdoc)*, A. Rossos *(PhD)*, E. Mouzourakis *(MSc)*, K. Dimos *(Postdoc)*, K.-M. Lyra *(MSc)*, A. Sima *(MSc)*, G. Varfi *(MSc)*, E. Skoura *(MSc)*, V. Manoloukou *(MSc)*

PUBLICATIONS
since 2006

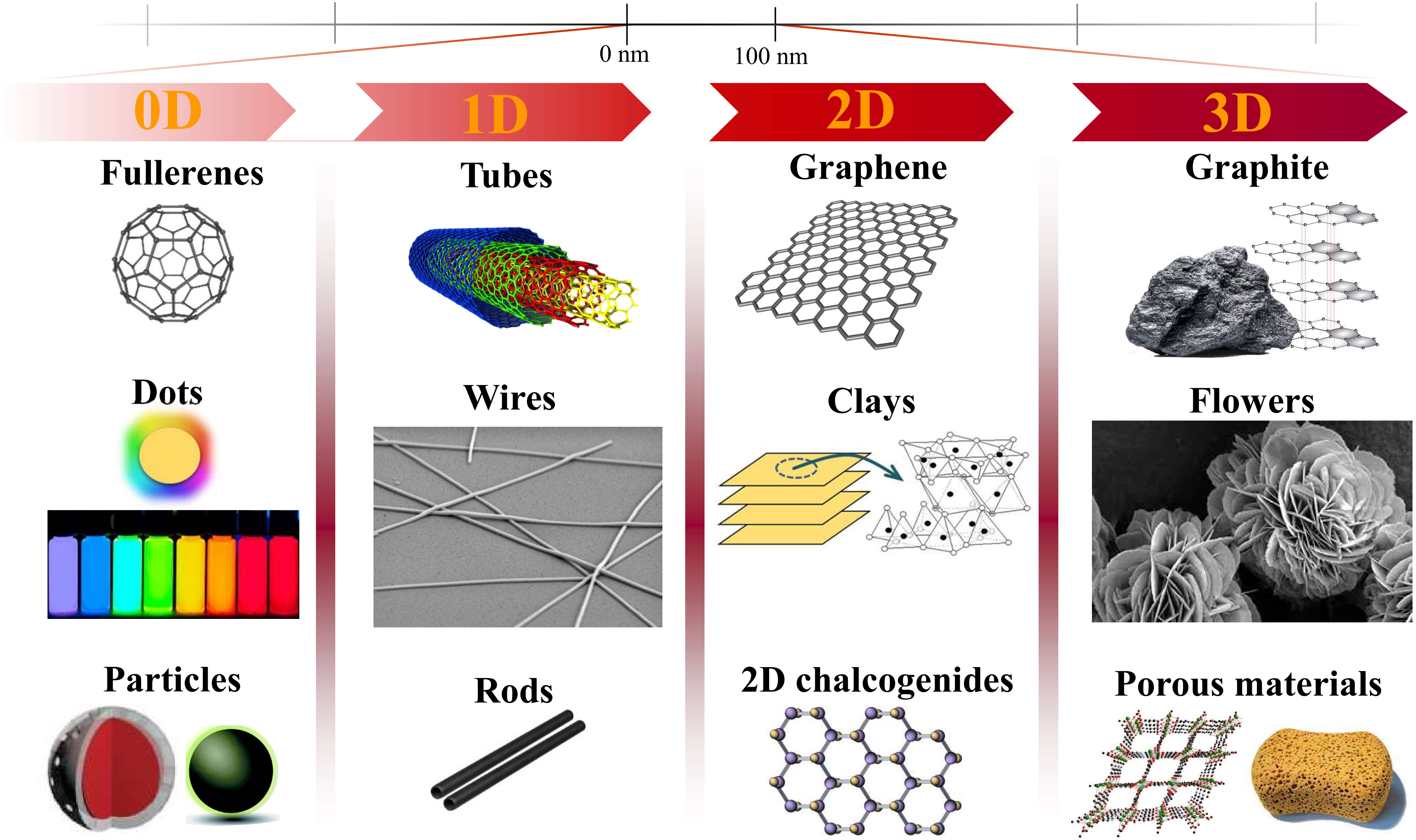
169 papers
~ 6500 citations
5 book chapters
2 international patents

@UoI
LNM GROUP

Dept. Mater. Sci. & Engineer.
the university of ioannina
THE UNIVERSITY OF IOANNINA

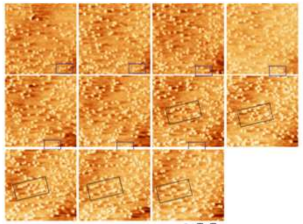
INSTITUTE OF MATERIALS SCIENCE AND COMPUTING

Nanostructured materials

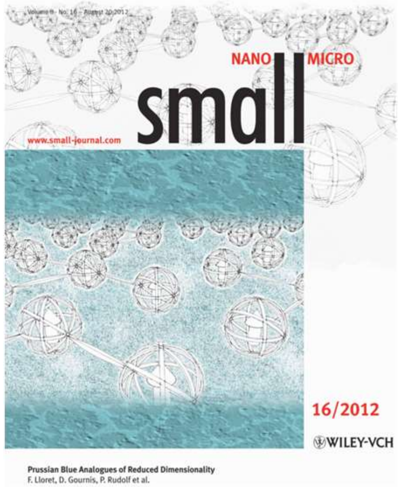


“Hybrids and composites can be developed by combining diverse nanomaterials”

INSTITUTE OF MATERIALS SCIENCE AND COMPUTING

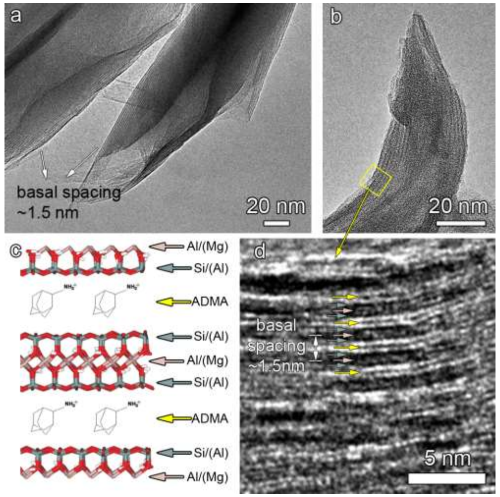


Research Activities

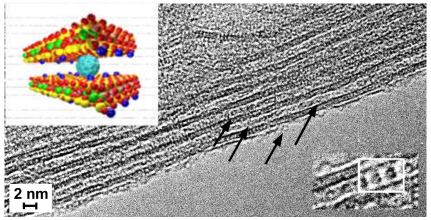


INORGANIC LAYERED MATERIALS

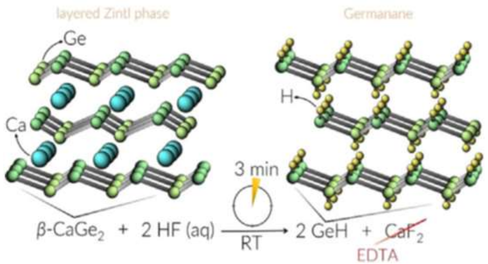
- **Pillared clays & organoclays** for catalytic, magnetic, electronic, optical and environmental applications
- **2D materials** (TMDs, germanane, silicene, Bi_2Se_3, etc)
- **Intercalation reactions/pillaring** (macromolecules, nanoparticles, **fullerene derivatives and carbon nanostructures, etc)** in/of layered materials
- **Biocatalysts & Biomimetic** materials based on layered materials
- Low dimensional solids based on **layer double hydroxides** with optoelectronic and selective sorption properties
- **Magnetic layered phyllosilicates**



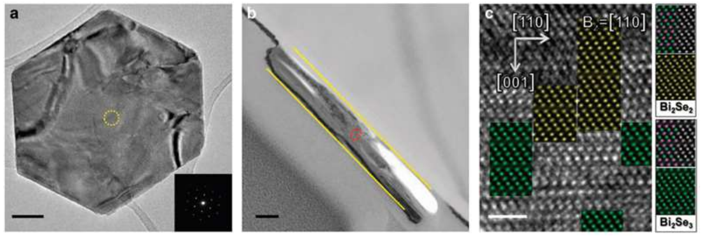
Adv. Funct. Mater. **2014**



JACS **2006**



Angew. Chem. Int. Ed. **2020**

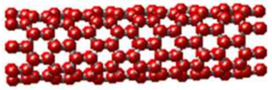


NPG Asia Mater. **2016**

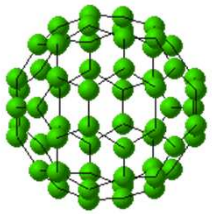
Research Activities

‘COMMON’ CARBON-BASED NANOSTRUCTURED MATERIALS

Graphene

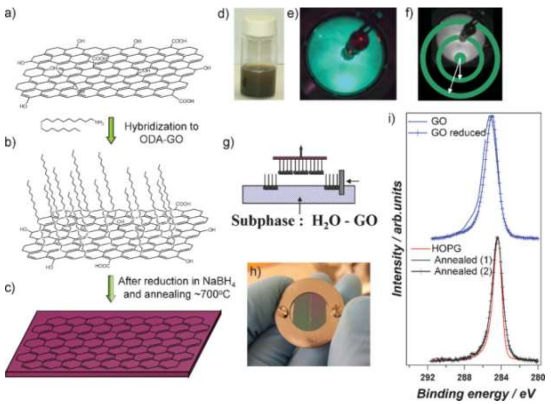


CNTs

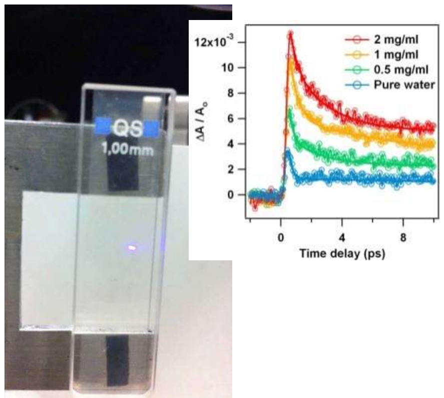


Fullerenes

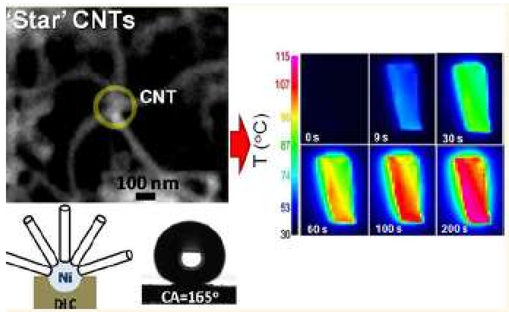
production → modification → Development of hybrid materials



Small **2010**, *6*, 35



Nature Commun. **2013**, *4*, 2560

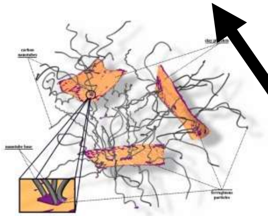


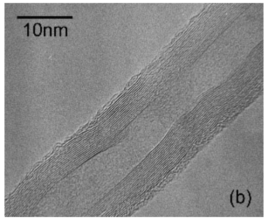
ACS Nano **2012**, *6*, 10475

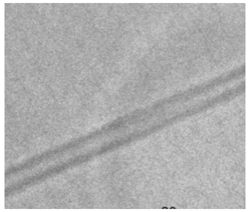
INSTITUTE OF MATERIALS SCIENCE AND COMPUTING

CNTs

Synthesis

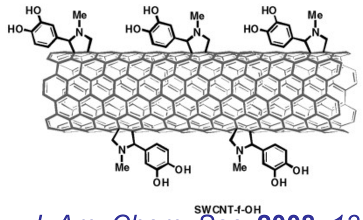






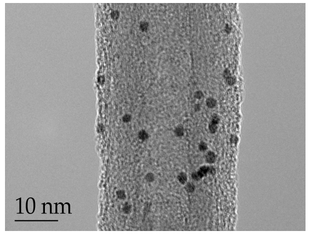
Carbon **2002**, *40*, 2641; **2010**, *48*, 3434; *Micropor. Mesopor. Mater.* **2008**, *110*, 128

Functionalization



J. Am. Chem. Soc. **2008**. *130*, 8733; *Carbon* **2004**, 4, 865

Decoration

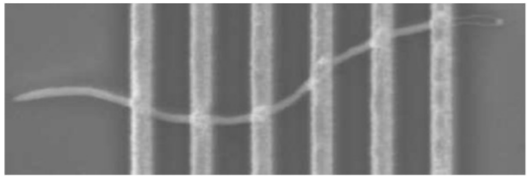


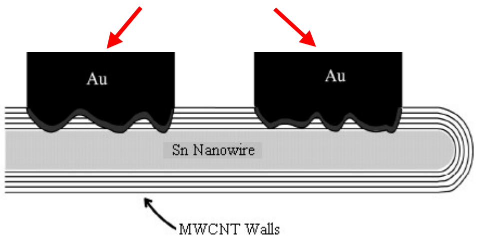
J. Mater. Chem. **2007**, *17*, 2679; *J. Nanosci. Nanotechn.* **2008**, 5941; *Nanotechn.* **2011**

(Bio)catalysis, (Bio)sensors etc.

Adv. Engineer. Mater. **2010**, *12*, B179; *Bioresour. Technol.* **2011**, 102

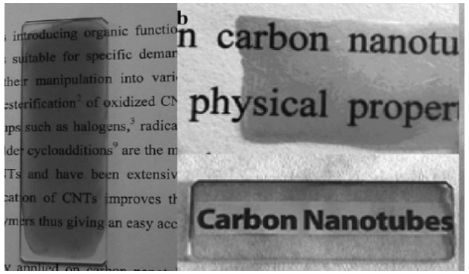
Nanotechnology





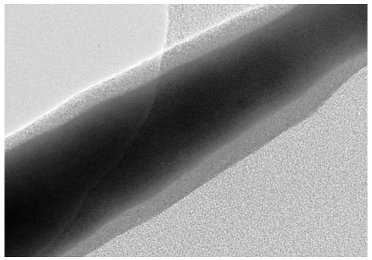
Nano Lett. **2008**, *8* 3060.

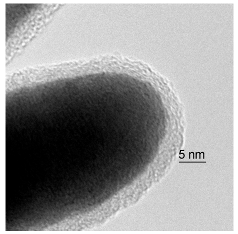
Nano-fillers: composites or hybrids



J. Am. Chem. Soc. **2008**. *130*, 8733.

Filling: 1D Nano-templates



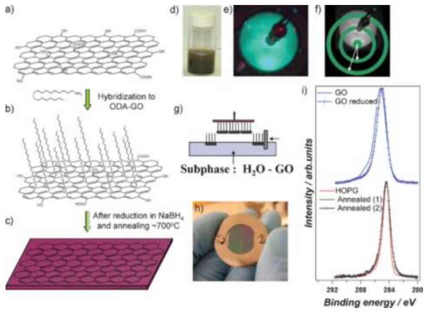


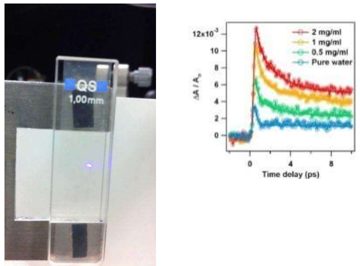
Nano Lett. **2006**, *6*, 1131.

