



PCAM/Thinface Summer School 2017

Surfaces and Interfaces

**Miramar Palace, Donostia - San Sebastian
Basque Country (Spain)
20-23 June 2017**

PROGRAM AND ABSTRACTS



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Chairman: Jose M. Pitarke (nanoGUNE and UPV/EHU, San Sebastian)

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PREFACE

The European network of doctorate programs in Physics and Chemistry of Advanced Materials (PCAM) organizes every year a summer school on a specific relevant scientific topic. The 2017 edition is being organized jointly with the THINFACE European Initial Training Network, in the framework of the Summer Courses of the University of the Basque Country (UPV/EHU). The local organizers are the Materials Physics Center CSIC-UPV/EHU, the Donostia International Physics Center (DIPC), and the Nanoscience Cooperative Research Center nanoGUNE. The lectures focus on Surfaces and Interfaces, more specifically on two-dimensional (2D) materials, thin-film solar cells, and core-level spectroscopies. The participation is open to PhD students, post-docs, and all researchers interested in the field. The summer school takes place on 20-23 June 2017 in a seaside palace in the scenic city of San Sebastian, Basque Country (Spain).

During the last decades, nanotechnology has enabled the fabrication of novel nanostructures like extremely thin films and 2D materials. A deep theoretical and experimental understanding of these nanostructures is necessary in order to get new insights and profit from the possibilities arising from their use and manipulation. This summer school provides attendees with state-of-the-art knowledge on the physical and chemical properties of thin films and 2D materials, most interesting in a variety of applications.

The lecturers and invited speakers are first-class scientists and world leaders in their fields. The program, based on lectures and invited talks, also includes oral contributions and posters as well as a special seminar on scientific presentations.

Donostia - San Sebastian, 20 June 2017



Jose M. Pitarke
Chairman

PROGRAM

Tuesday, 20 June

- 8:30 Registration
- 8:45 Welcome, opening remarks, and announcements
- 9:00 **O. Monti** (Arizona, USA)
Advances in 2D materials
- 11:00 Coffee & Posters
- 11:30 **F. Nüesch** (Dübendorf, Switzerland)
Introduction to thin-film solar cells
- 13:30 Lunch & Posters
- 14:30 **T. Rahman** (Florida, USA)
Tailoring chemical and optical properties of 2D transition-metal dichalcogenides
- 15:05 Discussion
- 15:15 **S. Agnoli** (Padova, Italy)
Surface-science studies of 2D materials and Van der Waals heterostructures
- 15:50 Discussion
- 16:00 Coffee & Posters
- 16:30 **J. Adam** (Sønderborg, Denmark)
Computational nanophotonics – concepts, algorithms, and applications
- 17:05 Discussion
- 17:15 **M. Farronato** (Paris, France)
Reactivity of lutetium bis-phthalocyanine thin films
- 17:30 Discussion
- 17:35 **M. Lorenzon** (Milan, Italy)
Single-particle ratiometric pressure sensing based on “double-sensor” colloidal nanocrystals
- 17:50 Discussion
- 17:55 **N. Marinova** (San Sebastian, Spain)
Light and oxygen resistant methylammonium lead iodide perovskite stabilized with hindered amine light stabilizer
- 18:10 Discussion

Wednesday, 21 June

- 9:00 **O. Monti** (Arizona, USA)
Advances in 2D materials
- 11:00 Coffee & Posters
- 11:30 **F. Nüesch** (Dübendorf, Switzerland)
Introduction to thin-film solar cells
- 13:30 Lunch & Posters
- 14:30 **K. Vandewal** (Dresden, Germany)
Intermolecular charge-transfer states for organic optoelectronics
- 15:05 Discussion
- 15:15 **K. Zojer** (Graz, Spain)
The role of interfaces in organic electronic devices
- 15:50 Discussion
- 16:00 Coffee & Posters
- 16:30 **D. Egger** (Regensburg, Germany)
Lead-halide perovskites on the move: structural dynamics from first-principles calculations
- 17:05 Discussion
- 17:15 **D. E. Martínez-Tong** (San Sebastian, Spain)
Ionic transport of polymer electrolyte thin films by nanodielectric spectroscopy
- 17:30 Discussion
- 17:35 **M. Müller** (San Sebastian, Spain)
Role of structural fluctuations in computing elastic charge-injection times on dye-sensitized TiO₂
- 17:50 Discussion
- 17:55 **B. Nell** (Dresden, Germany)
Investigating the doping efficiency of organic semiconductors by thermoelectric measurements
- 18:10 Discussion

Thursday , June 22

- 9:00 **L. Martín-Moreno** (Zaragoza, Spain)
Photonics/plasmonics in 2D materials
- 11:00 Coffee & Posters
- 11:30 **F. J. Himpsel** (Wisconsin, USA)
Core-level spectroscopies
- 13:30 Lunch, Posters & Group Photo
- 14:30 **Jean-luc Doumont** (Principia, Belgium)
Making the most of your presentation

Friday, 23 June

- 9:00 **L. Martín-Moreno** (Zaragoza, Spain)
Photonics/plasmonics in 2D materials
- 11:00 Coffee & Posters
- 11:30 **F. J. Himpsel** (Wisconsin, USA)
Core-level spectroscopies
- 13:30 Lunch & Posters
- 14:30 **R. Hillenbrand** (San Sebastian, Spain)
Nanoimaging and control of polaritons in 2D materials
- 15:05 Discussion
- 15:15 **J. O'Shea** (Nottingham, UK)
Resonant core-level spectroscopies for probing the electronic structure and charge-transfer dynamics of adsorbed molecules
- 15:50 Discussion
- 16:00 Coffee & Posters
- 16:30 **L. Floreano** (Trieste, Italy)
On-surface chemical modification of porphyrins: from metal to metal-oxide substrates
- 17:05 Discussion
- 17:15 **A. F. Fernandez** (Graz, Austria)
Suppressing short-channel effects by Schottky barrier manipulation
- 17:30 Discussion
- 17:35 **A. Ravikumar** (Milan, Italy)
Substrate-induced ultrafast electron injection dynamics at organic-graphene interfaces
- 17:50 Discussion
- 17:55 **A. Summerfield** (Nottingham, UK)
Van der Waals epitaxy of highly strained graphene and the growth of hexagonal boron nitride using high-temperature molecular-beam epitaxy
- 18:10 Discussion
- 18:15 Closing

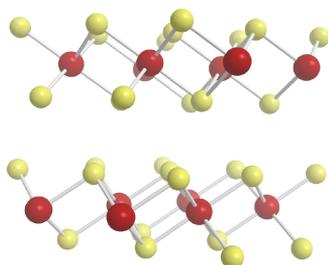
TUTORIALS

T1. Advances in 2D materials

O. L. A. Monti

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2D materials such as graphene and transition metal dichalcogenides are atomically thin crystalline solids which realize the fundamental size limit of device technologies and exhibit surprising new properties. In the few-layer limit, semiconducting 2D materials may transition from indirect to direct bandgap, enabling use of these materials in novel photovoltaic devices, light-emitting diodes, electro-absorption modulators, biosensors and photocatalysts. Importantly, spin and electronic degrees of freedom are coupled, which makes it uniquely possible to address and manipulate spin both optically and electronically. This lays the foundation for low-loss and quantum devices that use spin rather than charge (spintronics and quantum information). More recently, it was discovered that electronic properties are strongly strain-dependent in some 2D



materials, enabling the creation of flexible devices and field-deployable sensors whose electronic response is mechanically controlled and which, unlike Si-based devices, are still functional under strain.

In this tutorial, I will focus mostly on transition metal dichalcogenides. I will give an overview of some fundamental aspects and recent advances in 2D materials and their heterostructures. The tutorial will provide a survey of growth of single-layer, few-layer and heterostructures, and provide an overview over the different classes of 2D materials available to date. I will then introduce some key theoretical concepts which will enable us to explore characterization approaches, signatures of the different structures and phenomena such as valleytronics that play a prominent role in 2D materials. I will conclude with a review of devices and applications that make use of the unique properties of 2D materials.

T2. Introduction to thin-film solar cells

F. A. Nüesch^{1,2}

¹ *Empa, Swiss Federal Institute for Materials Science and Technology, Laboratory for Functional Polymers, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland*

² *Institut des Matériaux, Ecole Polytechnique Fédérale de Lausanne, EPFL, Station 12, CH-1015 Lausanne, Switzerland*

This course makes a link between the fundamental physics of solar cells and the technological development of thin film photovoltaics. Students will learn basic physical principles of solar cell operation, different technologies that are currently on the market and how solar cells are manufactured. Potential and drawbacks of inorganic solar cells (amorphous silicon, thin film chalco-genide and III-V solar cells) will be evaluated. Emerging technologies of polymer, dye-sensitized and hybrid technologies will be treated including device physics, manufacturing and technological development.

T3. Photonics/plasmonics in 2D materials

L. Martín-Moreno

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The interaction between light and matter is at the heart of a vast number of physical properties. Thus, by tailoring the electromagnetic fields we could open a full new range of possibilities. For instance, if we were able to concentrate the electric field in the optical or infrared regime so much as to address a single molecule, we could “see” it in real time (and thus follow its chemical reactions) or even change its photochemistry.

This task is not possible for *propagating* fields, as they cannot be concentrated in dimensions smaller than the wavelength (results known as the diffraction limit). However, close to surfaces, this limit does not hold and, in fact, the interface between a conductor and a dielectric supports bound electromagnetic modes (called surface plasmon polaritons). The ability of these modes to concentrate light, to enhance the electromagnetic field and to provide an ultrafast response has given rise to the active field of plasmonics.

The discovery of 2D materials has originated a boost of activity in the field, as these systems support surface plasmons that can concentrate light in in dimensions 100-1000 times smaller than the wavelength. Moreover, their plasmonic properties depend on the doping level, which can be controlled by an external gate, thus opening the possibility of controlling light with DC voltages. In this talk we will concentrate on the best study 2D material to date: graphene. But we will also cover the basic properties of other 2D materials that present different characteristics, as for instance hiperbolicity, anisotropy or chirality.

T4. Core-level spectroscopies

F. J. Himpsel

Physics Department, University of Wisconsin Madison, USA

There are several reasons why core level spectroscopies have found a wide range of applications. In addition to being element- specific, they are also bond-specific (as recognized by the 1981 Physics Nobel Prize to Kai Siegbahn). Furthermore, core levels yield well-defined peaks while valence states form broad energy bands. That facilitates the interpretation of core level spectra and enables applications to complex surfaces and interfaces. The first lecture introduces various core level spectroscopies and discusses their characteristics. The second lecture focuses on a broad range of applications, together with their characteristic experimental and theoretical methods. Suggestions of topics by the audience are welcomed.

Lecture I

1. Types of core level spectroscopies
2. Spectral ranges, probing depth, chemical resolution, sensitivity to dilute species
3. Connection to chemical bonding
4. Spectroscopic imaging, holography
5. Atom-specific structure determination
6. New developments: ultrafast, coherent

Lecture II

1. Photovoltaics and LEDs
2. Magnetic nanostructures
3. Semiconductor surfaces and interfaces
4. Two- and one-dimensional systems
5. Immobilization of biomolecules at surfaces
6. In-situ, in-operando spectroscopy
7. Resonant inelastic x-ray scattering (RIXS)
8. Optional topics on demand

SPECIAL SEMINAR

Making the most of your presentation

Jean-luc Doumont

Principiae, Belgium

Strong presentation skills are a key to success for engineers, scientists, and others, yet many speakers are at a loss to tackle the task. Systematic as they otherwise can be in their work, they go at it intuitively or haphazardly, with much good will but seldom good results. In this talk, Dr Doumont proposes a systematic way to prepare and deliver an oral presentation: he covers structure, slides, and delivery, as well as stage fright.

An engineer (Louvain) and PhD in applied physics (Stanford), Jean-luc Doumont is acclaimed worldwide for his no-nonsense approach, his highly applicable, often life-changing recommendations on a wide range of topics, and *Trees, maps, and theorems*, his book about “effective communication for rational minds” [1]. For additional information, visit www.principiae.be.

References

[1] Jean-luc Doumont, *Trees, maps, and theorems* (2009).

INVITED TALKS

11. Tailoring chemical and optical properties of 2D transition-metal dichalcogenides

T. S. Rahman

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Single-layer of molybdenum disulfide (MoS₂) and other transition metal dichalcogenides (TMDC) appear to be promising materials for next generation applications (optoelectronic and catalysis), because of their low-dimensionality and intrinsic direct band-gap which typically lies in the visible spectrum. Several experimental groups have already reported novel electronic and transport properties which place these materials beyond graphene for device applications. MoS₂ is also known to be a leading hydrodesulphurization catalyst. Efforts are underway to further tune these optoelectronic and catalytic properties through alloying, defects, doping, coupling to a substrate, and formation of bilayer stacks (homo- and hetero-structures). In this talk, I will present results from our joint theoretical and experimental investigations [1-2] which provide a framework for manipulating the functionality of these interesting materials. With emphasis on the chemical properties of defect-laden single layer MoS₂, I will examine modulations in its local atomic environment under which it could serve as a catalyst for the conversion of synthetic gas (CO and hydrogen) to methanol. With regard to the optical properties, I will present results of our analysis of the excitation spectrum and the ultrafast charge dynamics in both single- and bi-layer TMDCs obtained through the application of combined time-dependent density functional theory and many-body theory. In particular, I will show how the reduced electron screening in these systems leads to surprisingly large binding energy of the electronic bound states [3] - excitons (hundreds of meVs), trions (tens of meVs) and biexcitons (tens of meVs), in rather good agreement with available experimental data. I will also show that ultrafast (10-100 fs) transfer processes are possible in these materials as a result of strongly-delocalized hole orbitals.

References

- [1] D. Sun, D. Le et al., *Angew. Chem. Int. Ed.* **51**, 10284 (2012).
- [2] D. Le, T. B. Rawal, and T. S. Rahman, *J. Phys. Chem. C* **118**, 5346 (2014).
- [3] A. Ramirez-Torres, V. Turkowski, and T. S. Rahman, *Phys. Rev. B* **90**, 085419 (2014).

12. Surface-science studies of 2D materials and Van der Waals heterostructures

S. Agnoli

Department of Chemical Sciences University of Padova, Italy

The transition metal dichalcogenides (TMDs), such as MoS_2 , WS_2 are intriguing materials, displaying a diverse range of electronic properties as semiconductors, metals, and superconductors.¹ The rich variety of available MX_2 compounds coupled with the dramatic changes in electronic structure that arise as the layer thickness is reduced to the monolayer level, offers opportunities for new physics and device applications. Additionally, heterogeneously combining these atomic layered TMDs^{1,2} to form van der Waals heterostructures will be the ultimate route to tuning electronic and photonic properties. These exciting predictions are just now beginning to be realized experimentally through manual stacking of different layers,³ whereas the development of bottom-up syntheses of such heterostructures is a less travelled route. In this context, we decided to investigate new methods for the preparation of advanced heterostructures either using chemical vapour deposition, which is very suitable for practical applications^{4,5} or physical vapour deposition,⁶ which can be effectively coupled with advanced *in situ* investigation techniques that are fundamental to characterize the novel electronic properties of these systems.

