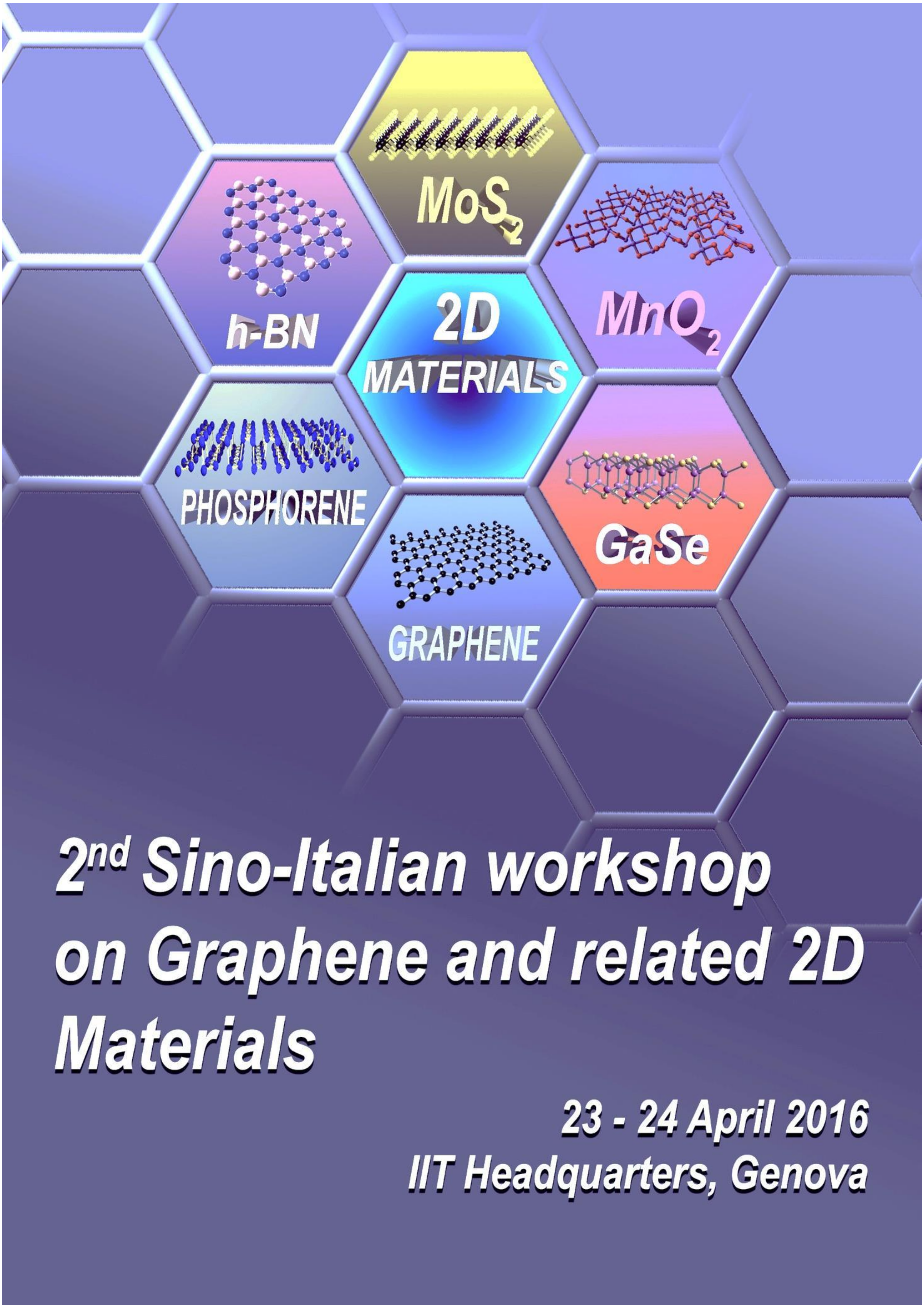

# 2nd Sino-Italian workshop on Graphene and related 2D Materials

23 - 24 April 2016
IIT Headquarters, Genova

ISTITUTO ITALIANO DI TECNOLOGIA
GRAPHENE LABS

UNIVERSITÀ
DEGLI STUDI
DI PADOVA

# 2nd Sino-Italian workshop on Graphene and related 2D Materials

Graphene is an extremely intriguing material that is rising a formidable interest in different research areas since it was first isolated in 2004. Since then, graphene has been and it continue to be one of the most investigated nanomaterials thanks to its exceptional properties, *e.g.*, outstanding charge carrier mobility, high surface area, excellent thermal conductivity, high intrinsic mechanical strength. Nowadays, the forefront of research has progressed from fundamental research challenges to a variety of applications in a large number of sectors. More recently, other 2D materials, *e.g.* chemically-modified graphene, h-BN, transition metal chalcogenides, topological insulators, just to cite a few, are gaining increasing attention. These have a combination of properties that could make them key enablers for many applications, generating new products that cannot (or may be difficult to) be obtained with current technologies or materials. The creation of new disruptive technologies based on graphene and other 2D materials is conditional to reaching a variety of objectives and overcoming several challenges throughout the value chain, ranging from materials to components and systems.

The research on graphene and other 2D materials is developing through large consortium such as the European Graphene Flagship or in the framework of Pancontinental programmes. Moreover, focused research programmes and bilateral collaborations are being set more recently. In this context, the first Sino-Italian Workshop on graphene and other 2D materials has been held in Dalian the 20th and 21th September 2014 to engage the Italian and Chinese communities working in this field. Such event was organized by the Scientific Office of the Italian Embassy in Beijing in cooperation with the Dalian Institute of Chemical Physics of the Chinese Academy of Sciences (CAS) and the Department of Chemical Sciences of the University of Padova. The Chinese delegation was composed by 15 researchers from the most renowned Chinese institutions (Beijing, Tsinghua, Nanjing, Tianjin, Sichuan Universities and several CAS institutes). The Italian delegation was composed by 15 researchers as well from Universities (i.e. Padova, Milano Bicocca, Sassari, Messina and Calabria) and from CNR and the Istituto Italiano di Tecnologia (IIT).

**The second Sino-Italian Workshop on Graphene and related 2D Materials is now held at the IIT Headquarters in Genova from 23 to 24 April 2016, as a side meeting of *Graphene 2016* event (April 19-22 2016) where almost a thousand of researchers worldwide are attending.** The workshop has been organized by the Graphene labs of the Istituto Italiano di Tecnologia, the Department of Chemical Sciences of the University of Padova and the Scientific Office of the Italian Embassy in Beijing.

Gaetano Granozzi
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## 2nd Sino-Italian Workshop on Graphene and related 2D Materials meeting Venue

The second Sino-Italian Workshop on Graphene and related 2D Materials will be taking place the 23rd and 24th April 2016 starting at 8.50 am at:

**Auditorium "Sala Leonado"**

***Istituto Italiano di Tecnologia** (IIT).*

*Via Morego, 30*
*16163 Genova,*
*Italy.*
*Tel: +39 010 71781*
*http://graphene.iit.it/*

Istituto Italiano di Tecnologia (IIT) is a public research institute that adopts the organizational model of a private law foundation. The Institute was set up with the objective of promoting excellence in basic and applied research and fostering Italy's economic development.

IIT has an overall staff of about 1,440 people. The scientific staff covers about 85% of the total. Out of 45% of researchers coming from abroad 29% are foreigners coming from more than 50 countries and 16% are returned Italians. The scientific staff currently consists of approximately 60 Principal Investigators, 110 researchers and technologists, 350 post-docs and 500 PhD students and grant holders and 130 technicians. Thanks to external funding, more than 330 positions have been created out of the staff overall amount. The average age is 34 and the gender balance proportion is 41% female against 59% male.

