

Part I. Invited Talks

Controllably Quenching a Single Chemical Reaction

Peter Sloan

Department of Physics, University of Bath

Atomic manipulation with the tip of a scanning tunnelling microscope is one of the limits of nanoscience. In general the tip is seen as a passive actor simply providing a convenient source of spatially well-defined electrons. Here I'll report on a new finding [1] whereby the proximity of the tip to the target molecule (toluene molecules on the Si(111)-7x7 surface) changes the excited state dynamics of the electron induced reaction – an example of dynamics induced by electronic transition. The core experiment result was that turning up the current did not lead to the usual increase in reaction rate. In this talk I will briefly outline what we think is really going on.

[1] Regulating the femtosecond excited-state lifetime of a single molecule, K. R. Rusimova, R. M. Purkiss, R. Howes, F. Lee, S. Crampin, P. A. Sloan, *Science* 07 Sep 2018, 361, pp. 1012-1016, DOI: 10.1126/science.aat9688

Changing Direction: Self-Assembly of Aromatic Carboxylic Acids at the Liquid/Solid Interface

Manfred Buck

School of Chemistry, University of St Andrews

Aromatic carboxylic acids (ArCAs) represent a versatile class of molecules which is one reason why they are extensively used as ligands in three dimensional metal-organic frameworks. Similarly, on surfaces they can be assembled to two-dimensional supramolecular networks, thus providing flexible means for the design of precisely defined nanostructures featuring sub-5 nm dimensions, both in vacuum and at the solid/liquid interface.

Contrasting 2D networks, where ArCAs are orientated parallel to the surface, self-assembled monolayers (SAMs), where these molecules adopt an upright orientation, have been studied very little, which is surprising considering that aliphatic carboxylic acids have been investigated since the early days of SAMs. From a series of recent microscopic and spectroscopic studies it is emerging that the structural and functional diversity of ArCAs introduces additional degrees of freedom in the design of SAMs.

Presenting examples of ArCA assembly on coordinating metals such as Cu and Ag, the talk addresses design principles and opportunities arising from variations in molecular geometry.

Non-Thermal Plasma Activated Catalysis

Christopher Hardacre

*School of Chemical Engineering & Analytical Science, University of
Manchester*

Hybrid non-thermal plasma catalysis has a significant potential to provide a low energy pathway to activate molecules and catalysts to enable processes to operate at lower temperatures than would occur if activated thermally. This presentation will show how plasma activation can be utilised to promote the water gas shift reaction, deNO_x reactions and methane combustion. The role of the plasma will be explored and the mechanism of thermal vs plasma activated processes will be shown.

Charge Transfer at the Single Molecule Level with Metal and Semiconductor Electrodes

Richard J. Nichols

*Department of Chemistry, University of Liverpool, Crown Street, Liverpool
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We have exploited STM based methods for making single molecule measurements on a wide variety of molecular targets from short molecular bridges, to redox active organometallic molecular wires and for complex supramolecular assemblies. Such measurements have been made as two-terminal determinations and also under electrochemical potential control with electrolytes varying from aqueous solutions to ionic liquids. Recently we have extended such measurements to semiconductor electrodes. In this lecture I will start by discussing charge transfer through single molecules at electrochemical interfaces and in particular discuss how the electrochemical environment can influence charge transfer. I will then focus on recent results with semiconductor contacts. In a recent publication in Nano Letters [1] we have shown that it is possible to make measurements of single molecules connected at one end to gallium arsenide and at the other end to a gold scanning tunnelling microscope tip. Using this methodology we can record current-voltage response of semiconductor – molecule – metal devices and measure the electrical conductance of single molecules in such junctions. As well as showing that it is possible to form single molecule devices contacted to the semiconductor gallium arsenide we have also recently demonstrated that such single molecule devices show a strong photocurrent response.[2] The photo-current response in these molecular junctions can be controlled through the choice of the semiconductor and its doping density, the molecular bridge and also the light intensity and wavelength. To conclude potential future applications in single-molecule semiconductor electrochemistry will be discussed.

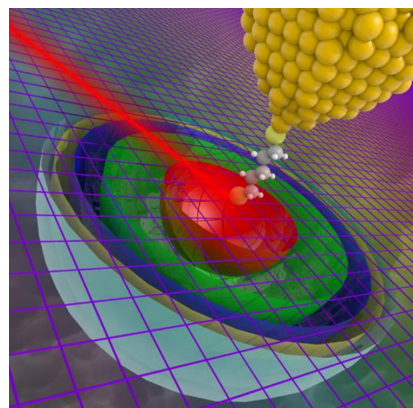


Figure 1: Image of GaAs-molecule-gold junction from Reference [2].

[1] Vezzoli, A.; Brooke, R. J.; Ferri, N.; Higgins, S. J.; Schwarzacher, W.; Nichols, R. J. Nano Lett. 2017, 17 (2), 1109-1115.

[2] Vezzoli, A.; Brooke, R. J.; Higgins, S. J.; Schwarzacher, W.; Nichols, R. J. Nano Lett. 2017, acs.nanolett.7b02762.

Electronic Structure and Charge-density Wave Order of Monolayer Transition-metal Dichalcogenides

Philip King

School of Physics and Astronomy, University of St Andrews

How the interacting electronic states and phases of layered transition-metal dichalcogenides (TMDs) evolve when thinned to the single-layer limit is a key open question in the study of two-dimensional materials. I will describe our recent work on single-layer TMD metals grown by molecular-beam epitaxy. I will show how their ubiquitous charge density-wave states not only persist, but can indeed be strengthened, in the single-layer systems as compared to the bulk parent compounds. I will further argue how a combination of surface spectroscopies can provide powerful insight on the evolution of the quantum many-body states in these systems, in particular using *in situ* angle-resolved photoemission (ARPES) as an ideal probe of the electronic structure of such epitaxial monolayers, and showing how low-energy electron diffraction provides a powerful measure of the order parameter of the charge-density wave. I will further discuss the delicate balance between competing interacting states and phases that the two-dimensional environment of such monolayer TMDs naturally provides, opening potential for the future targeted engineering of the collective properties in such systems.

[1] Feng *et al.*, Nano Lett. 18 (2018) 4493

[2] Watson *et al.*, arXiv: 1808.07141 (2018).

Near-ambient Pressure XPS/NEXAFS at Diamond Light Source

Georg Held

Department of Chemistry, University of Reading and Diamond Light Source

The near-ambient-pressure beamline B07 (Versatile Soft X-ray beamline) opened for users in July 2017 at Diamond Light Source. The beamline features a design, where beamline and electron analyser meet in the same flange; thus experimental chambers and reaction cells can be exchanged relatively easily. The energy range 250 – 2800 eV allows accessing a wide range of core levels and is optimised for the kinetic energy range necessary to penetrate gas phases in the 10 mbar range. The differentially pumped beamline entrance and analyser enable measurements routinely up to 30 mbar. The talk will discuss the beamline design and performance and present some of the first results of experiments studying industrial and model catalysts in ambient-pressure conditions. The experimental demonstrating the performance of the beamline and the research possibilities it offers.