In the present communication, we will present a few examples of vertical and in-plane van der Waals heterostructures based on some archetypal 2D materials such as graphene, h-BN and TMDCs. The resulting materials were investigated by using different surface science techniques including spatially resolved angle resolved photoemission spectroscopy, scanning tunnelling spectroscopy and low energy electron microscopy. The combination of all these techniques has allowed to gain a detailed understanding of the growth mode of 2D materials and to carry out a very systematic investigation of the electronic structure on several types of heterostructures made up by layers with different thickness.

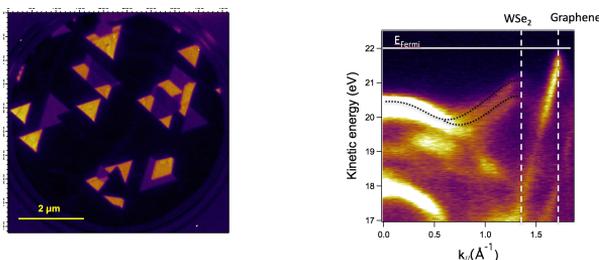


Figure 1. left: Dark field LEEM image of WSe_2 triangular islands on graphene obtained by chemical vapor deposition. Right: μ -ARPES measurements of the band dispersion from the Γ to the K point for the heterostructure formed by monolayer WSe_2 supported on monolayer graphene.

References

- [1] M. Chhowalla et al. *Nat. Chem.* **5**, 263–275 (2003).
- [2] Q. H. Wang et al. *Nat. Nanotechnol.* **7**, 699–712, (2012).
- [3] H. Fang et al. *Proc. Natl. Acad. Sci. U. S. A.* **111**, 6198–6202 (2014).
- [4] S. M. Eichfeld et al., *ACS Nano*, **9**, 2080–2087 (2015).
- [5] M. Cattelan et al. *Chem. Mater.*, **27** 4105–4113 (2015).
- [6] S. Nappini et al. *Adv. Func. Mater.* **26** 1120–1126 (2016).

I3. Computational nanophotonics – concepts, algorithms, and applications

J. Adam

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In recent years, we have encountered a vast increase in the number and diversity of photonics applications. The major driving factors for this development are advances and increased accessibility of computational modeling and design tools, the arising of new nanofabrication techniques, and the development of new optical and structural characterization methods. Nanophotonics, where the interplay of light with structures and devices with dimensions on the order of or below the wavelength of light are studied, is one of the prominent and prospective research fields in this area. Mainly due to the ease of fabrication and the prospect of mass production, especially thin-film devices incorporating corrugated, metallic or dielectric nanostructures are of particular interest. To fully understand the arising phenomena and, ultimately, the experimentally obtained device behavior, it is of paramount importance to develop, implement and verify appropriately tailored mathematical and physical modelling approaches. I will present numerical modelling approaches to investigate the near-field, far-field and modal behavior in nanostructured photonic devices. To this end, we apply finite-element, finite-difference, rigorous coupled-wave, and mode-coupling techniques [1, 2]. Our simulation results are closely related to and verified by NanoSYD's experimental outcomes. The applications range from photon and exciton management in organic solar cells [3] and light-emitting diodes [4] to label-free biosensing [5] and cold-atom trapping [6].

References

- [1] M. Paulsen, et al., *Opt. Quant. Electron.* 49, 107 (2017).
- [2] H. Lüder, et al., presented at: *Optical Wave and Waveguide Theory and Numerical Modeling Workshop* (2016).
- [3] A. J. Goszczak, et al., *Opt. Commun.* 370, 135 (2016).
- [4] C. Kluge, et al., *Opt. Express* 22(S5), A1363 (2014).
- [5] L. T. Neustock, et al., *J. Sensors*, 6174527 (2016).
- [6] A. Sierant, et al., presented at: *EMRS Fall Meeting, Symposium D* (2016).

14. Intermolecular charge-transfer states for organic optoelectronics

K. Vandewal

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Institute for Applied Physics, Technische Universität Dresden*

Intermolecular charge transfer (CT) states at the interface between electron-donating and electron-accepting materials in organic thin films are characterized by absorption and emission bands within the optical gap of the interfacing materials. Depending on the used donor and acceptor materials, CT states can be very emissive, or generate free carriers at high yield. The former can result in rather efficient organic light emitting diodes, via thermally activated delayed fluorescence, while the latter property is exploited in organic photovoltaic devices and photodetectors. In this contribution, we will discuss the fundamental properties of CT states and link them to organic opto-electronic device performance. In particular, we discuss the influence of the electronic coupling between donor and acceptor, molecular reorganization as well as non-radiative recombination pathways on free carrier recombination and the photo-voltage of organic solar cells. Furthermore, a new device concept will be introduced, using an optical cavity resonance effect to boost CT absorption at photon energies below the optical gap of both donor and acceptor, enabling narrow-band, near infrared (NIR) photo-detection. This new type of photodetector can compete with standard organic photodetectors but extends their detection range to longer wavelengths.

15. The role of interfaces in organic electronic devices

K. Zojer

Graz University of Technology and NAWI Graz, Graz, Austria

The field of organic electronics is continuously fueled by the promise of using organic chemistry to craft molecules tailor-made for a desired application. Owing to the peculiar properties of organic semiconductors, there is rich and unique physics taking place in organic devices. In fact, in many cases the device performance is critically or even solely determined by effects confined to interfaces.

To provide a broad context of the diverse roles interfaces can adopt in electronic devices, I will illustrate the interdependence of the device functionality on interface properties using examples mainly selected from the field of organic transistors [1–4] and organic solar cells.[5–7] In particular, I will rely on drift-diffusion or Kinetic Monte Carlo simulations of such devices or interfaces to provide a deeper understanding, inasmuch the properties of an interface locally affect charge transport and how such local phenomena determine the global device operation.

References

- [1] K. Zojer, E. Zojer, A. Fernandez, M. Gruber, *Phys. Rev. Appl.*, **4**, 44002 (2015).
- [2] K. Zojer, T. Rothländer, J. Kraxner, R. Schmied, U. Palfinger, H. Plank, W. Grogger, A. Haase, H. Gold, B. Stadlober, *Sci. Rep.*, **6**, 31387 (2016).
- [3] M. Gruber, E. Zojer, F. Schürerer, K. Zojer, *Adv. Funct. Mater.*, **23**, 2941–2952 (2013).
- [4] S. K. Possanner, K. Zojer, P. Pacher, E. Zojer, F. Schürerer, *Adv. Funct. Mater.*, **19**, 958–967 (2009).
- [5] R. Schueppel, K. Schmidt, C. Uhrich, K. Schulze, D. Wynands, J.-L. Bredas, E. Brier, E. Reinold, H.-B. Bu, P. Baeuerle, K. Leo, *Phys. Rev. B*, **77**, 85311 (2008).
- [6] B. Stickler, M. Gruber, G. Trimmel, F. Schürerer, K. Zojer, *Org. Electron.*, **12**, 1434–1445 (2011).
- [7] Y. Liu, K. Zojer, B. Lassen, J. Kjelstrup-Hansen, H.-G. Rubahn, M. Madsen, *J. Phys. Chem. C*, **119**, 26588 (2015).

16. Lead-halide perovskites on the move: structural dynamics from first-principles calculations

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Power-conversion efficiencies of lead-halide perovskite (LHP) solar cells have improved rapidly beyond 22%. Examining the phenomena that determine these impressive efficiencies is fundamentally and practically important. Often, a static ionic lattice displaced from the equilibrium positions by harmonic vibrations only is used to understand charge-transport and light-absorption in a semiconductor. In LHPs, several recent studies suggest that this picture is not sufficient, as different structurally dynamic effects, going beyond small harmonic vibrations, arise already at room temperature.¹

After introducing LHP solar cells,² I will present our results on structurally dynamic effects in LHPs, studied with first-principles calculations based on density functional theory. Starting from the canonical band structure picture,³ the relevance of ionic diffusion,^{4,5} optical phonons,⁶ and dynamic polar distortions,⁷ originating from a mechanically soft lattice,⁸ will be presented. From these, open questions with relevance for charge-carrier dynamics in LHPs will be discussed.⁹

References

- [1] Egger, D. A.; Rappe, A. M.; Kronik, L. *Acc. Chem. Res.* **49** (3), 573–581 (2016).
- [2] Brenner, T. M.; Egger, D. A.; Kronik, L.; Hodes, G.; Cahen, D. *Nat. Rev. Mater.* **1**, 15007 (2016).
- [3] Endres, J.; Egger, D. A.; Kulbak, M.; Kerner, R. A.; Zhao, L.; Silver, S. H.; Hodes, G.; Rand, B. P.; Cahen, D.; Kronik, L.; Kahn, A. *J. Phys. Chem. Lett.*, **7** (14), 2722–2729 (2016).
- [4] Egger, D. A.; Kronik, L.; Rappe, A. M. *Angew. Chem. Int. Ed.* **54** (42), 12437–12441 (2015).
- [5] Dastidar, S.; Egger, D. A.; Tan, L. Z.; Cromer, S. B.; Dillon, A. D.; Liu, S.; Kronik, L.; Rappe, A. M.; Fafarman, A. T. *Nano Lett.* **16** (6), 3563–3570 (2016).
- [6] Sendner, M.; K. Nayak, P.; A. Egger, D.; Beck, S.; Müller, C.; Epping, B.; Kowalsky, W.; Kronik, L.; J. Snaith, H.; Pucci, A.; Lovrinčić, R. *Mater. Horiz.* **3** (6), 613–620 (2016).
- [7] Yaffe, O.; Guo, Y.; Tan, L. Z.; Egger, D. A.; Hull, T.; Stoumpos, C. C.; Zheng, F.; Heinz, T. F.; Kronik, L.; Kanatzidis, M. G.; Owen, J. S.; Rappe, A. M.; Pimenta, M. A.; Brus, L. E. *Phys. Rev. Lett.* **118** (13), 136001 (2017).
- [8] Egger, D. A.; Kronik, L. *J. Phys. Chem. Lett.* **5** (15), 2728–2733 (2014).
- [9] Brenner, T. M.; Egger, D. A.; Rappe, A. M.; Kronik, L.; Hodes, G.; Cahen, D. *J. Phys. Chem. Lett.* **6** (23), 4754–4757 (2015).

17. Nanoimaging and control of polaritons in 2D materials

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A promising solution for active control of light on the nanometer scale are plasmons in graphene, which offer ultra-short wavelengths, long lifetimes, strong field confinement, and tuning possibilities by electrical gating. Here, we discuss scattering-type scanning near-field optical microscopy (s-SNOM) for real-space imaging of graphene plasmons [1-3] in nanoresonators [4] and hBN-graphene heterostructures [5]. We also introduce THz near-field photocurrent nanoscopy and discuss its application for imaging acoustic graphene plasmons in a graphene-based THz detector [6]. Further, we discuss ultraslow hyperbolic volume and surface phonon polaritons in boron nitride flakes [7,8].

References

- [1] J. Chen et al., *Nature*, **487**, 77 (2012).
- [2] Z. Fei et al., *Nature* **487**, 82 (2012).
- [3] P. Alonso-González et al., *Science* **344**, 1369 (2014).
- [4] A. Y. Nikitin et al., *Nat. Photon.* **10**, 239 (2016).
- [5] A. Woessner et al., *Nat. Mater.* **14**, 421 (2015).
- [6] P. Alonso-González et al., *Nat. Nanotechnol.* **12**, 31-35 (2016).
- [7] E. Yoxall et al., *Nat. Photon.* **9**, 674 (2015).
- [8] P. Li et al, *Nano Lett.* **17**, 225 (2017).

18. Resonant core-level spectroscopies for probing the electronic structure and charge transfer dynamics of adsorbed molecules

J. N. O'Shea¹, K. Handrup², R. H. Temperton¹, A. J. Gibson¹,
A. Nicolaou³, N. Jaouen³

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In devices such as dye-sensitised solar cells, the dynamics of charge transfer at the electron injection interface – from the molecule into the semiconductor substrate – play a key role and are typically very fast. The charge transfer dynamics of the molecule biisonicotinic acid adsorbed on a titanium dioxide surface was found to occur on the low femtosecond timescale – using a core-hole clock implementation of resonant photoemission (RPES) [1]. This process relies on the competing channels of core-hole decay and ultra-fast charge transfer to the surface. An electron emitted by a core-hole decay process in which the originally excited core-electron is a direct participant and is easily identified within the electronic debris by its kinetic energy and evinces electron localization in the excited molecular orbital on the timescale of the core-hole lifetime. It has long been proposed that the photons emitted during radiative core-hole decay should be equally informative, allowing femtosecond charge transfer to be probed in more realistic environments due to the large escape depth of the photons in what would be resonant inelastic x-ray scattering (RIXS) compared to the electrons of resonant photoemission (RPES). In the event that the originally excited core-electron is a direct participant in the decay process, radiative decay will give rise to what is essentially an elastically scattered soft x-ray photon, perhaps modified by any ultra-fast processes within the core-excited molecule. Moreover, the other photons emitted in the experiment – the inelastic scattering – provide valuable insight character of the occupied molecular orbitals and their relationship to each other. This is most evident when the RIXS is mapped over all the highest occupied molecular orbitals as a function of core-excitation into all the lowest unoccupied molecular orbitals.

In this talk I'll discuss RPES and RIXS maps of biisonicotinic acid molecules in the crystalline phase, multilayer film and the adsorbed monolayer on TiO₂(110) and show how these two complementary techniques reveal the ultra-fast charge transfer dynamics across the interface and also ultra-fast vibronic coupling within the molecules themselves.

References

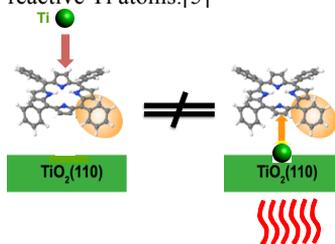
- [1] J. Schnadt, P. A. Brühwiler, L. Patthey, J. N. O'Shea, S. Södergren, M. Odelius, R. Ahuja, O. Karis, M. Bäessler, P. Persson, H. Siegbahn, S. Lunell & N. Mårtensson, *Nature* **418**, 620 (2002).
- [2] A. J. Britton, M. Weston and J N. O'Shea, *Phys. Rev. Lett.* **109**, 017401 (2012).

