



Joint Research Project

"Molecular assemblies on semiconductors and insulating surfaces"

Partners:

Jagiellonian University and University of Basel

Annual review meeting

Kraków, July 13-16, 2015









Molecular assemblies on semiconductors and insulating surfaces

joint program project of Jagiellonian University and University of Basel

The main aim of the project is to investigate processes taking place around the molecular assemblies formed on insulating and semiconducting substrate under irradiation by photons. The molecular assemblies grown either by evaporation or by electro-spray deposition will be examined by scanning probe methods, especially non contact atomic force microscopy (NC-AFM) and Kelvin probe force microscopy (KPFM) in order to determine dependence of the electrical properties of the assemblies of their morphology, and exploit that dependence to control the electrical properties of the assemblies. Within the project a number of molecule/substrate systems will be tested in order to find the most suitable ones for examination of the evolution of excitation in the assemblies induced by the incoming light. As the result we hope to gain deeper understanding of charge evolution and transport in the assembly which is crucial in many fields of the nanotechnology and research related to development of light-harvesting media.

The Project is supported by a grant from Switzerland through the Swiss Contribution to the enlarged European Union (Joint Polish-Swiss Research Programme) no PSPB-085/2010 "Molecular assemblies on semiconductors and insulating surfaces".

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WWW: http://molSurf.eu

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Molecular assemblies on semiconductors and insulating surfaces

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Agenda of the annual review meeting Kraków, July 13-16, 2015

Participation of the representatives of both Partners in the 8th International Workshop on Nanoscale Pattern Formation at Surfaces, July 12-16, 2015 Krakow, Poland. Oral and poster presentations showing the results obtained during Project realization and the present state of the art in the research field.

The Workshop is held in the Auditorium Maximum of the Jagiellonian University, Krupnicza 33, Kraków, Poland.

Monday - July 13, 2015

12:20-12:40	Rémy Pawlak:	Atomic structure and Majorana wavefunction of nano- structured Fe atoms on superconducting lead
18:00-19:30	Poster Session: Łukasz Zając:	Influence of carboxyl groups on the porphyrin morphology
20:00-22:00	dinner with the S the Jagiellonian U	cientific Committee and Invited Lecturers of the Workshop in Jniversity Rector's Conference and Reception Centre in

Modlnica (the Manor House in Modlnica)









Tuesday - July 14, 2015

15:30-15:50	Thilo Glatzel:	Patterning of C ₆₀ Islands on Organic Layer Compound Crystals
17:00-17:20	Res Jöhr:	Interaction of Metallo-Carboxyphenyl Porphyrins with Rutile and Anatase TiO ₂
17:20-17:40	Konrad Szajna:	Influence of $TiO_2(110)$ surface roughness on growth and stability of thin organic films
17:40-18:00	Marek Kolmer:	Aryl halide covalent coupling controlled by surface hydroxyl groups on rutile TiO ₂ surfaces
18:00-18:20	Ernst Meyer:	Manipulation of single molecules by NC-AFM

Wednesday - July 15, 2015

09:40-10:00 Ma r	rcin Kisiel:	Artificial	"cicada w	vings"	surfaces	for	antibacterial	l purpose
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Thursday - July 16, 2015

14:15-14:45	Bartosz Such:	Microscopic insight into the adsorption of organic dyes on
		titania

14:45-16:30 panel bilateral discussion concerning the progress, present state, plans and perspectives of the Project (regarding both financial and scientific side of the project)

16:30-22:00 hike through the Kraków Mounds and grill party in Przegorzały Castle, Kraków









Atomic structure and Majorana wavefunction of nano-structured Fe atoms on superconducting lead

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Majorana fermions (MF) are fermionic particles which are their own anti-particles. After more than 80 years search, this elusive particle has been recently observed by STM at the end of Fe chains nano-structured on lead [1]. In this contribution, the structure and electronic properties of such chains on Pb(110) are compared by means of STM, AFM and conductance mapping at low temperature. The conductance maps confirm the MF presence at the wire ends which are also used to determine the decay length of its wave-function. Interestingly, AFM imaging reveals the atomic structure along the chain with an additional force signature at the MF location.

[1] S. Nadj-Perge et al. Science 346, 602 (2014).