Raman Spectroscopy of Molecular Electronic Junctions

Heike Arnolds

Department of Chemistry, University of Liverpool

Vibrational modes play a key role in characterizing metal-molecule-metal junctions, but their detection currently either requires single-molecule sensitivity or the generation of defect-free large-scale junctions. Surface-enhanced Raman scattering (SERS) on roughened surfaces is a simple tool which can provide a significant amount of information on the kinetics of metal ion complexation and electrochemical reduction despite many defects in the layer. The key to success is to combine detailed spectral analysis with density functional calculations and careful application of Surface-enhanced Raman selection rules. SERS on non-ideal surfaces is thus revealed as a useful tool to rapidly establish the key process parameters in making molecular electronic junctions before embarking on more detailed studies on single molecules or single crystal surfaces.

Bioinspired Energy Materials and Processes – from Nanoscale Science and Surface Science to Applications

Lidija Šiller

School of Engineering, University of Newcastle

Many problems in materials synthesis have been solved in biological systems and can ‘guide’ the design and production of man-made analogues. A major feature that distinguishes biomaterials from synthetic materials are mild synthesis conditions, employing ambient temperatures and pressures, often in aqueous environments. Lightweight and porous materials are key elements of many biological structures: for example, the wings of Odonata – dragonflies and damselflies – which are among the fastest and most agile flying insects, consist of super-lightweight composite structures that have inspired us to novel routes for the production of lightweight, superinsulating aerogel materials¹.

In this talk we will show by exploring the life, structure and natural processes of two living organisms, sea urchins and the oldest insects in the world, dragonflies, at the nano-scale with surface science and nanoscale science experimental methods that it is possible to develop ‘nature-inspired sustainable solutions’ for carbon capture [2,3] and economical process of production of superinsulation [1], respectively. The key features discovered by this approach, further tests in laboratory and scale up will be discussed.

[1] Bioinspired Synthesis of Monolithic and Layered Aerogels, X. Han, K.T. Hassan, A. Harvey, D. Kulijer, A. Oila, M. R.C. Hunt and L. Šiller, *Advanced Materials*, 30 (2018) 1706294.

[2] L. Šiller and G. Bhaduri, ‘Carbon Capture’, World patent, WO2013/171480 A3

[3] G.A. Bhaduri and L. Šiller, *Catalysis Science & Technology* 3, (2013) 1234-1239.

He Spin-Echo Measurements as a Probe of Rate Theory

John Ellis

Department of Physics, Cambridge University

Quasielastic Helium Atom Scattering performed with the He spin echo technique provides a unique insight to thermally activated processes at surface on atomic length (Angstrom) and time (sub ps to ns) time scales.

In this talk, recent measurements will be presented in the context of the evaluation and development of rate theory. With recent advances in ‘first principle’ energetic calculations of reaction pathways for surface and processes are such that ‘chemical accuracy’ becomes a possibility.

Detailed measurements of surface dynamics, however, throw a spotlight on the very crude methods (typically transition state theory) used to predicate a rate based on these hard won potentials. Even for the simplest of systems, the reality is rarely the expected, and the challenge of how to work out what happens and how fast based on theoretical potentials needs to be readdressed. The roll of energy transfer rates between an adsorbate and substrate, the question of the minimum number of degrees of freedom that need to be included in modelling, the nature of multiple jumps, the role of lateral interactions, the transition from a requirement for quantum to classical methods and the fundamental and wide reaching problem of quantum propagation for systems connected to a heat bath are all probed. The current status of effective modelling is reviewed and the key points where data points to necessary theoretical developments are highlighted.

Part II. Posters

P1

Development of new equipment for clean catalyst synthesis

Ross Griffin¹, Chris Brown, Peter Ellis, Laura Ashfield, Peter Bishop, Quanmin Guo¹

¹Nanoscale Physics Research Laboratory, University of Birmingham, Birmingham, UK

We present the proof of principle and early development of a new ion gun based sputter system for the controlled deposition of metal onto oxide supports of Al₂O₃ and SiO₂. This atomic metal forms nanoparticles of approximately 2 nm diameter by surface agglomeration resembling standard catalysts. The consistency of this effect across different surfaces, temperature ranges and deposition rates is demonstrated using a test rig. Catalyst damage is induced by direct heating in atmosphere to demonstrate likely degradation effects post-catalysis.

The sputter system designed for this experiment consists of a high current Kauffmann ion gun and a rotatable prism shaped sputter target, able to clamp three separate metal films for the production of binary or even ternary nanoparticles. The powdered support is managed by a hopper-to-hopper system such that the powder can be rolled down a piezo-agitated pane of glass. This enables precise control over the exposure time of the powder particles to the metal beam, and hence particle size. In the case of multimetallic nanoparticles, compositional control can also be achieved.

Produced catalysts will be characterised using AC-STEM microscopy and ICP-MS to access their morphology and weight loading respectively. These catalysts will be tested for their activity in the selective hydrogenation of 1-Pentyne, the reduction 4-Nitrophenol and the oxidation of CO. This will enable direct comparison to previous work using the MACS system and more conventional catalysts made by wet impregnation in terms of activity, selectivity and durability.

P2

Degradation of size-selected Pt₉₂₃ nanoparticles through electrochemical methods studied through aberration corrected scanning transmission electron microscopy

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³*College of Engineering, Swansea University, Bay Campus, Fabian Way, Swansea, SA1 8EN, UK*

In the search for alternative energy sources hydrogen fuel is often tipped as a clean solution to energy storage[1]. Platinum is the de-facto standard electrocatalyst for the hydrogen evolution reaction (HER) in the electrolysis of water into hydrogen[2], yet the cost and rarity of Platinum Group Metals (PGMs) remain a large obstacle towards full-scale implementation[3].

Here we use physical methods to synthesize size-selected Pt₉₂₃ nanoparticles in vacuum using a magnetron sputtering cluster beam source⁴ directly onto amorphous carbon TEM grids. Atomic resolution Transmission Electron Microscopy reveals a Pt₉₂₃-monomer based degradation mechanism after electrochemical potentiostatic cycling in H₂SO₄. The structures formed after potentiostatic cycling resemble monomer chains which have been created by the sintering of monomers at common grain boundaries. The degree of sintering is shown to be a function of the anodic limit and nanoparticle density. Testing reveals that the HER performance of these nanoparticles improves with anodic activation (not shown) which is in part due to surface restructuring. We demonstrate that size-selected physically deposited nanoparticles can be used as model systems to optimize catalytic materials, and to study the fundamentals of surface processes under dynamic electrochemical conditions. Understanding the platinum catalyst-catalyst, and catalyst-surface interactions are fundamental to designing the next generation of catalysts with high performance and high stability.