19. On-surface chemical modification of porphyrins: from metal to metal-oxide substrates

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The large flexibility in porphyrin synthesis and functionalization is further enhanced in the contact layer with surfaces, where they can be modified following a bottom-up approach (e.g. sample heating, atom deposition, gas dosing). I will briefly review the large scenario of chemical and conformational modifications that can be achieved starting from thin films of free-base porphyrins, 2H-P. The most interesting reaction is certainly the on-surface incorporation of a metal atom in the tetra-pyrrolic macrocycle either by metal deposition on a 2H-P film or by extraction of a substrate metal atom through heating.[1] This approach permits the synthesis of an ultra-pure layer of metallo-porphyrins, M-P, with almost any element. Thermal treatments may even trigger partial cyclo-dehydrogenation and carbon-carbon rebonding at the peripheral terminations forming new porphyrin species.[2] On a few metals, such as Cu, the metal incorporation from the substrate may be further enhanced in presence of a surface oxide layer, which favors the recombination of pyrrolic hydrogen to form a H₂O molecule that is much less expensive than the formation of a H₂ molecule.[3] The situation is more complex in presence of a native transition metal oxide. I will present recent investigations by XPS, NEXAFS, STM, RHEED and DFT simulations of the interaction with the TiO₂(110) surface of free-base porphyrins with different peripheral terminations (2H-TTP, 2H-OEP, 2H-TBTTP), which represent archetypal interfaces for Dye-Sensitized Solar Cells, DSSCs. First of all, 2H-Ps are shown to spontaneously capture hydrogen atoms at the iminic nitrogen from the surface and subsurface nearby layers, irrespective of the peripheral functionalization.[4] The 2H-P layers can still be metalated by deposition of metal atoms (Fe, Co, Ti), however the most effective reaction is the self-metalation one, where 100% of first layer molecules are converted into Ti-metalated species. The self-metalation produces titanium(IV)-porphyrin species different from the titanyl-porphyrin obtained by Ti deposition. The self-metalated porphyrins are strongly bound to the substrate, preserving the same absorption site and molecular ordering from room temperature to 300°C, i.e. across the self-metalation reaction. The self-metalation reaction sets in already at 100°C, thus asking for special care when designing porphyrin/titania DSSCs in order to prevent metal-exchange with the highly reactive Ti atoms.[5]



References

- [1] R. Gonzalez-Moreno, C. Sanchez-Sanchez, M. Trelka, R. Otero, A. Cossaro, A. Verdini, L. Floreano, M. Ruiz-Bermejo, A. García-Lekue, J.A. Martín-Gago, and C. Rogero, *J. Phys. Chem. C* **115**, 6849 (2011).
- [2] G. Di Santo, C. Sfiligoj, C. Castellarin-Cudia, A. Verdini, A. Cossaro, A. Morgante, L. Floreano, and A. Goldoni, *Chem. Eur. J.* **18**, 12619 (2012).
- [3] A. Verdini, P. Shinde, G. L. Montanari, S. T. Suran-Brunelli, M. Caputo, G. Di Santo, C. A. Pignedoli, L. Floreano, D. Passerone and A. Goldoni, *Chem. Eur. J.* **22**, 14672 (2016).
- [4] G. Lovat, D. Forrer, M. Abadia, M. Dominguez, M. Casarin, C. Rogero, A. Vittadini, and L. Floreano, *Phys. Chem. Chem. Phys.* **17**, 30119 (2015).

ORAL CONTRIBUTIONS

O1. Reactivity of lutetium bis-phthalocyanine thin films

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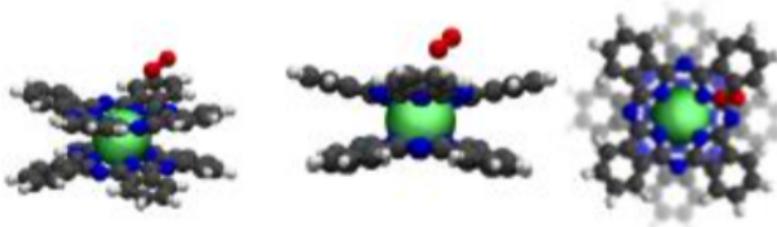
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Lutetium bis-Phthalocyanine thin films are gaining attention as candidate for efficient gas sensing applications. Their peculiar electronic structure, and in particular the presence of a Single Occupied Molecular Orbital (SOMO) makes them ideal candidates for different gas sensing, as they are available for both oxidation and reduction. However no fundamental studies exist yet about how the bonding takes place at the molecular level.

In this work we studied the low temperature reactivity towards molecular oxygen and water of a thick film of LuPc2 deposited on Au(111) single crystal in ultra-high vacuum (UHV). We characterized the reaction via X-Ray Photoelectron spectroscopy (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy. We showed a weak interaction, as oxygen desorbs as the sample is heated up to around 100K. We also showed that the reaction mostly affects the isoindole N atom, and only slightly the C atoms and the π system. We also show that the adsorption geometry is almost vertical. Also quantitative analysis showed that more than a ML was adsorbed, showing the possibility for the oxygen to diffuse inside the layer.

Instead we show that the desorption temperature for water is found at higher temperature, and the effects on the occupied as well as on the unoccupied states are weaker.

Therefore we can show the microscopic mechanism that lead to a degradation in the electronic properties of double decker phthalocyanine based devices as well as to their gas sensing capabilities.



References

- [1] M. Passard; J.P. Blanc; C. Maleysson, Thin Solid Films **271** 8-14 (1995).
- [2] L. Ottaviano, L. Lozzi, S. Santucci Surf. Sci. **431** 242 (1999).
- [3] F. Sedona, M. Di Marino, D. Forrer, A. Vittadini, M. Casarin, A. Cossaro, L. Floreano, A. Verdini and M. Sambi, Nat. Materials **11** 970 (2012).
- [4] I. Bidermane, J. Luder, S. Boudet, T. Zhang, S. Ahmadi, C. Grazioli, M. Bouvet, J. Ruzs, B. Sanyal, O. Eriksson, B. Brena, C. Puglia, and N. Witkowski, J. Chem. Phys. **138**, 234701 (2013).

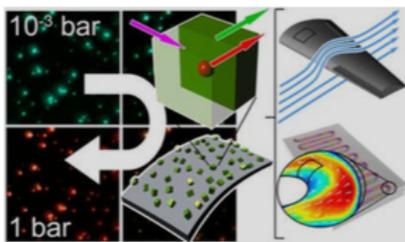
O2. Single-particle ratiometric pressure sensing based on “double-sensor” colloidal nanocrystals

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Ratiometric pressure sensitive paints (r-PSPs) are all-optical probes for monitoring oxygen flows in the vicinity of complex or miniaturized surfaces, with several applications spanning from aerodynamics, to microfluidics, to medicine and biology. They typically consist of a porous binder embedding mixtures of a reference and a sensor fluorophore exhibiting oxygen-insensitive and oxygen-responsive luminescence, respectively^{1,2}. Here, we realize the first example of an r-PSP based on a single two-color emitter that removes limitations of r-PSPs based on fluorophore mixtures such as different temperature dependencies of the two fluorophores, cross-readout between the reference and sensor signals and phase segregation³. In our paradigm-changing approach, we utilize a novel ‘double-sensor’ r-PSP that features two spectrally-separated emission bands with opposite responses to the O₂ pressure, which boosts the sensitivity with respect to traditional reference-sensor pairs. Specifically, we use two-colour-emitting CdSe/CdS core/shell nanocrystals, exhibiting red and green emission bands from their core and shell states^{4,5}, whose intensities are respectively enhanced and quenched in response to the oxygen partial pressure. This leads to strong and reversible ratiometric response at the single particle level and over 100% enhancement in the pressure sensitivity. Our proof-of-concept r-PSPs further exhibit suppressed cross-readout thanks to zero spectral overlap between the core and shell luminescence and temperature independent ratiometric response between 0°C and 70°C.



References

- [1] T. Liu, and J. Sullivan, Pressure and temperature sensitive paints. Springer, Berlin (2005).
- [2] M. Lorenzon, S. Christodoulou, G. Vaccaro, J. Pedrini, F. Meinardi, I. Moreels, and S. Brovelli, Nat. Commun. , **6**:6434 (2015).
- [3] Y. Feng, J. Cheng, L. Zhou, X. Zhou, H. Xiang, Analyst **137**, (21), 4885-4901 (2012).
- [4] S. Brovelli, W. K. Bae, C. Galland, U. Giovanella, F. Meinardi, V. I. Klimov, Nano Lett., **14**, (2), 486-494 (2013).
- [5] S. Brovelli, W. K. Bae, F. Meinardi, B. Santiago González, M. Lorenzon, C. Galland, V. I. Klimov, Nano Lett., **14**, (7), 3855-3863 (2014).

O3. Light and oxygen resistant methylammonium lead iodide perovskite stabilized with Hindered Amine Light Stabilizer

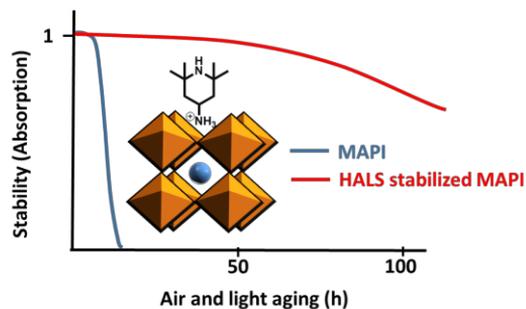
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Methylammonium lead iodide perovskite (MAPI) has been recognized as a promising material for highly-efficient photovoltaic devices. However, photoexcited MAPI is unstable in the presence of oxygen due to photooxidation. This imposes a strict requirement for MAPI processing and operation under controlled inert atmosphere. Herein we report the stabilization effect of hindered amine light stabilizer (HALS) on methylammonium iodide (MAI) and MAPI against photooxidation. We found that HALS prevents the degradation of MAI by inhibiting the oxidation of iodide to iodine. Chemical modification of HALS allows us to incorporate it in MAPI films which exhibit strongly enhanced stability at light and air. In this way the resistivity of photoexcited MAPI at ambient air could be extended from a couple of hours to several days (more than 20 times) while causing no significant changes in key properties as optical absorption and charge transport. Our results represent a significant advance in the stabilization of MAPI and demonstrate that HALS could be used as universal-like stabilizer.



O4. Ionic transport of polymer electrolyte thin films by nanodielectric spectroscopy

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Polymer electrolytes have been studied for decades, in connection with the promising applications for new energy storage devices.[1] In this application, poly(ethylene oxide) (PEO) has emerged as one of the most commonly used polymer matrices. This material has a semicrystalline nature that provides good mechanical properties, but the crystalline phase imposes restrictions to ionic transport. In this work we present a study on the ionic transport of poly(ethylene oxide) (PEO) thin films, using non-contact Atomic Force Microscopy (AFM), a technique called: nanoDielectric Spectroscopy (nDS). This is a technique based on amplitude modulation electrostatic force microscopy, and allows to measure the frequency dependent dielectric permittivity of thin films with good lateral resolution and over a broad frequency range. [2] nDS basis relates on measuring the phase of the cantilever oscillations produced by the electric force between the tip and the film sample when an AC voltage is applied to the AFM probe.[2,3] We studied the influence of film preparation conditions on the ionic conductivity of the PEO amorphous phase. We have found high conductivity values for films crystallized from the melt, while a strong reduction of the amorphous phase conductivity was observed for PEO films prepared from solutions at room temperature, more pronounced when using a highly polar solvent.

References

- [1] Long, L., et al. *J. Mater. Chem. A* **4**, 10038 (2016).
- [2] Schwartz, G. A., et al. *Ultramicroscopy* **111**, 1366 (2011).
- [3] Miccio, L. A., et al. *J. Appl. Phys.* **115**, 184305 (2014) .

05. Role of structural fluctuations in computing elastic charge-injection times on dye-sensitized TiO₂

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Finite temperature fluctuations cause geometrical changes at the picosecond time-scale, while fast electronic processes like electron transfer occurring within few femtoseconds depend strongly on the precise atomic structure at an instance of time. This renders a statistical analysis of such processes with respect to structure indispensable.

We theoretically investigate electron injection times from isonicotinic acid into extended rutile TiO₂(110) at room temperature. We couple a large set of snapshots from a finite-slab Car-Parinello molecular dynamics simulation [1] to a semi-infinite substrate by means of Green's function embedding [2,3] along with gradient corrected density functional theory. We scrutinize the charge-injection times from different molecular orbitals into the substrate in two cases: one in which the molecule is considered in its ground state, and a second case including a core-excitation in the Nitrogen 1s-level for comparison with core-hole-clock experiments [4]. For the core-excited case we find a temperature-averaged elastic lifetime of 6 fs in much better agreement with the experiment (5 fs) as found for the equilibrium structure (45 fs).

Our results, validated by this improved agreement, also allow to rationalize the effects of the dynamics on the energy levels and their interplay with the core-level excitation. The perturbation due to the core-hole reduces the electron-vibrational coupling of the molecular resonances resulting in narrowed Gaussian-like profiles in the cumulative spectra. Additionally, the molecular resonances are consistently down-shifted in energy with respect to the substrate density of states. Our statistical analysis highlights the emergence of characteristic Voigt-type line-shapes. A direct relation between the structure in terms of low frequency vibrational modes and calculated lifetimes remains difficult.

References

- [1] H. Lin *et al.*, *J.Phys. Chem. C* **7**, 3899 (2016).
- [2] D. Sánchez-Portal, *Prog. Surf. Sci.* **82**, 313 (2007).
- [3] G. Fratesi *et al.*, *J. Phys. Chem. C* **118**, 8775 (2014).
- [4] J. Schnadt *et al.*, *J. Chem. Phys.* **119**, 12462 (2003).

O6. Investigating the doping efficiency of organic semiconductors by thermoelectric measurements

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The introduction of p- and n-doped layers into the device architecture of organic opto-electronic devices can greatly improve their performance. Charge carrier extraction or injection from or into the organic photo-active layer is enhanced by doping, resulting in a reduction of ohmic losses. Transparent conductive layers can be realized by molecular doping of organic host materials moving the Fermi level to the appropriate position, enabling electron or hole selectivity.

In this work, we use thermovoltage (Seebeck effect) and temperature-dependent conductivity measurements to determine the dominating type of charge carriers introduced by the dopant and to gain insight into the position of the transport level with respect to the Fermi level. The investigation of fullerene dopants with a high degree of fluorination in various amorphous host materials allows us to tune the energy level offset between host and dopant and to study their influence on Fermi level position and overall doping efficiency systematically. From the thermoelectric measurements it is possible to observe a clear influence of the energy level offset between matrix and dopant on doping efficiency. Combining thermoelectric measurements with Kinetic Monte Carlo simulations gives further insight into the influence of Coulomb interactions on the trapping of mobile charge carriers in doped organic semiconductors.

We find that at low doping concentrations a high amount of charge carriers is immobilized in trap states, leading to a reduced doping efficiency. Upon increasing the doping concentration, the trap states are subsequently passivated and an increased doping efficiency can be observed. Furthermore the doping efficiency is increased upon fluorination of the dopant molecules and we find a correlation between the energy level offset and the doping efficiency, at the same molar concentration.

O7. Suppressing Short-Channel Effects by Schottky barrier manipulation

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High switching speeds constitute one of the optimization targets for organic thin film transistors (OTFT). Reducing the OTFTs channel length is a major handle to boost the switching speed. However, upon reducing the channel length one has to cope with undesired short-channel effects, i.e., a loss of saturation, a reduced ON-OFF ratio, and a disproportionately larger impact of the contact resistance. We demonstrate by virtue of device simulations that the ON-OFF-ratio of a short channel transistor is enhanced by orders of magnitude when a Schottky barrier at the injecting contact is intentionally introduced. The key effect is the efficient suppression of the OFF-current while trading in only a small loss in the ON current. We show that, in fact, it is possible to establish a minimal Schottky barrier such that the short channel transistors can be operated without premature turn-on while retaining an ON current as large as expected from Gradual Channel approximation. This strategy is suited for staggered and coplanar transistor architectures.