[2] R. Pawlak, M. Kisiel, J. Klinovaja, T. Meier, S. Kawai, T. Glatzel, D. Loss, E. Meyer. Submitted









Influence of carboxyl groups on the porphyrin morphology

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Understanding and engineering the molecule-substrate interaction is essential for technologies relevant for dye-sensitized solar cells (DSSC). In the presentation we present the results of studies into the influence of carboxyl groups on the molecular structure of the thin porhpyrin layer. Porphyrins were one of the first sensitizers used in dye-sensitized light harvesting applications[1]. The presence of anchoring carboxylic group plays important role in the adsorption as well as the electron transfer processes[2]. We have used carboxyphenyl-substituted porphyrin, tetrakis(4carboxyl-phenyl)porphyrin cooper(II) (CuTCPP), 5-(4-Carboxyphenyl)-10,15,20-triphenylporphyrin-Zn(II), meso-Tetraphenylporphine-Zn(II) as shown in Fig.1(a). Depending on the number of anchoring groups, we have noticed different behaviour of molecules. The CuTCPP molecules are immobilized and adsorbed flat on surface in the positions which allows the binding of the carboxylic groups into surface oxide rows (a square geometry). The COOH-ZnTPP are absorbed in two forms: stable and mobile. The stable molecules adsorbed flat in cross geometry. The mobile molecules are observed as dashed lines. In the case of the ZnTPP molecules there are no stable molecules.



Fig.1(a) Molecular structure of CuTCPP;(b) 5-(4-Carboxyphenyl)-10,15,20-triphenylporphyrin-Zn(II), (c) meso-Tetraphenylporphine-Zn(II)

This work was supported by a grant from Switzerland through the Swiss Contribution to the enlarged European Union (Joint Polish-Swiss Research Programme) no PSPB-085/2010 "Molecular assemblies on semiconductors and insulating surfaces". www.molsurf.eu

[1] A. Hagfeldt, G.Boschloo, L. Sun et al., Chem. Rev. 110,6595-6663, (2010).

[2] A. Karhiravan, R. Renganathan, Jourmal of Colloid and Interface Science 331, 401-407, (2009).









Patterning of C₆₀ Islands on Organic Layer Compound Crystals

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Organic layered compound crystals offer the possibility to design surfaces with different chemical compounds and molecular orientations [1]. The analysis of the frictional behaviour showed variations in the lateral force down to the single molecular scale highlighting the exceptional properties and possibilities of such materials [2]. However, also the adsorption and formation of molecular assemblies is likely be influenced and the patterning by molecular assemblies of such surfaces can be tuned and adopted.

In this presentation, the behaviour of adsorbed fullerene (C_{60}) molecules on the organic layered compound crystal bis(benzylammonium)bis(oxalate)cupurate(II) (BNL) will be discussed. The C_{60} molecules were deposited on the substrate by thermal deposition and high resolution AFM images of the C_{60} nanopatterns were obtained. Manipulations of the molecular islands have been induced by controlled tip interactions. It was observed that they can be split up and redistributed by these interactions to form larger patterns. Furthermore, also tip-induced shape modifications were observed. The figure below shows such a C_{60} island which was transformed by the AFM tip from a triangular to a hexagonal shape.



Fig. 1: nc-AFM images of a C60 nanopattern on the organic layer compund BNL. The shape was modified by the AFM tip from triangular a) to hexagonal b).

S. Decurtins, et al., Mol. Cryst. Liq. Sci. Technol., Sec A 305, 227, (1997).
G. Fessler, I. Zimmermann, Th. Glatzel, et al., APL 98, 083119, (2011).









Interaction of Metallo-Carboxyphenyl Porphyrins with Rutile and Anatase TiO₂

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Dye-sensitized titanium dioxide is of great interest for photocatalysis and photovoltaics. The structure of the deposited monolayer and the configuration of the single molecules within such layers are of great importance for the device performance. It is therefore necessary to understand the sensitization process and the interaction of single molecules with the surface and among the molecules. In our work we focused mainly on the interaction of metallo-carboxyphenyl porphyrins with the rutile (110) and anatase (101) surface. In order to assess the adsorption configurations of different porphyrins and their electrical properties, we used atomic force and Kelvin probe force microscopy at room temperature. We found that even though the chemical composition of the two surfaces is identical, the adsorption behavior is completely different, indicating that it depends on the surface structure of the substrate. On rutile (110) the evaporated porphyrins aligned themselves with respect to the bridging oxygen rows on the surface, resulting in two main orientations. For anatase (101), exhibiting a similar surface structure, the same porphyrins did hardly bind on the terraces but rather stuck to the step edges. The insight of our work is critically discussed with respect to the formation processes of monolayers and their application in dye-sensitized solar cells.