In its first 9 years of activity IIT has won 11 European Research Council (ERC) grants, of which the Consolidator Grants are amongst the most prestigious competitive research projects in Europe. The ERCs have been granted to high-profile scientists to allow them to accomplish challenging scientific projects.

**Dinner Venue: Palazzo del Principe**

Palazzo del Principe Andrea Doria or Palazzo del Principe a Fassolo was commissioned by Andrea Doria in 1521 and built between 1521 and 1529 outside the city walls, on an estate he had purchased from the Lomellini family.

The interiors, recently restored by the Doria Pamphili family feature a wealth of frescoes, tapestries and wooden furnishings. Of particular note is the hall with the fresco depicting the Giganti fulminati da Giove (Giants struck by Jupiter's lightening), by Perin del Vaga (1533), and the tapestries dedicated to the battle of Lepanto in 1571.

Revealing Roman influences in Renaissance design, it was built before the palaces of the Strada Nuova, marking the passage of Genoese architecture from the Middle Ages to the Renaissance and from the city palace to the suburban villa.

**Venue: IIT Headquarters, Via Morego, 30, 16163 Genova**

**Bus departure from Genova Downtown, Piazza Caricamento (in front to the Aquarium)**

**to IIT Headquarters at 8.00 am**

***23 April 2016***
***Saturday***

| | |
|---|---|
| **8:50 – 9:00** | **Opening ceremony (Dr. Bonaccorso, Prof. Granozzi, Prof. Liu)** |
| **Chair: Prof. Gaetano Granozzi** | |
| **9:00 - 9:30** | ***Graphene: A Road towards Controlled Growth***<br>**Prof. Zhongfan Liu**<br>Center for Nanochemistry, College of Chemistry and Molecular Engineering, Peking University |
| **9:30 - 10:00** | ***Electrochemical functionalization of graphene at the nanoscale with self-assembling diazonium salts***<br>**Dr. Vincenzo Palermo**<br>Istituto per la Sintesi Organica e la Fotoreattività - CNR, Bologna, Italy |
| **10:00 - 10:30** | ***Graphene and beyond: CVD growth on metals***<br>**Prof. Wencai Ren**<br>Institute of Metal Research, CAS, Shengyang |
| **10:30 - 11:00** | ***Surface Science studies of novel heterostructures based on 2D materials***<br>**Prof. Stefano Agnoli**<br>Department of Chemical Sciences, University of Padova, Italy |
| **Coffee break & Group photo** | |
| **Chair: Prof. Zhongfan Liu** | |
| **11:30 - 12:00** | ***Monolayer $MoS_2$ and $MoS_2$/Graphene heterostructures synthesized on Au foils by chemical vapor deposition method***<br>**Prof. Yanfeng Zhang**<br>Center for Nanochemistry, College of Engineering, Peking University |
| **12:00 - 12:30** | ***Graphene/$TiO_2$ interface in catalysis and photocatalysis***<br>**Prof. Cristiana Di Valentin**<br>Department of Materials Science, University of Milano-Bicocca |
| **12:30 - 13:00** | ***Synthesis of Near Zizgag Single-walled Carbon Nanotubes using Tandem-Plate CVD***<br>**Prof. Jin Zhang**<br>College of Chemistry and Molecular Engineering, Peking University |
| **13:00 - 14:00** | **Lunch** |

| *23 April 2016*<br>*Saturday* | |
|---|---|
| **Chair: Prof. Alberto Morgante** | |
| **14:00 - 14:30** | **Graphene Enhanced Raman Scattering in Nanocomposite Mesoporous Films**<br>**Dr. Luca Malfatti**<br>Laboratorio di Scienza dei Materiali e NanoTecnologie- Università di Sassari |
| **14:30 - 15:00** | **Optical spectroscopy of individual nano-materials with defined atomic structure**<br>**Prof. Kaihui Liu**<br>Center for Nanochemistry, School of Physics, Peking University |
| **15:00 - 15:30** | **Graphene and related 2D crystals for energy storage**<br>**Dr. Haiyan Sun**<br>Istituto Italiano di Tecnologia (IIT), Graphene Labs, Italy |
| **15:30 - 16:00** | **New two-dimensional crystals: controlled synthesis and optoelectronic devices**<br>**Prof. Hailin Peng**<br>Center for Nanochemistry, College of Chemistry and Molecular Engineering, Peking University |
| **Coffee break** | |
| **Chair: Prof. Wencai Ren** | |
| **16:30 - 17:00** | **In-situ atomic-scale investigation of CVD graphene on nickel substrates under realistic conditions**<br>**Dr. Cristina Africh**<br>CNR-IOM, Laboratorio TASC, Trieste, ITALY |
| **17:00 - 17:30** | **Graphene-based materials in catalysis**<br>**Prof. Dr. Dangsheng Su**<br>Institute of Metal Research, Chinese Academy of Science, Shenyang, China |
| **17:30 - 18:00** | **Electronics enabled by two-dimensional materials**<br>**Prof. Gianluca Fiori**<br>Information Engineering Department, University of Pisa, Italy |
| **18:00 - 19:00** | **Round table on future perspectives of Sino-Italian interactions**<br>**Chaired by Prof. Granozzi, Prof. Liu, Dr. Bonaccorso** |
| **19:00** | **Leaving for Museum visit and social dinner**<br>**(Palazzo del Principe, Genova Downtown)** |

**Location: IIT Headquarters, Via Morego, 30, 16163 Genova**

**Bus departure from Genova Downtown, Piazza Caricamento (in front to the Aquarium)**

**to IIT Headquarters at 8.00 am**

**24 April 2016**
**Sunday**

| | |
|---|---|
| **Chair: Dr. Francesco Bonaccorso** | |
| **9:00 - 9:30** | **Mechanics of 2d materials in 3d composites**<br>**Prof. N. Pugno**<br>Dipartimento di Ingegneria Civile, Ambientale e Meccanica, University of Trento, Italy |
| **9:30 - 10:00** | **Dielectric Property in Graphene doped Barium Titanate**<br>**Dr. Simon Xiaoyue Xiao**<br>Nanjing SCF Nanotech Ltd, Nanjing |
| **10:00 - 10:30** | **Graphene-supported Fe, Co, Ni carbon nitride electrocatalysts for the ORR in alkaline environment**<br>**Prof. Vito Di Noto**<br>Department of Industrial Engineering, University of Padova, Italy |
| **10:30 - 11:00** | **Enhanced Raman Scattering on Graphene and Beyond**<br>**Prof. Lianming Tong**<br>Center for Nanochemistry, College of Chemistry and Molecular Engineering, Peking University |
| **Coffee break** | |
| **Chair: Prof. Dangsheng Su** | |
| **11:15 - 11:45** | **Measuring the Refractive Index of Highly Crystalline Monolayer $MoS_2$ with High Confidence and A Simple and Scalable Graphene Patterning Method**<br>**Prof. Lun Dai**<br>Peking University |
| **11:45 - 12:15** | **Surface chemical reactions at epitaxial graphene and materials “beyond graphene”**<br>**Dr. Antonio Politano**<br>Department of Physics, University of Calabria, Italy |
| **12:15 - 12:45** | **Band structure, morphology of suspended and supported exfoliated graphene and charge transfer processes at graphene hybrid interfaces**<br>**Prof. Alberto Morgante**<br>CNR-IOM, Laboratorio TASC, Trieste, ITALY |
| **12:45 - 13:00** | **Closing** |
| **13.00 - 14.00** | **Lunch** |
| **14:00 - 15:00** | **IIT Lab tour** |

# Graphene: A road towards controlled growth

Zhongfan Liu

*Center for Nanochemistry, Beijing Science and Engineering Center for Nanocarbons, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China;*

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We have been working on the controlled chemical vapor deposition (CVD) growth of graphene since 2008. The research emphasis and representative achievements include: 1) Bimetal alloy catalysts for precise layer control; 2) Super graphene glass by directly growing graphene on traditional glasses; 3) Controlled growth of graphene/*h*-BN heterojunctions; 4) Controlled growth of large single crystalline graphene on Cu foils; 5) kg-CVD technique for growing graphene powders on biotemplates, 6) Scalable growth techniques for mass production of high-quality graphene. A brief overview will be made in the talk following a general concept of CVD process engineering.