O8. Substrate-induced ultrafast electron injection dynamics at organic-graphene interfaces

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We explore the interplay between the charge transfer lifetime of core excited organic molecules adsorbed on graphene and the modification of the electronic structure by a variable coupling with a metal substrate. Nitrogen 1s core electron of 1,1'-bipyridine (C₅H₄N)₂ is photo-excited and adsorbed on bilayer graphene/nickel(111) (BP/BLG/Ni) and epitaxially grown graphene on nickel(111) (BP/EG/Ni). We predict from first principle calculations that the charge transfer time of core excited molecules [1] depends strongly on the coupling of graphene to the underlying Ni substrate.

In the ground state, the LUMO of the molecule is strongly coupled with the substrate in both the cases (BP/BLG/Ni and BP/EG/Ni) and the charge transfer lifetime is ~7 fs and ~4 fs respectively. In the case of BP/BLG/Ni, the layer of graphene in contact with nickel substrate strongly hybridizes while the top layer of graphene remains fairly decoupled. Upon N 1s core excitation of the molecule, the LUMO* of the molecule is partially filled and shifts to the Fermi level. The molecular LUMO* finds very few states of graphene close to the Dirac point at the Fermi level to hybridize with. This leads to a decoupled molecular LUMO* and the lifetime increases significantly (~116 fs). But considering BP/EG/Ni case, the strong hybridization of graphene with the underlying nickel substrate significantly distorts the electronic structure of graphene generating states close to the Fermi level. The LUMO* of the molecule strongly couples with these states resulting in a substantially smaller lifetime (~33 fs). We also find experimental evidence to confirm this trend by performing core-hole-clock spectroscopy. The resonant charge transfer lifetime we find is ~35 fs for the BP/BLG/Ni and ~5 fs for the BP/EG/Ni [2], thus clearly demonstrating the effect of substrate on the charge transfer dynamics of organic molecules on graphene.

References

- [1] G. Fratesi, C. Motta, M. I. Trioni, G. P. Brivio, and D. Sánchez-Portal, *J. Phys. Chem. C* **118**, 8775 (2014).
[2] O. Adak, G. Kladnik, G. Bavdek, A. Cossaro, A. Morgante, D. Cvetko, L. Venkataraman *Nano Letters*, vol. 15, no. 12, 8316–8321 (2015).

O9. Van der Waals epitaxy of highly strained graphene and the growth of hexagonal boron nitride using high-temperature molecular-beam epitaxy

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To scale up the production of graphene-hexagonal boron nitride (hBN) and other 2D material heterostructure devices, direct epitaxial wafer-scale growth of these materials will be necessary. Commonly reported techniques for the fabrication of 2D material heterostructures such as exfoliation or chemical vapour deposition typically require time-consuming fabrication steps or transfer from a metal surface. However, we have investigated direct growth using high-temperature molecular beam epitaxy (HT-MBE) as a route to produce high-quality graphene and hBN monolayers [1].

We show that graphene grown using HT-MBE on hBN surfaces forms continuous domains with a maximum size of order $\sim 20 \mu\text{m}$ [2]. The graphene is found to exhibit moiré patterns with large periodicities, up to $\sim 30 \text{ nm}$, when imaged using atomic force microscopy (AFM), indicating that the layers are highly strained. We confirm the presence of strain using Raman spectroscopy which show that for large moiré periods, the G and 2D peaks of graphene are split and shifted. Topological defects are also observed in the moiré patterns which are attributed to the relaxation of graphene islands which nucleate at different sites and subsequently coalesce. In addition, cracks are formed leading to strain relaxation, highly anisotropic strain fields, and abrupt boundaries between regions with different moiré periods. We show that these cracks can also be formed by modification of the layers with a local probe resulting in the contraction and physical displacement of graphene layers.

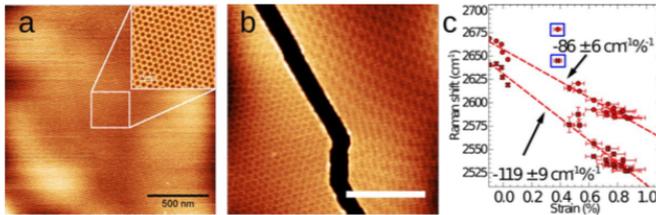


Fig. 1. a) AFM images of moiré patterns on the surface of epitaxially grown graphene on hBN, (inset) high resolution image of the central region of the main image. b) AFM image of a crack in a graphene monolayer exhibiting regular and highly anisotropic moiré patterns. Scale bar 175 nm. c) Raman shift of graphene 2D peak positions as a function of strain, determined by spatial correlation of local moiré periodicity with Raman peak position.

POSTER CONTRIBUTIONS

P1.Crystalline MoOx thin-films as hole transport layers in DBP/C70 based organic solar cells

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Transition Metal Oxides such as Molybdenum oxide (MoOx) have been intensively used as hole transport layers in different organic, inorganic and hybrid technologies, demonstrating also important improvements on the power conversion efficiency as well as on the stability of different types of solar cells. Among several different deposition methods available for fabrication of MoOx thin-films, reactive sputtering arises as an interesting option due to its full control over the deposition parameters such as the deposition power, reactive gas partial pressure and the deposition rate¹.

In the work presented here, MoOx thin-films fabricated from reactive sputtering are investigated as hole transport layers in organic photovoltaic devices. The MoOx thin films are prepared by ex situ reactive sputtering ($x \sim 3.16$) followed by post-annealing in ultra-high vacuum, and compared to reference devices prepared by in situ thermal evaporation ($x \sim 2.85$). Devices based on 10, 30 and 50 nm of sputtered and thermally deposited MoOx were prepared on pre-patterned ITO samples. The MoOx post-fabrication annealing experiments, carried out under 10-8mbar, included heating at different temperatures to induce different degrees of crystallization of the MoOx layer. Subsequently, the samples were transferred to the nitrogen glovebox (connected to cluster deposition system) for device fabrication. Transmission Electron Microscopy (TEM) and Low-Energy Electron Microscopy (LEEM) were used to shed light on the crystallinity and work function of the MoOx films², respectively. Standard configuration OPV devices based on DBP (5,10,15,20-Tetraphenylbisbenzo[5,6]indeno[1,2,3-cd:1',2',3'-lm]perylene) as the electron donor, C70 ((C70-D5h)[5,6]fullerene) as the electron acceptor and BCP (2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline) as the exciton blocking layer were fabricated using different MoOx films fabricated on glass/ITO substrates, in order to evaluate their effect on the efficiency and long-term stability of the devices. Interestingly, the samples fabricated by reactive sputtering and annealed at 350°C showed improved power conversion efficiency (PCE) reaching up to 4%, while the in situ thermally deposited MoOx devices showed a rapid decay in performance with the increase in the annealing temperature. The long-term stability measurements showed that devices based on the post-annealed (350°C) sputtered films are of superior device stability as compared to the thermally evaporated ones, remaining within nearly 90% of their initial PCE upon 7 days of 1 sun (1000W/m²) intensity irradiation at $\sim 60^\circ\text{C}$.

References

- [1] A.L. Fernandes Cauduro, Z.E. Fabrim, M. Ahmadpour, P.F.P. Fichtner, S. Hassing, H.-G. Rubahn, and M. Madsen, *Appl. Phys. Lett.* 106, 202101 (2015).
- [2] A.L. F. Cauduro, R. dos Reis, G. Chen, A.K. Schmid, C. Méthivier, H.-G. Rubahn, L. Bossard-Giannesini, H. Cruguel, N. Witkowski, and M. Madsen, *ACS Appl. Mater. Interfaces* 9, 7717 (2017).

P2. Improving the thermal and mechanical properties of Kevlar through MPI

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Due to their extraordinary mechanical properties and cost effective processability, polyaramides (e.g Kevlar®) are among the most used polymers in mechanically demanding applications, such as sport equipment and aircrafts. However, the mechanical properties of Kevlar are sensitive to temperature and especially to UV radiation, therefore it is crucial to protect Kevlar in applications where the material is directly exposed to high temperatures and/or UV light. For this purpose, Kevlar has traditionally been coated with UV absorbing resins or metal oxides which add extra weight and reduce the flexibility of Kevlar fabrics. In this work, we show a novel strategy to improve the thermal and UV stability of Kevlar's mechanical properties while maintaining its flexibility namely by infiltration with ZnO through Multiple Pulsed Infiltration (MPI)¹. The thermal stability was measured showing that the infiltration (I-ZnO) of ZnO enhance the thermal stability of Kevlar increasing the decomposition temperature in almost 10 °C, while the coating (C-ZnO) just increase it in 2 °C. Besides, tensile test were performed to analyze the effect of the temperature and the UV light in the toughness modulus. It was observed that while the non-treated Kevlar loses the 25% of its modulus toughness due to the processing temperature (150 °C), the I-ZnO fibers just lost the 9%. In terms of UV resistance, after 24 hours of irradiation the C-ZnO Kevlar loses significantly its mechanical strength. In contrast, infiltration with ZnO protects Kevlar from degradation with 88% of the modulus of toughness value of native Kevlar having been maintained. The structure of the ZnO-Kevlar hybrid material was theoretically modelled using DFT calculations, showing that the improved stability of the I-ZnO arises from the covalent cross-linking of Kevlar chains through the infiltrated ZnO. In this presentation, we will show that the infiltration of ZnO into Kevlar through MPI is a valuable technique to improve the thermal and UV stability of Kevlar while maintaining its flexibility.

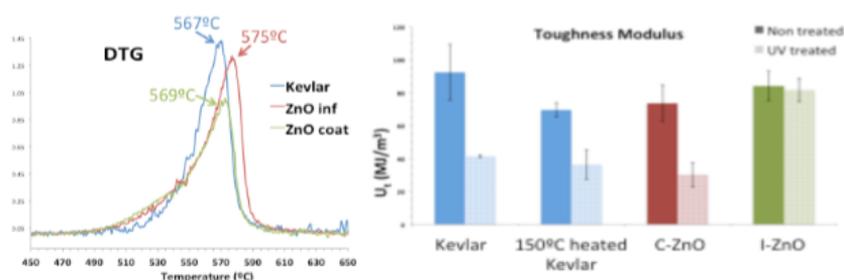


Figure: Derivative of the TGA curve showing the increase on the degradation temperature and the toughness modulus of all the samples before and after UV irradiation.

References

[1]Parsons, G. N., George, S. M. & Knez, M. MRS Bull. **36**, 865–871 (2011).

P3. Impact of K-doping on the electronic and optical properties of PTCDA monolayer on Ag(111)

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We study the impact of K doping of a PTCDA (sub)monolayer domain on Ag(111) to gain profound insights into the doping- induced changes of the optical and electronic properties of this prototypical interface. A particular advantage of the KxPTCDA/Ag(111) system is that it is known to form distinct stoichiometric phases, which allows associating the observed spectra with well-defined adsorbate structures. Unfortunately, the interpretation of the measured differential reflectance spectra is highly ambiguous, which prompted us to perform state-of-the-art density-functional theory based calculations. These provide full atomistic insight into interfacial charge rearrangements and in conjunction with photoelectron spectra and X-ray standing wave data allow a comprehensive explanation of the interface properties. In particular, we find coincidentally similar positions for photon absorption maxima for neutral PTCDA layers on only weakly interacting substrates with the data obtained for the strongly interacting PTCDA/Ag(111) interface subsequent to K-doping. The presence of the K atoms is found to increase the electron density in the organic layer and in the Ag substrate; at the same time it reduces the coupling between the adsorbate and the substrate. The latter, on the one hand, is evidenced by the decreasing dispersion and hybridization of the PTCDA-derived bands in potassium-rich phases and, on the other hand, can be concluded from an increasing adsorption distance upon K intercalation found both in theory and experiments. In combination with the full structural characterization of the KxPTCDA interface by low-energy electron diffraction and scanning-tunneling microscopy experiments [1], the present study provides a fully characterized reference system for a well-defined metal-organic interface in the presence of alkali atoms that will be useful as a benchmark for future studies.

References

[1] Zwick, C.; Baby, A.; Gruenewald, M.; Verwüster, E.; Hofmann, O. T.; Forker, R.; Fratesi, G.; Brivio, G. P.; Zojer, E.; Fritz, T. . ACS Nano, **10**, 2365–2374 (2016).

P4. Nanoplasmonics from large-scale *ab initio* calculations: opposite trends in Ag and Na clusters

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An accurate description of electronic excitations is indispensable for understanding material properties and designing nanoscale devices. For instance, using large-scale TDDFT calculations, we have recently demonstrated the importance of taking into account the details of the atomic-scale structure [1] and the quantization of electron transport [2] in metal nanostructures in order to accurately describe their plasmonic properties. In this contribution we will compare the surface plasmon resonance of sodium and silver clusters within the same framework of iterative TDDFT [3]. Recent progress in our implementation made it possible to perform calculations of large clusters of diameters ranging from a few Å to 4–5 nm (see the Figure), counting up to 5000 silver atoms and using only modest computational resources (a 32-core node with 500GB RAM). With these new capabilities, we have characterized the size-scaling of the SPR frequency for both sodium and silver clusters. As expected these two materials show opposite behaviors that can be related to the different spill out of charge at the surface and to the additional screening created by the 4d electrons in silver.

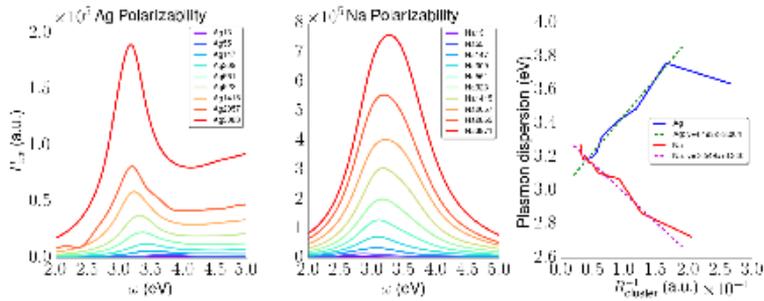


Figure: First and second column: optical polarizability for icosahedral silver and sodium clusters of different sizes. Third column: plasmon dispersion for silver and sodium cluster from *ab-initio* calculations, the dashed lines show the linear interpolations.

References

- [1] M. Barbry et al., Nano Letters, **15**, 3410 (2015).
- [2] F. Marchesin et al., ACS Photonics, **3**, 269 (2016).
- [3] P. Koval et al., J. Phys: Condens Matter, **28**, 214001 (2016).

P5. Synthesis and characterization of novel triphenylamine-based hole transporting material for perovskite solar cells

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Hybrid organic-inorganic perovskite represent a class of emerging materials in optoelectronics semiconductors, and since the last few years represent the raising star of the photovoltaic technology. The power conversion efficiency of perovskite-based solar cells arose from 3.8% in 2009[1], value which has increased exponentially in few years, until the last certified value of 22.1% [2]. Photovoltaic research is therefore focusing on the optimization of materials, architectures and configurations of this technology to further increase the power conversion efficiency and pave the way to future commercialization.