Dept. Mater. Sci. & Engineer.
the university of ioannina
THE UNIVERSITY OF IOANNINA

Graphene

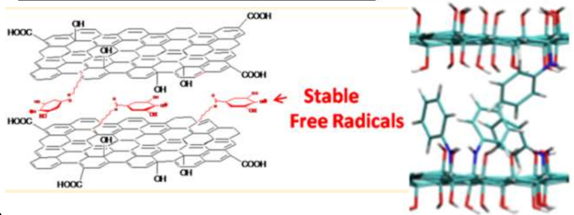
Production





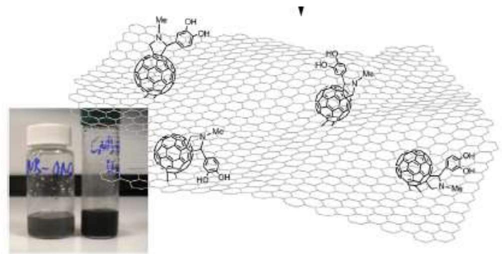
Langmuir **2003**, *19*, 6050; *Smaill* **2010**, *6*, 35; *Nature Commun.* **2013**, *4*, 2560; *Nanoscale* **2016**, *8*, 2908

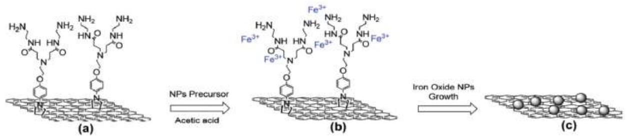
Modification

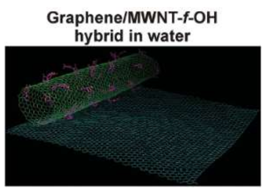


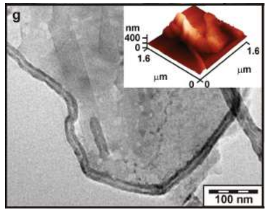
Adv. Funct. Mater. **2015**. *25*, 236; *Langmuir* **2015**, *31*, 10508

Hybrids



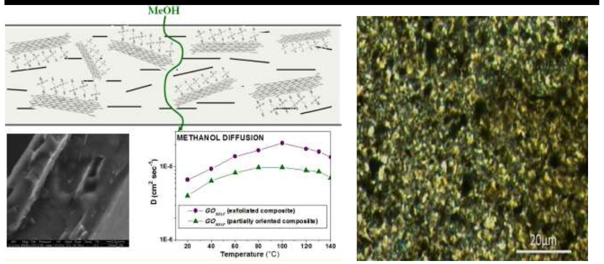


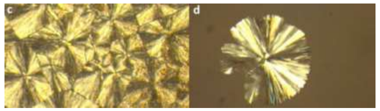




Carbon. **2016**, *110*, 51; *Nanoscale.* **2015**, *7*, 8995; *Adv. Funct. Mater.* **2015**, *25*, 1481; *Adv. Funct. Mater* **2014**, *24*, 5841

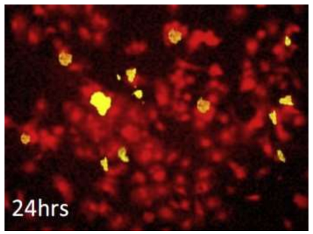
Nano-fillers for composites

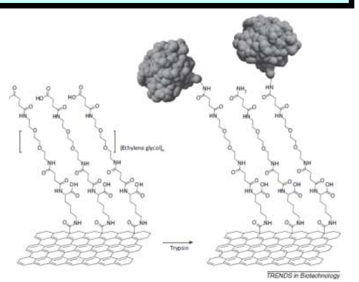




Small **2012**. *8*, 3388; *J. Phys. Chem. C* **2014**, *118*, 24357; *Polymer* **2013**, *54*, 4604

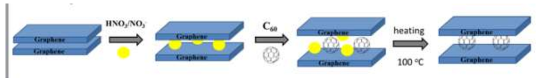
(Bio)-catalysis, -sensors drug delivery

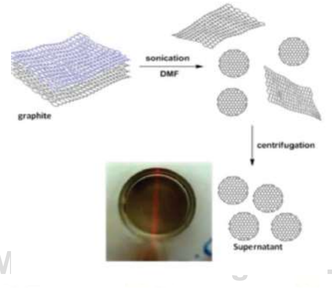




Eur. J. Pharm. Biopharm. **2015**, *93* 18; *Trends Biotech.* **2014**, *32*, 312; *Proc. Biochem.* **2013**, *48*, 1010; Bioresource Techn. **2012**, *115*, 164

Graphene forms



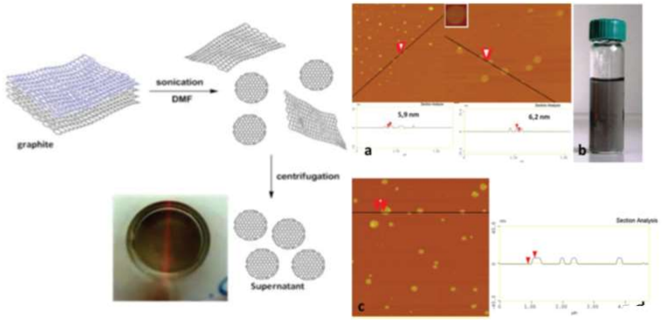


Nanoscale **2015**, *7*,15059; *Carbon* **2013**, *61*,313

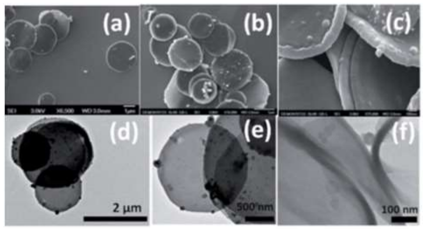
Research Activities

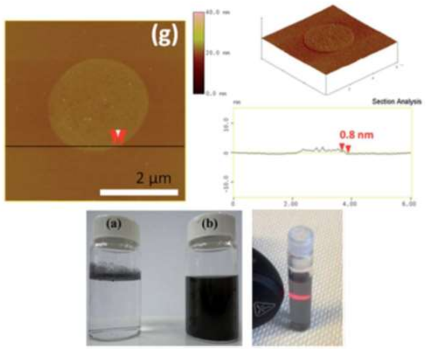
‘ALTERNATIVE’ CARBON NANOSTRUCTURES

Nanodiscs



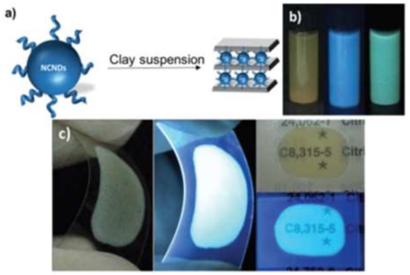
Nanoscale **2015**, *7*, 1509



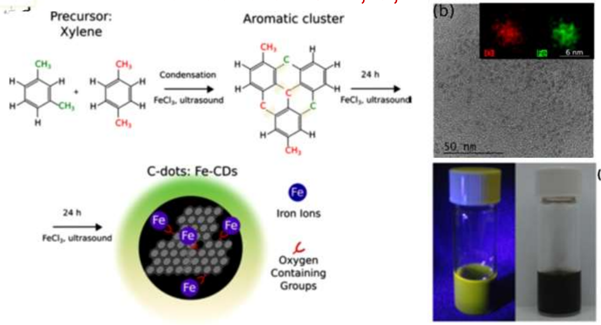


RSC Advances **2018**, *8*, 122

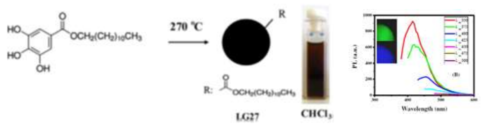
Dots



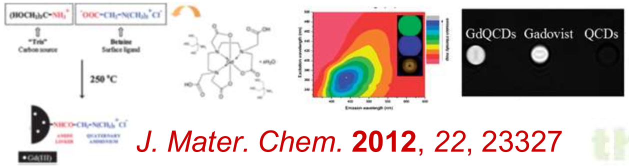
Nanoscale **2017**, *9*, 10256



Appl. Mater. Today **2017**, *7*, 179

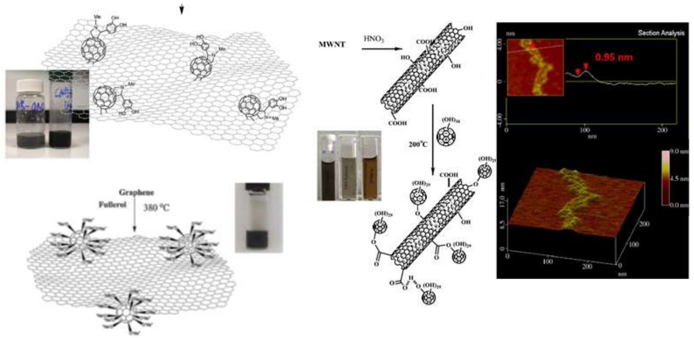


Carbon **2015**, *83*, 173; **2013**, *61*, 640



J. Mater. Chem. **2012**, *22*, 23327

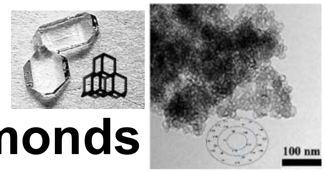
Nanobuds



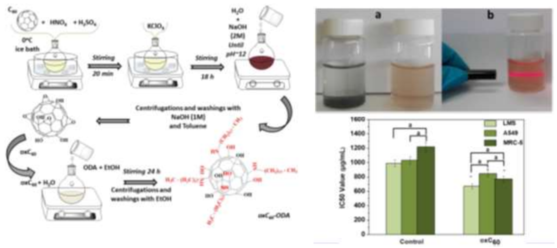
Appl. Mater. Today **2017**, *9*, 71; *Carbon* **2016**, *110*, 51; *Mater. Lett.* **2012**, *82*,48

Nanorings

Molecular diamonds



‘Fullerene oxide’

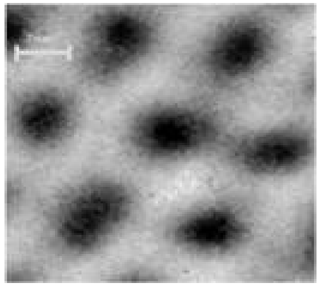


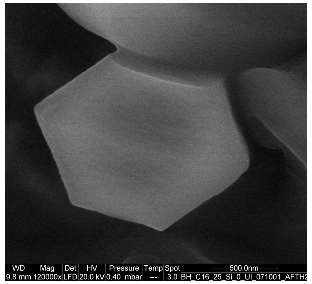
Sci. Rep. **2020**, *10*, 8244

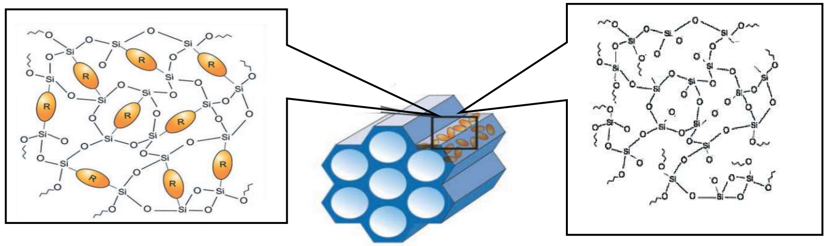
Research Activities

NANOPOROUS (MICRO-, MESO-) MATERIALS

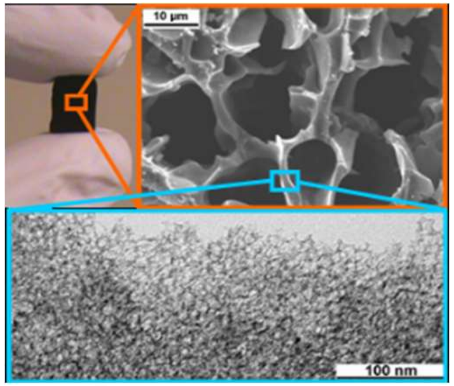
- **Mesoporous silicate molecular sieves** such as MCM-41, SBA-15, HMS with functional groups for targeted applications
- **Periodic mesoporous organosilicas** (PMOs) for hydrogen and methane storage
- **Hierarchical porous carbons (HPC)** for gas storage and biomedical applications
- **Carbon cuboids (CC)** for environmental remediation, antimicrobial, biocatalysis and gas storage



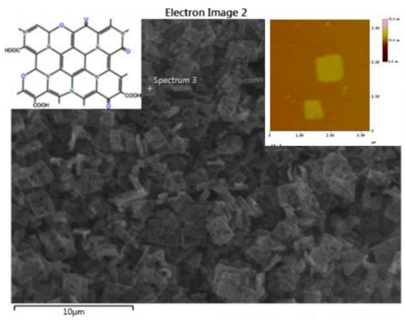




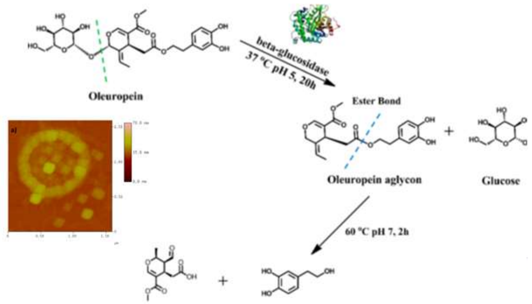
Int. J. Hydrog. Energ. **2014,** *39*, 2104



Pharmaceutics **2020,** *12*, 227;
Biores. Techn. Rep. **2020**, 9 100372



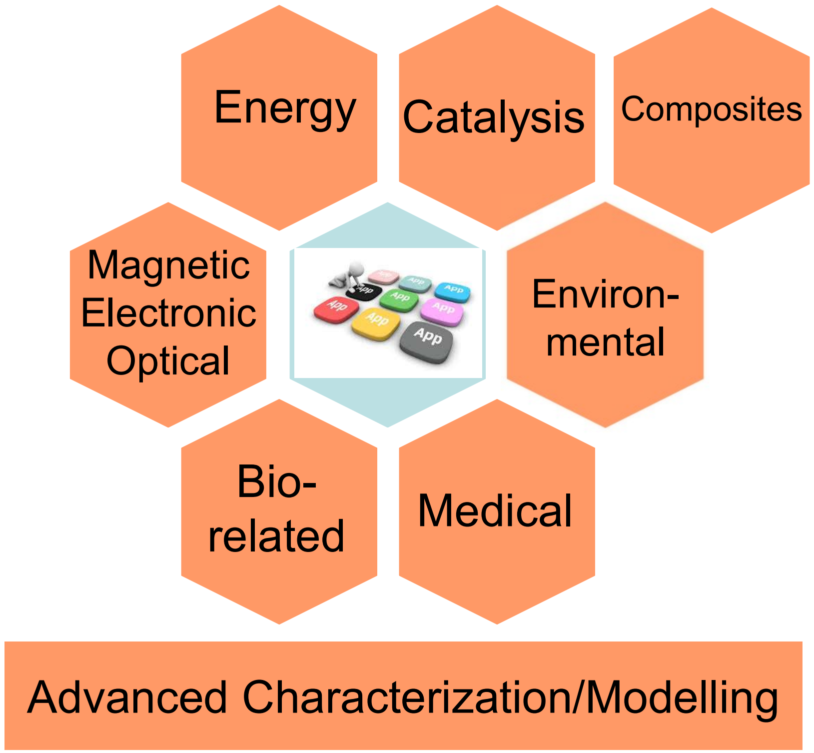
ACS Omega **2019,** *4*, 4991



Nanomater. **2019,** *9*, 1166

INSTITUTE OF MATERIALS SCIENCE AND COMPUTING

Active Collaborations



University of Ioannina
- M.A. Karakassides *group*
- I. Deligiannakis *group*
- A. Bourlinos
- A. Douvalis
- Ch. Stamatis *group*
- M. Patila
- E. Ntounousi
- Y. V. Simos
- D. Peschos *group*

جامعة خليفة Khalifa University
- S. Alhassan *group*
- Y. Al Wahedi *group*
- G. Karanikolos *group*

University of Trieste
- M. Prato *group*

University of Patras
- V. Georgakilas *group*
- K. Avgoustakis *group*

Technical University of Crete
- Y. Yentekakis *group*

university of groningen
- P. Rudolf *group*
- B. van Wees *group*

Aristotle University of Thessaloniki
- D. Bikiaris *group*
- K. Triantafyllidis *group*

Demokritos National Center for Scientific Research
- T. Steriotis *group*
- G. Charalampopoulou
- G. Papavasileiou *group*
- Z. Sideratou *group*
- F. Katsaros *group*
- I. Karatasios *group*

Università della Calabria
- I. Nicotera *group*
- R. Agostino *group*

Universitat Politècnica de Catalunya BarcelonaTech (UPC)
- R. Macovez
- J. L. Tamarit *group*

Universiteit Antwerpen
- G. Van Tendeloo *group*
- X. Ke

University of Crete
- G. Froudakis *group*
- P. Trikalitis *group*

Palacký University Olomouc
- R. Zboril *group*
- M. Otyepka

Alma Mater Studiorum Università di Bologna
- F. Zerbetto *group*

INSTITUTE OF MATERIALS SCIENCE AND COMPUTING

Funding

Presently active:

- Inter. Res. Grant –Petroleum Institute, UAE (2016-2020) *"CO_2 from tail gas for EOR"*
- Research-Create-Innovate (2018-2021) *"A novel process for the efficient and eco-friendly valorization of biogas and CO_2 emissions: complete conversion to ethylene"* , **ECO-ETHYLENE**
- Research-Create-Innovate (2018-2021) *"Production of innovative high energy efficiency pipes for underfloor heating-cooling systems"* , **SETHYEA**
- Research-Create-Innovate (2018-2021) *"Self-healing and self-sensing nano-composite conservation mortars",* **AKEISTHAI**
- Research-Create-Innovate II (2020-2023) *"Design and develpopment of a sweat-based glucose monitoring graphene nanodevice (closed-loop) with controlled transdermal nanoemulsion release for hypoglycemic drug delivery",* **DEMIGOD**
- Research-Create-Innovate II (2020-2023) *"Development and pilot scale demonstration of an innovative, effective and eco-friendly process for the production of clean hydrogen and electrical power generation from biogas",* **Eco-Bio-H2-FCs**
- Special Actions: Industrial Materials (2020-2023) *"Advanced aluminosilicate and magnesia refractories of high efficiency using nanotechnology"*
- Research-Create-Innovate II (2020-2023) *"Advanced energy upgrading building components containing phase change composite and/or ceramic foams with electromagnetic shielding properties"*
- HFRI Postodoc I (2019-2022) *"Hierarchical Porous Carbon—PLLA and PLGA Hybrid Nanoparticles for Intranasal Delivery of Galantamine for Alzheimer's Disease Therapy",* K. Spyrou

Recently concluded:

- Inter. Res. Grant –Petroleum Institute, UAE (2015-2019) *"Magnetic Nanoparticles (**MNPs**) for Reservoir Characterization"*

innova TECHNOLOGY SOLUTIONS

DeltaE Srl

Dept. Mater. Sci. & Engineer.