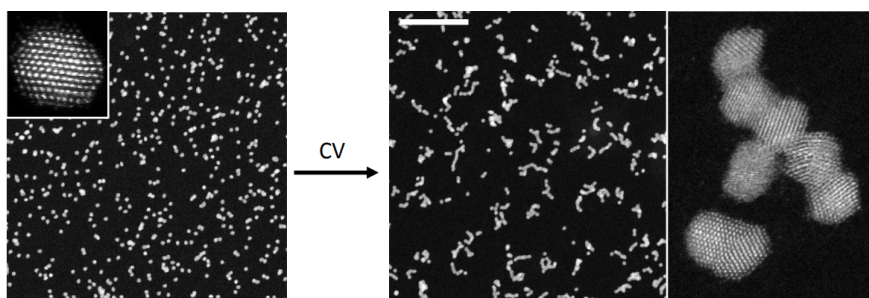


Figure 1: Aberration corrected HAADF-STEM imaging. Left) the as-deposited Pt_{923} nanostructured surface, with high magnification inset of one Pt_{923} nanoparticle. Right) the nanostructured surface distribution changes significantly after 25 cyclic voltammograms in 0.5M H_2SO_4 in the potential window (0, 1.25) V vs RHE. Far right) a high magnification image of one of the chain-like structures reveals Pt_{923} monomer sintering.

P3

Atomic resolution electron tomography of nanoparticles on tungsten tips

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National*

Laboratory, Berkeley, CA, United States

A major challenge in electron tomography is the degradation of the signal-to-noise ratio at high tilt angles, which is due to the increase in thickness of the support that the beam must pass through as the sample is tilted. This restricts the range of tilt angles from which information can be gathered, thereby limiting the resolution of the final reconstruction. This so-called ‘missing wedge’ problem can be avoided by placing the sample on the apex of a tungsten tip rather than a planar support like a TEM grid. By orienting the tip perpendicular to the direction of the beam, the beam will only pass through the sample and avoid the support altogether. The tip can then be rotated about its axis to access the full range of tilt angles ($\pm 180^\circ$), thereby avoiding missing wedges. Nanoparticles can be deposited onto the apex of an electrochemically-etched crystalline tungsten tip by thermal evaporation or drop-casting from solution. Preliminary analysis of a Au nanoparticle dataset with 60 projections over 180° is presented here. The dataset was taken with a beam energy of 300 keV and a probe convergence angle of 17 mrad in annular dark field STEM mode.

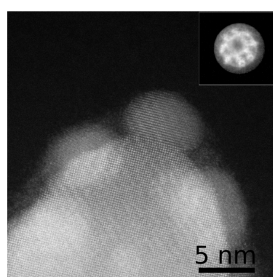


Figure 1: ADF STEM image of the apex of a tungsten tip with Au nanoparticles formed by Au evaporation. The lattice structure of the Au nanoparticle and tungsten tip can be clearly seen and the interface can be identified. The inset shows the corresponding convergence beam electron diffraction (CBED) pattern of the tungsten tip at 400 nm from the apex.

P4

Orientational epitaxy of van der Waals molecular heterostructures

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¹*Nanoscale Physics Research Laboratory, University of Birmingham, Birmingham,
UK*

The shape of individual building blocks is an important parameter in bottom-up self-assembly of nanostructured materials. A simple shape change from sphere to spheroid can significantly affect the assembly process due to the modification to the orientational degrees of freedom. When a layer of spheres is placed upon a layer of spheroids, the strain at the interface can be minimized by the spheroid taking a special orientation. C₇₀ fullerenes represent the smallest spheroids, and their interaction with a sphere-like C₆₀ is investigated. We find that the orientation of the C₇₀ within a close-packed C₇₀ layer can be steered by contacting a layer of C₆₀. This orientational steering phenomenon is potentially useful for epitaxial growth of multilayer van der Waals molecular heterostructures.

P5

Mixing of C₆₀ and C₇₀ in closed-packed molecular layers on Au(111) substrate

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¹*Nanoscale Physics Research Laboratory, University of Birmingham, Birmingham, UK*

C₆₀ and C₇₀ are two model molecules for the investigation of molecular self-assembly on surfaces. Both molecules, when deposited onto a solid substrate, have the tendency to form close-packed molecular layers. Because of the similarity between C₆₀ and C₇₀, there is an interest in exploring the possibility of making a molecular “alloy” with tunable properties. The different geometric shapes of the two molecules, however, seem to prevent a regular structured molecular alloy to form [1]. In addition to the idea of a molecular alloy, it is also interesting to see how the molecules move within a mixed layer. For purely imaging purposes, we are also interested in how to identify C₆₀ and C₇₀ based on their spectroscopic response since they have different HOMO-LUMO gaps.

We have conducted experiments to study molecular transport between a layer of C₆₀ in contact with a layer of C₇₀. First, 0.3 ML C₆₀ is deposited on a Au(111) substrate at room temperature in ultra-high vacuum. We then add a 0.3 ML C₇₀. We image the molecular layers using an Omicron VT-STM. Images are acquired before and after the sample has been annealed to 573 K for a fixed period of time, so changes due to annealing can be monitored.

[1] Frederic Rossel, Marina Pivetta, Elizabeta Cavar, Ari P. Seitsonen, and Wolf-Dieter Schneider, *Phy. Rev. B.* 84, 075426 (2011).

P6

Growth of icosahedral and truncated octahedral Ni nanocrystals on a SrTiO₃ (111) support

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We have investigated the structure and morphology of self-assembled nickel nanocrystals supported on a SrTiO₃ (111) substrate using UHV scanning tunneling microscopy. The substrate was sputtered (0.5 keV, 2.6 μ A, 10 min) and annealed (900 °C, 1 h) to generate terraces with (4 \times 4) and (6 \times 6) reconstructions. 1 ML of Ni was deposited using an electron beam evaporator on substrate preheated at 320 °C. The system was then post-annealed at 320 °C for 6 h. Ni formed clusters with five-fold symmetry which have an icosahedral shape. Nanocrystals with point, edge, and face orientation (five-fold, two-fold, and three-fold symmetry, respectively) have been studied. The truncated octahedral nanocrystals were also observed that resulted from the epitaxial growth of fcc Ni on SrTiO₃ (111). The icosahedral and truncated octahedral nanocrystals coexisted on the SrTiO₃ (111) substrate. Wulffman simulations were also generated to estimate $\gamma_{001}/\gamma_{111}$ energy ratios and were compared with theoretical values. The edge ratios of the truncated octahedral nanocrystal facets at equilibrium and an energy minimization calculation resulted in $W_{adh} = (3.851 \pm 0.150) \text{ J/m}^2$.

P7

What can be seen with atom beams?

Sam Lambrick¹, David Ward, Matthew Bergin, Susanne Schulze, Bill Allison, John Ellis, and Andrew Jardine.

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Microscopy has been a major enabling technique for the development and understanding of materials from the bottom up. Some of the major insights in the development of modern materials have come from scanning probe, electron and ion microscopies, with advances in resolution and sensitivity enabling new science. Unfortunately charged beam techniques tend to cause surface damage and scanning probe techniques are limited to relatively flat surfaces and samples with a small aspect ratio – imaging with a neutral helium beam[4] overcomes some of these issues.

In the current work we present experimental measurements demonstrating a variety of features detected with our Scanning Helium Microscope (SHeM)[2] and discuss the origins of the observations. Further potential contrast mechanisms[3,5] are examined in the context of their application. The most significant mechanism of contrast observed is correlated with topographic features[5,6], as might be expected. We also present evidence of intensity variation dependent on the helium surface interaction which has the potential to reveal nontopographic features. Comparison between experimental data and a ray-tracing model[1] enables us to comment on the scattering distribution between helium and technological samples which is of some fundamental interest.