Triphenylamine (TPA)-based compounds are one of the most studied and most effective small molecule hole-transport materials (HTMs) in optoelectronic devices [3]. Among these HTMs, 2,2',7,7'-tetrakis(N,N'-di-p-methoxy-phenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) represents the state of the art p-type material used as electron blocking-hole transporting material[4] in perovskite sensitized solar cells. However, its multistep synthetic route and its complex purification make its price too high for industrial-scale process. Furthermore, due to its relatively poor hole mobility and conductivity, it required the addition of dopants, in order to extract and conduct the holes efficiently. Although Spiro-OMeTAD continues to be the best performing candidate HTM, several small molecules, as well as classical polymers were extensively investigated in organic photovoltaic devices [5]. The aim of the present work is to design synthesize and characterize TPA-based novel small organic molecules as cheaper and more efficient HTMs. The opto-electrical properties of the novel molecules were measured, and were tune as such to yield better photovoltaic parameters for efficient device fabrication. Advantages such as low cost fabrication, easy synthesis and purification, and good cell performance provide a potential application as the replacement of the expensive Spiro-OMeTAD.

References

- [1] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **131**, 6050–6051 (2009).
- [2] S. Kazim, M. K. Nazeeruddin, M. Graetzel, S. Ahmad, *Angewan Chem. Int. Ed.*, **53**, 2812–2824 (2014).
- [3] F. Zhang, C. Yi, P. Wei, X. Bi, J. Luo, G. Jacopin, S. Wang, X. Li, Y. Xiao, S. M. Zakeeruddin, et al., *Adv. Energy Mater.*, **6**, 1–7 (2016).
- [4] D. Bi, W. Tress, M. I. Dar, P. Gao, J. Luo, C. Renevier, K. Schenk, A. Abate, F. Giordano, J. C. Baena, et al., *Sci. Adv.*, **2**, 1-7 (2016).
- [5] L. Calió, S. Kazim, M. Graetzel, S. Ahmad, *Angew. Chemie - Int. Ed.*, **55**, 14522–14545 (2016).

P6. Chemical reactivity of pristine and defected graphene grown on nickel(111)

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Due to its exceptional properties graphene (G) is considered as one of the most promising materials for the future. Its possible use as gas sensor has been demonstrated [1], but the underlying chemistry is still unclear since “clean” G was reported to be nearly unreactive for ammonia [2]. The sensitivity towards CO was thereby even lower.

To unravel the CO adsorption mechanisms, we investigated the reactivity of pristine [3] and defected [4] single layer G grown on polycrystalline Cu and Ni(111) under ultra high vacuum conditions by High Resolution Electron Energy Loss Spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS) and Low Temperature Scanning Tunneling Microscopy (LT-STM).

We have found non-dissociative chemisorption at cold, pristine G on Ni(111). The adlayer remains stable up to 125 K, allowing to estimate an adsorption energy of 0.58 eV/molecule at low coverage, much higher than for unsupported G films (0.014 eV/molecule) [1]. Among the different configurations of G on Ni(111), the top-fcc resulted to be the most reactive [5]. No adsorption occurs, on the other hand, at G supported on the less interacting polycrystalline Cu substrate.

The nature of the substrate plays a key role also in presence of defects created by low energy Ne⁺ ion beam bombardment. CO penetrates then through the vacancies created in the G layer and adsorbs at the interface close to the holes, thereby detaching G from the substrate.

Therefore, the sensing activity of Single Layer free standing G, cannot be ascribed to pristine sites nor to vacancies, but to modification of the G layer by reactive species.

References

- [1] Varghese C et al, *Sensors and Actuators B* **218**, 160 (2015).
- [2] Dan et al, *Nanolett* **9**, 1472 (2009).
- [3] M. Smerieri et al, *ChemCatChem* **7**, 2328 (2015).
- [4] E Celasco et al, *PCCP* **18**, 18692 (2016).
- [5] E. Celasco et al, *JCP* **146**, 104704 (2017).

P7. Effects of surface reactivity on the self-assembly of methylamine-terminated molecules

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The chemical and morphological properties of the 1-naphthylmethylamine (NMA) self-assemblies on Ag(111) and Ni(111) substrates have been investigated with a multi-technique approach. In particular, X-ray and ultraviolet photoemission spectroscopies (XPS and UPS) as well as near-edge absorption (NEXAFS) and scanning tunneling microscopy (STM) were used to obtain a detailed characterization of the system. On the Ag(111) surface, NMA molecules displayed poor hybridization, which led to results similar to those already reported for Au(111). [1] Instead, on Ni(111), the strong interaction between the NMA films and the substrate induced considerable changes in the chemistry of the adsorbed molecules. In this case, XPS measurements revealed the presence of different chemical species, derived from the dehydrogenation of the molecule. Moreover, upon annealing NMA thin films to 350°C, we observed the formation of 2D structures, which display a band dispersion resembling the N-doped graphene one. The present study is thus suggesting a novel and effective method for functionalizing the Ni(111) surface with doped graphene, which can be exploited for applications in organic electronics.

References

[1] C. Dri, G. Fronzoni et al., *J. Phys. Chem. C* **120**, 6104 (2016).

P8. Catalysis under cover: enhanced reactivity at the interface between (doped) graphene and anatase TiO₂

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The “catalysis under cover” involves chemical processes which take place in the confined zone between a 2D material, such as graphene, h-BN, or MoS₂, and the surface of an underlying support, such as a metal or a semiconducting oxide [1,2]. The hybrid interface between graphene and anatase TiO₂ is extremely important for photocatalytic and catalytic applications because of the excellent and complementary properties of the two materials [3]. We investigate and discuss the reactivity of O₂ and H₂O on top and at the interface of this hybrid system by means of a wide set of dispersion-corrected hybrid density functional calculations [4]. Both pure and boron- or nitrogen-doped graphene are interfaced with the most stable (101) anatase surface of TiO₂ in order to improve the chemical activity of the C-layer. Especially in the case of boron, an enhanced reactivity toward O₂ 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 observed where the boron atom bridges the two systems by forming very stable B-O covalent bonds. Interestingly, the B defect in graphene could also act as the transfer channel of oxygen atoms from the top side across the C atomic layer into the G/TiO₂ interface. On the contrary, the same conditions are not found to favor water dissociation, proving that the “catalysis under cover” is not a general effect, but rather highly depends on the interfacial material properties, on the presence of defects and impurities and on the specific reaction involved [5].

References

- [1] C. Di Valentin, L. Ferrighi, G. Fazio, *ChemSusChem* **9**, 1061 (2016).
- [2] Y. Zhang, X. Weng, et al. *Nano Lett.* **15**, 3616 (2015).
- [3] L. Ferrighi, G. Fazio, C. Di Valentin, *Adv. Mater. Interfaces* **3**, 1500624 (2016).
- [4] B. Civalleri, C. M. Zicovich-Wilson, L. Valenzano, P. Ugliengo, *CrystEngComm* **10**, 405 (2008).
- [5] L. Ferrighi, M. Datteo, G. Fazio, C. Di Valentin, *J. Am. Chem. Soc.* **138**, 7365 (2016).

P9. Controlling the Au/Iron Oxide interface to optimize plasmonic resonance for magneto-optic diagnostics

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Anisotropic magnetic nanoparticles coated in plasmonically active metals (e.g., gold) have a number of applications such as surface enhanced Raman spectroscopy (SERS). Their combination of plasmonic and magnetic properties makes them uniquely suited to homogenous magneto-optic nanoprobe analysis. Unlike their counterparts in SERS, these particles require smooth surfaces for reliable analysis. However, the crystallinity of such nanoparticles may result in rough coatings when gold is nucleated upon their surface. In the present study, Iron Oxide particles were precipitated from ferric chloride with aspect ratios controlled by phosphate concentration. To maximise smoothness, sandwich like anisotropic nanoparticles were prepared consisting of a hematite core, silicon intermediate and an outer gold coat. The structure and surfaces of these particles were analysed by TEM, UV and XPS.

References

- [1] Frandsen, C. et al.. *Crystengcomm* **16**, 1451–1458 (2014).
- [2] Nikoobakht, B. & El-Sayed, M. A. *Chem. Mater.* **15**, 1957–1962 (2003).
- [3] Ma, Z., Han, H., Tu, S. & Xue, J. *Colloids Surfaces A Physicochem. Eng. Asp.* **334**, 142–146 (2009).
- [4] S. Schrittwieser, B. Pelaz, W. J. Parak, S. Lentijo-Mozo, K. Soulantica, J. Dieckhoff, F. Ludwig, T. Altantzis, S. Bals, and J. Schotter *ACS Appl. Mater. Inter.* **8** (14), 8893-8899 (2016).

P10. A new class of carbon allotropes

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Carbon naturally exists mainly in two well-known allotropes, characterized by different atomic hybridization: graphite and diamond. The first consists of sp² hybridized carbon atoms stack in parallel planes, individually known as graphene, interacting by mean of Van der Waal forces. The second is made up of sp³ atoms, arranged in a tetrahedral configuration. The different kinds of bonds are responsible for both the structural and electric properties: diamond is an insulator with a well-defined indirect gap, while graphite is a conductor [1]. The basis of the studied new classification [2] resides on the combination of hexagonal diamond [3,4] and ring carbon (graphene [5]). Since hexagonal diamond acts as an insulator and graphene bonded rings act as conductors, these predicted materials have potential applications for transistors and other electronic components [6]. Further on, we suggest how hundreds of allotropes of carbon could arise by different arrangement of higher number of carbon rings [7].

We studied the proposed series of carbon allotropes and carry out a detailed computational analysis, based on DFT techniques [8], of the structural and electronic properties of two hybrid compounds: the single-ring novamene, which share some structural features with fullerenes [9] and protomene. We performed calculation for analyze their structural stability, finding that these new allotropes are slightly less stable than diamond and graphite at zero T. We also investigated the possibility of induce a transition from metallic to semiconductor regime, which consist of a Peierls transition for few specific atoms, which can flip from sp³ to sp² and back, with just a slight variation in cohesive energy [2].

References

- [1] M.R. Salehpour, S. Satpathy, Phys. Rev. B, **41**, 3048 (1990).
- [2] L.Burchfield, M.A.Fahim, R.S.Wittman, F.Delodovici, N.Manini; Heliyon **3**, e00242 (2017).
- [3] C. Frondel, U.B. Marvin: Lonsdaleite, a new hexagonal polymorph of diamond; Nature, **214**, 58 (1967).
- [4] F.P. Bundy, J.S. Kasper, J. Chem. Phys., **46**, 3437 (1967).
- [5] K.S.Novoselov, A.K.Geim et Al. Science **5696**, 666-669 (2014).
- [6] Y.Y. Zhang, S. Chen, H. Xiang, X.-G. Gong, Carbon, **109**, 246 (2016).
- [7] G. Brinkmann, G. Caporossi, P. Hansen, J. Algorithms, **45**, 155 (2002).
- [8] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G.L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. Fabris, G. Fratesi, S. de Gironcoli, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A.P. Seitsonen, A. Smogunov, P. Umari, R.M. Wentzcovitch, J. Phys.: Condens. Matter, **21**, 395502 (2009).

P11. Thin films of anisotropic particles: equilibrium and growth

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The dynamic adsorption process of particles at surfaces (or interfaces) addresses fundamental questions as well as has several applications (smooth coatings, functionalized surfaces, efficient organic solar cells) [1]. This dynamic adsorption leads to evolution of thin films mainly consisting of anisotropic particles and is observed in the self-assembly of organic monolayers [1], growth of organic semi-conductors thin films by deposition [2, 3] etc.

We investigate the phase behavior of equilibrated structures of rod-like particles near a substrate as well as their dynamic deposition using "dynamic" Monte-Carlo (MC) simulations. We compare our MC data to density-functional theory and kinetic MC simulations [4, 5]. We also write rate equations (REs) for film growth of organic rod-like particles inspired by an attachment-detachment film growth model [6].

References

- [1] F. Schreiber, *Prog. Surf. Science*, **65**, 151 (2000).
- [2] F. Schreiber, *Phys. Stat. Sol. A*, **201**, 1037 (2004).
- [3] G. Witte, and C. Woll; *J. Materials Res.*, **19**, 1889 (2004).
- [4] M. Oettel, M. Klopotek, M. Dixit, E. Empting, T. Schilling, and H. Hansen-Goos, *J. Chem. Phys.* **145**, 074902, (2016).
- [5] M. Klopotek, H. Hansen-Goos, M. Dixit, T. Schilling, F. Schreiber, and M. Oettel, accepted by *J. Chem. Phys.*, arXiv:1701.05830, (2017).
- [6] M. Einax, W. Dieterich, and P. Maass, *Rev. Mod. Phys.*, **85**, 3, (2013).

P12. Manipulation of graphite via graphite oxidation to produce functionalized and few-layered graphene for incorporation into aluminium meta phosphate coatings for electrical steel

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Economic and environmental considerations are driving increased efficiency and technological advances in all industries. This work focuses on electrical steels which are used in the steel laminations of electrical transformers. Transformers are subject to electrical power losses of up to 10%¹. These losses come about from eddy currents, hysteresis losses and magnetostriction. The latter is responsible for up to 5% of these losses and are also responsible for the humming noise of a transformer. The electrical steel industry have been using carcinogenic CrVI coatings on their steel to reduce this loss. There is need to come up with a replacement. Aluminium ortho and meta-phosphate coatings give good magnetostriction properties but are not suitable for particular markets. Therefore, there is a need to develop coatings for specific markets. One solution is to incorporate film modifiers. Graphene is a strong candidate for incorporation in the phosphate coating due to its strength and heat resistance. This paper describes the production of functionalised graphite oxide (GO) using both direct acid treatments and the Hummers method² and its incorporation into novel magnetostrictive resistant coatings. There are two potential benefits. Firstly, that the additional functionality of epoxide, ketone, hydroxide and ester along with intercalating sulfates³ and nitrates give good dispersion of graphene in the phosphate mix as well as bonding to the phosphates. Secondly, graphite oxidation with subsequent reduction is a method of exfoliating⁴ graphene from graphite which will aid a reduced coating thickness. The products were characterised with XPS, XRD⁵, FTIR, Raman⁶ and SEM.

References

- [1] A. J. Moses, *Scripta Materialia*, **67**, 560–565 (2012).
- [2] H. L. Poh, F. Sanek, A. Ambrosi, G. Zhao, Z. Sofer and M. Pumera, *Nanoscale*, **4**, 3515–3522 (2012).
- [3] S. Eigler,* C. Dotzer, F. Hof, W. Bauer, and A. Hirsch. *Chem. Eur. J.* **19**, 9490 – 9496 (2013).
- [4] M. J. McAllister, J.-L. Li, D. H. Adamson, H. C. Schniepp, A. A. Abdala, J. Liu, M. Herrera-Alonso, D. L. Milius, R. Car, R. K. Prud'homme and I. A. Aksay, *Chem. Mater.*, **19**, 4396–4404 (2007).
- [5] A. Ganguly, S. Sharma, P. Papakonstantinou and J. Hamilton, *J. Phys. Chem. C*, **115**, 17009–17019 (2011).
- [6] K. N. Kudin, B. Ozbas, H. C. Schniepp, R. K. Prud'homme, I. A. Aksay and R. Car, *Nano Lett.*, **8**, 36–41 (2008).