THE UNIVERSITY OF IOANNINA

INSTITUTE OF MATERIALS SCIENCE AND COMPUTING

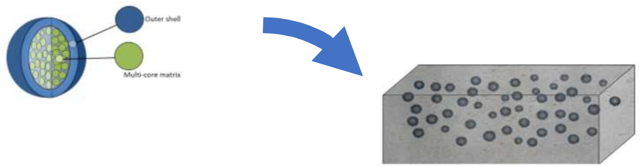
ΕΥΔΕ ΕΤΑΚ — Ερευνώ, Δημιουργώ, Καινοτομώ

ΑΚΕΙΣΘΑΙ

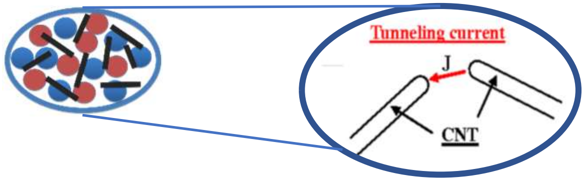
ΚΑΙΝΟΤΟΜΑ, ΠΟΛΥ-ΛΕΙΤΟΥΡΓΙΚΑ ΚΟΝΙΑΜΑΤΑ ΚΑΙ ΕΝΕΜΑΤΑ ΑΠΟΚΑΤΑΣΤΑΣΗΣ ΜΝΗΜΕΙΩΝ, ΜΕ ΙΚΑΝΟΤΗΤΑ ΑΝΙΧΝΕΥΣΗΣ ΚΑΙ ΕΠΟΥΛΩΣΗΣ ΤΩΝ ΒΛΑΒΩΝ

The concept

- **Development of self-healing repair mortars,** based on **encapsulated healing agents**.



- **Development of self-sensing, repair mortars,** based on **functionalized C-nanostructures** (CNTs,GnPs,GOx,rGOx)



Deliverables Impact

- **12 new research jobs**
- **3 PhD projects**
- **new production methodologies**
- **new design & experimental protocols**
- **10 research papers**

and counting…

Ευρωπαϊκή Ένωση
Ευρωπαϊκό Ταμείο Περιφερειακής Ανάπτυξης
ΕΠΑνΕΚ 2014-2020
ΕΠΙΧΕΙΡΗΣΙΑΚΟ ΠΡΟΓΡΑΜΜΑ ΑΝΤΑΓΩΝΙΣΤΙΚΟΤΗΤΑ ΕΠΙΧΕΙΡΗΜΑΤΙΚΟΤΗΤΑ ΚΑΙΝΟΤΟΜΙΑ
ΕΣΠΑ 2014-2020
Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης

Partners

DEMOKRITOS
UNIVERSITY OF IOANNINA
UNIVERSITY OF THE AEGEAN
TITAN

INSTITUTE OF MATERIALS SCIENCE AND COMPUTING

ΕΥΔΕ ΕΤΑΚ — Ερευνώ, Δημιουργώ, Καινοτομώ

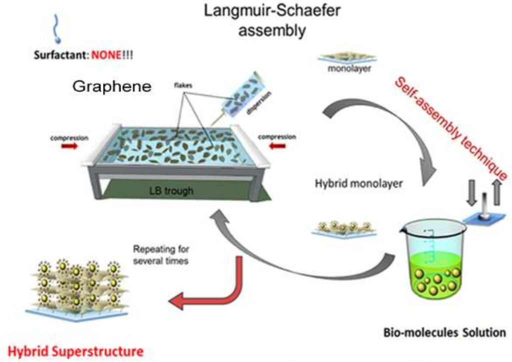
DEMIGOD

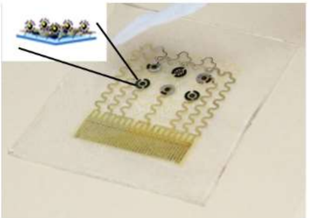
Nanotechnology · Medicine · Computer Engineering · Biotechnology · Pharmaceutics

UNITED AGAINST DIABETES MELLITUS

Design and development of a sweat-based glucose monitoring graphene nanodevice (closed-loop) with controlled transdermal nanoemulsion release for hypoglycemic drug delivery

Development of a very sensitive glucose bio-sensor based on graphene

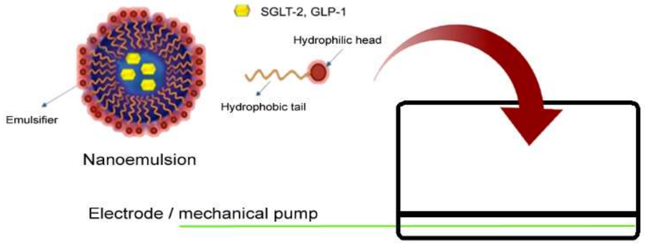


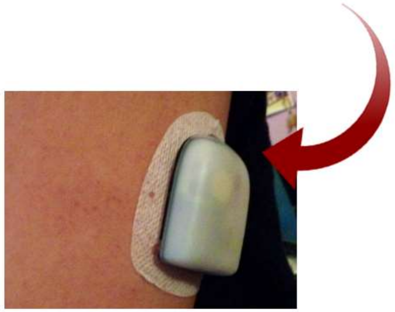


Sensor

Device/Software

Nanoemulsion of SGLT-2 inhibitors and GLP-1 analogues





Development of a release system for hypoglycemic treatment

UNIVERSITY OF IOANNINA

University of Western Macedonia

Pharmadata Business Development Pharmaceutics

Dept. Mater. Sci. & Engineer.

THE UNIVERSITY OF IOANNINA

Ευρωπαϊκή Ένωση
Ευρωπαϊκό Ταμείο Περιφερειακής Ανάπτυξης

ΕΛΛΗΝΙΚΗ ΔΗΜΟΚΡΑΤΙΑ
ΥΠΟΥΡΓΕΙΟ ΟΙΚΟΝΟΜΙΑΣ & ΑΝΑΠΤΥΞΗΣ
ΕΙΔΙΚΗ ΓΡΑΜΜΑΤΕΙΑ ΕΤΠΑ & ΤΣ
ΕΙΔΙΚΗ ΥΠΗΡΕΣΙΑ ΔΙΑΧΕΙΡΙΣΗΣ ΕΠΑνΕΚ

ΕΠΑνΕΚ 2014-2020
ΕΠΙΧΕΙΡΗΣΙΑΚΟ ΠΡΟΓΡΑΜΜΑ
ΑΝΤΑΓΩΝΙΣΤΙΚΟΤΗΤΑ
ΕΠΙΧΕΙΡΗΜΑΤΙΚΟΤΗΤΑ
ΚΑΙΝΟΤΟΜΙΑ

ΕΣΠΑ 2014-2020
ανάπτυξη - εργασία - αλληλεγγύη

Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης

SINGLE RTDI STATE AID ACTION
RESEARCH - CREATE - INNOVATE

"A NOVEL PROCESS FOR THE EFFICIENT AND ECO-FRIENDLY VALORIZATION OF BIOGAS AND CO2 EMISSIONS: COMPLETE CONVERSION TO ETHYLENE"
(Acronym: ECO-ETHYLENE)
Co-ordinator, Scientific director: Professor Ioannis V. Yentekakis

1. TECHNICAL UNIVERSITY OF CRETE (TUC), Co-Ordinator: Prof. Ioannis V. Yentekakis.
2. UNIVERSITY OF IOANNINA (UoI), Team Leader: Professor Dimitris Gournis
3. TECHNOLOGICAL EDUCATIONAL INSTITUTION OF WESTERN MACEDONIA (TEIWM), Team Leader: Professor Maria Goula
4. INTERGEO EPE (Abbreviation: INTER), Team Leader: Dimitrios Gelezis

Special Managing and Implementation Service in the areas of Research, Technological Development and Innovation (RTDI)

www.eyde-etak.gr

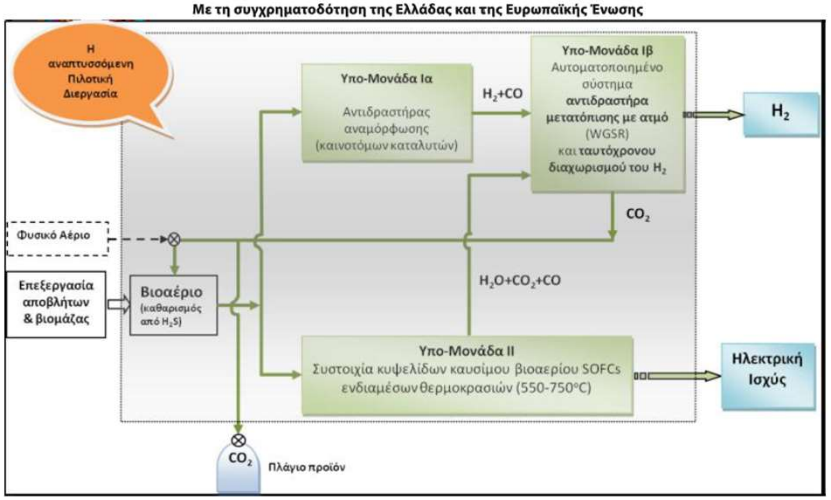
European Union
European Regional Development Fund

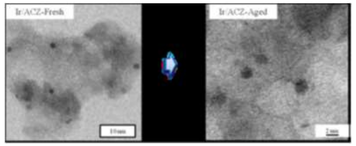
EPAnEK 2014-2020
OPERATIONAL PROGRAMME
COMPETITIVENESS•ENTREPRENEURSHIP•INNOVATION

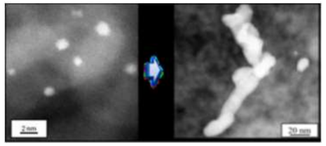
ΕΣΠΑ 2014-2020

Co-financed by Greece and the European Union

- **Develop, design and demonstrate in pilot scale, a novel, eco-friendly, automated process for the production of ethylene (C_2H_4) from the complete conversion of biogas (i.e., both CO_2 and CH_4 components), or from CO2 emissions.**
- The new concept is based on synergistically interacting catalytic sub-processes that converting in one-step biogas (CO_2+CH_4), or any independent CO_2 emissions, towards clean C_2H_4.
- The advanced design of the novel process overcomes the well known intrinsic constrains of the involved sub-processes, leading the system to offer very high ethylene yields.
- The novel process will initially be applied on a bench-scale and after will be scaled-up to Pilot size.







- **Design, develop and demonstrate in pilot scale, an innovative, eco-friendly, automated and stand alone process for the production of pure H_2 and/or electricity from biogas.**
- The production unit will comprise of two separate components that will work in harmony, either individually or synergistically, distributing the product (H_2 or electrical power) depending on the business requirements and demands of the user.
- The H_2 production component includes a biogas dry reforming reactor, followed by “a beyond the state of the art” H_2 purification system. The system will yield pure H_2, which means that both CO and CO_2 will be removed upstream. The electrical power generation component is based on a novel Solid Oxide Fuel Cell stack that will be fueled directly with Biogas (DBFC). This will ensure the efficient and low energy loss exploitation of biogas.
- The DBFC will be characterized by high efficiency in the intermediate temperature interval (650-800^{o}C) regardless of biogas quality, and by long lifetime, without efficiency losses due to C deposition or electrodes’ structure degradation.

INSTITUTE OF MATERIALS SCIENCE AND COMPUTING

H.F.R.I. Hellenic Foundation for Research & Innovation

Hierarchical Porous Carbon—PLLA and PLGA Hybrid Nanoparticles for Intranasal Delivery of Galantamine for Alzheimer's Disease Therapy

Dr. K. Spyrou

In the present study, poly(L-lactic acid) (PLLA) and poly(lactide-co-glycolide) (PLGA) hybrid nanoparticles were developed for intranasal delivery of galantamine, a drug used in severe to moderate cases of Alzheimer's disease. Galantamine (GAL) was adsorbed first in hierarchical porous carbon (HPC).

The intranasal (IN) delivery of GAL: alternative strategy to orally-administered GAL and has recently gained attention

Drawback →

Nose to-brain delivery of GAL, the inability of IN administration to retain constant therapeutic levels of GAL in the brain

Solution →

incorporation of the drugs in nanoparticles and their further incorporation in polymeric microparticles was found to lead to the controlled release of the drugs.

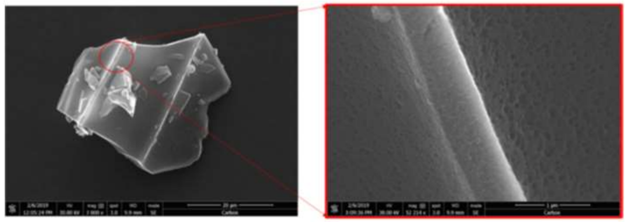
Benefits

IN administration overcomes the selective permeability of the blood–brain-barrier and the first pass metabolism in liver, leading to high drug accumulations in the brain

The nose-to-brain drug delivery also avoids gastrointestinal and other systemic side effects that are triggered by the direct interaction of GAL molecules with cells of the intestinal mucosa

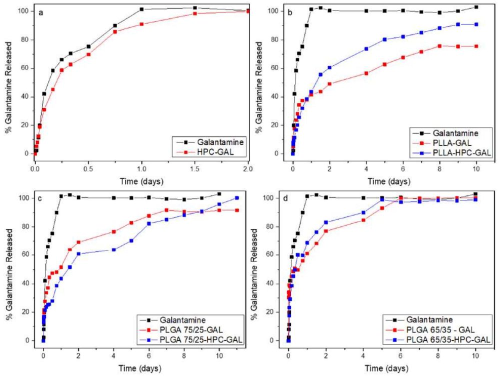
Table 1. Textural characteristics of hierarchical porous carbon (HPC).

	BET Surface Area [m² g⁻¹]	*t*-Plot Micropore [m² g⁻¹]	Mesopore Surface [m² g⁻¹]	Total Pore Volume [cm³ g⁻¹]	Mesopore Volume [cm³ g⁻¹]	Micropore Volume [cm³ g⁻¹]	Vmeso/Vtotal
HPC	2211	233	1978	4.014	3.90	0.112	97

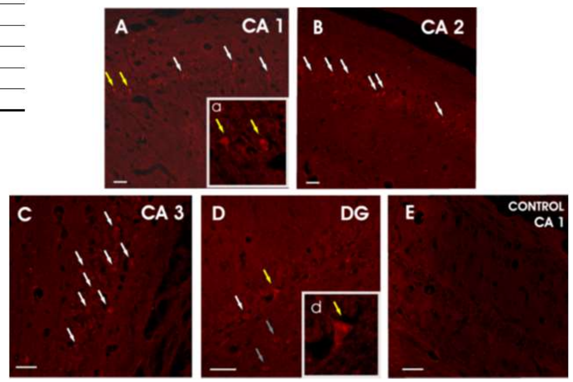


Representative SEM images of hierarchical porous carbon showing surface morphology and texture.

Nanoparticles	Drug Loading (%)	Entrapment Efficiency (%)	Nanoparticle Yield (%)
PLLA–GAL	5.34 ± 0.24	25.14 ± 2.57	87.26 ± 2.05
PLGA 75/25–GAL	8.49 ± 0.72	28.49 ± 1.08	92.86 ± 1.98
PLGA 65/35–GAL	9.57 ± 0.61	29.04 ± 2.19	89.71 ± 2.14
PLLA–HPC–GAL	28.35 ± 1.06	54.04 ± 2.46	82.18 ± 1.57
PLGA 75/25–HPC–GAL	32.83 ± 1.84	59.23 ± 2.75	88.83 ± 2.34
PLGA 65/35–HPC–GAL	31.24 ± 1.75	58.76 ± 3.51	90.29 ± 3.08



In Vitro Galantamine Release Profile



Photomicrographs illustrating the uptake of PLGA 65/35-HPC–GAL–Rhod nanoparticles by neurons of all layers of the entire hippocampal formation at 48 h after their intranasal (IN) delivery. Administered nanoparticles were found intra-neuronally in the pyramidal neurons of the CA1 (white and yellow arrows) (A), CA2 (white arrows) (B), and CA3 (white arrows) (C) fields and also in the mossy cells (grey arrows) (D) and granule cells of the DG (white and yellow arrows) (D). PLGA 65/35– HPC–GAL–Rhod nanoparticles formed aggregates that were distributed in the cytoplasm of hippocampal neurons (yellow arrows, a and d). No fluorescence was seen in hippocampal sections of the IN saline-treated rats (E). Scale bar = 50 μm.

UNIVERSITY OF IOANNINA

ARISTOTLE UNIVERSITY OF THESSALONIKI

Dept. Mater. Sci. & Engineer.

THE UNIVERSITY OF IOANNINA

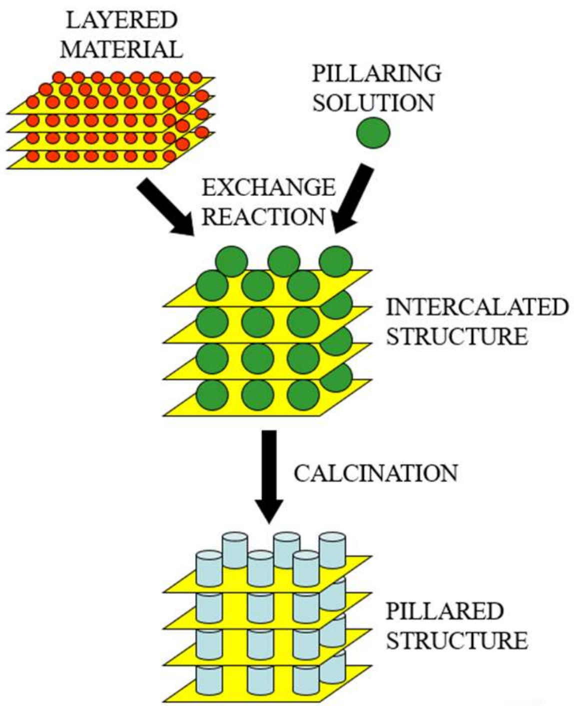
INSTITUTE OF MATERIALS SCIENCE AND COMPUTING

Graphene pillaring

- Graphene hybrids
- Light
- Open 3D structures
- High surface area
- Tunable pore size
- Aromatic functionna-lities

Lack of permanent porosity (a normal layered material swells upon hydration, but looses its interlayer after dehydration)

Taking advantage of the concept of **intercalation chemistry** and the so-called **pillaring method** which involves the insertion of suitable and robust organic and/or inorganic species as pillars between the layers.