**Recent publications:**

[1] C. H. Zhang, S. L. Zhao, C. H. Jin, A. L. Koh, Y. Zhou, W. G. Xu, Q. C. Li, Q. H. Xiong, H. L. Peng, Z. F. Liu, Direct growth of large-area graphene and boron nitride heterostructures by a co-segregation method, *Nature Commun.*, 6 (2015) 6519.
[2] T. Gao, X. J. Song, H. W. Du, Y. F. Nie, Y. B. Chen, Q. Q. Ji, J. Y. Sun, Y. L. Yang, Y. F. Zhang, Z. F. Liu, Temperature-triggered chemical switching growth of in-plane and vertically stacked graphene-boron nitride heterostructures, *Nature Commun.*, 6 (2015) 6835.
[3] J. Y. Sun, Y.B. Chen, M. K. Priydarshi, A. Bachmatiuk, Z.Y. Zou, Z.L. Chen, X.J. Song, M. H. Rummeli, Y.F. Zhang, Z. F. Liu, Direct chemical vapor deposition-derived graphene glasses targeting wide ranged applications, *Nano Lett.*, 15 (2015) 5846.
[4] J. Y. Sun, Y.F. Zhang, Z.F. Liu et al., Direct Growth of High-Quality Graphene on High‑κ Dielectric $SrTiO_3$ Substrate *J. Am. Chem. Soc.* 136 (2014) 6574.
[5] K. Yan, L. Fu, H. L. Peng, Z. F. Liu, Designed CVD Growth of Graphene via Process Engineering, *Acc. Chem. Res.*, 10 (2013) 2263.

# Electrochemical functionalization of graphene at the nanoscale with self-assembling diazonium salts

Zhenyuan Xia[1], Francesca Leonardi[1], Yi Liu[2], Marco Gobbi[3], Emanuele Treossi[1], Xinliang Feng[2], Emanuele Orgiu[3], Paolo Samorì[3], Vincenzo Palermo[1*]

*[1] Istituto per la Sintesi Organica e la Fotoreattività - Consiglio Nazionale delle Ricerche, Bologna, Italy*
*[2] Center for Advancing Electronics Dresden and Department of Chemistry and Food Chemistry, Technical University Dresden, Germany. School of Chemical and Chemical Engineering Shanghai Jiao Tong University, Shanghai, P. R. China*
*[3] Nanochemistry Laboratory, ISIS & icFRC Université de Strasbourg & CNRS, Strasbourg, France*

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Single layer graphene (SLG) has been widely studied in academia and industry for its fantastic electronic, mechanical, and thermal properties. However, this semi-metal material has some drawback: zero band-gap limited its application in electronic devices. Although thermal or photo-induced [2+1] cycloadditions of graphene with nitrene and carbene intermediates are common approaches for covalent functionalization, the long reaction time and low yield hinders an efficient tailoring of graphene [1,2].

Compared to the above methods, electrochemical grafting of diazonium salt is a well-established functionalization route, which ensures a stable grafting of aryl molecules with short reaction time and high surface coverage [3]. Anyhow, this method has poor spatial control and random deposition of the diazo radicals from the bulk solution. Meanwhile, the active radicals in solution could further react with the grafted aryl molecules on graphene, forming a thick poly-aryl multilayer.

Hereby, we describe a fast, efficient and versatile method combining supramolecular and covalent approaches to functionalize high quality graphene with organic molecules (fig. 1). The rationally designed molecule is an alkylbenzene derivative bearing a long alkyl chain fostering supramolecular array on graphene, and a diazonium salt moiety for successive covalent grafting (DBT). First, a thin molecular layer is physically adsorbed on graphene from solution. Then, the sample is transferred in a non-solvent, to fix the molecules on the surface and avoid desorption. Quantitative covalent grafting is finally achieved in a three-electrode setup by applying a negative voltage to the graphene surface. The successful grafting is monitored *in situ* using cyclic voltammetry, and *ex situ* with Raman spectroscopy, atomic force microscopy (AFM, fig. 2) and Kelvin Probe Force Microscopy (KPFM).

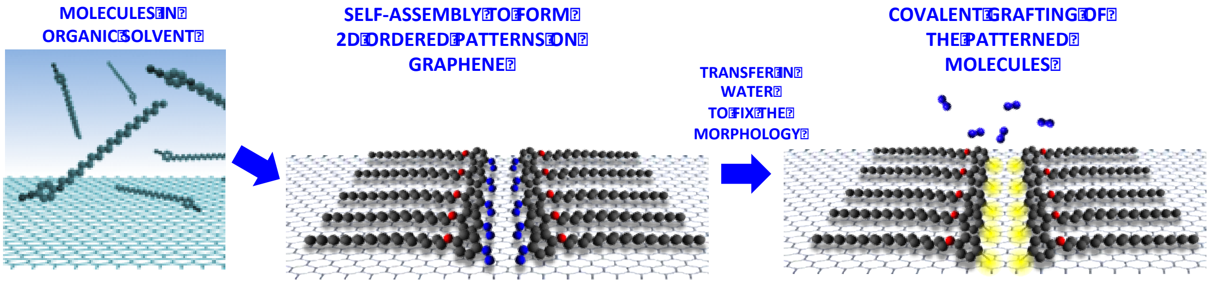

***Figure 1.*** *Schematic representation of a two-steps self-assembly + electrochemical grafting procedure.*

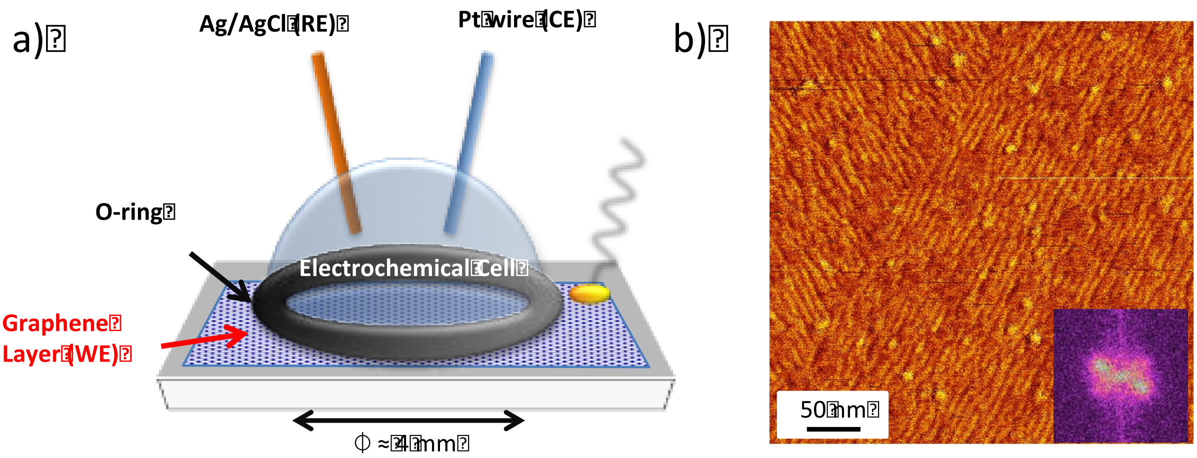

***Figure 2.*** *a) Schematic representation of the electrochemical setup used for grafting. WE (working electrode)= graphene; CE (counter electrode)= Pt; RE (reference electrode)= Ag/AgCl (3 M KCl). b) AFM phase image of a graphite surface after DBT spin-coating from an organic solvent and electrochemical grafting in* $H_2SO_4$*/water solutions. The inset shows the respective fast Fourier transform images. Z-range=10 deg.*

## References

[1] L. Elliot, et al., Chemistry of Materials. 23 (2011) 3470.
[2] J. Park, et al., Accounts of Chemical Research. 46 (2013) 181.
[3] L. Gan, et al., Small, 8 (2012) 1326.
[4] This research was supported by the European Union Seventh Framework Programme under Grant Agreement No. 604391 Graphene Flagship. The project UPGRADE acknowledges the financial support of the Future and Emerging Technologies (FET) programme within the Seventh Framework Programme for Research of the European under FET-Open Grant Number: 309056.