[1] S. M. Lambrick, M. Bergin, A. P. Jardine, and D. J. Ward, “A ray tracing method for predicting contrast in neutral atom beam imaging,” *Micron*, vol. 113, pp. 61–68, Oct. 2018.

[2] M. Barr et al., “A design for a pinhole scanning helium microscope,” *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, vol. 340, pp. 76–80, Dec. 2014.

[3] M. Barr et al., “Unlocking new contrast in a scanning helium microscope,” *Nature Communications*, vol. 7, p. 10189, Jan. 2016.

[4] M. Koch et al., “Imaging with neutral atoms—a new matter-wave microscope,” *Journal of Microscopy*, vol. 229, no. 1, pp. 1–5, Jan. 2008.

[5] P. Witham and E. Sánchez, ‘Exploring neutral atom microscopy’, *Crystal Research and Technology*, vol. 49, no. 9, pp. 690–698, Sep. 2014.

[6] A. Fahy, M. Barr, J. Martens, and P. C. Dastoor, ‘A highly contrasting scanning helium microscope’, *Review of Scientific Instruments*, vol. 86, no. 2, p. 023704, Feb. 2015.

P8

Development of a combined scanning tunnelling microscope

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scanning electrochemical microscope (STM- SECM)

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Since the conception of scanning tunnelling microscopy (STM) in 1981, many other scanning probe microscopy (SPM) techniques have been developed, including in the field of electrochemistry, where scanning electrochemical microscopy (SECM) has found many applications.[1] While scanning electrochemical probe microscopes are powerful tools for the spatial mapping of electrochemical reactivity (e.g., electrocatalytic activity) at the micro- to nanoscale, they are often limited in their ability to reliably map topography.[2,3] Herein, a combined STM-SECM technique is proposed for simultaneous high resolution topographical and electrochemical imaging (mapping). The challenge of bridging the differing length scales of the two individual techniques (i.e., nano- to Angstrom-scale for STM versus micro to nanoscale for SECM) has been addressed using a “hopping mode” regime, thereby allowing for the study of features that are larger than are normally observable in STM whilst still being able to map smaller features. Significant progress has been made in the fabrication of robust and reproducible STM-SECM probes, manufactured from laser-pulled quartz capillaries filled with pyrolytic carbon,[4] on which electrocatalytically active metals (e.g., Pt) can be electro-deposited,[5] resulting in well-defined and stable probe tips. Herein, these probes have been used to carry out joint STM-SECM studies on sample systems to correlate topography and electrocatalytic activity at the nanoscale, using {111}-oriented two-dimensional Au nanocrystals, AuNCs, as an exemplar system (e.g., see Fig. 1).

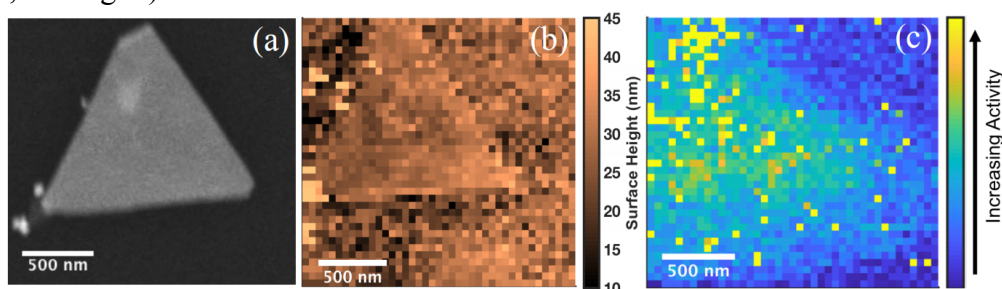


Figure 1: SEM, STM and SECM (left to right) images of a single AuNC. The STM (topography) and SECM (electrochemical activity) maps were obtained synchronously using

a “hopping pulse mode” of STM-SECM in 0.1 M HClO₄. SECM was operated in the substrate generation/tip collection mode, detecting the product (H₂) of the hydrogen evolution reaction at the substrate.

- [1] D. Polcari, et al., *Chem. Rev.*, 2016, 116, 13234-13278.
- [2] M. O’Connell & A. Wain, *Anal. Meth.*, 2015, 7, 6983-6999.
- [3] T. Treutler & G. Wittstock, *Electrochim. Acta.*, 2003, 48, 2923-2932.
- [4] Y. Takahashi, et al., *Angew. Chem. Int. Ed.*, 2014, 50, 9638-9642.
- [5] M. Şen, et al., *Anal. Chem.*, 2015, 87, 3484-3489.

P9

Charge transfer at the single molecule level with metal and semiconductor electrodes

Richard J. Nichols^{1,*}, Edmund Leary¹, Nicola Kay¹, Samantha Catarelli¹, Andrea Vezzoli¹, Richard J. Brooke², Nicolò Ferri¹, Simon J. Higgins¹, Walther Schwarzacher², Jens Ulstrup³ and Richard J. Nichols¹

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²*H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK*

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We have exploited STM based methods for making single molecule measurements on a wide variety of molecular targets from short molecular bridges, to redox active organometallic molecular wires and for complex supramolecular assemblies. Such measurements have been made as two-terminal determinations and also under electrochemical potential control with electrolytes varying from aqueous solutions to ionic liquids. Recently we have extended such measurements to semiconductor electrodes. In this lecture I will start by discussing charge transfer through single molecules at electrochemical interfaces and in particular discuss how the electrochemical environment can influence charge transfer. I will then focus on recent results with semiconductor contacts. In a recent publication in Nano Letters [1] we have shown that it is possible to make measurements of single molecules connected at one end to gallium arsenide and at the other end to a gold scanning tunnelling microscope tip. Using this methodology we can record current-voltage response of semiconductor – molecule – metal devices and measure the electrical conductance of single molecules in such junctions. As well as showing that it is possible to form single molecule devices contacted to the semiconductor gallium arsenide we have also recently demonstrated that such single molecule devices show a strong photocurrent response.[2] The photo-current response in these molecular junctions can be controlled through the choice of the semiconductor and its doping density, the molecular bridge and also the light intensity and wavelength. To conclude potential future applications in single-molecule semiconductor (photo-) electrochemistry will be discussed.

[1] Vezzoli, A.; Brooke, R. J.; Ferri, N.; Higgins, S. J.; Schwarzacher, W.; Nichols, R. J. Nano Lett. 2017, 17 (2), 1109-1115.

[2] Vezzoli, A.; Brooke, R. J.; Higgins, S. J.; Schwarzacher, W.; Nichols, R. J. Nano Lett. 2017, acs.nanolett.7b02762.

XPS study of Tin Oxide passivation film for packaging application

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Packaging tinplate comprises of 5 layers: mild steel base, Fe-Sn intermetallic, pure tin, passivation layer and lacquer coating. Its wide use, mainly within the packaging steel sector for food and beverage cans, where approximately a third of world tin production goes towards the manufacture of tinplate.[1] Some soups and fruits stored by tinplate packing will have a very acidic pH due to the naturally occurring acids inside them [2] as well as high salt content which accelerates the corrosion process thus requiring good protection. The viability of Sn passivation is an alternative idea [3] as it wouldn't require any other material, due to the tin already being present. Proposed tin passivation also allows for the reduction in the amount of raw tin required compared to that of conventional tinplate thus making it more financially viable and sustainable.