NANO LETTERS

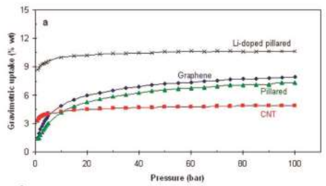
2008
Vol. 8, No. 10
3166-3170

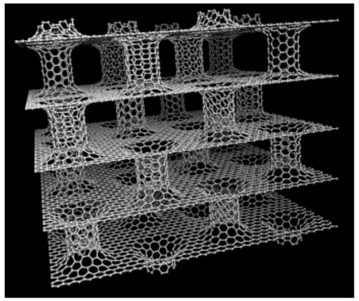
Pillared Graphene: A New 3-D Network Nanostructure for Enhanced Hydrogen Storage

Georgios K. Dimitrakakis,[†] Emmanuel Tylianakis,[‡] and George E. Froudakis[*,†]

Department of Chemistry, and Materials Science and Technology Department, University of Crete, P.O. Box 2208, 71003 Heraklion, Crete, Greece

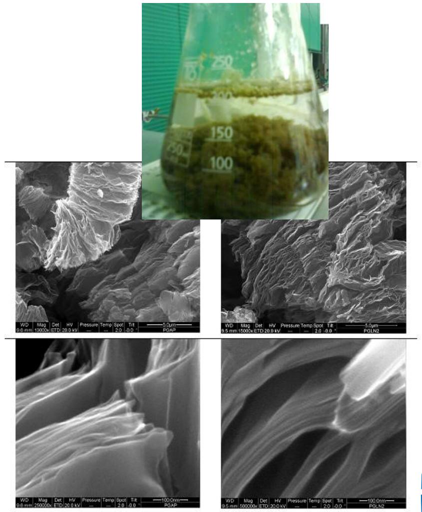
Received May 16, 2008; Revised Manuscript Received July 11, 2008

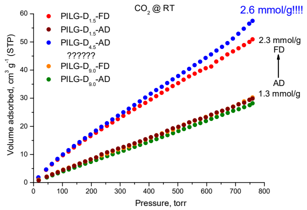


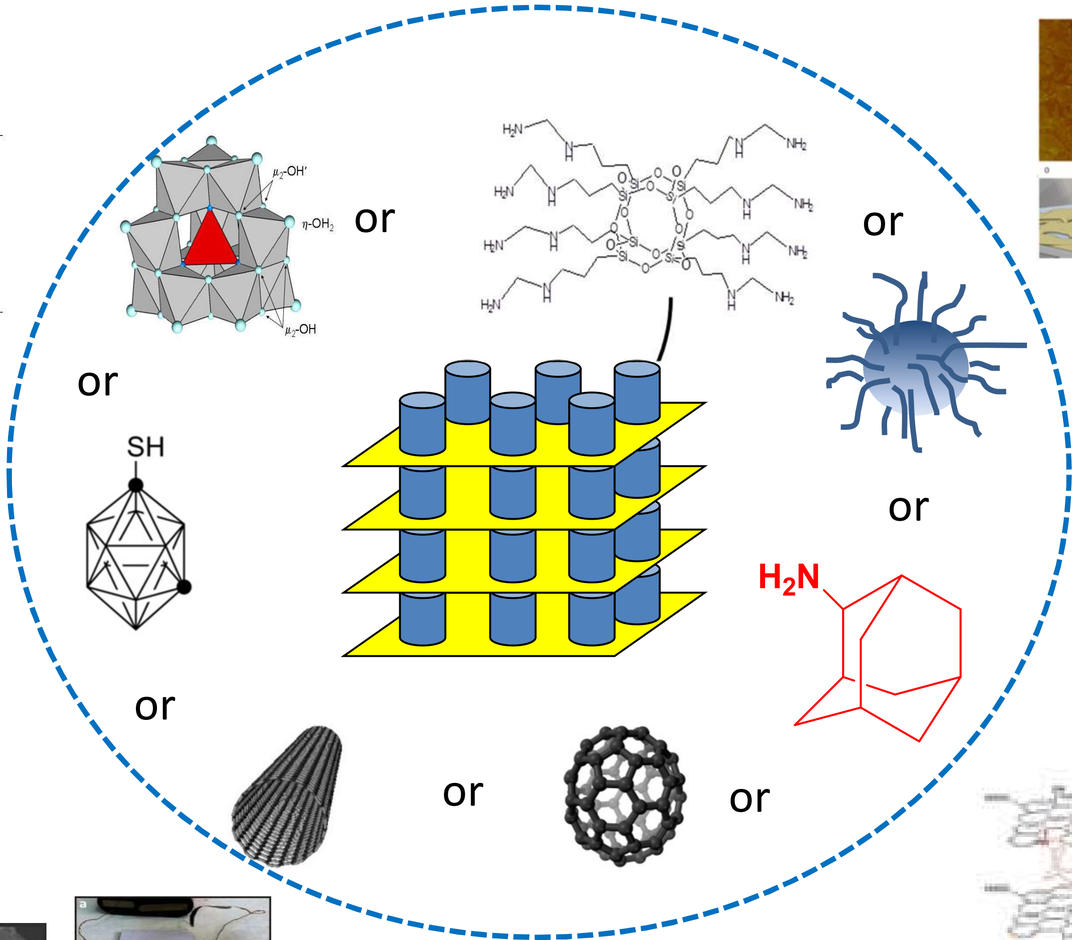


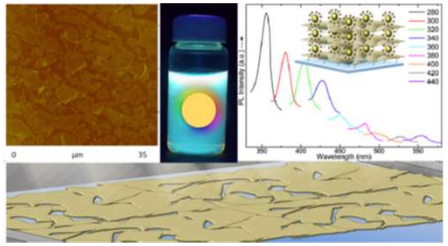
INSTITUTE OF MATERIALS SCIENCE AND COMPUTING

Pillared graphenes

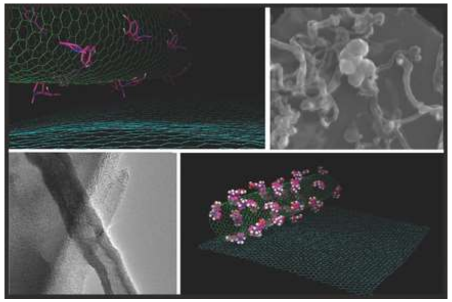


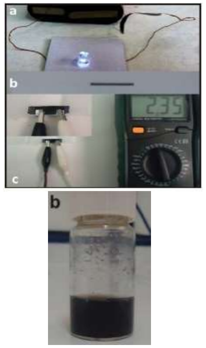




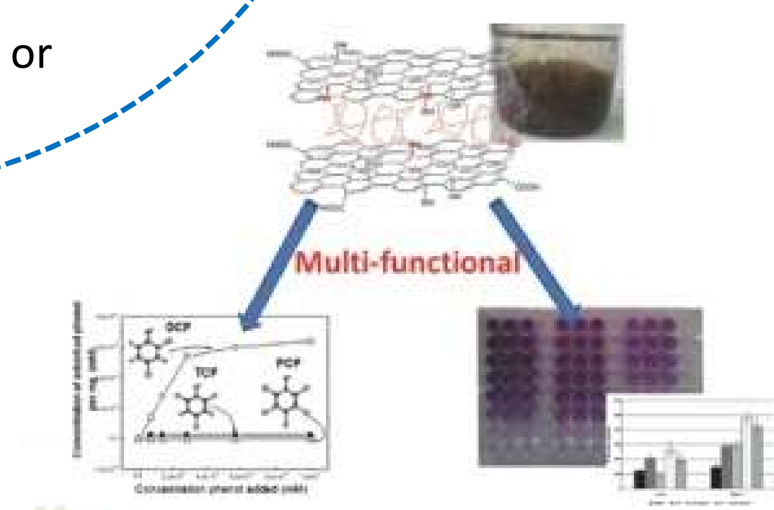


ACS Omega **2017**, *2*, 2090



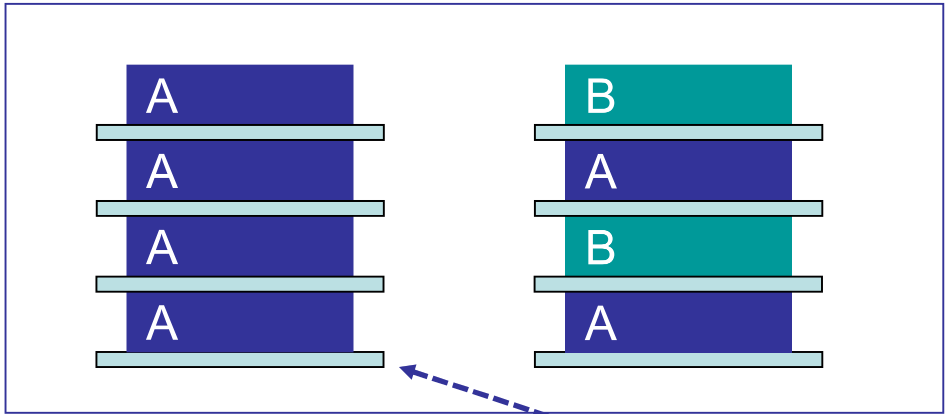


Adv. Funct. Mater.. **2015**, *25*, 1481

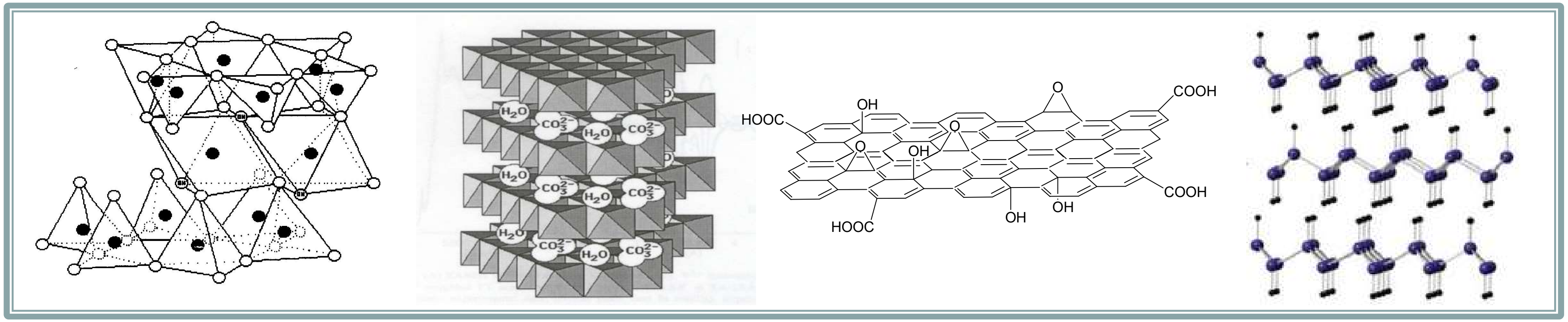


Adv. Funct. Mater.. **2014**, *24*,5841

BOTTOM-UP APPROACH:
Nanotechnology using 2D materials as templates



Montmorillonite
Graphene-based materials
LDHs
Germananes
…….



But how ?

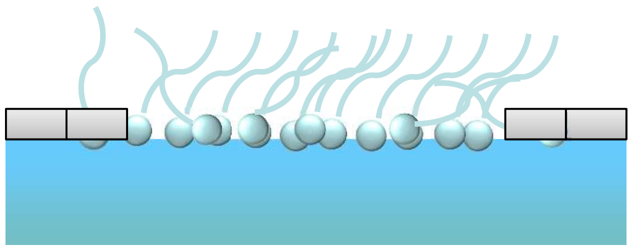
Using self-assembly and Langmuir-Blodgett technique

Self-assembly and Langmuir-Blodgett technique

Aim at the creation of a monolayer at the air water interface and its transfer to a substrate

Air

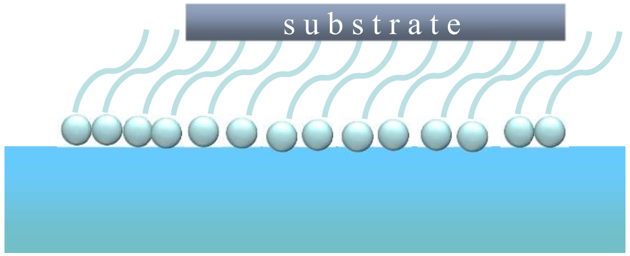
Water



Amphiphilic

K.B.Blodgett, *J. Am. Chem. Soc., 57* (1935) 1007

V.J.Schaefer, *J. Am. Chem. Soc., 60* (1938) 1351



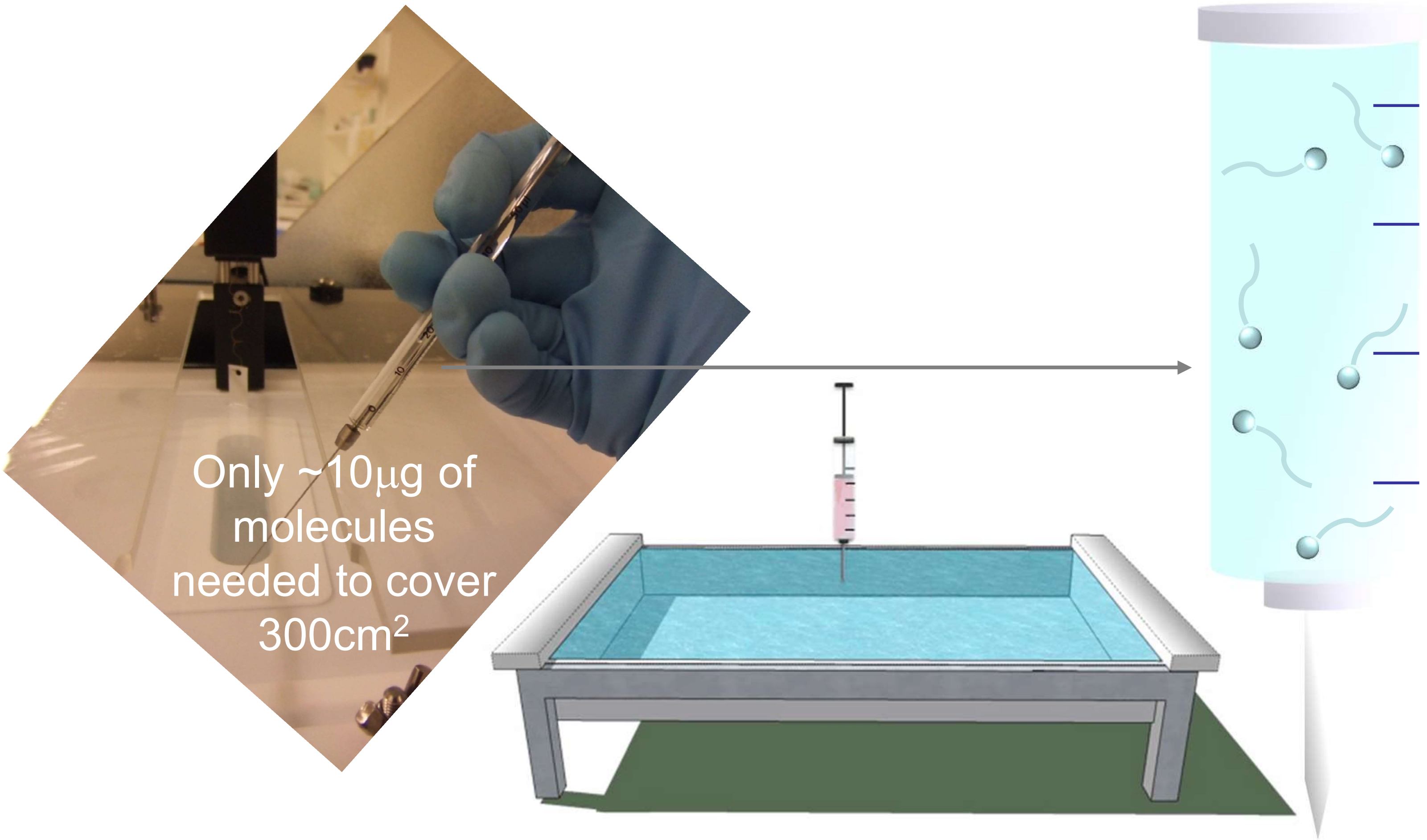
Air

Water

- Precise control of the monolayer thickness and packing density
- Homogeneous deposition over large areas
- Multilayer structures with varying layer composition
- Deposition on any kind of solid substrate