Influence of TiO₂(110) surface roughness on growth and stability of thin organic films

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We have investigated growth and stability of molecular ultra-thin films on ion beam modified $TiO_2(110)$ surfaces. The surface morphology of developed *para*-hexaphenyl (6P) structures was examined with AFM, tapping and contact mode, and SEM techniques. The $TiO_2(110)$ surface was modified with low energy, 2 keV, noble gas (Ar, Kr, Xe) ion beam irradiating the surface at oblique, 75 degree off normal, incidence. Under the experimental conditions used, the ion bombardment of the $TiO_2(110)$ surface resulted in the formation of a nanoripple pattern. We have found that the ripples' period, height, and length depend on fluence, projectile type, and temperature. The 6P sub-monolayer deposition was carried out in UHV by organic MBE at room temperature. The deposition process was performed on two kind of substrate surfaces: on freshly prepared ion beam-modified $TiO_2(110)$ and on identically prepared pre-patterned surfaces air passivated prior to deposition.

It has been found that the 6P deposition on rippled substrates both, fresh and air-passivated, results in formation of anisotropic islands composed of upright-standing molecules [1]. In the case of shallow rippled surface (surface height variation lower than the length of 6P molecules of 2.7 nm), the islands are stable and can be imaged by AFM and SEM. On the other hand, for deeper ripples (surface height variation in the range of 10 nm) the created 6P islands are not stable against the interaction with the AFM tip. They can be imaged only with SEM. We have found that the local curvature of the substrate surface influences the bonding between the nearest standing molecules in the island. Higher local slope angles result in larger shift between the nearest standing molecules along their length. This induces weaker bonding between them and, finally, leads to a less stable island.

For the case of stable islands, we have also found that the islands can be moved by the AFM tip in contact mode. However, the strength of the substrate-island interaction depends on the $TiO_2(110)$ surface conditions. For the case of manipulating the islands grown on freshly prepared ripples, a higher load has to be applied compared to the case of the islands grown on air-passivated ripples. We will show how the substrate surface anisotropy and AFM scanning conditions influence the possibility of moving the islands.

[1] M. Kratzer, D. Wrana, K. Szajna, F. Krok and C. Teichert, Phys. Chem. Chem. Phys., 2014, 16, 26112.









Aryl halide covalent coupling controlled by surface hydroxyl groups on rutile TiO₂ surfaces

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Molecular nano-architectures formed by the on-surface chemical reactions have attracted great attention over the last few years [1-3]. The bottom-up strategies allow assembling of covalently coupled molecular structures of well-defined morphologies, including: molecular wires, 2D molecular networks, or confined graphene nanostructures. So far, surfaces of selected noble metals have been mostly used as substrates. Recently we could demonstrate for the first time the feasibility of the on-surface covalent coupling of aryl halide precursors on a semiconducting oxide. Low temperature STM (LT-STM) studies and DFT-D modelling showed that thermally activated 10,10'-dibromo-9,9'-bianthryl (**DBBA**) monomers form polyanthrylene chains on the rutile TiO₂(011)-(2x1) surface [4].

Following our recent work, here we report on the role of surface hydroxyl groups in the onsurface polymerization on rutile TiO₂(011) and demonstrate univocally that OH groups are in this case essential for the reaction to occur [5]. We show that the polymerization of diiodoterfluorene (**DITF**) molecules proceeds most effectively when the reduced TiO₂(011) is prepared with a moderate density of surface hydroxyls (~5% coverage), leading to formation of long molecular wires. Increasing the density of the surface hydroxyls (to ~20%) by surface exposure to atomic hydrogen results in formation of shorter oligomers, whereas the hydroxyl-free surface (<0.5%) suppresses the polymerization reaction completely.

- [1] L. Grill et al., Nat. Nanotechnol. 2 (2007) 687.
- [2] J. Cai et al., Nature 466 (2010) 470.
- [3] L. Lafferentz et al., Nat. Chem. 4 (2012) 215.
- [4] Kolmer et al., Angew. Chem. Int. Ed. 52 (2013) 10300.
- [5] Kolmer et al., Chem. Comm. (2015) DOI: 10.1039/C5CC02989A.