Tin has two primary oxides that are able to form; Stannous (SnO) and Stannic (SnO₂). SnO is naturally formed, however it's thermodynamically unstable when compared to SnO₂ [4], this instability is unwanted when another coating would be applied upon it. An advantage of having SnO₂ is that an amphoteric SnO is more susceptible to react with the water in the air and form hydroxide Sn(OH)₂ which is a problem for tinplate, especially in a humid and warm environment. The hydroxyl groups are forming a porous fluffy structure compared to that of compact SnOx, providing direct transport of oxygen for further oxidation of tin and subsequently the steel substrate, thus greatly decreasing the corrosion performance of the tinplate and adhesion strength between the lacquer and the passivation layer. Another disadvantage of a thick tin oxide layer is that it causes dust formation in the tooling of the can-maker as it's brittle and cannot withstand deformations applied during the can making process, moreover the tinplate loses its lubrication ability by soft free tin at the surface. Therefore selective growth of SnO₂ is needed.

Present XPS study of the SnO and SnO₂ powders (Sigma-Aldrich, 99.99%) revealed that indeed the thin layer of Sn(OH)₂ hydroxide forms only on SnO surface (p-type semiconductor has many oxygen vacancies). While SnO₂ (n-type) does not react with water from the air, and the grown hydroxide can preferentially be removed by either a mild Ar⁺ sputtering or annealing in UHV below 200°C. Then the XPS chemical shift in Sn 3d spectrum confirms the further oxidation of SnO powder [5] to SnO₂ + Sn₃O₄

at 500°C for 2 hours in N₂O environment [6] (performed in a reaction chamber directly attached to XPS); resulted in a transformation from a fine dark SnO powder to a more clumpy yellow/off white, similar to that of SnO₂ powder. This study also demonstrated that the surface of non-passivated tinplate exposed for 2 years in normal conditions consists of naturally grown SnO + Sn(OH)₂, and that hydroxide removal by annealing below 200°C can improve the corrosion resistance prior to the lacquering. Furthermore the thermal transformation of SnO to SnO₂ at higher temperatures is an interesting avenue for future exploration.

[1] S. Blunden and T. Wallace. Tin in canned food: a review and understanding of occurrence and effect. *Food and chem. Toxicology*, 41(12):1651-1662, December 2003.

[2] B.F. Giannetti et al. Electrochemical dissolution and passivation of tin in citric acid solution using electron microscopy techniques. *Electrochimica Acta*, 37(1):143 – 148, 1992.

[3] D.R. Gabe. Mixed oxide films on tin. *Surface Technology*, 5(6):463 – 478, 1977.

[4] G. L. Humphrey and C. J. O'Brien. Heats of formation of stannic and stannous oxides from combustion calorimetry. *American Chemical Society*, 75(12):2805–2806, 1953.

[5] Leo. Brewer. Thermodynamic properties of the oxides and their vaporization processes. *Chemical Reviews*, 52(1):1–75, 1953.

[6] Zu Dai et al. Growth and structure evolution of novel tin oxide diskettes. *American Chemical Society*, 124(29):8673–8680, 2002.

P11

Reversible reaction of CO₂ with superbasic ionic liquid [P₆₆₆₁₄][benzim] studied with in situ photoelectron spectroscopy

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Ionic liquids have been widely investigated as potential CO₂ capture agents. The regeneration of some ionic liquids after CO₂ capture is a relatively low energy process compared to current industrial solutions such as monoethanolamine [1,2]. Superbasic ionic liquids, or SBILs, have received considerable attention for CO₂ capture applications due to their excellent CO₂ capacity [1]. Their reaction with CO₂ leads to the formation of carbamate at one or more of the deprotonated amine sites [3]. An additional benefit of SBILs is, unlike some other ionic liquids, they do not undergo a large increase in viscosity upon CO₂ saturation, which makes them potentially useful in large-scale applications. In an experimental and theoretical study of SBILs, tetra-alkylphosphonium benzimidazolide (or [P66614][benzim]), was able to absorb equimolar quantities of CO₂ in the dry state, but when wet its capacity for CO₂ decreased [1,3]. Here we examine the absorption and reaction of the SBIL [P66614][benzim] with CO₂, with H₂O, and with CO₂/water vapour mixtures, using in situ photoelectron spectroscopy. Results indicate a reaction takes place between the CO₂ and aromatic nitrogen atoms to form a carbamate species, which is reversible via reduction of the surrounding gas pressure. Results also appear to indicate that the SBIL appears to preferentially react with CO₂ over H₂O vapour.

[1] Taylor, S. F. R.; McCrellis, C.; McStay, C.; Jacquemin, J.; Hardacre, C.; Mercy, M.; Bell, R. G.; de Leeuw, N. H., *Journal of Solution Chemistry*, 44, 511-527 (2015)

- [2] Blanchard, L. A.; Hancu, D.; Beckman, E. J.; Brennecke, J. F., *Nature*, 399, 28-29 (1999)
- [3] Mercy, M.; Rebecca Taylor, S. F.; Jacquemin, J.; Hardacre, C.; Bell, R. G.; De Leeuw, N. H., *Physical Chemistry Chemical Physics*, 17, 28674-28682 (2015)

P12

Structural characterisation of conjugated polymers using scanning Tunnelling microscopy

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The ability of Scanning Tunnelling Microscopy (STM) to be used as a unique and novel characterisation tool for complex heterogeneous conjugated polymers has been demonstrated. The polymers analysed in this work, poly[2,5-bis(3-alkylthiophen-2-yl)thieno(3,2-b)thiophene] (PBTtT) and indacenodithiophene-co-benzothiadiazole (IDT-BT) have particular importance in solar and electronic applications respectively^{1,2} Recently, diketopyrrolopyrrole (DPP) based polymers have also been investigated.³ Images were obtained by using a combination of electrospray ionisation (ESI) and STM under ultra-high vacuum (UHV) and liquid nitrogen temperatures. DPP STM images showed that the conjugated polymers structures and self-assembly can be analysed effectively. Images for IDT-BT showed changings of the conformation adopted within the backbone which are not detectable by other analytical tools. Future work will focus on further development of a more effective combination of ESI and STM as an analytical tool for characterising polymers.

[1] D. Alberga, D. Perrier, I. Ciofini, G. F. Mangiatordi and C. Adamo, Phys. Chem. Chem. Phys., 2015, 17, 18742

[2] X. Zhang, H. Bronstein, A. J. Kronemeijer, J. Smith, Y. Kim, R. J. Kline, L. J. Ritcher, T. D. Anthopoulos, H. Sirringhaus, K. Song, M. Heeney, W. Zhang, I. McCulloch and D. M. Delongchamp, Nat. Commun., 2013, 4, 2238

[3] Warr et al., Sci. Adv. 2018, 4, 1

P13

Work function control in III-V semiconductors

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The work function is a fundamental semiconductor parameter but has received relatively scant attention in the literature. Ionization potential and electron affinity depend on the work function and are practically important for hybrid organic-inorganic solar cells. Apart from variation due to doping, one expects that work function can change due to the crystallographic orientation of the surface (for polar materials) and presence of surface dipoles (through native oxides or deliberate surface modification). Zhou et al. [Science 336 (2012) 328] showed that surface modification using poly(ethylenimine) (PEI) reduced the work function of several metals, metal oxides and organic materials by up to 1 eV, calling the method “universal”.