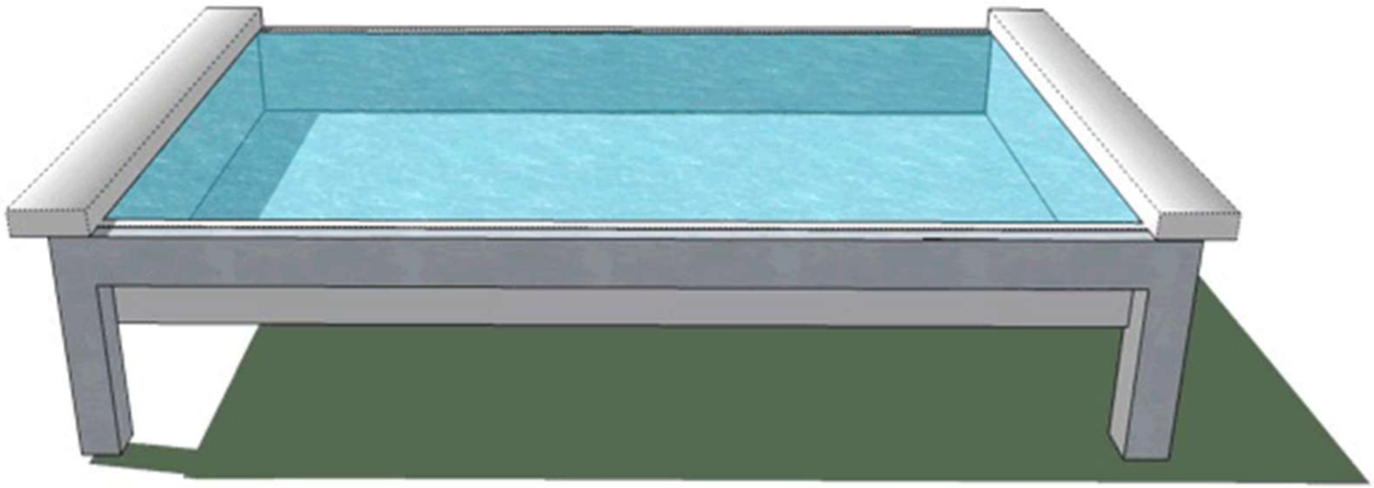
1st step

spreading of the molecules onto water



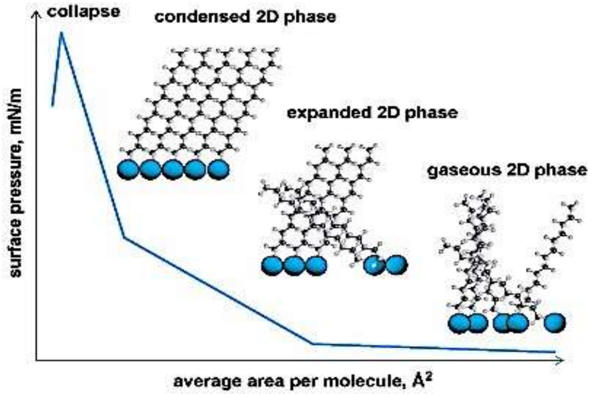
1st step

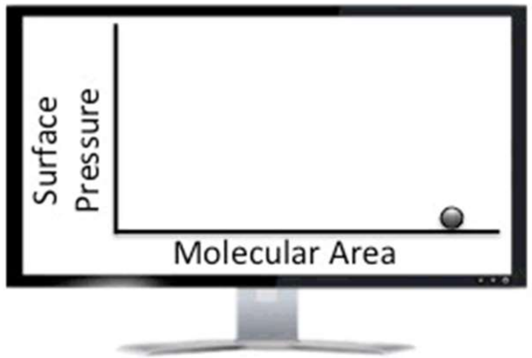
spreading of the molecules onto water

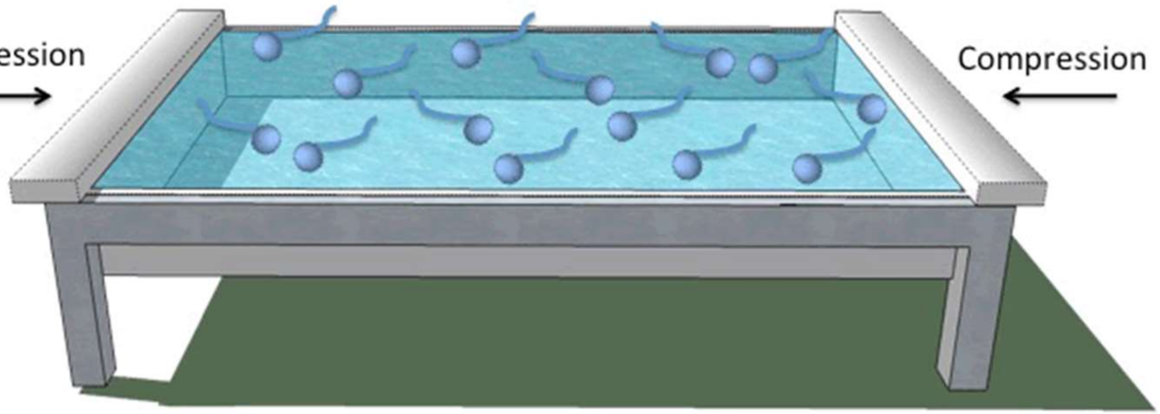


2nd step

compression of the molecules to form a monolayer





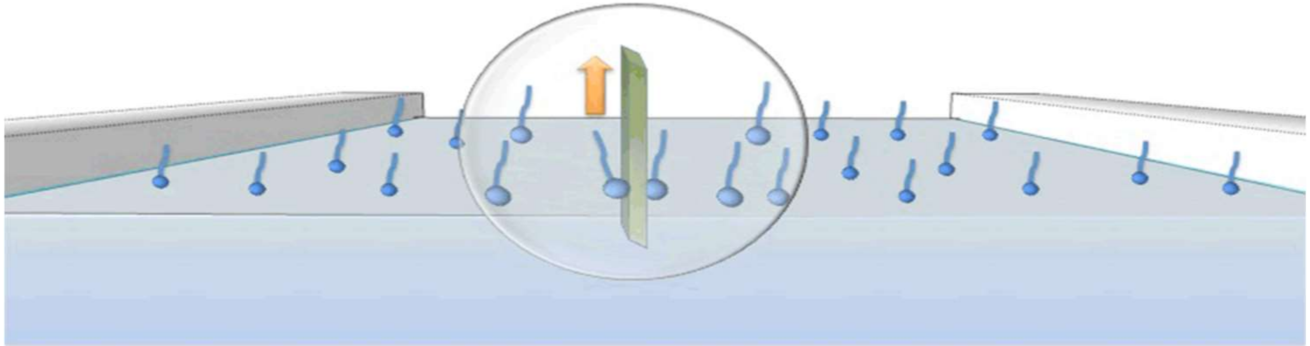


INSTITUTE OF MATERIALS SCIENCE AND COMPUTING

3nd step

transfer of the monolayer onto a solid hydrophilic substrate; *vertical dipping*

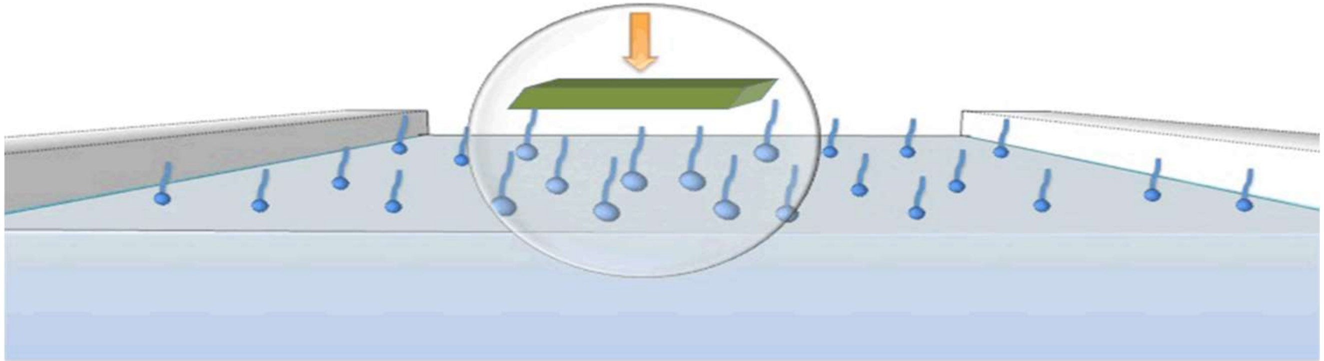
*(**Langmuir-Blodgett**)*



3nd step

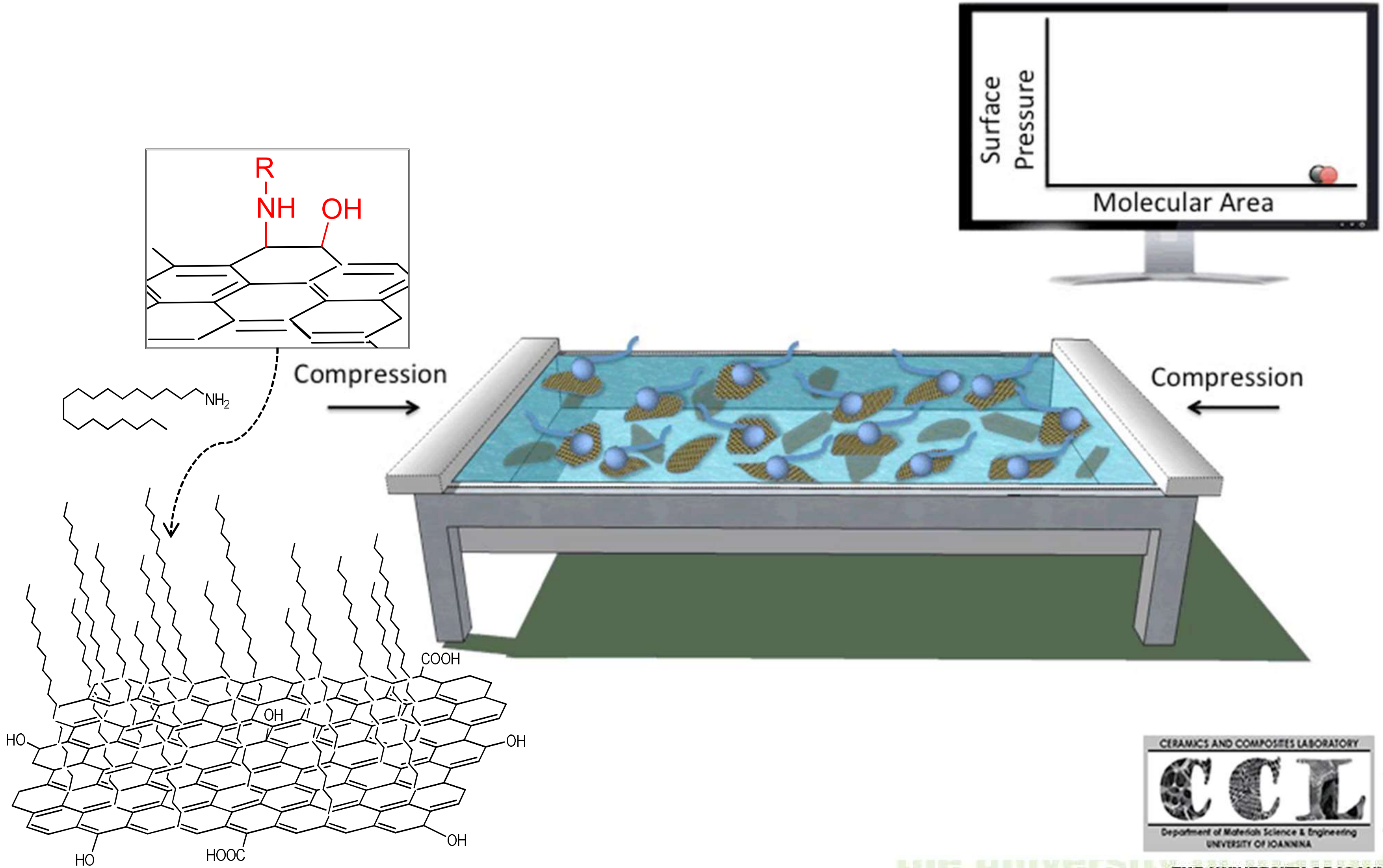
transfer of the monolayer onto a solid hydrophobic substrate; *horizontal dipping*

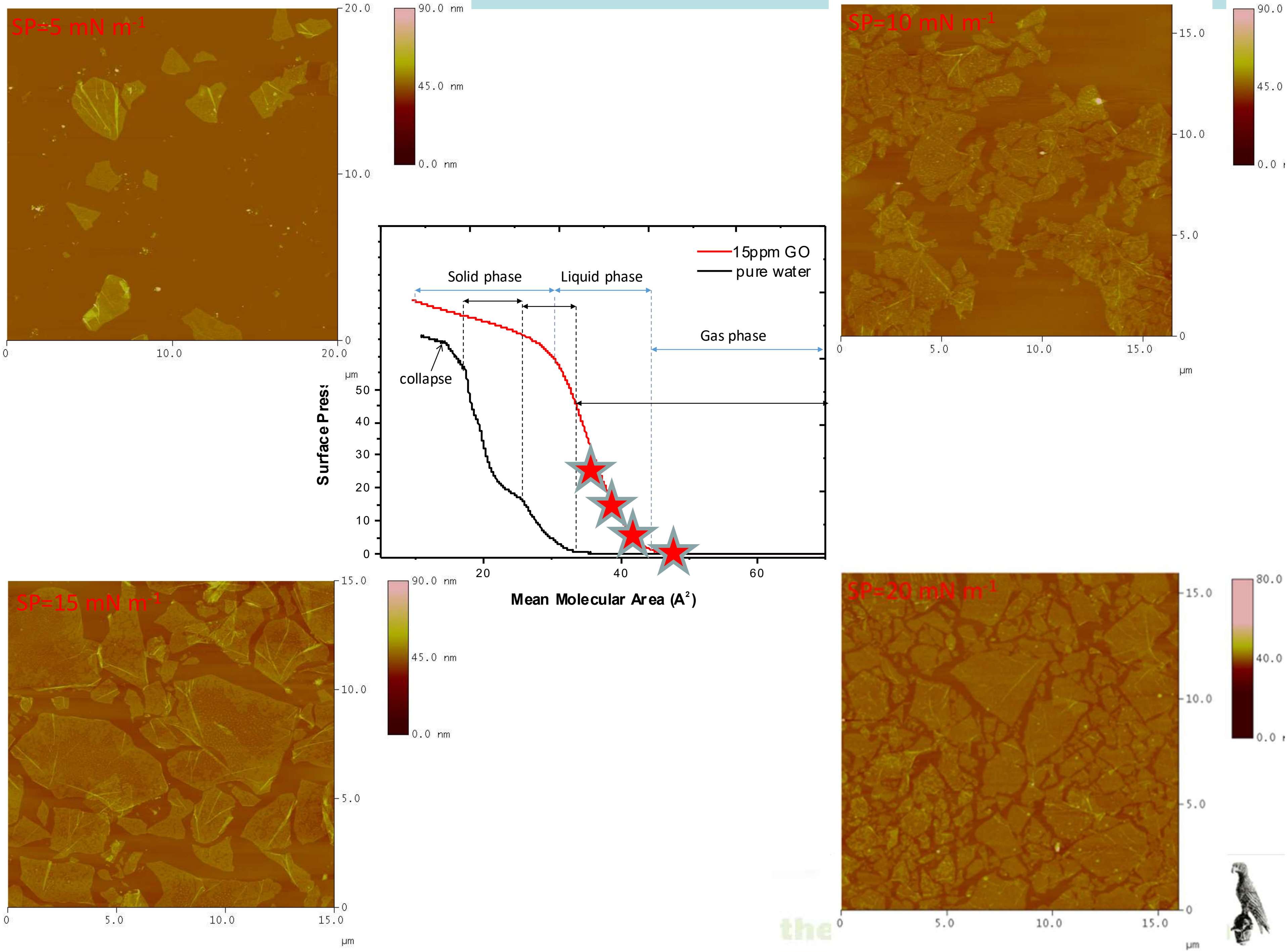
(Langmuir-Schaefer)