# Graphene and beyond: CVD growth on metals

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In this presentation, I will show our recent progress on the chemical vapor deposition (CVD) growth of graphene and other two-dimensional (2D) materials. For the CVD growth of graphene, we have developed an ambient-pressure CVD process to grow millimeter-size single-crystal graphene on Pt [1], observed the edge-dependent growth behavior of graphene [2], and found an efficient way to heal the defects in graphene [2,3]. Importantly, we have proposed a nondestructive electrochemical bubbling transfer method [1,4], and realized the continuous production of large-area graphene transparent conductive films (TCFs) by integrating the bubbling method with the scalable roll-to-roll process. With these graphene TCFs as electrodes, we have fabricated 7 inch flexible touch panels and 4 inch flexible OLEDs.

For the CVD growth of other layered 2D materials, we have developed an ambient-pressure CVD process with Au foils as substrate to realize the self-limited catalytic surface growth of uniform monolayer $WS_2$ single crystals of millimeter size and large-area films [5]. The weak interaction between the $WS_2$ and Au enables the intact transfer of the monolayers to arbitrary substrates using the electrochemical bubbling method without sacrificing Au. The $WS_2$ shows high crystal quality and optical and electrical properties comparable or superior to mechanically exfoliated samples. We also demonstrated the roll-to-roll/bubbling production of large-area flexible films of uniform monolayer, double-layer $WS_2$ and $WS_2$/graphene heterostructures, and batch fabrication of large-area flexible monolayer $WS_2$ film transistor arrays.

Beside layered 2D materials, we have also realized the CVD growth of large-size high-quality non-layered ultrathin 2D transition metal carbides (TMC) crystals, such as $Mo_2C$, WC, and TaC, by using Cu/transition metal foils bilayer as substrate [6]. For instance, the 2D $\alpha$-$Mo_2C$ crystals obtained are a few nanometers thick, over 100 μm in lateral size, and very stable under ambient conditions. They show 2D characteristics of superconducting transitions that are consistent with Berezinskii–Kosterlitz-Thouless behavior and show strong anisotropy with magnetic field orientation, and strong dependence of superconductivity on thickness of the crystals. These ultrathin TMC crystals further expand the large family of 2D materials.

## References

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[4] W.C. Ren, H.M. Cheng, *Nature Nanotechnology* 9, 726 (2014).
[5] Y. Gao, H.M. Cheng, W. C. Ren, et al., *Nature Communications* 6, 8569 (2015).
[6] C. Xu, H.M. Cheng, W.C. Ren, et al., *Nature Materials* 14, 1135 (2015).

# Surface Science studies of novel heterostructures based on 2D materials

Stefano Agnoli, Roberto Sant, Francesco Carraro, Mattia Cattelan and Gaetano Granozzi

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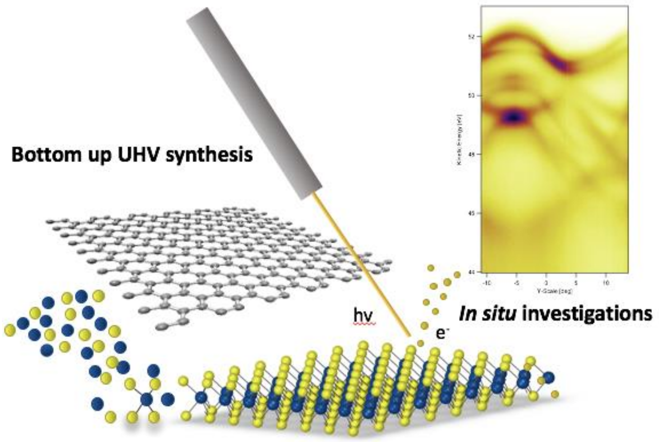
Heterostructures made up by 2D materials are emerging as a test ground for new physics and new chemistry, and represent a treasure trove for innovative applications in electronics, sensors, photovoltaics etc.[1]

Actually, the rational combination of different nanosheets provides a way to control in a surgical way the physicochemical properties of the assembled 2D heterostructures and sometimes it allows even inducing totally new properties. However, basic research is only at the beginning of its journey into this multi-material flatland. Actually, one major obstacle toward the full comprehension of heterostructures and in particular for a fundamental understanding of structure-activity relationships, is represented by the complex methods needed for producing highly perfect interfaces with low defectivity, extreme purity, and atomic scale control of structural properties.

In this contribution, we present a general bottom-up method for the synthesis under ultra high vacuum conditions, e.g. physical and chemical vapor deposition, of different types of vertically stacked heterojunctions such as $WSe_2$/graphene and $WS_2$/h-BN,[2] as well as in-plane graphene/h-BN nanojunctions.[3] These systems have been investigated *in situ* without using any transfer method or exposing them to the atmosphere, by means of advanced spectroscopy and microscopy techniques, in order to determine their pristine electronic and structural properties. In addition, we report the results of a study where an aerosol processing enables the preparation of hierarchical graphene/$MoS_2$ nanocomposites where nitrogen-doped crumpled graphene nanosacks wrap finely dispersed $MoS_2$ nanoparticles.[4] The activity of these materials is tested toward the photoelectrochemical production of hydrogen, obtaining seven times more efficient materials with respect to single $MoS_2$, because of the formation of p-n MoS /graphene nanojunctions, which allow an efficient charge carrier separation.



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[3] S. Nappini et al. *Adv. Func. Mater.* 2016, doi10.1002/adfm.201503591
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# Monolayer $MoS_2$ and $MoS_2$/Graphene heterostructures synthesized on Au foils by chemical vapor deposition method

Yanfeng Zhang

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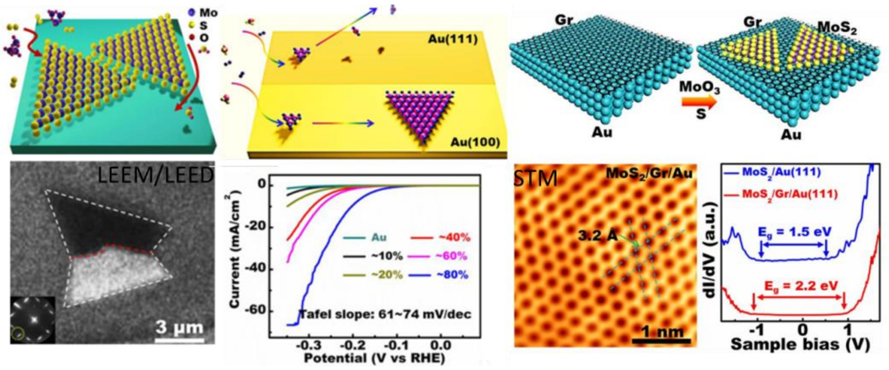
Controllable synthesis of monolayer $MoS_2$ on conducting substrates is essential for exploring the atomic-scale structure, intrinsic electronic property, and engineering its application in various aspects. Recently, we have achieved the domain size tunable (with the edge length of the triangular domains tunable from several hundred nanometers to a hundred microns) growth of monolayer $MoS_2$ directly on Au foils, *via* a facile low-pressure chemical vapor deposition (LPCVD) [1]. We also demonstrate an obvious substrate-crystal-facet-dependent growth behavior at relative high growth temperatures (>680 °C), where large-domain single-crystal $MoS_2$ triangles are more preferentially evolved on Au(100) and Au(110) facets than that on Au(111), and this substrate effect can be weakened at relative low growth temperature (~530 °C). The preferential growth behavior are then explained from the facet-dependent binding energy of $MoS_2$ according to density functional theory calculations[2]. We have also presented that the crystal orientations and domain boundaries of monolayer $MoS_2$ flakes as-grown on Au foils can be on-site identified by using low-energy electron microscopy/diffraction (LEEM/LEED) method [3]. Of particular interest, the nanosized $MoS_2$ flakes on Au foils are proven to be excellent electrocatalysts for hydrogen evolution reaction (HER).