We have investigated the work functions of III-V semiconductors and their modification with PEI. We focus on different low-index orientations of n-type GaAs with spin-coated PEI films, also allowing the films to age for weeks or months in air. Using a Kelvin probe in ambient conditions we monitor the work function reduction after coating (Fig. 1a) via the contact potential difference to the gold probe tip. The reduction begins at around -500 mV settling at around -200 mV after a few months. XPS measurements indicate a dramatic increase in the O=C-O and N-(C=O)-O (Fig. 1b/c) components of the C 1s spectra after exposure to the atmosphere for 10 months, which is in agreement with reaction mechanisms described in the literature, and a good indicator for the condition of the polymer after application to the surface.

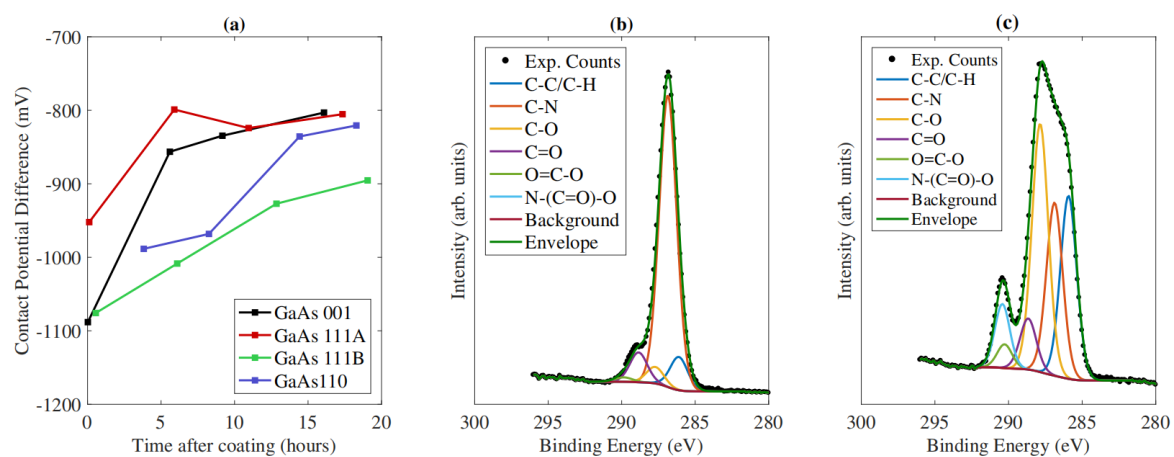


Figure 1: (a) Contact Potential Difference measurements by Kelvin probe showing the gradual decay over the course of several hours. (b)&(c) C 1s spectra measuring a freshly coated sample, and a sample that's 10 months old respectively.

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The surface chemistry of 2-butanol on Au , Cu and AuCu single crystal surfaces. Alternative sources of atomic H for “hydrogen free” hydrogenation reactions.

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Supported gold is a highly selective catalyst for the hydrogenation of alcohols, however it is very poor at promoting the dissociation of molecular hydrogen; in turn this severely limits the achievable reaction rate of hydrogenation reactions and leads to the requirement for high pressures of H₂. [1] An alternative approach is to use “hydrogen-free” hydrogenation whereby atomic hydrogen is generated in situ by the dehydrogenation of an alcohol. [2] In this project, we are interested in the coupled reaction of 2-butanol dehydrogenation and furfural hydrogenation. Furfural can be derived from corn husk making it a renewable feedstock. The desired product, furfuryl alcohol is an important feedstock in the production of rubber resins and glues. [3]

The Cu/Au system has been shown to be effective for this coupled reaction demonstrating excellent selectivity for the formation of furfuryl alcohol, as well as greater activity when compared to a supported Au catalyst. [4,5] The current catalyst developed by the group of MK at HWU is a physical mixture of Au/SiO₂ and Cu/CeO₂. In this system, atomic hydrogen is thought to be generated by 2-butanol dehydrogenation on the Cu component, before diffusing to the Au particles, where it is used for the hydrogenation of furfural.

In this work the surface chemistry of 2-butanol has been studied with Scanning Tunnelling Microscopy (STM), Thermal Desorption Spectroscopy (TDS) and High Resolution Electron Energy Loss Spectroscopy (HREELS) on Au(111) and Cu(111) as well as ultrathin Cu films on Au(111). Finally, adsorption was studied on a Cu₅₀Au₅₀ surface alloy prepared on Au(111). This is the first instance of this surface alloy being synthesised. [6] The implications of our work for understanding the catalytic system are discussed.

[1] A. Stephen and K. Hashmi, *Angew. Chemie - Int. Ed.*, 2005, 44, 6990–6993.

[2] M. Li, Y. Hao, F. Cárdenas-Lizana, H. H. P. Yiu and M. A. Keane, *Top. Catal.*, 2015, 58, 149–158.

[3] Z. Guo, B. Liu, Q. Zhang, W. Deng, Y. Wang and Y. Yang, *Chem. Soc. Rev.*, 2014, 43, 3480–

- [4] M. Li, Y. Hao, F. Cárdenas-Lizana and M. A. Keane, *Catal. Commun.*, 2015, 69, 119–122.
- [5] M. A. Keane, M. Li, L. Collado and F. Cárdenas-Lizana, *React. Kinet. Mech. Catal.*, 2018, 125, 25–36.
- [6] F. Grillo, R. Megginson, J. Christie, S. M. Francis, N. V. Richardson and C. J. Baddeley, *e-Journal Surf. Sci. Nanotechnol.*, 2018, 16, 163–171.

High intensity electrospray source for UHV deposition of large functional molecules for in-situ STM studies

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Electrospray ionisation beam deposition (ESI-BD) is quickly becoming a versatile technique for depositing large thermally labile molecules for study on surfaces in vacuum. The technique has been used to demonstrate deposition and study of a wide range of molecules such as molecular magnets, biomolecules, and porphyrin nanorings. A new ESI-BD instrument will be presented, which has been designed for high efficiency and high transmission, coupled with a variable temperature Scanning Tunnelling Microscope (STM), that offers the ability to study complex systems with the ultimate spatial resolution. Molecules are delivered from solution in atmospheric conditions to a sample surface located in ultrahigh vacuum (UHV), by electrospray ionisation, followed by several ion optic elements that guide and mass-select ions through successive differential pumping chambers with high transmission. By adjusting deposition voltage it is also possible to adjust the molecule impact energy, from the soft landing to the ballistic impact regime. STM images and analysis of a selection of large molecules will be presented, demonstrating the capabilities of this scientific instrument for nanoscale molecular visualisation.