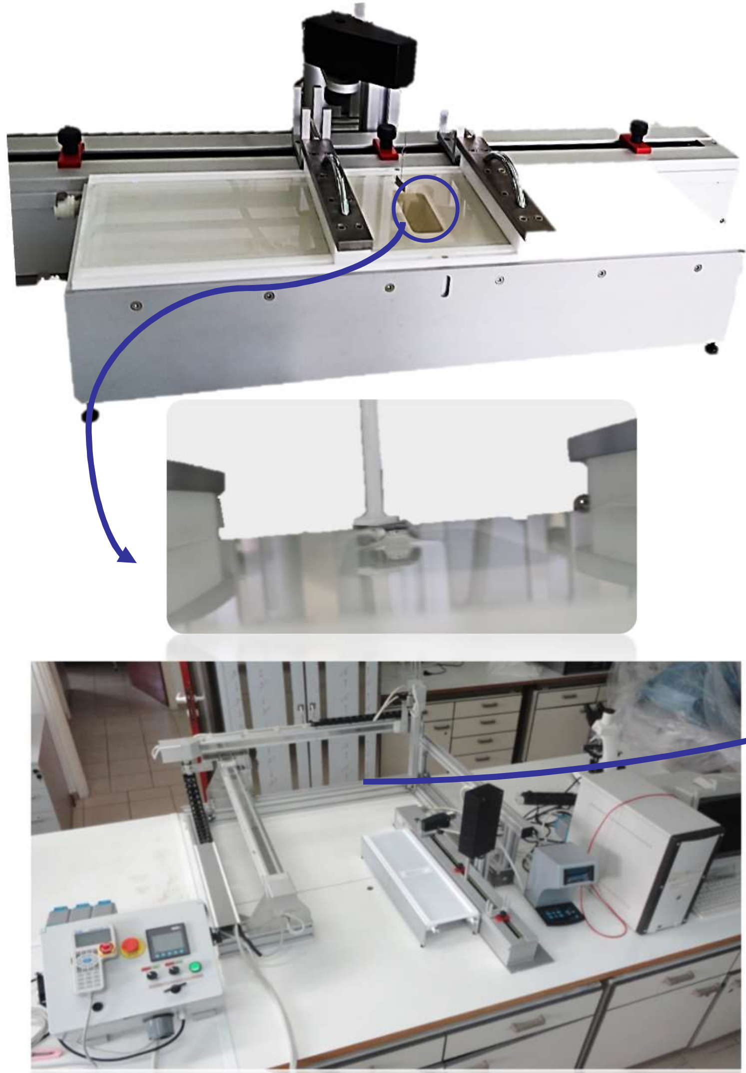
GO as template

Langmuir-Schaefer technique

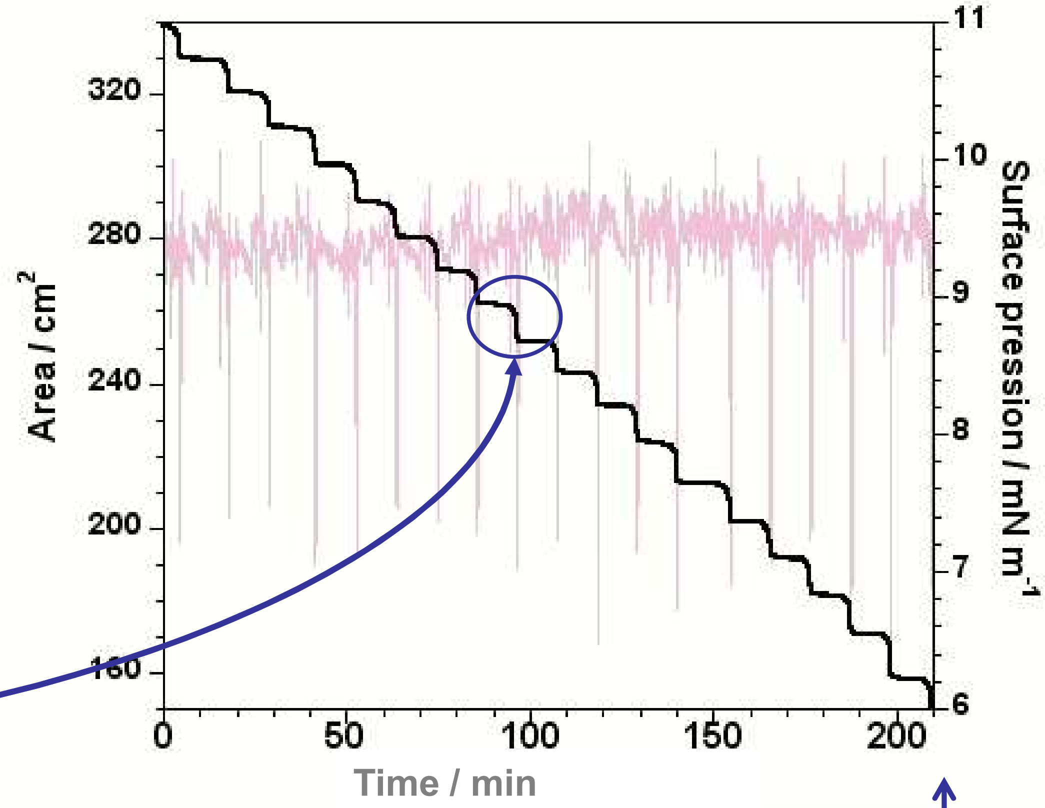


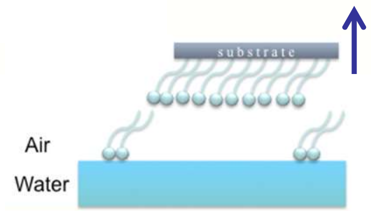

SP=5 mN m-1
SP=10 mN m-1
SP=15 mN m-1
SP=20 mN m-1
90.0 nm
45.0 nm
0.0 nm
µm
15ppm GO
pure water
Solid phase
Liquid phase
Gas phase
collapse
Surface Pres
Mean Molecular Area (A²)

LB horizontal deposition

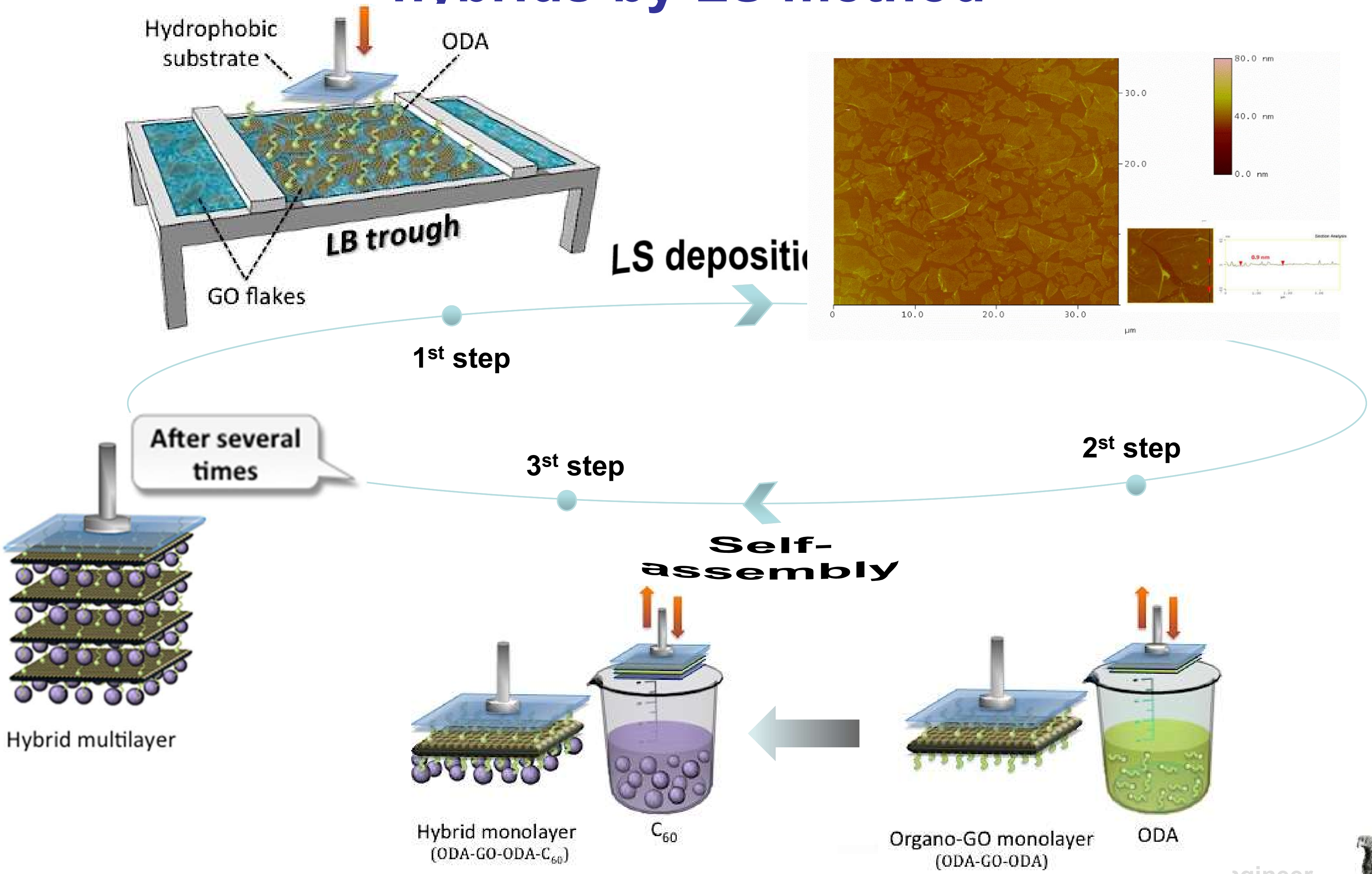


Deposition robotic system
CCL, Dep. Mater. Sci. & Engineer, UoI

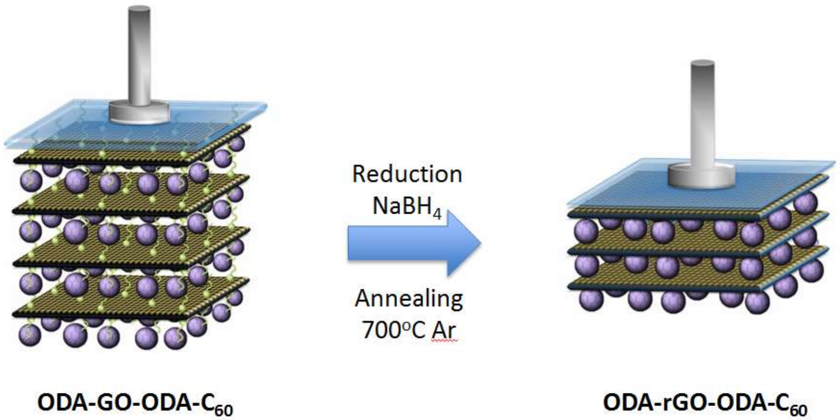


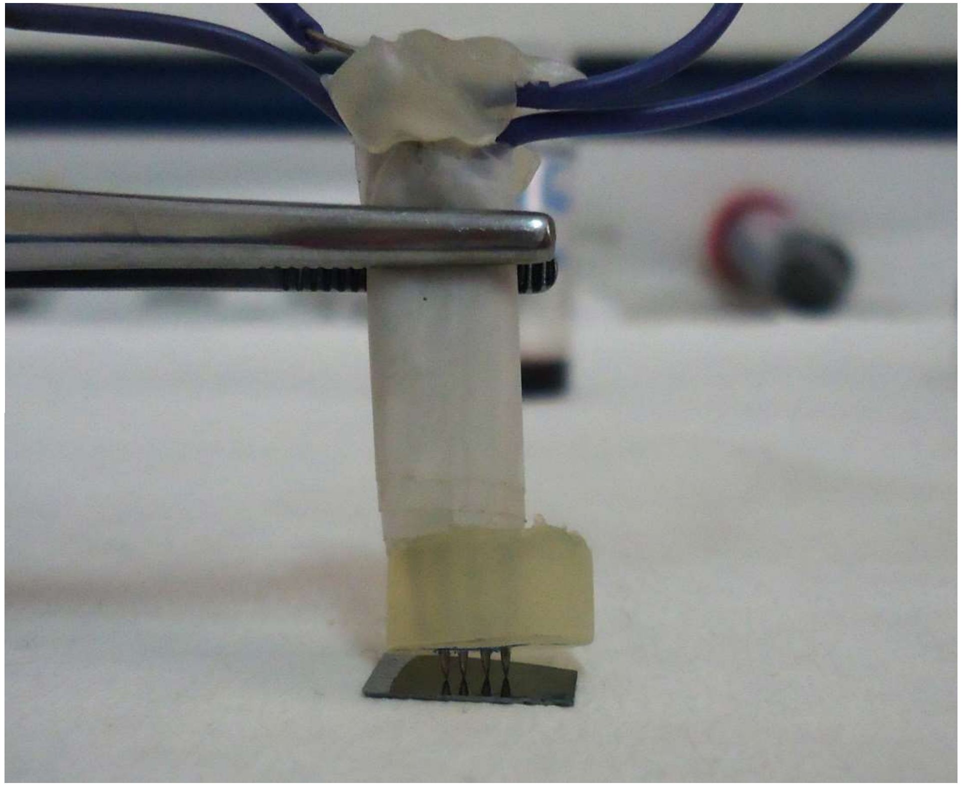


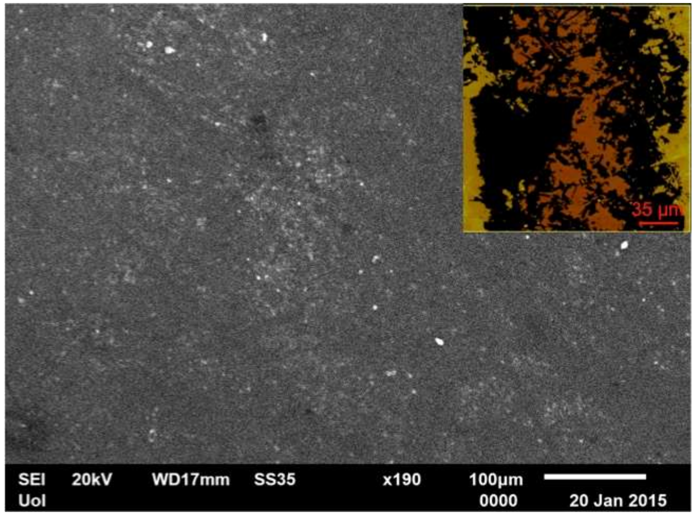
Highly ordered fullerene-intercalated graphene hybrids by LS method



Kouloumpis et al. *Front. Mater.* **2015**, *2, doi:10.3389/fmats.2015.00010*







	Electrical Conductivity ($S\ m^{-1}$)
ODA-rGO-ODA	714
ODA-rGO-ODA-C_{60}	2800

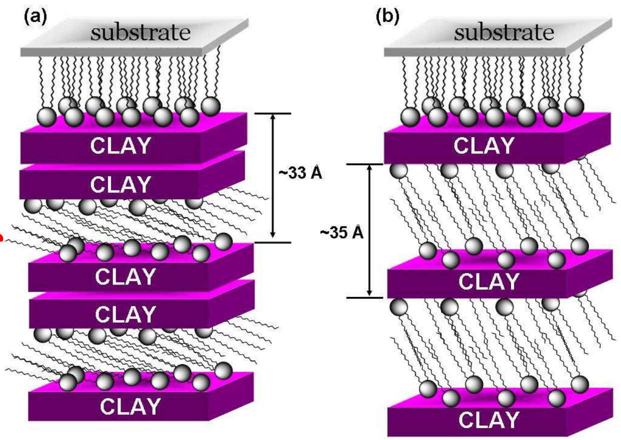
ODA-rGO-ODA-C_{60}
Mean roughness (RMS): 3 nm

Kouloumpis et al. *Front. Mater.* **2015**, *2, doi:10.3389/fmats.2015.00010*

INSTITUTE OF MATERIALS SCIENCE AND COMPUTING

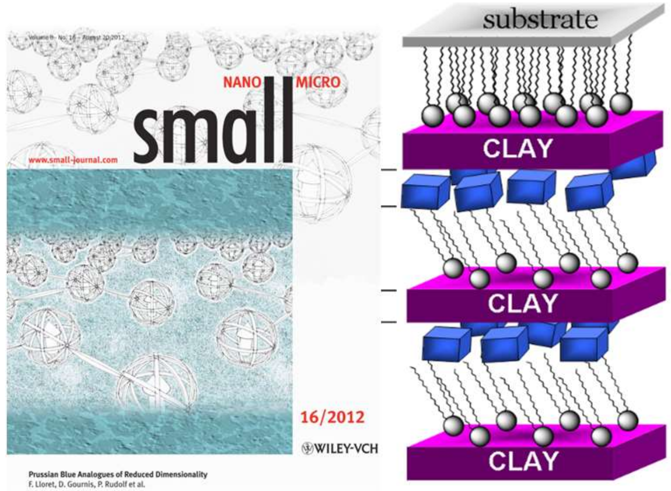
Organo-clays

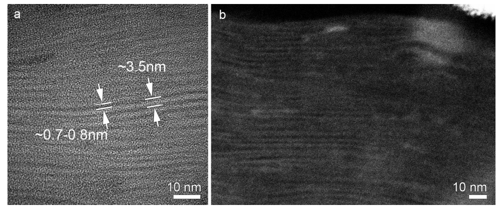
“mixed-ion heterostructured clays”



Toma et. al. *Phys. Chem. Chem. Phys.* **2010**, *12,* 1248

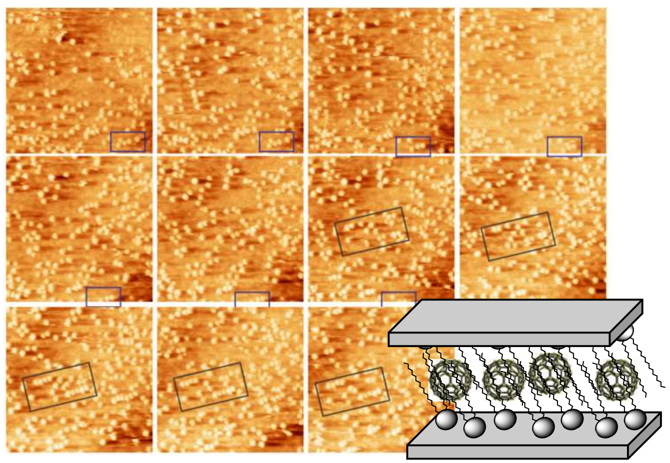
Prussian-blue analogues of reduced dimensionality





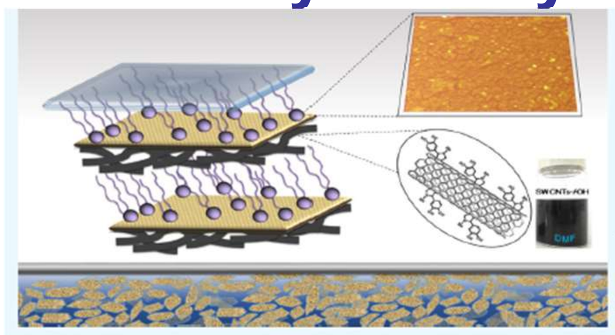
Gengler, et al. *Small* **2012**, *8*, 2532