By using a facile all chemical vapor deposition (all-CVD) approach, we have also realized the direct growth of monolayer $MoS_2$ on CVD graphene (Gr) ($MoS_2$/Gr) on the Au foil substrate. Spectroscopic characterizations reveal that the in-between Gr monolayer substantially weakens the interface interaction between $MoS_2$ and Au, leading to electronically quasi-freestanding $MoS_2$. This is evidenced by a very weak n-doping effect and an intrinsic bandgap of $MoS_2$ for $MoS_2$/Gr/Au sandwich by scanning tunneling microscopy/spectroscopy (STM/STS) characterizations. Moreover, the exciton binding energy is also obtained by combining variable temperature photoluminescence measurements[4].



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# Graphene/$TiO_2$ interface in catalysis and photocatalysis

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Graphene/$TiO_2$ nanocomposites are successfully applied both in photocatalysis and photovoltaics.[1,2,3] The enhanced performances are attributed to their improved interfacial charged transfer and charge separation, reducing the recombination rate of photoexcited electron and hole pairs. In the first part of the talk we show that only density functional methods which provide corrections for the spurious self-interaction and for the Van der Waals forces can correctly describe the electronic structure, the adhesion energy and the atomic distances of this hybrid interface. We also provide evidences that electrons are preferentially trapped at subsurface layers of $TiO_2$, while holes are preferentially delocalized on the G sheet. This opposite tendency is proposed to be at the basis of the lower recombination rate leading to the observed improved outcomes in technological applications. [4]

In the second part of the talk we present $O_2$ and $H_2O$ reactivity on top and at the interface of pristine or B-doped Graphene/$TiO_2$. An enhanced reactivity towards $O_2$ dissociation is observed as a result of both the contribution of the dopant and of the confinement effect in the bidimensional area between the two surfaces. Extremely stable dissociation products are formed where the boron atom bridges the two systems by forming very stable B-O covalent bonds. On the contrary, the same conditions are not found to favour water dissociation, proving that the "catalysis under cover" is not a general effect, but highly depends on the interfacing material properties, on the presence of defects and impurities and on the specific reaction involved. [5]

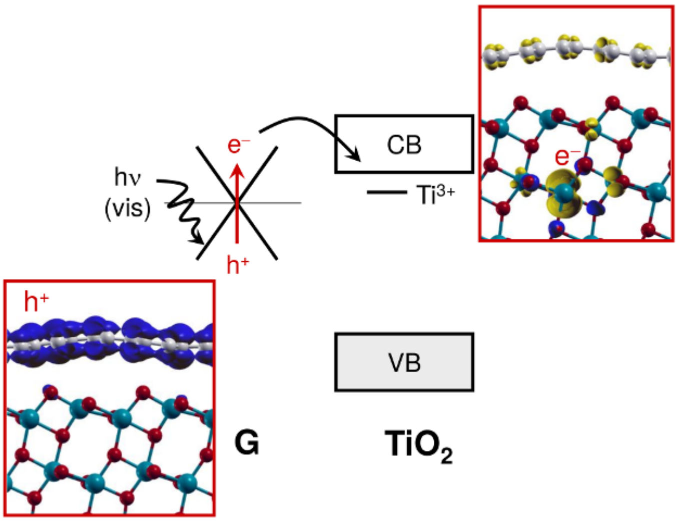

***Figure 1*** *Photoexcited electron and hole separation at the graphene/anatase (101) $TiO_2$ interface.*

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# Synthesis of near zizgag single-walled carbon nanotubes using tandem-plate CVD

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Chemical vapor deposition (CVD) method is regarded as the most potential method for realizing the structure-specific single-walled carbon nanotubes (SWNTs) growth. However, normal CVD growth under a constant conditions could not take the full advantage to optimize the chirality because of the randomly formed cap structure allows the nucleation of all types of SWNTs. Here, we report a CVD process that allows temperature to be changed periodically to vary a SWNT' chirality frequently in order to build up a more stable catalyst-SWNT interface. With this strategy, SWNTs with small helix angles (less than 10°), which are predicted to have lower interfacial formation energy than others, are enriched up to 72%. Kinetic analysis of the process suggests a multiple re-distribution features that a large chiral angle SWNT tends to reach the near zigzag chirality step by step with a small chiral angle change every step, hence we named this method as "Tandem-Plate CVD".