Manipulation of single molecules by NC-AFM

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Though the frequency shift of tuning fork force microscopy is primarily related to normal force gradients, there are some examples of experiments, which provide valuable information about lateral forces or energy barriers in the lateral direction. Either 2d- or 3d-frequency data are acquired and transferred into force or energy fields by integration, where instabilities limit the applicability of this method. Alternatively, models are used, where the essential parameters are included to simulate the frequency shift data. An example is given by the pulling of polymeric chains on Au(111) [1], where the detachment of the chain leads to oscillations of the normal and lateral forces. The comparison with the model allows to determine the adhesive energy per subunit of the molecular chain. Lateral manipulation gives insight about the movement of one dimensional chains on surfaces, which is close to the ideal of the Frenkel-Kontorova model.





^[1] S. Kawai, M. Koch, E. Gnecco, A. Sadeghi, R. Pawlak, T. Glatzel, J. Schwarz, S. Goedecker, S. Hecht, A. Baratoff, L. Grill, and E. Meyer, Quantifying the atomic-level mechanics of single long physisorbed molecular chains, Proc. Natl. Acad. Sci. USA, 111, (11), (2014), 3968–3972.





Artificial "cicada wings" surfaces for antibacterial purpose

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In recent years the number of harmful bacteria which are resistant to antibiotics has steadily risen which spurs the research on non drug-mediated bactericidal agents. High aspect ratio nanostructures on cicada wings have been shown to mechanically kill bacteria during contact [1]. The most probable mechanism is based on the physical interaction of nanoasperities with bacteria membranes, which leads to elastic strain and eventual rupture of the bacteria membrane.

We expand the ongoing research to polymer nano – patterned surface, which has great implications for the design of medical items like catheters as well as consumer goods like food packaging materials and single use protective clothes. The plasma exposed polystyrene (PS) and Polyether ether ketone (PEEK) samples mimic bactericidal cicada wing surfaces. Their morphological and elastic properties are investigated by means of Atomic Force Microscopy under ambient and liquid conditions – which is a natural environment for the most of bacteria. The influence of the geometrical parameters of the nano – structured surface as well as the chemical surface modifications on the attachment of E. Coli bacteria is investigated, as well.



Figure 1: left – sketch of the bacteria membrane rapture onto nano – paterrned surface, right – AFM topography image of low power (P=50W) plasma exposed PS "cicada wing" surface.

[1] E. P. Ivanova, et.al., Small 8, (2012) 2489 - 2494.









Microscopic insight into the adsorption of organic dyes on titania

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Adsorption of molecules on titania surfaces plays an important role in various modern technologies. One of the most prominent is the technology of construction of dye-sensitized solar cells (DSSC). In DSSCs the titania is used as a substrate for the light-harvesting molecules. Therefore, the molecule-substrate interaction is of paramount importance since their connection has to assure the stable structure of a cell while allowing for efficient charge transfer. In the presentation we will focus on the microscopic data concerning the morphology of the assemblies of prototypical molecular dyes at low coverages. Our molecules of choice are Zn-porphyrines equipped with carboxylic groups acting as anchoring groups. Many existing studies concerning the efficiency of DSSCs assume that the molecules tend to adsorb in the upright position with their molecular board perpendicular to the surface. Microscopic data do not support such a claim. We will present the evolution of the morphology of molecular layer starting from adsorption of isolated molecules up to coverages slightly exceeding a monolayer. We explore the role of number of anchoring groups in the process of the layer building as well as effect of substrate comparing the behavior of the molecules on reactive (110) an more inert (011) surfaces of rutile. Additionally, we will show the possibility of using the porphyrines as a buffer layer between titania and other molecules forming molecular 'sandwich' of well defined geometric structure.



Figure 1. STM image of 5-(4-Carboxyphenyl)-10,15,20-triphenylporphyrin-Zn(II) molecules on TiO(011)

This work was supported by a grant from Switzerland through the Swiss Contribution to the enlarged European Union (Joint Polish-Swiss Research Program) no PSPB-085/2010 "Molecular assemblies on semiconductors and insulating surfaces".









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