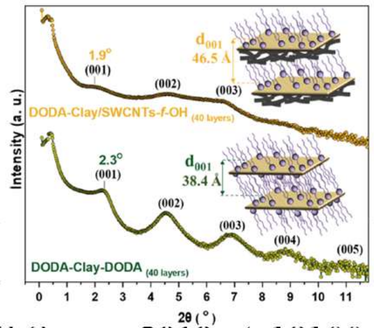
Clay-fullerene hybrids



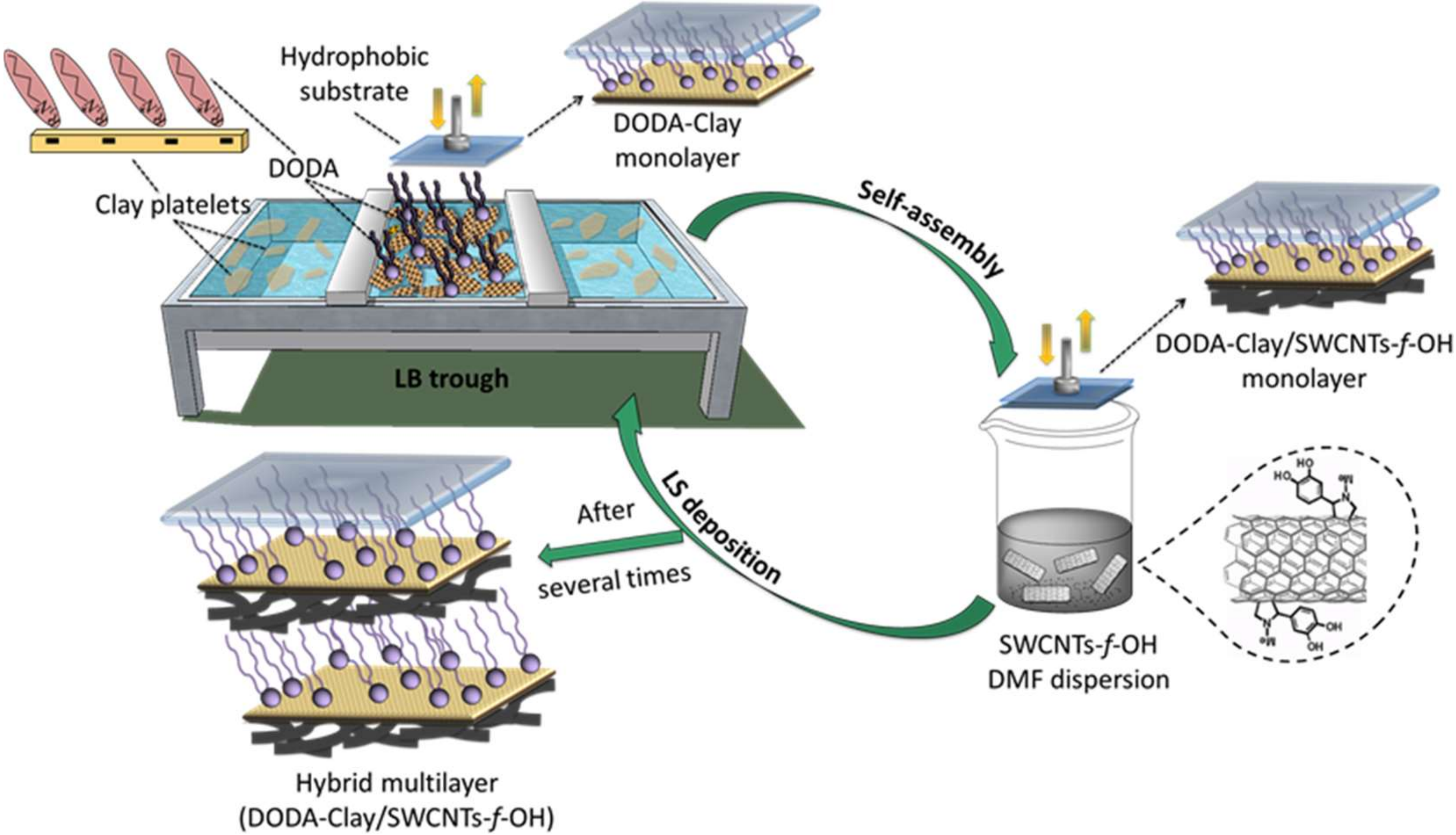
Gengler, et. al. *Chem.-Eur. J.* **2012,** *18*, 7594

Clay-CNT hybrids





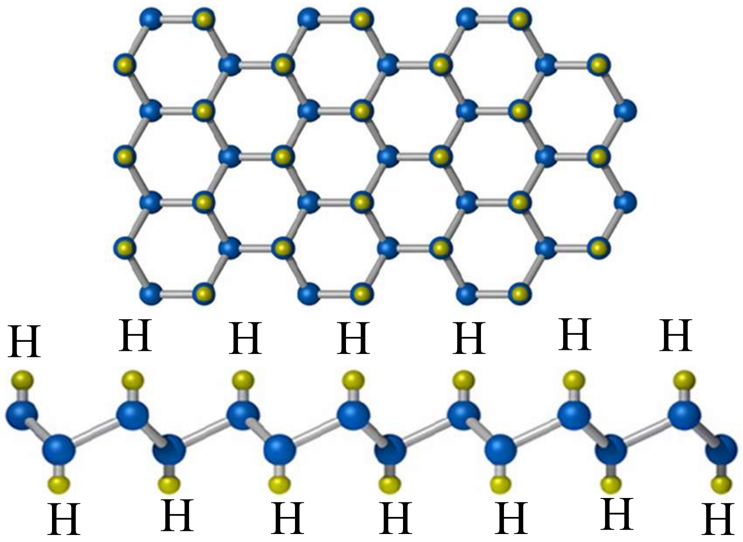
Chalmpes, et al. *ACS Omega* **2019**, *4*, 18100



Chalmpes, Kouloumpis, Zygouri, et al. *ACS Omega* **2019**, *4*, 18100−18107

Germanane: a germanium graphane analogue

New generation of semiconductors



Single-layer crystal composed of **germanium** with **one hydrogen** bonded in the **z-direction** for each atom

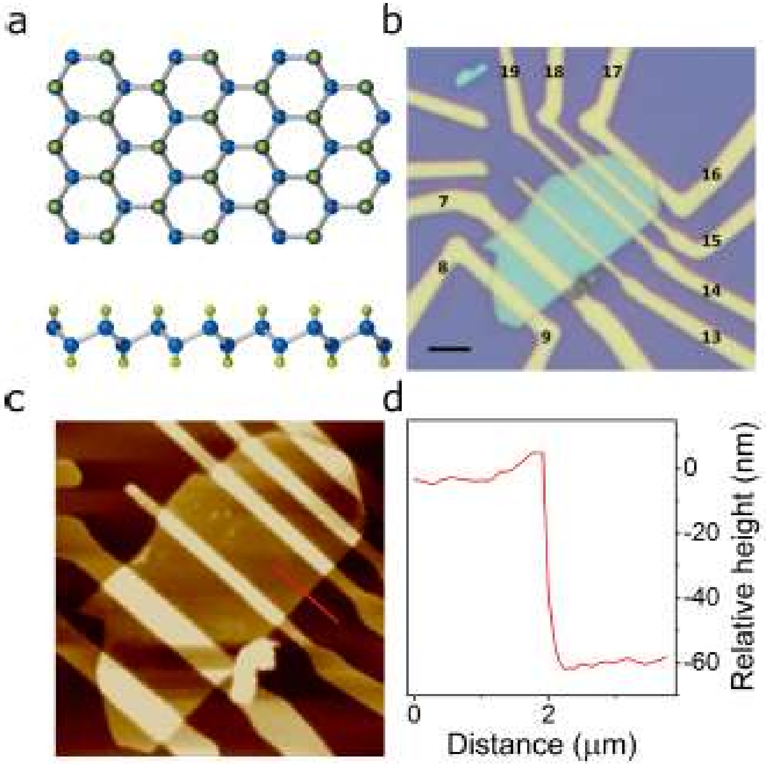
Applications

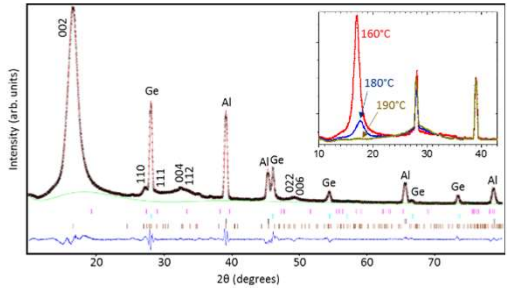
Solar cells Electronics Photocatalysis

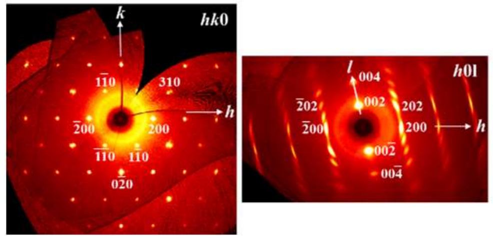
Properties

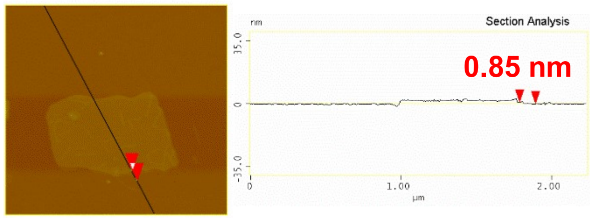
- **Electron mobility** is predicted to be more than ten times that of silicon & five times more than conventional germanium.
- **Chemically & physically stable** when exposed to air & water (black phosphorus degrades with oxidation).
- "**Direct band gap**" easily absorbing & emitting light (graphene zero band gap while graphane is insulating)
- Ge atoms have higher **spin-orbit coupling** (as compared to C in graphene/graphane) possible to explore physical phenomena such as quantum spin Hall effect at room temperature.

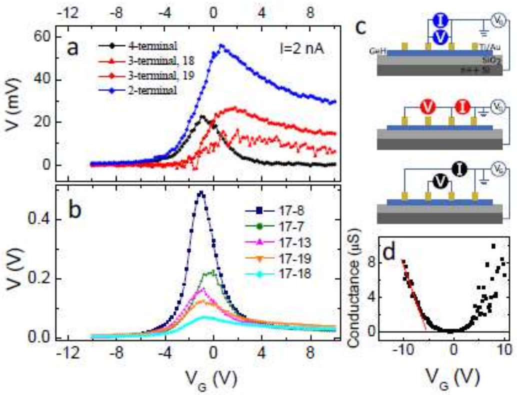
Germanane field effect transistors

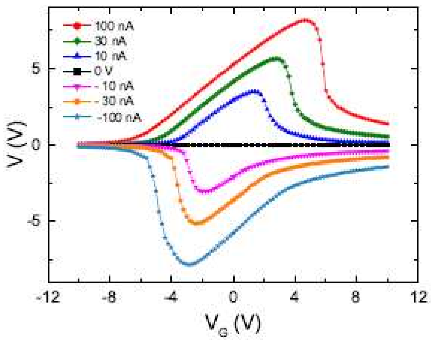


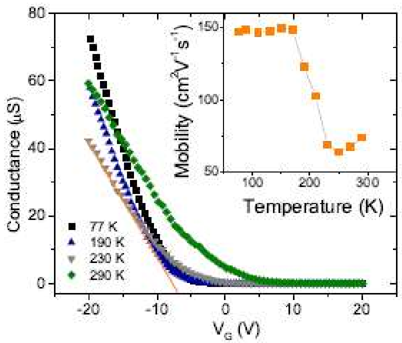


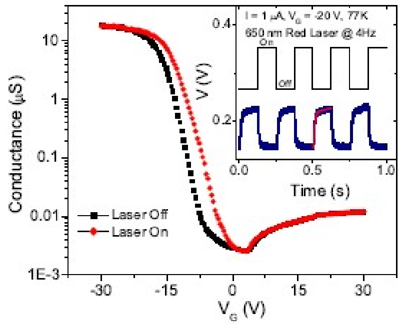












Madhushankar, Kaverzin, Giousis et al. *2D Mater*. **2017,** *4*, 021009

NANO LETTERS

Letter

Cite This: *Nano Lett.* 2019, 19, 1520−1526

pubs.acs.org/NanoLett

Highly Conductive Metallic State and Strong Spin−Orbit Interaction in Annealed Germanane

Qihong Chen,[†] Lei Liang,[†] Georgia Potsi,[‡] Puhua Wan,[†] Jianming Lu,[†,§] Theodosis Giousis,[‡,∥] Eleni Thomou,[‡,∥] Dimitrios Gournis,[∥] Petra Rudolf,[‡] and Jianting Ye*[,†]

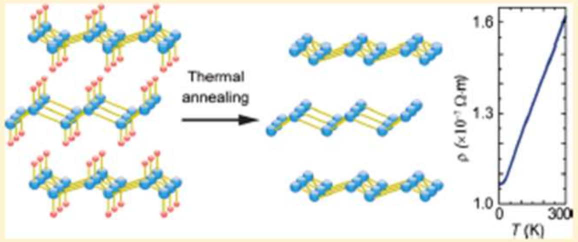
[†]Device Physics of Complex Materials, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

[‡]Surfaces and Thin Films, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

[§]State Key Laboratory for Mesoscopic Physics, Department of Physics, Peking University, No. 5 Yiheyuan Road Haidian District, 100871 Beijing, P. R. China

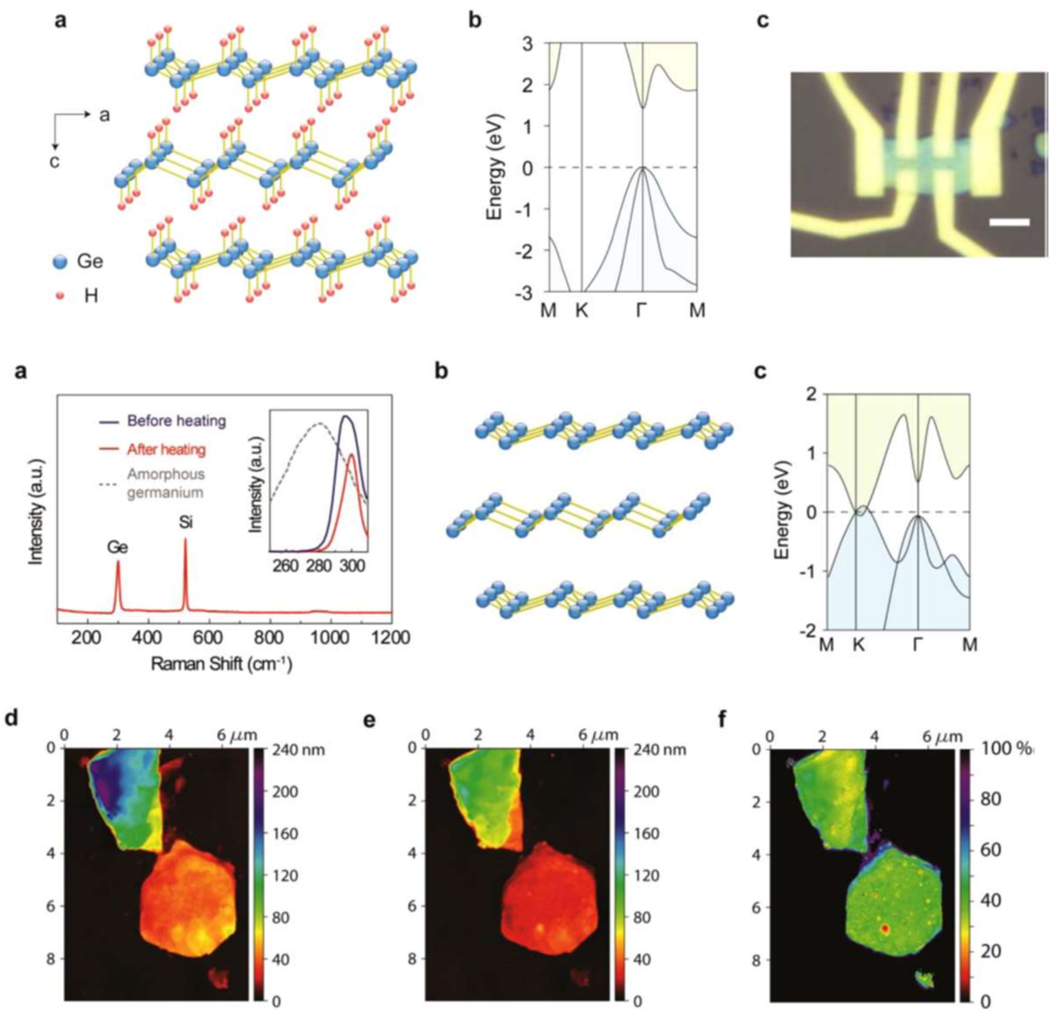
[∥]Department of Materials Science & Engineering, University of Ioannina, 45110 Ioannina, Greece

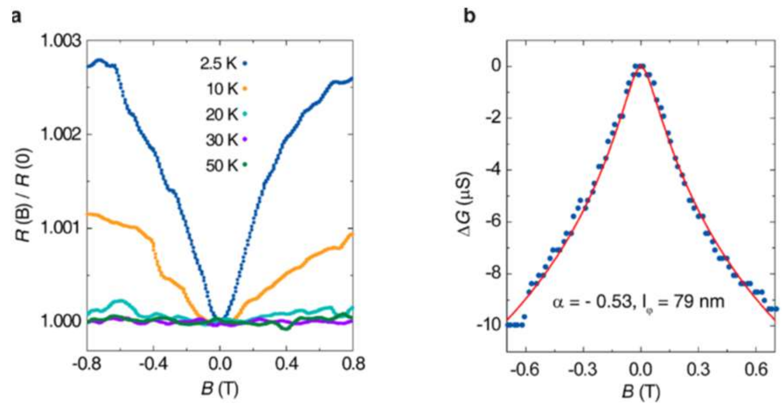
Supporting Information



ABSTRACT: Similar to carbon, germanium exists in various structures such as three-dimensional crystalline germanium and germanene, a two-dimensional germanium atomic layer. Regarding the electronic properties, they are either semiconductors or Dirac semimetals. Here, we report a highly conductive metallic state in thermally annealed germanane (hydrogen-terminated germanene, GeH), which shows a resistivity of $\sim10^{-7}$ Ω·m that is orders of magnitude lower than any other allotrope of germanium. By comparing the resistivity, Raman spectra, and thickness change measured by AFM, we suggest the highly conductive metallic state is associated with the dehydrogenation during heating, which likely transforms germanane thin flakes to multilayer germanene. In addition, weak antilocalization is observed, serving as solid evidence for strong spin−orbit interaction (SOI) in germanane/germanene. Our study opens a possible new route to investigate the electrical transport properties of germanane/germanene, and the large SOI might provide the essential ingredients to access their topological states predicted theoretically.