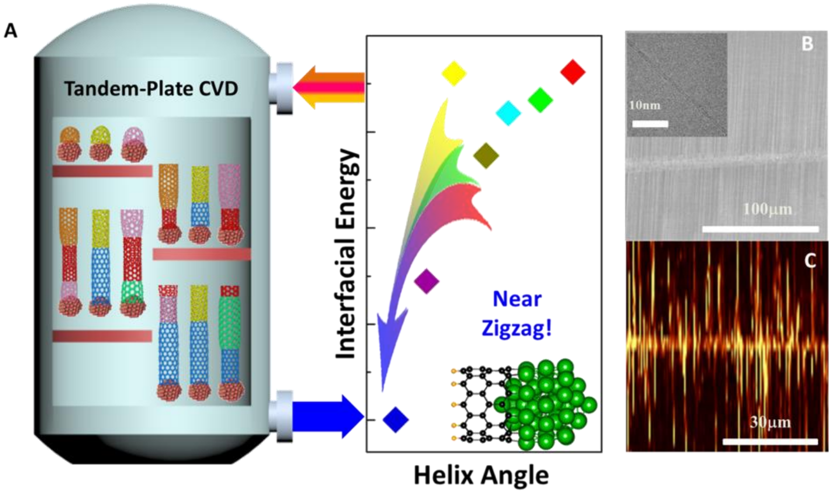

***Figure 1.*** *A schematic illustration of TPCVD process*

# Graphene enhanced raman scattering in nanocomposite mesoporous films

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The first report on Graphene Enhanced Raman Scattering (GERS) of molecules deposited onto graphene layer has arisen a great deal of interest in the scientific community boosting the need of developing new graphene-based substrates capable of improving this property. However, one issue that hampers the use of graphene-based substrates is the low enhancement factor associated with the GERS effect, which is several orders of magnitude lower than conventional Surfaced Enhanced Raman Scattering (SERS) based on noble metals nanoparticles. Since the analytical enhancement factor (AEF) is strictly dependent upon the number of molecules adsorbed onto the ERS-active substrate, an increase in the number of adsorbed molecules in contact with the substrate would improve the AEF and thus its efficiency. This increase can be achieved, for instance, by using highly porous scaffolds where a large number of molecules can be adsorbed into a well-defined volume bigger than that of a corresponding flat surface. In this case, the ERS-active surface would be described by the volume defined by the laser spot size, the thickness and porosity of the matrix. On the base of this assumption we have developed several ERS-active 3D platforms based on nanocomposite mesoporous films embedding exfoliated graphene (EG) and characterised by a high surface area. In particular, by using Rhodamine 6G as a Raman probe we have investigated the possibility of using these matrices as a versatile tool for new sensing devices. This approach led to the preparation of silica nanocomposite mesoporous films embedding 2-layers EG through a one-pot route capable of nucleating gold nanoparticles onto the graphene surfaces.[1] The resulting silica mesoporous matrix embedding both gold nanoparticles and EG showed an AEF ranging from 80 up to 136 fold increase, depending on the Raman mode, whilst the corresponding mesoporous films embedding either EG or gold nanoparticles reached a maximum of less than 10. Such a difference can be ascribed to the effect named Graphene-mediated SERS (G-SERS) that was there evidenced in a mesoporous matrix for the first time. The use of this 3D approach was investigated further by analysing the extent of the GERS effect induced into titania mesoporous films.[2] This allowed evidencing a co-operative ERS effect between graphene and crystalline titania leading to the discovery of a new effect that we have named Ti-GERS (Titania-induced GERS).[3] In fact, the enhancement due to crystalline mesoporous titania embedding EG (Ti-GERS) exceeded the sum of the enhancements due solely to EG and crystalline titania (Figure 1 a and b). Very recently we have started investigating the possibility of using hybrid organic-inorganic silica matrices embedding EG as flexible thick GERS substrates particularly suitable for providing molecular recognition properties through a molecular imprinting approach. This, in fact, would allow developing new enhanced Raman scattering protocols based on a selective pre-concentration of the analyte, due to a molecular selectivity of the substrate, followed by a selective determination of the molecular species, exploiting the GERS effect.

Giving the interesting results reported for these GERS-active mesoporous matrices, it is possible to envisage their use in the near future as versatile 3D tuneable platforms for sensing applications.

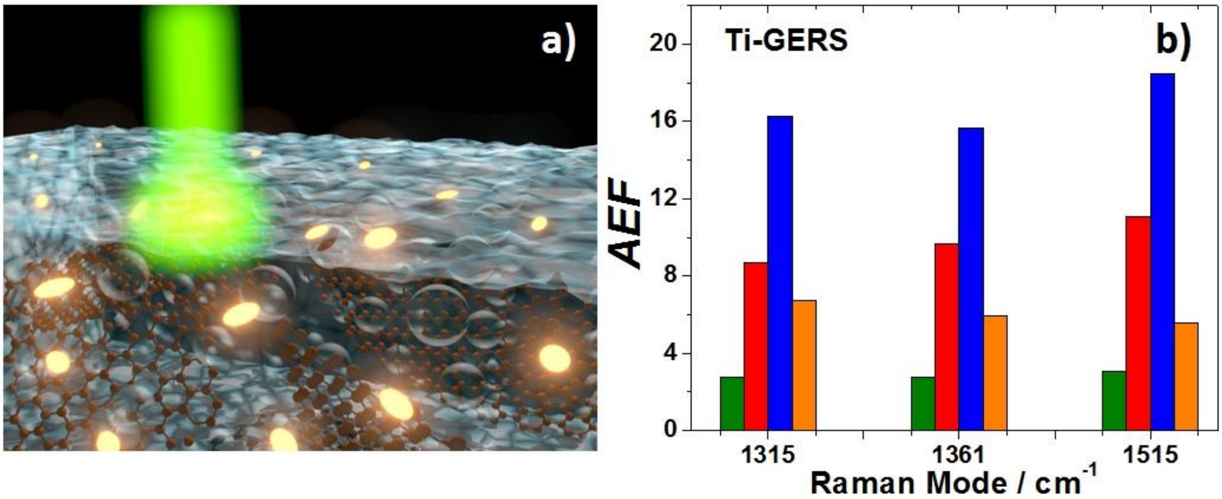

**Figure 1.** a) Schematic of the Ti-GERS process. b) Bar plot showing the analytical enhancement factors (AEFs) of Rh6G for mesoporous films embedding exfoliated graphene with respect to bare mesoporous silica: silica treated for 2 h at 450 °C under an inert atmosphere (green), titania treated for 2 h at 350 °C in air (orange), and titania treated for 2 h at 450 °C under an inert atmosphere (anatase phase) with (blue) and without (red) embedded graphene.

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# Optical spectroscopy of individual nano-materials with defined atomic structure

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When the characteristic length of a material shrinks to 1 nm scale, many distinct physical phenomena, such as quantum confinement, enhanced many-body interactions and strong van der Waals inter-material couplings, will appear. To investigate these related fascinating low-dimensional physics, we need a tool to quantitatively link the atomic structures to the physical properties of very small nano-materials. In this talk, I will introduce our recently developed in-situ TEM + nanooptics technique [1,2], which combines capability of structural characterization in TEM and property characterization in nanooptics on the same individual nano-materials. Several examples of using this technique to study the physics in 1D carbon nanotube system [3-6] and 2D atomic layered materials [7-8] will be demonstrated.

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# Graphene and related 2D crystals for energy storage

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Graphene, thanks to its outstanding materials properties, has the opportunity to enable new technology and products.[1] Graphene is just the first of a new class of two dimensional (2D) crystals, derived from layered bulk crystals counterpart.[2]

New materials and processes[1] can improve the performance of existing devices or enable new ones,[1-5] which are also environmentally benign. In this context, graphene and other 2d crystals are emerging as promising materials.[1-6] A key requirement for application in the energy storage and conversion field is the development of industrial-scale, reliable, inexpensive production processes,[2] while providing a balance between ease of fabrication and final material quality with on-demand properties.

Solution-processing[2] offers a simple and cost-effective pathway to fabricate various 2d crystal-based energy devices, presenting huge integration flexibility compared to conventional methods. Here, we will present an overview of graphene and other 2D crystals for energy storage applications, starting from solution processing of the raw bulk materials,[2] the fabrication of large area electrodes[3] and their integration in the final devices.[6,7,8,9,10]

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# New two-dimensional crystals: controlled synthesis and optoelectronic devices

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The unique structure and properties of two-dimensional (2D) crystals have a large impact on fundamental research as well as applications in electronics, photonics, optoelectronics and energy sciences. Here our recent studies on the controlled synthesis of high-quality 2D crystals such as large graphene single crystals, bilayer twisted graphene, topological insulator V2VI3 nanostructures, other layered metal chalcogenides and their hybrid materials, as well as their optoelectronic properties will be discussed. We propose several methods including roll-to-roll CVD, micro-contact printing growth, and van der Waals epitaxy to achieve the controlled growth of various high-quality 2D crystals, which can be used for high-performance electronics and efficient photodetection applications. Our studies suggest that functional 2D crystals hold great promise for future electronic and optoelectronic applications.

# In-situ atomic-scale investigation of CVD graphene on nickel substrates under realistic conditions

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The understanding of growth mechanisms, at the atomic level and on substrates suitable for scalable CVD production, is a key step for the use of graphene in industrial applications. However, most studies so far are based on the interpretation of post-growth experiments on model surfaces, which can sometimes be misleading, while real-time information on realistic substrates is usually missing.

By means of variable-temperature scanning tunnelling microscopy, we studied the graphene growth process in the 380-500ºC temperature range with a time resolution down to 100 ms and on commercially available polycrystalline Ni substrates. (111) and (100) facets were identified in the examined regions of the polycrystalline sample and growth mechanisms were investigated on both flat (100) terraces and highly-stepped regions. On flat terraces, graphene can grow directly on top of the metal or via in-plane carbide conversion, as already evidenced in our previous work on model (111) substrates. On (100) grains, a variety of moiré superstructures are present, which can be well explained in atomistic models by the mismatch with the substrate and whose appearance in the STM images is well reproduced by density functional theory simulations. These moiré structures were found to be able to influence carbide segregation under graphene, thus providing a new route to tune its electronic properties on a nanometre scale. Furthermore, with the aid of an add-on FAST module allowing for the acquisition of STM time-series up to video rate, novel growth mechanisms at stepped areas are unveiled, which rationalize the continuity of the graphene layer even when it lies on highly stepped polycrystalline substrates.