P13. Functional coatings of nanoparticles applying atomic layer deposition in a fluidized bed reactor

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Coating technologies are important for adding or improving functionalities of diverse materials. The use of atomic layer deposition (ALD) as a deposition technology allows generating very precise and homogeneous coatings on top of various substrates. Nanoparticles (e.g. TiO₂, ZnO, MgO, Al₂O₃ and Fe₂O₃) are playing an increasingly important role for numerous applications, but their chemical and physical properties often still need to be improved or stabilized. ALD has proven to be a viable option to apply conformal, pinhole-free films with Ångstrom-level control to the surfaces of ultrafine primary particles [1]. Such films will increase the stability and durability and will add value to the functionalities of nanoparticles without seriously altering their weight or size. However, a coating of particles in a traditional chamber type reactor without agitation or mobility of the particles will induce non-conformality of the coatings wherever the particles are in touch with each other. To overcome such issues, the use of a fluidized bed reactor (FBR) was proposed. A fluidization of the particles allows creating a dynamic environment with the particles being in steady motion, while a parallel coating process enables a conformal coating of those. The objective of this research is to design a fluidized bed reactor in which variety of parameters can be optimized for obtaining functional coatings of nanoparticles for an anticipated use in energy storage applications.

Figure 1 shows the setup of a fluidized bed reactor. Nitrogen is used as an inert carrier gas, which facilitates the fluidization of the bed as well as the transport and purging of precursors to and from the reactor column [2]. After the coating process, nanoparticles are characterized using various techniques including, X-Ray diffraction (XRD), Environmental Scanning-Electron Microscopy (E-SEM), Energy Dispersive X-Ray analysis (EDX) and the analysis of the specific surface area.



Figure. The fluidized bed reactor (FBR) configuration for coating nanoparticles using ALD.

References

- [1] D. M. King, J.A. Spencer II, X. Liang, L.F. Hakim and A.W. Weimer, Science Direct, Surf. Coat. Tech. **201**, 9163-9171 (2007).
- [2] D. Valdesueiro, G.M.H. Meesters, M.T. Kreutzer and J.R. van Ommen, Materials **8**, 1249-1263, (2015).

P14. Structure and reactivity of lutetium bis-phthalocyanine thin films

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Lutetium bis-Phthalocyanine thin films are gaining attention as candidate for efficient gas sensing applications. Their peculiar electronic structure, and in particular the presence of a Single Occupied Molecular Orbital (SOMO) makes them ideal candidates for different gas sensing, as they are available for both oxidation and reduction. However no fundamental studies exist yet about how the bonding takes place at the molecular level.

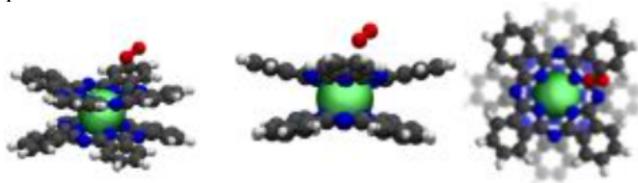
In this work we studied structure and the low temperature reactivity towards molecular oxygen and water of a thick film of LuPc2 deposited on Au(111) single crystal in ultra-high vacuum (UHV).

The structure was characterized by Scanning Tunneling Microscopy (STM) and Grazing Incidence X-ray Diffraction (GIXD). We showed the different orientation of the polycrystalline film on the substrate and the effect of the deposition on the herringbone reconstruction of the Au(111) surface. Also by STM we show the morphology of the film and the layer growth in the multilayer regime.

We characterized the reaction via X-Ray Photoelectron spectroscopy (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy. We showed a weak interaction, as oxygen desorbs as the sample is heated up to around 100K. We also showed that the reaction mostly affects the isoindole N atom, and only slightly the C atoms and the π system. We also show that the adsorption geometry is almost vertical. Also quantitative analysis showed that more than a ML was adsorbed, showing the possibility for the oxygen to diffuse inside the layer.

Instead we show that the desorption temperature for water is found at higher temperature, and the effects on the occupied as well as on the unoccupied states are weaker.

Therefore we can show the microscopic mechanism that lead to a degradation in the electronic properties of double decker phthalocyanine based devices as well as to their gas sensing capabilities.



References

- [1] M. Passard; J.P. Blanc; C. Maleysson, Thin Solid Films 271 8-14 (1995).
- [2] L. Ottaviano, L. Lozzi, S. Santucci Surface Science 431 242 (1999).
- [3] F. Sedona, M. Di Marino, D. Forrer, A. Vittadini, M. Casarin, A. Cossaro, L. Floreano, A. Verdini and M. Sambri, Nature Materials 11 970 (2012).
- [4] I. Bidermane, J. Luder, S. Boudet, T. Zhang, S. Ahmadi, C. Grazioli, M. Bouvet, J. Ruzs, B. Sanyal, O. Eriksson, B. Brena, C. Puglia, and N. Witkowski, Journal of Chemical Physics 138, 234701 (2013).

P15. Platinum nanoparticle patterning of graphene using inkjet printing

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Graphene belongs to Europe's flagship materials. It is a zero band gap semiconductor with remarkable electron mobility and unusually thermal conductivity which make it an interesting material for transparent electrodes. [1,2] The goal of the presented work is to modify the graphene electronic structure with regular patterns of metal dots by using mild 2D ink jet printing as a novel, low-cost solution for printed electronics. The metal dots may act as scattering centers for the strongly delocalized electrons of graphene. Experiments on platinum nanoparticles (Pt NPs) based inks including colloidal synthesis will be presented. The well dispersed NP ink was composed of Pt colloids with an average particle diameter less than 10 nm. These NPs were protected by trisodium citrate hydrate as a capping agent. [3] Stable aqueous inks were formulated by using a combination of solvent (milli-Q water) and co-solvents (ethylene glycol). Different factors affecting the adhesion between the ink and various substrates (silicon wafer and graphene) were investigated. The ink containing 20 wt% Pt, has a viscosity and a surface tension suitable for inkjet printing requirements at room temperature. Successful synthesized Pt NPs were characterized after cleanup by transmission electron microscope (TEM) (Figure 1a). Printed dots on graphene were characterized by optical camera, scanning electron microscope (SEM) and atomic force microscope (AFM) (Figure 1b-d). Furthermore the strategy for the best ink formulation will be presented.

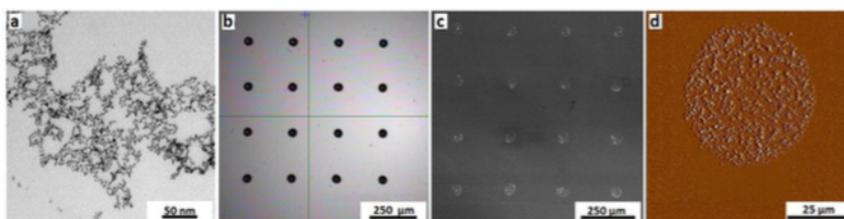


Figure 1: a. TEM image of the Pt NP's after cleanup; b. Optical image of printed dots on graphene; c. SEM image of printed dots; d. AFM image of one of printed dots

References

- [1] I. Meric, et al. *Digest*, **23.2.1–23.2.4**, 556–570 (2010).
- [2] Kim, K. S., et al. *Nature*, **457**, 706–710 (2009).
- [3] G. Wei Wu, et al. *Anal. Chem.*, **86**, 10955–10960 (2014).

P16. Intentional modification of electronic structure in MoS₂ monolayer

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In recent years there has been an increased interest in 2D materials because of their unique properties. Molybdenum disulphide (MoS₂) is one such 2D material that exhibits thickness-dependent electronic properties and is in the focus of contemporary research. Building upon the idea of using collective electrostatic effects for tuning the electronic structure of graphene [1], here we extend this strategy to pristine and doped molybdenum disulphide. By means of dispersion-corrected density functional theory simulations we find that compared to graphene, MoS₂ is more viable for electrostatic design as the shift in electrostatic potential due to adsorption of a polar molecule is significantly larger than what has been predicted for graphene. For doped MoS₂ layer we furthermore investigate to what degree electrostatically patterning the MoS₂ surface can be useful for spatially localizing the doping-induced excess charges. Finally, we outline strategies for using (structurally) more complex molecules on MoS₂ for achieving complicated patterns in the electronic landscape such as valleys and islands.

References

[1] G. J. Kraberger, D. A. Egger, and E. Zojer, *Adv. Mater. Interfaces* **2**, 1500323 (2015).

P17. Microchannel formation in fused silica via ultra-short pulse laser induced chemical etching

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Ultra-short laser pulse interaction with matter is a fascinating field that has attracted a lot of attention over the recent years [1]. High peak power, ultra-short electromagnetic pulses interact with matter in a non-linear way, thus creating potential for advanced micro-machining technologies to emerge. Modifications in transparent materials employing femtosecond laser pulses has recently received a lot of attention [2, 3]. It relies on non-linear absorption, which leads, depending on the tightness of the focused beam, to very small affected volumes. This provides new access to create materials and micro-devices that cannot be obtained by other means [4]. One of the approaches for such fabrication is femtosecond laser induced chemical etching (FLICE).

Using this technique, a tightly focused femtosecond laser beam is scanned inside a transparent material, drawing an arbitrary shape. Due to non-linear interaction, part of the light is absorbed. This alteration of the material changes its etching selectivity – laser illuminated silicon rich areas become soluble in KOH or HF. By providing proper windows for the etchant to reach laser-exposed parts, any arbitrary shape can be fabricated inside a transparent material. However, there are plenty of laser writing parameters to consider when searching for optimal fabrication speed, which is necessary as both laser writing and subsequent etching are rather time consuming processes. This research is dedicated to figure out the influence of pulse density, scanning speed and pulse energy on the etching rate in KOH.

As described in literature [4], three types of transparent material alterations are possible – a slight refractive index change when the pulse energy is below the necessary threshold, formation of nanostructures when it is above the threshold and finally void formation when the pulse energy is exceedingly large. The second type modifications demonstrate reasonable etching selectivity. Fig. 1 depicts channels in fused silica etched by KOH after a single-pass scan of individual lines at varying intervals of 5 μm , 3 μm and 1 μm using a second harmonic of Yb:KGW femtosecond laser PHAROS (Light Conversion) and XYZ sample translation performed with laser microfabrication setup FemtoLAB (Altechna R&D). Thus achieved validation of FLICE technique will enable to further investigate non-linear processes of light-matter interaction and develop an advanced technology for realization of novel 3D microfluidic channels towards lab-on-a-chip devices.

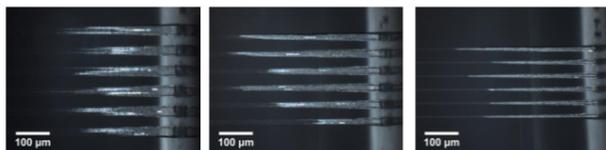


Fig.1. Optical dark field micrographs of etched channels in fused silica with varied line intervals: 5 μm , 3 μm , 1 μm . This research was partly supported by Kaunas University of Technology Interdisciplinary Project No. PP35/161.

References

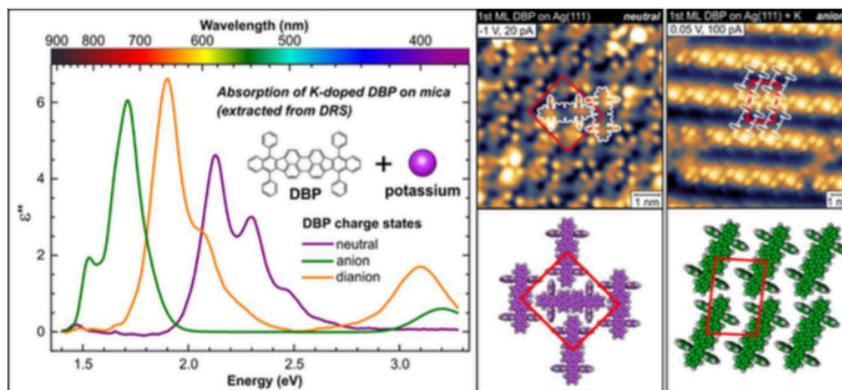
- [1] K. Sugioka, J. Xu, D. Wu, et al., *Lab. Chip*, **14**, 3447-3458 (2014).
- [2] M. Beresna, M. Gecevičius, P. G. Kazansky, *Adv. Opt. Photonics*, **6**, 293-339 (2014).
- [3] R. R. Gattass, E. Mazur, *Nat. Photonics*, **2**, 219–225 (2008).
- [4] D. Tan, K. N. Sharafudeen, Y. Yue, et al, *Prog. Mater. Sci.* **76**, 154–228 (2016).

P18. How K-doping affects the properties of DBP monolayers on Ag(111)

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Doping is a suitable tool to tune the electronic properties and the absorption of organic semiconductors for the purpose of specific technical applications. Recently, tetraphenylidibenzoperiflanthene (DBP), which is applicable as a donor or acceptor for other molecules,¹ was used as a component of optoelectronic devices. Here, we investigate how doping affects DBP itself, by studying the interplay between the optical and electronic properties, as well as the structure of potassium doped epitaxial DBP thin films on Ag(111). For DBP sub-monolayers several different laterally ordered structures depending on the local K:DBP stoichiometry are observed using low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). As concluded from ultraviolet photoelectron spectroscopy (UPS) experiments, an electron transfer from potassium to DBP is achieved. Our differential reflectance spectroscopy (DRS) measurements show that this lowest unoccupied molecular orbital (LUMO) filling leads to tremendous alterations of the molecular absorption and even reduces the molecule-substrate interactions significantly. The optical fingerprints of DBP anions with reduced hybridization to the silver surface and dianions, which are rather effectively decoupled from the substrate, are identified by comparison to optical spectra of K-doped DBP films on inert mica.



References

- [1] A. N. Bartynski et al., *J. Phys. Chem. C* **120**, 19027 (2016).

P19.Integrating periodic gold nano-triangle arrays in organic solar cells

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Using plasmonic nanostructures in organic photovoltaic devices is a promising approach to enhance the light absorption within the active layer and thus improve the solar cell performance. To date, different light management techniques such as the use of plasmonic nanostructures, patterned metal electrodes and plasmonic metamaterials have been proposed for improving both the optical and electrical properties of organic solar cells¹.

In this work, we investigate the plasmonic effect of periodic gold nano-triangle arrays in organic solar cells. We fabricate large-area periodic gold nano-triangle arrays on indium tin oxide (ITO) substrates using a nano-sphere lithography method. The nano-sphere lithography technique is based on the self-assembly of polystyrene nano-spheres achieving a well-packed hexagonal mask, which leads to the formation of metal triangle nanostructures after metal deposition and mask removal. Subsequently, we incorporate the nanostructures into organic solar cells based on PTB7:PC71BM active layers. The field enhancement properties induced by the triangularly shaped nanostructures arranged in hexagonal arrays are characterized by a laser ablation technique² alongside absorption measurements. To shed further light on the impact of the nano-triangle arrays on the light absorption enhancement in the cells, we furthermore perform numerical studies to model the electromagnetic field distribution inside the target devices.

Our study thus presents the light harvesting ability of periodic gold nano-triangles and the feasibility of integrating these inexpensive and easily scalable nanostructures into organic solar cells. We expect that the presented generic technique can be applied in various future optoelectronic devices.

References

- [1] Sungmo, A., Devin, R. & Wounjhang, P. J. Optics-UK **18**, 033001 (2016).
- [2] Goszczak, A. J. *et al.* Opt. Commun. **370**, 135-139 (2016).