Thin film growth of pentacene (Pn) on the two-fold surface of the icosahedral Ag-In-Yb quasicrystal

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Quasicrystals are intermetallic alloys which exhibit long-range order but lack periodicity. The structure of the i-Cd-Yb material can be modelled using to a larger rhombic triacontahedron, or RTH cluster. The two-fold surface of an icosahedral (i)-Ag-In-Yb quasicrystal has been used as a substrate to study the adsorption pentacene molecules.

The results of previous study of deposition of Pn on five-fold (i)-Ag-In-Yb gives quasicrystalline overlayer. In that study, Pn molecules were found to selectively adsorb on Yb sites.[1] Therefore, in this study, we have investigated if Pn molecules can form a quasicrystalline line overlayer on the two-fold surface. In addition, we have checked the hypothesis of Pn molecules adsorbing on Yb atoms.

Scanning Tunnelling Microscopy (STM) indicates that Pn molecules form a multilayer on the clean surface. The molecules are arranged in rows, which reflect the zigzag structure, which is a feature of two fold Ag-In-Yb.[2] The distance between two rows either a short (0.86 nm) or long one (1.43nm). The ratio between them is 1.66... which is close to the golden mean. The rows order follows a Fibonacci sequence. Also, there are three possible directions of Pn molecules -20° , 40° , and 20° . The two main directions correspond to two five-fold symmetry axis of the RTH cluster.

In summary, Pn molecules deposited on the two-fold i-Ag-In-Yb appear to form a quasicrystalline thin film. In addition. The main orientations of Pn molecules correspond to two five-fold symmetry axes of the RTH cluster. Further work is needed to firm up these conclusions.

[1] JA Smerdon, KM Young, M Lowe, SS Hars, TP Yadav, D Hesp, VR Dhanak, AP Tsai, HR Sharma, and R McGrath. Templated quasicrystalline molecular ordering. Nano letters, 14(3):1184-1189, 2014.

[2] C Cui, PJ Nugent, M Shimoda, Julian Ledieu, Vincent Fourn'ee, AP Tsai, R McGrath, and HR Sharma. Structure of the twofold surface of the icosahedral Ag-In-Yb quasicrystal. Journal of Physics: Condensed Matter, 26(1):015001, 2013.

P17

Quasicrystalline overlayers with crystallographic orders of rotational symmetry

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Quasicrystals (QCs) are a class of materials with non-periodic long-range order [1]. They have been discovered in a range of phases including colloids, perovskites, and intermetallic alloys [2]. These phases exhibit ‘unusual’ orders of rotational symmetry, i.e. rotational symmetries which are not permitted by conventional crystallography, such as 5-fold, 10-fold, and 12-fold. Here, we present a series of QC substrate-adsorbate systems that display ‘allowed’ orders of rotational symmetry yet retain quasicrystalline structure.

First, the two-fold surface of an icosahedral Al-Pd-Mn QC has been used to grow a quasicrystalline molecular film of C₆₀. The C₆₀ molecules form a Fibonacci square grid – a structure which is quasicrystalline yet has 4-fold rotational symmetry [3]. This is the first unfabricated (i.e. natural) example of the Fibonacci square grid. Scanning Tunnelling Microscopy (STM) and Low Energy Electron Diffraction (LEED) are used to compare a structural model of the clean surface, whilst STM is used to uncover the C₆₀ ordering, Figure 1. The refined model structure predicts a network of Mn atoms that form a Fibonacci square grid. The C₆₀ molecules adsorb exclusively at this network [4].

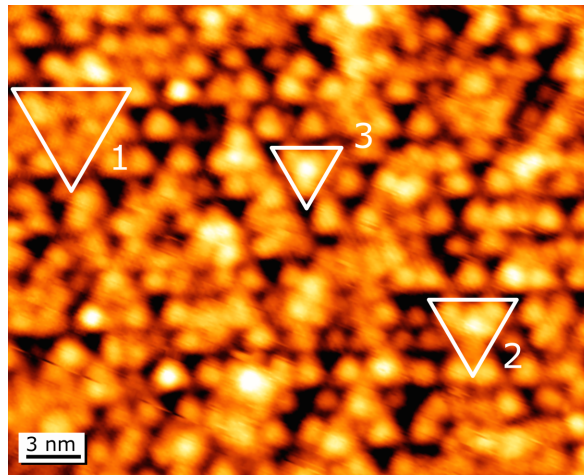
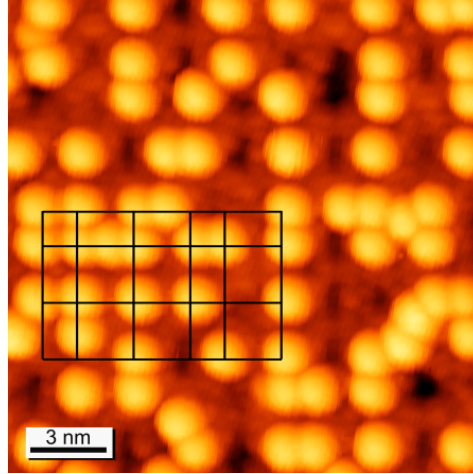


Figure 1: STM image of C_{60} forming a Fibonacci square grid at the 2-fold AlPdMn surface. Figure 2: STM image of Pb on 3-fold AgInYb. Highlighted are 4 τ -scaled motifs, where $1 = 2 \cdot \tau$, $2 = 3 \cdot \tau$ etc.

Second, the 3-fold surface of the Ag-In-Yb system has been used to grow 3-dimensional quasicrystalline nano-structures of Pb. This is to directly compare with previous work in the group, in which we explored the growth mode of Pb on the 5-fold Ag-In-Yb surface [5]. There, Pb grows in QC multi-layers, with each layer's structure dependent on vacant sites of rhombic-triacontahedron (Tsai-type [6]) clusters which are created by surface truncation. The 3-fold surface was investigated to ascertain whether this was a phenomenon unique to the 5-fold orientation. Using STM, we find that Pb does indeed grow on the 3-fold termination in the same fashion, yet not in a layer-by-layer manner. The first layer of Pb is dense and completed before the second layer starts to grow, Figure 2. However, the second and third layer appear to grow almost simultaneously, in a quasi-island-growth manner, resulting in sparse triangular nano-structures.

- [1] D. Shechtman, I. Blech, D. Gratias, J. W. Cahn, *Phys. Rev. Lett.*, **53**, (1984), 1951.
- [2] S. Förster, K. Meinel, R. Hammer, M. Trautmann, W. Widdra, *Nature.*, **503**, (2013), 215.
- [3] R. Lifshitz, *Journal of alloys and compounds.*, **342**, (2002), 186.
- [4] S. Coates, J. A. Smerdon, R. McGrath, H. R. Sharma, *Under review for publication*.
- [5] H. R. Sharma, K. Nozawa, J. A. Smerdon, P. J. Nugent, I. McLeod, V. R. Dhanak, M. Shimoda, Y. Ishii, A. P. Tsai, R. McGrath, *Nat. Comms.*, **2715**, (2013).
- [6] H. Takakura, C. P. Gomez, A. Yamamoto, M. De Boissieu, A. P. Tsai, *Nat. Mat.*, **6**, (2007), 58.