Finally, preliminary results on the influence of exposure of the graphene covered substrate to ambient gases in the 1-10 torr pressure range will also be briefly discussed.

# Graphene-based materials in catalysis

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For sustainable chemistry metal-free catalysis has gained broad interests. Graphene-based materials for catalysis is one green option for alternative to replace traditionally metal-based catalysts. This is documented by the numerous reports on gas phase dehydrogenation and selective oxidation where carbon provides successful alternatives to metal oxide systems. Graphene-based materials are interesting for many liquid phase reactions, especially for organic synthesis, and are forming a newly established research discipline and experienced a rapid development in recent years. This presentation gives a critical analysis on the state-of-the-art of graphene-based materials for liquid phase reactions, with the focus on the possible underlying mechanisms, advantage and limitation.

# Electronics enabled by two-dimensional materials

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Two-dimensional materials have shown so far exceptional properties, which could pave the way towards their exploitation in a wide range of electronic applications. Their ultimate thinness as well as their excellent electrical properties could represent the enabling ingredients in order to obtain end-of-the-roadmap transistors.

Actually, both Industry and Academy are fighting against the main issue of breaking the sub-5nm channel length limit in next-generation field effect transistors, since short channel effects (SCE) as well as quantum tunnelling phenomena are greatly affecting device performance.

Here we will show that ultimately thin devices based on two-dimensional materials will manage to accomplish this goal, being able to both reduce SCE and intra-band tunnelling, if materials with sufficiently large effective mass along the longitudinal direction are properly chosen.

In the talk, we will also cover other important issues, like flexible electronics, and optoelectronic applications, like the exploitation of graphene as a transparent conductive electrode in flexible organic solar cells.

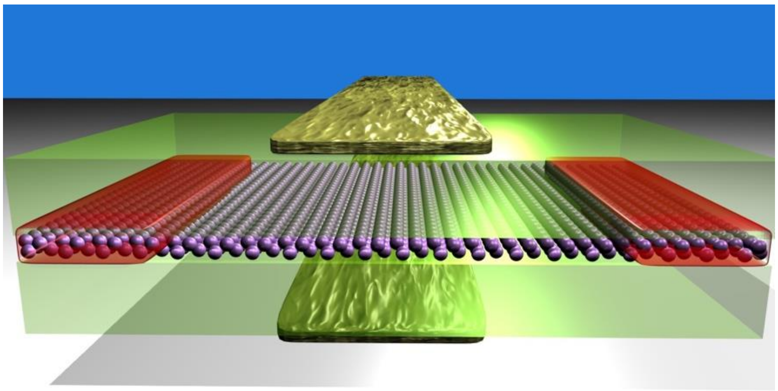

***Figure.*** *Sketch of a 2D-material based Field Effect Transistors for digital applications*

# Mechanics of 2d materials in 3d composites

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In this lecture I will present our recent results on the mechanics of 2D materials in 3D composites, specifically our numerical and analytical tools ad hoc developed for designing optimized nanocomposites, from the lab to the industrial size-scale, well surpassing the commonly used and abused trial and error approach.

## References

see http://www.ing.unitn.it/~pugno/

# Dielectric property in graphene doped barium titanate

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GN/BT nanocomposites were fabricated via colloidal processing methods and ceramics were sintered through two-step sintering methods. The microstructure and morphology were characterized by X-ray diffraction, high-resolution transmission electron microscopy, and field emission scanning electron microscopy. XRD analysis shows all samples are perovskite phases and the lattice parameter *a* and *c* almost decrease linearly with the increase of graphene nanosheets. The dielectric properties were tested by using precision impedance. The maximum dielectric constant at Curie temperature for the nanocomposites with graphene addition of 3 wt% is about 16000, almost two times more than that of pure BaTiO3 ceramics. The relaxation, band structure, density of states, and charge density distribution of GN/BT superlattices were calculated first-principles calculations for the first time, and results showed the strong hybrid interactions between C 2p states and O 2p and Ti 3d orbitals.

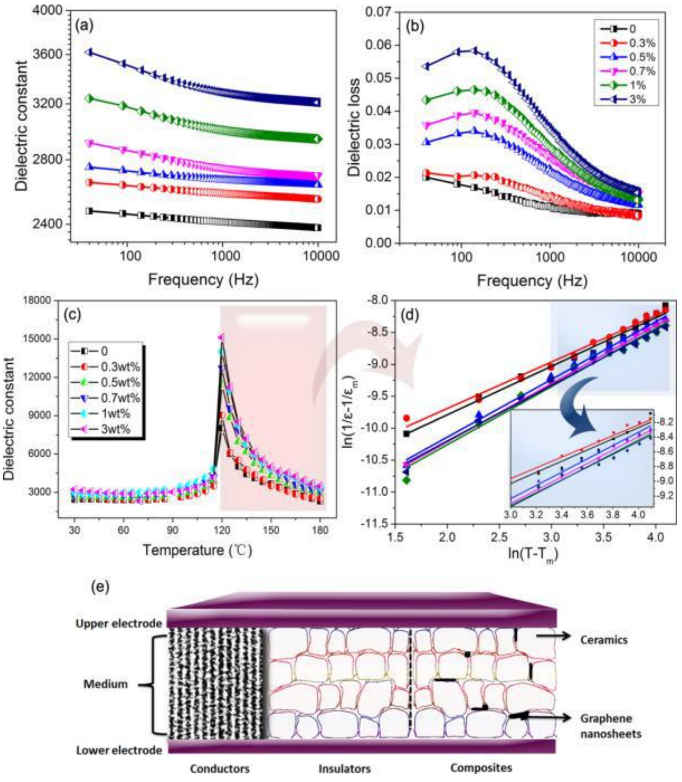

**Figure 1.** Frequency dependence of dielectric constant (a) and dielectric loss (b) of GN/BT composites. Temperature dependence of dielectric constant(c) and (d) curie Weiss fitting curves of GN/BT nanocomposites. (e) Schematic images of the microstructure of GN/BT nanocomposites.

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# Graphene-supported Fe, Co, Ni carbon nitride electrocatalysts for the ORR in alkaline environment

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One of the major obstacles for the development of feasible low-temperature fuel cells (e.g., proton-exchange membrane fuel cells, PEMFCs, and anion-exchange membrane fuel cells, AEMFCs) is the sluggishness of the oxygen reduction reaction (ORR) kinetics. As of today, carbon-supported Pt-based nanocrystals are the most efficient electrocatalysts (ECs) for the ORR. However, the low abundance of platinum and the insufficient durability of these ECs, which results from the degradation of the carbon support, constitute some of the major obstacles for large-scale commercialization of PEMFC and AEMFC technology [1, 2].

In this study, new "Pt-free" electrocatalysts are prepared and studied for the ORR process. These ECs consist of alloyed Fe-Sn nanoparticles embedded in a carbon nitride "shell" a few nanometers thick, supported on conducting micrometric graphene sheets that act as the "core". The electrocatalytic precursors are prepared by a sol-gel/gel-plastic process following a protocol previously developed in our laboratory [3]; afterwards, they undergo suitable pyrolysis and activation processes. The proposed electrocatalysts, both pristine (e.g., $FeSn_{0.5}$-CN 900/Gr) and activated (e.g., $FeSn_{0.5}$-CN 900/$Gr_a$) are extensively characterized in order to gain a full understanding of their structural features, proprieties and electrocatalytic performance [4]. The chemical composition is determined by inductively-coupled plasma atomic emission spectroscopy (ICP-AES). The structure is elucidated by powder X-Ray diffraction (XRD); the morphology is inspected by high-resolution scanning electron microscopy (HR-SEM) and high-resolution transmission electron microscopy (HR-TEM). Finally, "ex situ" cyclic voltammetry with the rotating ring-disk electrode (CV-TF-RRDE) and "in situ" single fuel cell measurements are carried out to evaluate the electrocatalytic performance as well as to study the ORR mechanism. The preliminary CV-TF-RRDE investigations in an alkaline medium exhibit promising results. Indeed, the catalysts exhibit an overpotential ca. 70 mV higher with respect to a 20 wt.% Pt/C reference.