P20. Conformational Switching in Benzothiadiazole-Graphene Nanojunctions

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A variety of switching mechanisms have been studied for the development of molecular electronics, considering hydrogen transfer reactions, redox reactions and ring isomerization in a finite bias region [1]. Most investigations on single-molecule charge transport have been thoroughly employed metal electrodes. With improvement of experimental technologies, various kind of carbon-based materials such as carbon nanotubes and carbon nanoribbons would be also promising materials for electrodes. In particular, carbon graphene nanoribbons (GNR), showing excellent electronic properties such as rectification [2] negative differential resistance (NDR) [3], spin filtering [4], field-effect and switching [5] characteristics.

In the present work, we theoretically investigated the charge transport phenomena in benzothiadiazole (BT) molecular wires attached to zigzag-edged GNR electrodes. The rotation of BT wires with respect to the GNR electrodes forms two geometries of devices; parallel and perpendicular conformers. The calculated transport characteristics of the systems have shown a systematic decrease of the conductivity with the increased length of the molecules in perpendicular symmetry (low conductance) than the ones obtained for parallel junctions (high conductance). The in plane orientation represent perfect delocalized π -conjugated electron framework with stable conductance as molecular wire extended. On the other hand, dramatically reducing of conductance occurs in perpendicular orientation related to the interruption of the conjugated π -system along the electrode direction. As a consequence, involvement of the conformational switch was confirmed in our simulated devices.

All the first-principles calculations are carried out on the basis of density functional theory (DFT), as implemented in the SIESTA ab initio simulation package. The electronic transport properties are computed by non-equilibrium Green's function (NEGF) techniques within the Keldysh formalism as implemented in the TranSIESTA module.

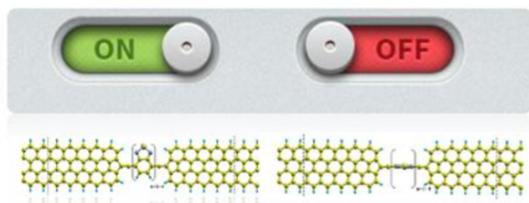


Figure. Benzothiadiazole-graphene molecular switches investigated in this work.

References

- [1] V. Pohl and C. Tremblay, *J. Phys. Chem. C* **120**, 28808 (2016).
- [2] J. Zeng, K.-Q. Chen, J. He, X.-J. Zhang and W. Hu, *Org. Electron.* **12**, 1606 (2011).
- [3] J. Huang, K. Xu, S. Lei, H. Su, S. Yang, Q. Li, J. Yang, *J. Chem. Phys.* **136**, 064707(2012).
- [4] H. Wan, B. Zhou, X. Chen, C. Q. Sun, G. Zhou, *J. Phys. Chem. C* **116**, 2570 (2012).
- [5] C. Jia, A. Maigilior, N. Xin, S. Huang, J. Wang, Q. Yang, S. Wang, H. Chen, D. Wang, *Science* **352**, 1443 (2016).

P21. Characterization of the potential organic superconductor 1,2;8,9-dibenzopentacene on Ag(111) and Au(111)

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The emerging field of superconductivity in doped polycyclic aromatic hydrocarbons has attracted much interest in the last few years. The organic molecule 1,2;8,9-dibenzopentacene (DBPen, C₃₀H₁₈) was reported to have one of the highest critical temperatures in the range of 33 K [1]. However, the mechanisms and even the existence of superconductivity in these systems are still under debate [2]. As yet there are only a few studies dealing with the structural and electronic properties of this molecule, cf. [3], for instance. We deposited DBPen films up to a few monolayers thick on Ag(111) and Au(111) to elucidate, on the one hand, the thickness-dependent and, on the other hand, the substrate-influenced structural and electronic properties. The information gathered from ultraviolet and x-ray photoelectron spectroscopy (UPS, XPS) was combined with an optical in situ characterization of the film growth with differential reflectance spectroscopy (DRS) and low-energy electron diffraction (LEED) measurements. On Au(111) we observe a modification of the Shockley surface state with the amount of molecules being varied. Furthermore, a splitting of the highest occupied molecular orbital (HOMO) indicates the formation of a dimer structure. The observation of an asymmetric shape of the HOMO in the monolayer regime is discussed in terms of vibronic states. The experiments on Ag(111) yield also notable alterations of the occupied states, which were evaluated with the help of photoelectron momentum maps.

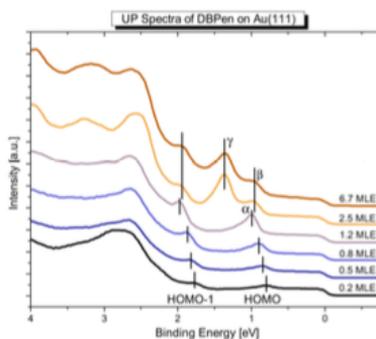


Figure 1. Film thickness dependent ultraviolet photoelectron spectra of 1,2;8,9-dibenzopentacene on Au(111). Above two monolayer equivalent (MLE) a splitting of the highest occupied molecular orbital (HOMO) is observed.

References

- [1] M. Xue, T. Cao, D. Wang, Y. Wu, H. Yang, X. Dong, J. He, F. Li, and G. F. Chen, *Sci. Rep.* **2**, 389 (2012).
- [2] S. Heguri, M. Kobayashi, and K. Tanigaki, *Phys. Rev. B* **92**, 014502 (2015).
- [3] B. Mahns, F. Roth, A. König, M. Grobosch, M. Knupfer, and T. Hahn, *Phys. Rev. B* **86**, 035209 (2012).

P22. Investigation of surface interaction between polymer film and carbon nanotube sheets

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Carbon nanotubes (CNTs) [1] have been studied for nearly two decades and their amazing properties continue to spur intense investigation in the area of nanoscience and nanotechnology. In terms of potential commercialization, multiwall CNTs (MWCNTs) are currently the most prevalent and economically viable form of nanotubes. Uncovering innovative means to take full advantage of their properties remains a fundamental issue. Aligned multiwall carbon nanotube sheets drawn from CNT forests [2] can be deposited on glass or flexible polymer substrates (see figure 1). Since these sheets are electrically conductive and optically transparent [3], they have great potential as transparent electrodes. In addition, their anisotropic morphology can be useful to unidirectional align liquid crystals in display [4]. However, good adherence between the substrate and CNT sheet is important to maintain the uniformity, order, coverage and give time stability to the structure. In our investigations, we have introduced a spin coated polymer film on a glass substrate equipped with an indium tin oxide (ITO) layer. The polymer will play the role of an insulating layer between CNT sheet and substrate. Initial results shows that a film of polyvinylpyrrolidone (PVP) works well as an insulating layer between CNTs and ITO. Indeed, the polymer layer is not more than few hundred nanometer thick and it improves the adhesion, however a strong adhesion is still a challenge. In this presentation, the insulating effect and the interfacial characteristics of PVP on CNT sheets will be discussed and compared with other polymers but also with other surface treatments. Since the surface of CNTs induces planar alignment on liquid crystal molecules [5] the role of the interface between the CNT coated substrate and a deposited LC film will also be discussed.

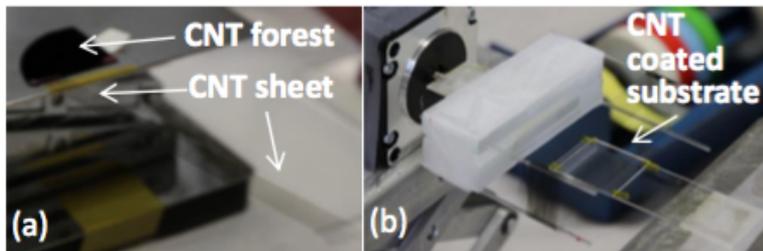


Figure 1. a) Realization of CNT sheets: b) Substrate coated with layer of aligned CNTs

References

- [1] S. Iijima, *Nature* **354**, 56–58 (1991).
- [2] M. Zhang et al., *Science* **309**, 5738, pp. 1215-1219 (2005).
- [3] T. K. Truong et al., *Curr. Appl. Phys.* **16**, 1250 (2016).
- [4] J. M. Russell et al., *Thin Solid Films* **509**, 53-57 (2006); W. Fu et al. *Carbon*, **48**, 1876-1879 (2010).
- [5] G. Scalia et al., *Phys. status Solidi B* **243**, 3238-3241 (2006).

P23. Impedance biosensor interface based on nanostructured porous silico

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Biosensing technology is a rapidly advancing field that benefits from the possibility to use the properties of functional advanced materials to analyse biological systems. Electrical biosensors, and in particular impedance biosensors, have potential for simple, rapid, label-free and low-cost detection of biomolecules [1]. On the other hand, among all the functional materials, porous silicon (PS) constitutes an ideal substrate for developing new chemistries owing to its biocompatibility, well-established fabrication methods and large adsorption surface, which allows an enhanced sensitivity [2].

In the present work, we use PS as a conductive and biocompatible platform in order to fabricate an impedance biosensor. The first step involves the formation of a conductive PS structure. For that, two parallel slots created by ion sputtering and filled with metal by electron beam evaporation are formed on the PS surface. The second step consists of the formation of a biorecognition interface. Indeed, after modification of the surface by a self-assembled monolayer to trigger its sensitivity and allow a molecular selectivity and a control of the biomolecular interactions, the surface of the functionalized material is biologically activated for the detection of specific genomic or proteomic species. Indeed, we perform a sandwich assay in which the biomarker is first recognized by a surface-anchored antibody and then by an antibody in solution that identifies a free region of the captured biomarker. This second antibody is tethered to a gold nanoparticle. Finally, the changes in the interfacial impedance upon analyte binding are detected. The gold nanoparticles act as a mass-electric label and allow increasing the impedance changes and consequently the sensitivity of the detection.

References

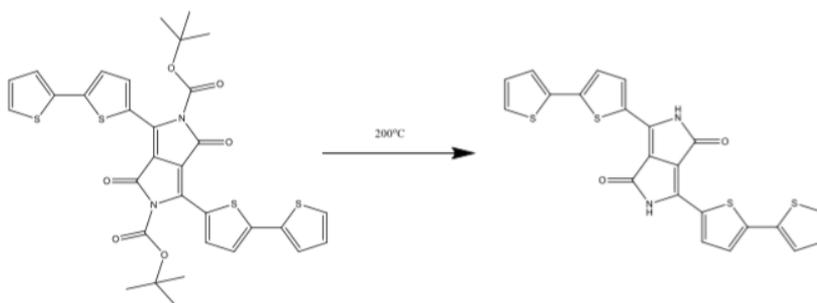
- [1] J. S. Daniels, N. Pourmand, *Electroanalysis*, **19** (12), 1239-1257 (2007).
- [2] S. Stolyarova, S. Cherian, R. Raiteri, J. Zeravik, P. Skladal, Y. Nemirowsky, *Sensors and Actuators B*, **131**, 509-515 (2008).

P24. Latent pigment semiconductors for organic optoelectronics

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Organic electronics have now taken their first steps into commercialization. For many fields, such as Organic photovoltaics scalability is still a problem. Benchmark performances often comes from small scale devices, incorporating expensive active layer deposition techniques such as thermal evaporation. To address this issue, we have developed a method where common small molecule semiconductors can be easily solution processed into thin films for devices such as photovoltaics or transistors. Following deposition, we remove a thermally labile solubilizing chain while simultaneously annealing our films. This results in an insoluble pigment layer that can have subsequent layers' solution processed on top of it from the same solvent. In effect this latent pigment process removes the requirement for orthogonal solvents when solution processing multilayer devices.



References

- [1] F. Bruni, M. Sassi, M. Campione, U. Giovannella, R. Ruffo, S. Luzzati, F. Meinardi, L. Beverina and S. Brovelli, *Adv. Funct. Mater.* **47** (2014).
- [2] J.S. Zambounis, Z Hao, and A Iqbal, *Nature* **388**, no. 6638 (1997).
- [3] H. Yanagisawa, J. Mizuguchi, S. Aramaki, Y. Sakai, *JPN J. Appl. Phys.*, **47** (6), 4728-473 (2008).

P25. Role of interface between perovskite and hole selective layer on the performance of perovskite solar cells

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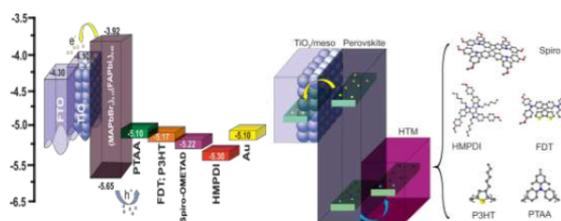
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In recent years, organic-inorganic halide perovskite for solar cells (PSCs) application has received huge attention in the photovoltaic community due to its excellent power conversion efficiency. The merit of organic-inorganic halide perovskite lies due to its broad light absorption in the UV-Vis part of spectra and the ambipolar characteristic of charge transport. Although the current record efficiency of PSCs has reached >22%, a thorough understanding is required to understand the processes occurring inside the devices¹.

In accordance with the working principle, the incident photons which are absorbed by the perovskite layer, creates free carriers. These free carriers then diffuse through the perovskite to the charge selective contacts interfaces, where they are selectively extracted. However losses exist mainly at the grain boundaries of perovskites crystal structure, which acts as recombination sites. Sincere efforts have been made to improve the quality of perovskite layers by process engineering (sequential deposition, vacuum evaporation, vapor assisted deposition or solvent engineering approach). However, at interfaces, there exist energy level mismatch and/or undesirable interface. The introduction of hole transport layers (HTL) and electron transport layers (ETL) can facilitate the selective carrier extraction and collection. Thus it is important to understand and control carrier extraction across the interfaces in order to minimize the energetic losses, to improve device performance.

To elucidate this, we have investigated PSCs fabricated with range of high performance HTLs, including the classical Spiro-OMeTAD and polymeric semiconductors like poly triarylamine (PTAA) and poly 3-hexylthiophene (P3HT), and the small molecules coded as FDT and HMPDI. To reveal the role of HTLs, the solar cell configuration (FTO/bl-TiO₂/mesoporous-TiO₂/perovskite) was kept unaltered in devices and the influence of the different HTMs was probed. We have employed an array of small- perturbation electrochemical techniques to hypothesize the recombination losses caused by each HTLs.



References

- [1] L. Calio, S. Kazim, M. Grätzel and S. Ahmad, *Angew. Chem. Int. Edit.* **55**, 14522-14545 (2016).
- [2] M. Salado, J. Idigoras, L. Calio, S. Kazim, M. K. Nazeeruddin, J. A. Anta, and S. Ahmad. *ACS Appl. Mater. Inter.* **8**, 34414-34421 (2016).

P26. Study of different phases of α -Fe₂O₃ (0001) surface and its templating effect

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The atomic scale studies of various oxide surfaces have been a remarkable challenge in the field of surface science. Different physical and chemical properties of the oxide surfaces, such as the exact atomic structure, catalytic activity or homogeneity depend strongly on the stoichiometry and the treatment of the samples. A rather subtle change in the preparation parameters can have a significant impact on the phase composition of a particular oxide surface and the overall morphology [1, 2].

In this work, we exploit the potential of the scanning probe microscopy (SPM) to study the surface phases of the α -Fe₂O₃ (0001). We investigate its complex reconstructions that emerge as a result of varying the preparation conditions in ultra high vacuum. The standard cleaning of the monocrystalline sample usually results in coexisting phases of different-stoichiometry iron oxides on the surface of α -Fe₂O₃, as they have similar thermodynamic stability [3]. The α -Fe₂O₃ is supposed to reduce to Fe₃O₄ upon performing repeated cycles of sputtering with Ar⁺ ion and annealing in ultra high vacuum. In contrast, on annealing in the presence of O₂ gas, the Fe₃O₄ layers formed on the surface should be partially oxidized back to Fe₂O₃ [4].