Growth of C₆₀ on the 2-fold Surface of the *i*-Ag-In-Yb Quasicrystal

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Since Shechtman's discovery of quasicrystals in 1982,[1] a range of stable quasicrystals displaying icosahedral symmetry have been discovered. One example is *i*-Ag-In-Yb, which is isostructural to binary *i*-Cd-Yb - a quasicrystal whose structure is unambiguously known.[2] This structure involves an aperiodic arrangement of rhombic triacontahedral (RTH) clusters, separated by rhombohedral 'glue' units. These RTH clusters consist of five successive atomic shells. The *i*-Cd-Yb system has been utilised to describe structural features at the high symmetry surfaces of *i*-Ag-In-Yb as bulk planes intersecting the centres of the RTH clusters.

Atomically resolved scanning tunnelling microscopy (STM) images of the 5-fold and 3-fold surfaces of *i*-Ag-In-Yb show features which can be explained by truncated *i*-Cd-Yb clusters.[3-4] However, in previous investigations, atomic resolution on the 2-fold surface could not be achieved, leaving open questions regarding comparison with the bulk structure model.[5] Here, new STM images of the clean twofold *i*-AgInYb surface are presented. These results suggest a major contribution from the 4th Cd shell.

Also discussed here are the preliminary results of an epitaxial investigation involving the deposition of fullerene molecules (C₆₀) onto the 2-fold surface. Quasicrystalline ordering of C₆₀ molecules on a range of icosahedral Al-based has been reported previously.[6-8] Low-coverage STM images of C₆₀ on the 2-fold surface of *i*-Ag-In-Yb indicate local quasicrystalline order, where examples of τ scaled distances between adsorbed molecules is observed. At higher coverage, a 2-fold FFT is observed, taken by only considering the molecular positions. The corresponding real-space vertical row separation directly relates to clean surface observations, indicating preferential adsorption sites.

[1] D. Shechtman, I. Blech, D. Gratias, and J.W. Cahn. *Physical Review Letters*, 53(20):1951-1953, 1984.

[2] H. Takakura, C. P. Gómez, A. Yamamoto, M. De Boissieu, and A. P. Tsai. *Nature Materials*, 6(1):58-63, 2007.

[3] H. R. Sharma, M. Shimoda, K. Sagisaka, H. Takakura, J. A. Smerdon, P. J. Nugent, R. McGrath, D. Fujita, S. Ohhashi, and A. P. Tsai. *Physical Review B*, 80(12), 2009.

[4] C. Cui, P. J. Nugent, M. Shimoda, J. Ledieu, V. Fournee, A. P. Tsai, R. McGrath, and H. R. Sharma. *Journal of Physics-Condensed Matter*, 24(44), 2012.

- [5] C. Cui, P. J. Nugent, M. Shimoda, J. Ledieu, V. Fournee, A. P. Tsai, R. McGrath, and H. R. Sharma. *Journal of Physics-Condensed Matter*, 26(1), 2014.
- [6] J. A. Smerdon, K. M. Young, M. Lowe, S. S. Hars, T. P. Yadav, D. Hesp, V. R. Dhanak, A. P. Tsai, H. R. Sharma, R. McGrath. *Nano Letters*, 14(3), 2014.
- [7] V.Fournée, É. Gaudry, J. Ledieu, M. C. de Weerd, D. Wu, T. Lograsso. *ACS Nano*, 8(4), 2014.
- [8] S. Coates, J. A. Smerdon, R. McGrath, H. R. Sharma. *Nature Communications*, 9(5), 2018.

Smart switchable biological surfaces for on-demand biosensing

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Advances in biology research and clinical diagnosis require new biological inspired tools and technology platforms to measure, understand and control biological systems.[1] Surface confined self assembled monolayers (SAMs) of electroswitchable peptides have the capacity to regulate biomolecular interactions in response to an applied electrical potential.[2-4] This study aims to understand the organization of charged peptides together with nanobody [5] molecules (NbVCAM1) on a gold surface, in order to devise switchable surfaces with the capability to control the activity of NbVCAM1 binding to the human vascular cell adhesion hVCAM1, a molecule that attracts inflammatory cells, having an important role in the initiation of atherosclerosis.[6-8]

Contact Angle, Ellipsometry and X-ray Photon Spectroscopy (XPS) techniques have been used to characterize the surfaces with SAMs of charged peptides, namely, oligolysines, Cys-Lys(ϵ -Lys)₄ (C5K) or Cys-Lys(ϵ -Lys)₇ (C8K) on gold, individually or in the presence of the support molecule triethylene glycol mono-11-mercaptopundecyl ether (TEG11) and the NbVCAM1 nanobody. Results on mixed SAMs of C5K:TEG11 and C8K:TEG11 indicated the solution ratio of 40:1 as the optimal candidate for the switching studies. XPS results showed that the actual surface ratios are 1:(3 \pm 0.4) for C5K:TEG11 and 1:(3 \pm 0.2) for C8K:TEG11. Further characterization has been performed by Time-of-Flight Secondary Ion Mass Spectrometry (TOF SIMS) to demonstrate the covalent binding of the NbVCAM1 nanobody to the gold surface. Electrochemistry Surface Plasmon Resonance (E-SPR) is being used to study the switching capabilities of these SAMs that include the NbVCAM1 at the surface. SPR results confirm the binding of hVCAM1 to the surface-tethered NbVCAM1 nanobody under open circuit (OC) conditions, with an electrical potential being able to switch the binding capabilities.

[1] B. S. Gomes, B. Simões and P. M. Mendes, Nat. Rev. Chem., 2018, 2, 0120.

- [2] E. CanHni, X. Wang, P. Koelsch, J. A. Preece, J. Ma and P. M. Mendes, *Acc. Chem. Res.*, 2016, 49, 1223-1231.
- [3] M. Lashkor, F. J. Rawson, A. Stephenson-Brown, J. A. Preece and P. M. Mendes, *Chem. Commun. (Camb)*, 2014, 50, 15589-15592.
- [4] M. Lashkor, F. J. Rawson, J. A. Preece and P. M. Mendes, *Analyst*, 2014, 139, 5400-5408.
- [5] S. Muyldermans, T. Atarhouch, J. Saldanha, J. A. Barbosa and R. Hamers, *Protein Eng.*, 1994, 7, 1129-1135.
- [6] G. Bala, A. Blykers, C. Xavier, B. Descamps, A. Broisat, C. Ghezzi, D. Fagret, G. Van Camp, V. Caveliers, C. Vanhove, T. Lahoube, S. Droogmans, B. Cosyns, N. Devoogdt and S. Hernot, *Eur. Heart J. Cardiovasc. Imag.*, 2016, 17, 1001-1008.
- [7] M. I. Cybulsky, K. Iiyama, H. Li, S. Zhu, M. Chen, M. Iiyama, V. Davis, J. C. GuHerrez-Ramos, P. W. Connelly and D. S. Milstone, *J. Clin. Invest.*, 2001, 107, 1255-1262.
- [8] D. T. Ta, W. Guedens, T. Vranken, K. Vanschoenbeek, E. Steen Redeker, L. Michiels and P. Adriaenssens, *Biosens. (Basel)*, 2016, 6.