KEYWORDS: *Germanane, multilayer germanene, dehydrogenation, metallic state, weak antilocalization, strong spin−orbit interaction*





Evidence for strong spin−orbit interaction!

Table 1. Room Temperature Resistivity for Crystalline Germanium,[48] Amorphous Germanium,[49] Heavily Doped Germanium,[50] Graphite,[51] Annealed Germanane, and Graphene[52]

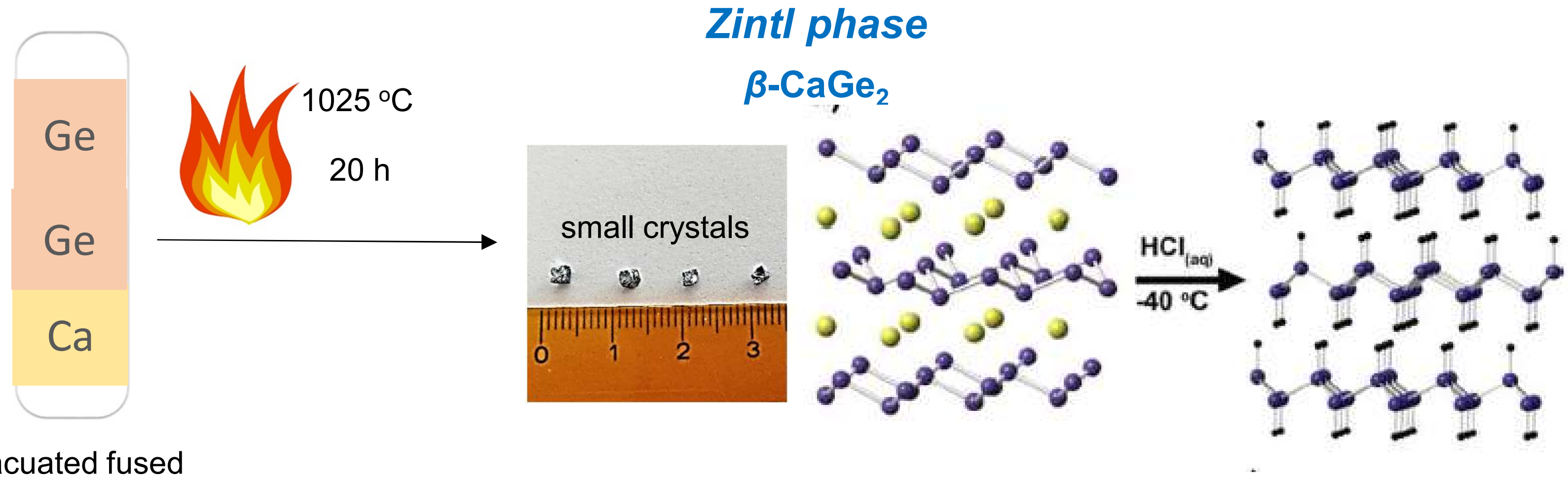
material	resistively (Ω·m)
germanium (crystalline)	0.1
germanium (amorphous)	1
germanium (heavily doped)	2×10^{-6}
graphite	6×10^{-6}
annealed GeH	1.6×10^{-7}
graphene	1×10^{-8}

Creation of **Germanene!**

Chen, Liang, Potsi et al. *Nano Lett.*. **2019,** *19*, 1520

Synthesis

Topotatic deintercalation of β-$CaGe_2$ ***in aqueous HCl at -40 °C for 8 days***



evacuated fused quartz tube

Table 2 Different synthesis conditions for GeH

Acid (K_a)	Temperature (°C)	Time (days)	Amorphization temperature from DRA (°C)
Conc. HCl (10^6)	−40	8	75
Conc. HI (10^{10})	−40	11	75
Conc. HBr (10^9)	−10	6	75
Conc. HCl (10^6)	25	5	75
Acetic acid (1.7×10^{-5})	25	14	75
1.6 M HCl (10^6)	25	10	75

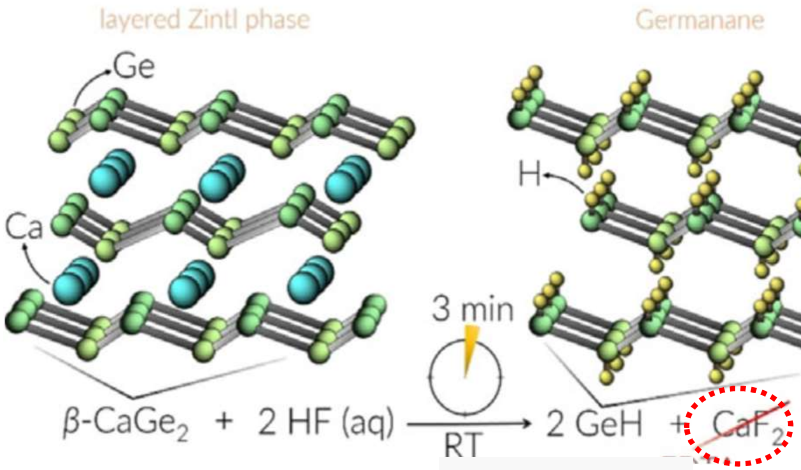
Germanane

How to cite:
International Edition: doi.org/10.1002/anie.202010404
German Edition: doi.org/10.1002/ange.202010404

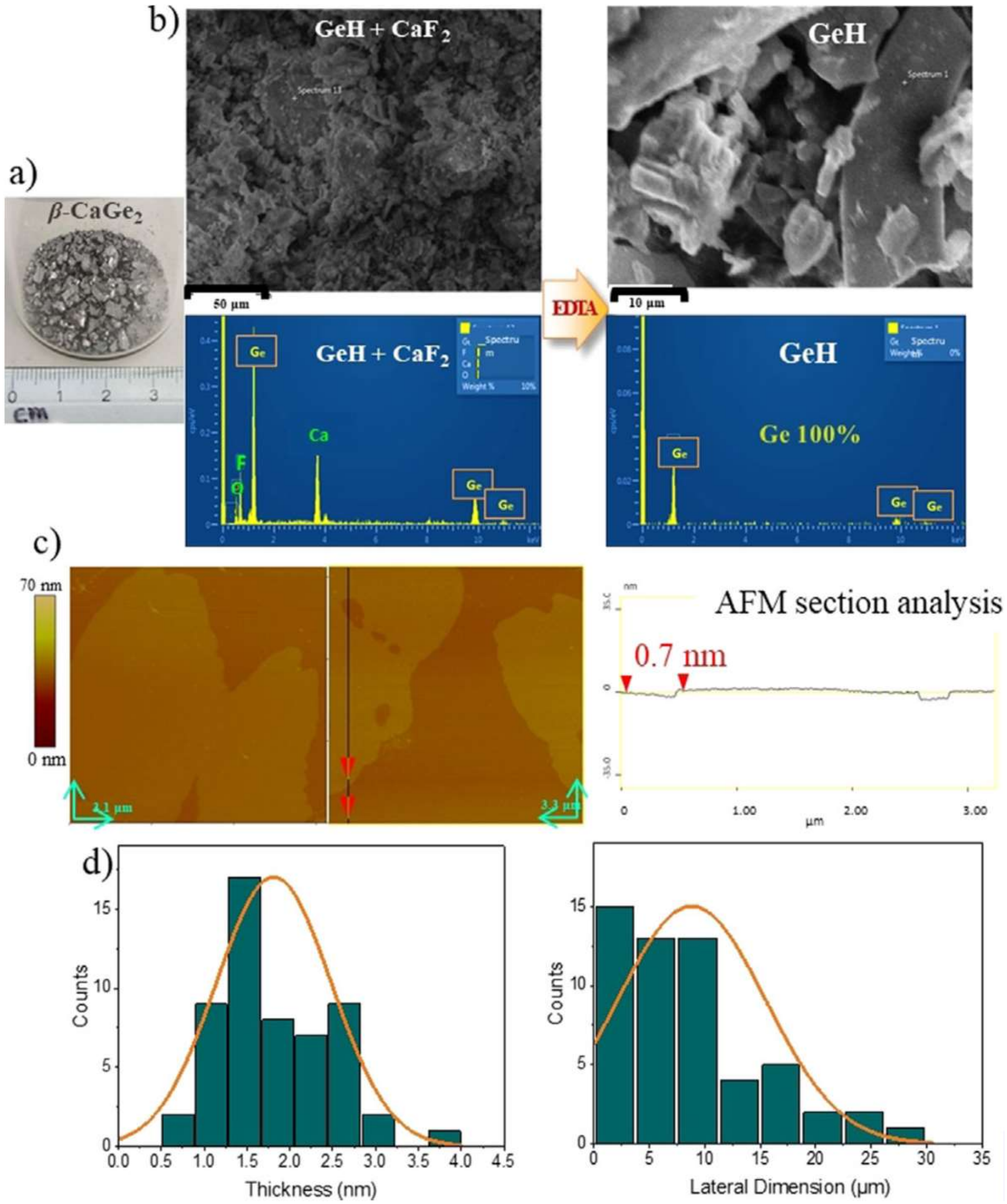
Synthesis of 2D Germanane (GeH): a New, Fast, and Facile Approach

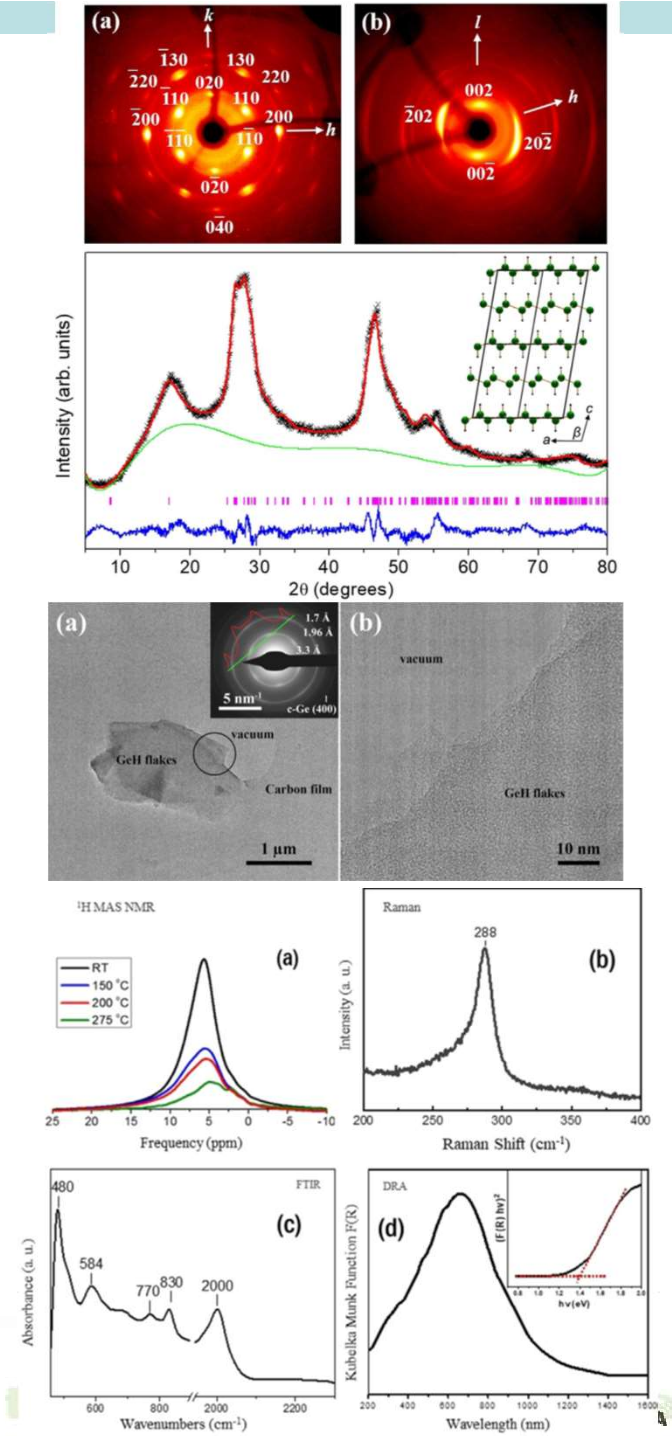
Theodosis Giousis, Georgia Potsi, Antonios Kouloumpis, Konstantinos Spyrou, Yiannis Georgantas, Nikolaos Chalmpes, Konstantinos Dimos, Myrsini-Kiriaki Antoniou, Georgios Papavassiliou, Athanasios B. Bourlinos, Hae Jin Kim, Vijay Kumar Shankarayya Wadi, Saeed Alhassan, Majid Ahmadi, Bart J. Kooi, Graeme Blake, Daniel M. Balazs, Maria A. Loi, Dimitrios Gournis, and Petra Rudolf**

Germanane was synthesized by the *topotatic deintercalation* of β-$CaGe_2$ in ***aqueous HF (10% w/w)*** **at room temperature for few seconds** (under stirring)



EDTA!!!!





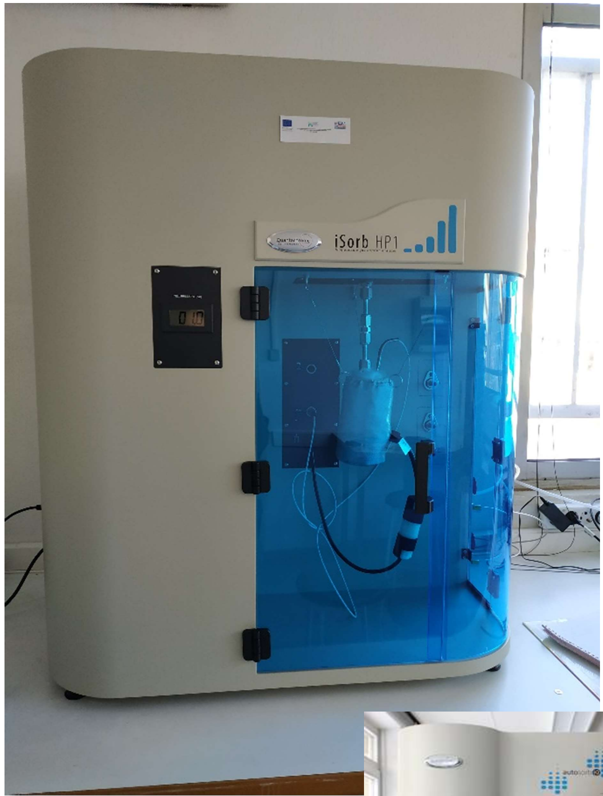
Giousis et al. *Angew. Chem. Int. Ed.* **2020**, https://doi.org/10.1002/anie.202010404

Additional in CCL

INSTITUTE OF MATERIALS SCIENCE AND COMPUTING

High pressure gas sorption analyser

Quantachrome INSTRUMENTS | iSorb™ HP1



autosorb® iQ -MP
automated gas sorption analyzer

AFM/MFM microscope

Bruker (Veeco) Multimode/Nanoscope 3D

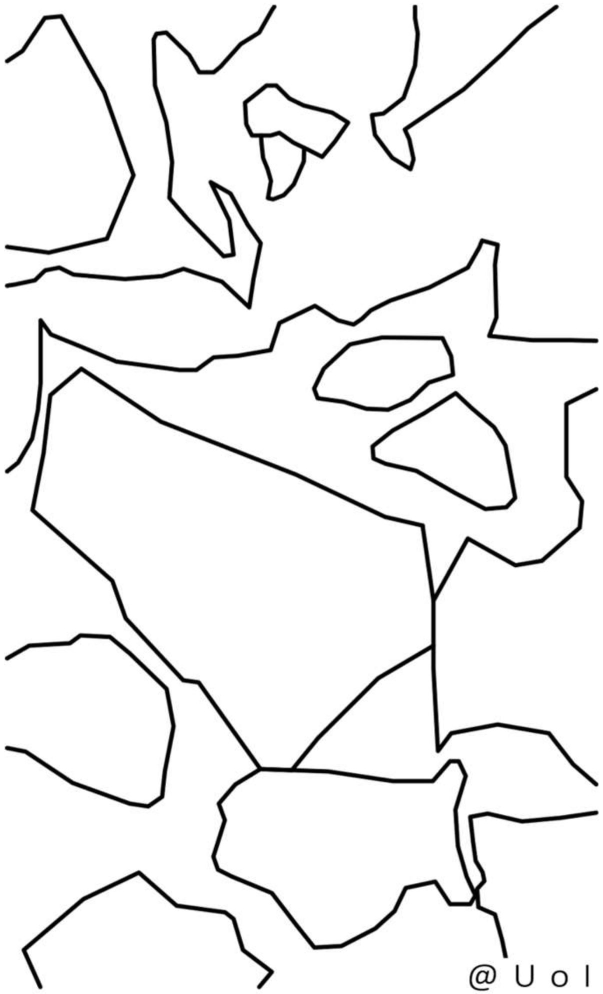
SETSYS Evolution -SETARAM

(DTA/TGA/TMA)

KSV LB apparatus

(+ **Condor** robotic system)

INSTITUTE OF MATERIALS SCIENCE AND COMPUTING



@ U o I

L N M   G R O U P

Dept. Mater. Sci. & Engineer.

the university of ioannina

THE UNIVERSITY OF IOANNINA

follow us on twitter **@lnm_uoi**