We analyze the images obtained at the room temperature with the SPM and identify two majority surface reconstructions: the regular "R" superstructure and the honeycomb superstructure. We show how the ratio of the phases is influenced by the selection of the preparation method and propose an atomic model. Moreover, we deposit submonolayers of the 4,4'-dibromo-1,1'-biphenyl molecules and observe their interaction with these phases. We discover that the honeycomb phase has a templating effect on the molecules, which preferentially attach to its least-conductive regions.

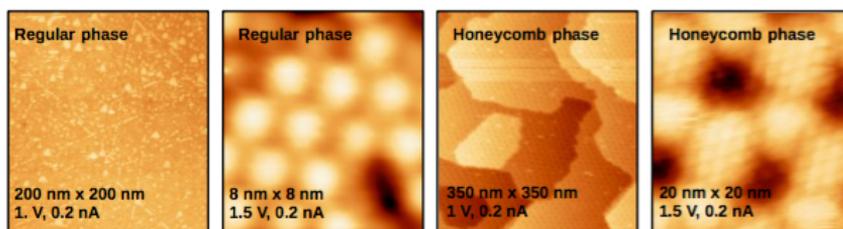


Figure: STM images of regular and honeycomb superstructure on α -Fe₂O₃ (0001) surface

References

- [1] N.G. Condon, F.M. Leibsle, T. Parker, Phys. Rev. B **55** (1997).
- [2] T. K. Shimizu, J. Jung, H. S. Kato, Y. Kim, M. Kawai, Physical Review B **81** (2010).
- [3] Y. Tang, H. Qin, K. Wu, Q. Guo, J. Guo, Surf. Sci. **609** (2013).
- [4] M. Paul, M. Sing, R. Classen, Phys. Rev. B **76** (2007).

P27. The role of charge-transfer (CT) states in degradation of DBP-C₇₀ based organic solar cells

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Over the course of past years, organic solar cells (OSCs) have become an emerging competitive photovoltaic technology. However, despite their advantages over conventional inorganic solar cells, such as low fabrication cost, light weight, semi- transparency and mechanical flexibility, OSCs still have comparably low power conversion efficiencies and rather short lifetime. These disadvantages are the most critical factors hampering their successful implementation on the energy market. In order to overcome these barriers, a detailed understanding of the device degradation mechanism is required.

Charge transfer (CT) states, representing intermediate states between exciton dissociation and recombination at the donor-acceptor interface, play a crucial role in performance of the devices, and the energy of the CT state defines the maximum achievable VOC for a particular D-A junction. In the work presented here, we study the energy of the CT states in DBP-C70 based organic solar cells in inverted and standard architectures. The results from sensitive external quantum efficiency (sEQE) measurements show an unexpected difference in CT state energies for the two architectures. Moreover, we observe different values for the reorganization energy, which determines the energy loss upon deformation of the molecule during charging. These results suggest a morphological sensitivity at the D-A interface, which depends on the deposition sequence, here investigated amongst others by means of atomic force microscopy studies. Aging of the devices at various ISOS testing protocols and the detection of changes in the previously obtained parameters follow these investigations in order to gain deeper insight into the degradation mechanisms of the devices.

P28. Strain-engineered graphene grown on boron nitride by molecular-beam epitaxy

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We show that graphene grown by high temperature molecular beam epitaxy (MBE) on hexagonal boron nitride (hBN) forms continuous domains with dimensions of order 20 μm , and exhibits moiré patterns with large periodicities, up to ~ 30 nm, indicating that the layers are highly strained. Topological defects in the moiré patterns are observed and attributed to the relaxation of graphene islands which nucleate at different sites and subsequently coalesce. In addition, cracks are formed leading to strain relaxation, highly anisotropic strain fields, and abrupt boundaries between regions with different moiré periods. These cracks can also be formed by modification of the layers with a local probe resulting in the contraction and physical displacement of graphene layers. The Raman spectra of regions with a large moiré period reveal split and shifted G and 2D peaks confirming the presence of strain. Our work demonstrates a new approach to the growth of epitaxial graphene and a means of generating and modifying strain in graphene.

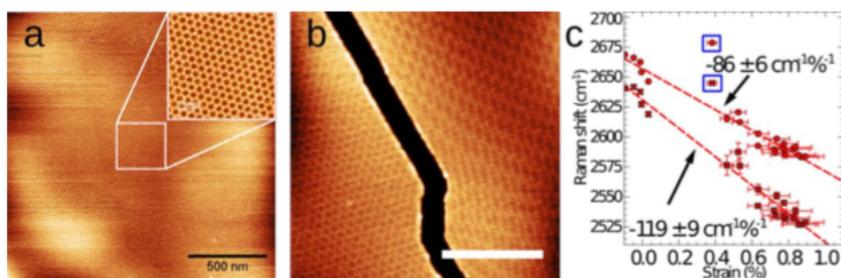


Fig. 1. a) AFM images of moiré patterns on the surface of epitaxially grown graphene on hBN, (inset) high resolution image of the central region of the main image. b) AFM image of a crack in a graphene monolayer exhibiting regular and highly anisotropic moiré patterns. Scale bar 175 nm. c) Raman shift of graphene 2D peak positions as a function of strain, determined by spatial correlation of local moiré periodicity with Raman peak position.

P29. Deposition of Fingerprint on Surfaces with Different Wettability

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Fingerprints have always played a pivotal role as a form of evidence in a crime scene even though there are still many areas that need to be explored. Since, fingerprints are indispensable method of identification, an attempt has been made in the present work to analyse the impact of wetting properties of different surfaces with the fingerprint residue left on it. In this study, fingerprints were deposited on different surfaces of polymers with different water contact angle and were then recovered using the cyanoacrylate fuming technique. Two methods were employed to study the fingerprint development process during the fuming process. In the first method, pictures of the deposited fingerprint on polymer coated glass slides fumed in a chamber were taken. In the second method, deposition poly-ethyl-cyanoacrylate is monitored using Fourier Transform Infrared (FTIR) Spectroscopy via Attenuated Total Reflectance (ATR) sampling. The physical and chemical changes experienced by the fingerprint residue on different surfaces were analysed in three different ways. The rate at which fingerprints undergo fuming is determined by plotting the kinetics of the change in intensity of the fingerprint image from camera and absorbance of cyanoacrylate in peaks from FTIR. The amount of fingerprint residue deposited along with changes in their visibility or absorbance at initial and final of the fuming process was also observed from the same kinetics plot. At time, t equals 20 minutes of fuming, both methods show agreement that the absorbance and brightness value of the fingerprint decrease as the surface water contact angle the fingerprint deposited on increases. Thus, the fingerprint deposited on low water contact angle (higher wetting) surface fumes faster compared to fingerprint deposited on lower wetting surfaces.

P30. Understanding the bond of pentacene to platinum (111) surface

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Aromatic molecules are promising building blocks for active and carrier-injection layers in hybrid metal-organic opto-electronic devices [1]. A complete characterization of the interface is of paramount importance in defining the properties and the efficiency of such systems, therefore they have to be carefully modelled. For example, the van der Waals (vdW) interactions play a crucial role in determining the correct adsorption geometry and energy [2].

In our work we investigated theoretically and experimentally the adsorption of a member of the acene family, namely Pentacene (Pc) (C₂₂H₁₄), on the (111) surface of Platinum (Pt). We determined the adsorption energetics and geometry for several configurations by the means of density functional theory, also accounting for vdW dispersion. We performed our simulations using Quantum ESPRESSO and VASP softwares, employing the Grimme D2 [3] and the modified Tkatchenko-Scheffler [4,5] TS surf vdW correction schemes.

We investigated several adsorption sites. The two most favorable geometries are: the first one displaying a flat molecular profile and the second a more distorted one. The former also has the long molecular axis parallel to the Pt surface crystal directions. We verified our findings by comparison with scanning tunnelling microscopy (STM) data. In all the configurations that we tested, we observed a strong re-hybridization of the molecular orbitals with the substrate states. This result, along with the high adsorption energy and the short C-Pt distances, suggests that the Pc is undergoing chemisorption with the substrate. To get a deeper understanding of this effect we performed an X-ray absorption analysis, by the means of the photoemission (XPS) and near-edge fine structure (NEXAFS) spectra, both experimental and theoretical. In XPS we accounted for the different C- atom contributions to the spectra, due to the varying chemical environment. In NEXAFS we observed a broadening of the features, supporting our hypothesis of strong interaction.

References

- [1] Fratesi G. et al., *Phys. Chem. Chem. Phys.* 16, 14834 (2014)
- [2] Yildirim H. et al., *J. Phys. Chem. C* 117, 20572–20583 (2013)
- [3] Grimme S., *J. Comput. Chem.* 27, 1787–1799 (2006)
- [4] Tkatchenko A. et al., *PRL* 102, 073005 (2009)
- [5] Ruiz V.G. et al., *PRL* 108, 146103 (2012)

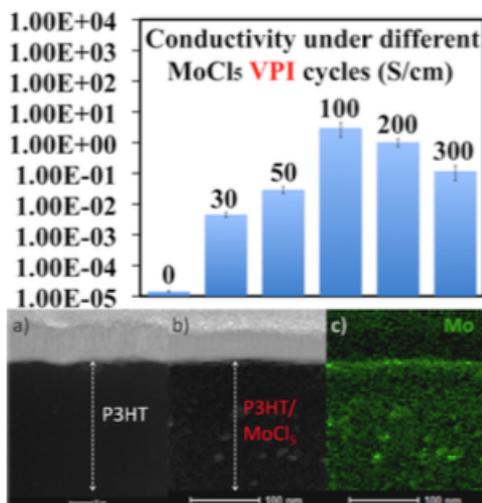
P31. Efficient and controllable vapor to solid doping of the polythiophene P3HT by low-temperature vapor phase infiltration

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Efficient doping of organic semiconductors is an important prerequisite for the fabrication of high performance organic electronic devices. In this work, we describe a novel single precursor low-temperature (70 °C) vapor phase infiltration (VPI) process to dope poly(3-hexyl)thiophene (P3HT). The infiltration is performed with the metal containing atomic layer deposition (ALD) precursor MoCl₅. The conductivities of the polymer are assessed with four-point probe measurements and showed significant enhancement by up to 5 orders of magnitude, confirming the efficiency of the VPI process. The chemical changes resulting from the infiltration of P3HT are characterized applying UV-Vis-NIR, Raman spectroscopy, and FTIR. The crystalline state of the material is analyzed by X-ray diffraction (XRD). SEM micrographs and AFM images show that the morphologies of the samples before and after MoCl₅ infiltration process do not seriously change. TEM images of cross-sections of the thin film clearly show that the vapor phase infiltration process results in the incorporation of Mo into the bulk of the polymer.



P32. Excitation of surface-plasmon polaritons with a scattering-type scanning near-field optical microscope

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Scattering-type Scanning Near-field Optical Microscopy (s-SNOM) is a powerful tool to investigate the optical properties of samples at the nanoscale as well as for the huge emerging field of nanophotonics. In addition to the normal Atomic Force Microscope (AFM), which provides topographical images of the sample, in the s-SNOM, a laser illuminates the tip-sample region and the scattered light contains information about the sample at the tip's position. The resolution is not limited by the wavelength anymore, but rather by the tip geometry, so nanometer resolution is possible for in principle any arbitrary wavelength. Very sophisticated signal processing is required to extract the pure near-field signal from the strong background signal, e.g. interferometric detection and higher harmonic demodulation [1].

Surface Plasmon Polaritons (SPPs) are confined electromagnetic waves at an interface, like metal air interface. Due to the k-vector mismatch, they cannot be excited by means of free light propagation on a flat surface, but a grating, edges, defects or AFM tips can launch them. The s-SNOM technology is very successful in mapping different kind of polaritons since the polaritons interfere coherently with the incident laser and a standing wave pattern is formed in the acquired images, e.g. graphene plasmons in the infrared range [2].

Here we measure SPP in the near-infrared regime ($\lambda=850$ nm). The SPPs excite at four edges of a window in an Au layer (thickness ~ 100 nm) on top of an ITO substrate. The incoming light - figure 1(a)- interferes with edge-launched SPPs -figure 1(b)-, tip-launched SPPs -figure 1(c)- and edge-launched SPPs from a tip-reflected beam path -figure 1(d). The latter channel is required to understand the measured pattern in figure 1(e). In addition, we find an evidence for non-symmetrical SPP generation of the probe tip [3].

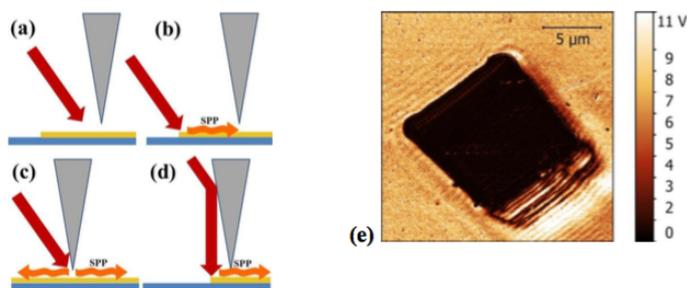


Figure 1 (a)-(d) Different contributions to s-SNOM pattern: (a) incident s-SNOM laser (b) edge excited SPPs (c) tip-launched SPPs (d) tip reflected edge excited SPPs (e) Resulting s-SNOM image (second harmonic of the AFM vibration) of a window in an Au layer on ITO substrate reveals the superposition of the different contributions.

References

- [1] F. Keilmann and R. Hillenbrand, *Phil. Trans. R. Soc. Lond. A*, **362**, 787 (2004).
- [2] Z. Fei et. al., *Nature*, **487** (2012).
- [3] Walla et. al., submitted (2017).

P33. Electrostatically tuned van der Waals heterostructures

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The family of two-dimensional (2D) materials has been growing rapidly since the discovery of graphene. This creates new scientific challenges as well as opportunities because the properties of layered, van der Waals bonded systems are often different from their bulk counterparts, requiring a new approach to electronic-structure engineering.

In this work, using first principles approaches, we propose a novel strategy for engineering the level alignment in van der Waals (vdW) heterostructures. In particular, we focus on the inclusion of polar molecules (e.g. Titanyl phthalocyanine) into stacks consisting of 2D transition metal dichalcogenides (TMDCs) sheets (MoX_2 and WX_2 where $X = \text{S}$ or Se). For structures of the type $\text{TMDC}|\text{TiOPc}|\text{TMDC}$ we observe a shift in the frontier levels of successive TMDC layers by as much as 0.4 eV. Remarkably, for $\text{WSe}_2|\text{TiOPc}|\text{MoS}_2$ the results show that the type of band alignment can be changed from type II to type I. We further extend the idea to intercalating vdW heterostructures, consisting of more than two TMDC sheets, and multiple TiOPc layers to realize complicated structures such as quantum cascades and quantum wells.

Thus, the results obtained strongly suggest that such an electrostatic design approach is a viable way to tune the electronic structure of vdW heterostructures, making it especially interesting for future optoelectronic devices.

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