## Acknowledgements

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# Enhanced raman scattering on graphene and beyond

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Surface-enhanced Raman scattering (SERS) on graphene has stimulated increasingly interests and has become a unique platform to study the chemical effects in SERS [1,2]. Other two-dimensional (2D) materials, including hexagonal boron nitride (h-BN), molybdenum disulfide ($MoS_2$), and black phosphorous (BP), have also been shown active for Raman enhancement [3, 4]. The enhancement is attributed to the charge interaction between the 2D materials and molecules, in reciprocal, the Raman enhancement could also reveal information on the charge interaction, and further on the fundamental electronic properties of the 2D materials. In addition, the atomic flatness and flexibility of 2D materials promise unique potential in certain applications superior to traditional metallic SERS substrates. Here, we report our recent progress on graphene-based Raman enhancement and its application in quantitative analysis, and Raman enhancement on anisotropic 2D materials such as BP and rhenium disulphide ($ReS_2$) [4, 5].

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# Measuring the refractive index of highly crystalline monolayer $MoS_2$ with high confidence and a simple and scalable graphene patterning method

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Monolayer molybdenum disulphide ($MoS_2$) has attracted lots of attention, due to its attractive properties, such as two-dimension, direct-bandgap, valley-selective circular dichroism, and valley Hall effect. However, because of some technique difficulties, some of its fundamental physical parameters, *e. g*. refractive index, are still not studied in detail. In this work, we have synthesized highly crystalline monolayer $MoS_2$ on $SiO_2$/Si substrates via chemical vapor deposition (CVD) method and found a way to measure their optical contrast spectra. Based on these contrast spectra, we fit out the complex refractive index spectrum of monolayer $MoS_2$ in a wavelength range from 400 nm to 750 nm with high confidence. The clear difference between the obtained complex refractive index spectrum and that of bulk $MoS_2$ is analyzed in detail. The method presented here has some advantages over conventional methods for small-scale two-dimensional materials. Furthermore, we have calculated the color plot of the contrast as a function of both $SiO_2$ thickness and incident light wavelength for monolayer $MoS_2$ using the obtained refractive index spectrum, which is useful in both experimental study and device fabrication.

We have also developed a simple and scalable graphene patterning method using electron-beam or ultraviolet lithography followed by a lift-off process. This method, with the merits of: high pattern resolution and high alignment accuracy, free from additional etching or harsh processes, universal to arbitrary substrates, and compatible to Si microelectronic technology, can easily be applied to diverse graphene-based devices, especially in array-based application, where large-scale graphene pattern is desired.

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# Surface chemical reactions at epitaxial graphene and materials “beyond graphene”

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Graphene (Gr) is a promising material in the fields of energy and catalysis [1]. By means of a combination of surface-science spectroscopies and theory, we have investigated the mechanisms ruling the catalytic role of epitaxial Gr grown on transition-metal substrates for the production of hydrogen from water. Water decomposition at the Gr/metal interface at room temperature provides a hydrogenated Gr sheet, which is buckled and decoupled from the metal substrate. We have evaluated the performance of Gr/metal interface as a hydrogen storage medium, with a storage density in the Gr sheet comparable with state-of-the-art materials (1.42 wt.%). It is expected that decoration of Gr by Ca or transition-metal atoms and, moreover, the substitutional doping of Gr by N or B could further increase the gravimetric capacity.

Moreover, thermal programmed reaction experiments show that molecular hydrogen can be released upon heating the water-exposed Gr/metal interface above 400 K. The Gr hydro/dehydrogenation process might be exploited for an effective and eco-friendly device to produce (and store) hydrogen from water, i.e. starting from an almost unlimited source.

The surface catalytic activity is also important for the prospect of electronic devices using ultrathin flakes of black phosphorus (few-layer phosphorene) [2-4].

Many studies have reported the oxidation of black phosphorus and the formation of $P_2O_5$ upon air exposure [5]. However, the reactivity of phosphorene toward CO has been not studied yet. By means of vibrational spectroscopy and density functional theory, we have investigated CO adsorption on phosphorene-based systems. We find stable CO adsorption at room temperature on both phosphorene and bulk black phosphorus. The adsorption energy and the vibrational spectrum have been calculated for several possible configurations of the CO overlayer. We find that the vibrational spectrum is characterized by two different C-O stretching energies. The experimental data are in good agreement with the prediction of the DFT model and unveil the unusual C-O vibrational band at 165-180 meV, activated by the lateral interactions in the CO overlayer.

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# Band structure, morphology of suspended and supported exfoliated graphene and charge transfer processes at graphene hybrid interfaces

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Exfoliated graphene is expected to behave like a flexible membrane where intrinsic thermal fluctuations or interactions with the substrate can induce substantial crystal deformations. These deformations can affect conductivity and increase local chemical reactivity in graphene sheets. Thus, an understanding of the surface morphology in both suspended and supported graphene is essential to making high quality devices. Crystal deformation can affect also the band structure of graphene. Until now many Angle Resolved Photo Emission (ARPES) measurements of epitaxially grown graphene have been reported where interaction with the substrate instead of crystal deformation can play a major role in modifying the details of the band structure. However, because of the inherent difficulties associated with studying exfoliated graphene with conventional ARPES techniques due to the small size of presently available samples, there have been no direct band structure measurements of this material.

We have combined low energy electron microscopy (LEEM) and micro-spot low energy electron diffraction (□-LEED), micro Angle Resolved Photo Emission (ARPES) and XPEEM techniques to study the morphology and the band structure of both suspended and $SiO_2$ supported exfoliated graphene. LEEM measurements allow real space imaging of surface features above 10 nm while a careful analysis of □-LEED measurements can reveal details of surface morphology on length scales down to interatomic distances. Thus, by combining these two probes we are able to access both the microscopic and mesoscopic regimes to obtain a full characterization of the corrugation in suspended and supported exfoliated graphene.

Moreover we describe experimental approaches for obtaining high-resolution ARPES data from a non-planar free-standing, single-crystal films, like exfoliated single-layer graphene. The extrinsic and intrinsic surface roughness of these samples impacts ARPES measurements in two ways: deviation from planarity induces lifetime broadening in initial states and, additionally, causes decoherence in electron waves through the photoemission process. We demonstrate use of experimental and analytical methods to allow electronic band mapping of micrometer-scale samples of monolayer graphene. After corrections for surface corrugation, we measure the energy dependent quasi-particle lifetime and band structure.

The use of graphene in organic electronics and photovoltaics (as an electrode or charge collector/separator) is expected to improve the efficiency of the devices based on these materials. In these devices Interface processes strongly affect the performances and efficiency. There is a need therefore to more clearly understand and control interface processes like charge transfers between materials such as organic films, graphene and metals. Charge injection occurs at the femtosecond time scale (or shorter) so that the study of the dyanmics fo these processes is in most cases still out of reach of the pump probe spectroscopies. Here we use X-ray spectroscopies to investigate charge injection in complex ethero-structures that include organic molecules, graphene and metallic substrates. We show that the Core hole clock implementation of the Resonant Photoemission spectroscopy (RESPES) allows us to determine charge dynamics in both directions at these interfaces and can give clues on the interface parameters that can increment/decrement the charge transfer efficiency. Examples of model systems will be discussed.

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