Project no. NMP4-CT-2004-013817

NanoMesh project

Nanomesh – Boron nitride Nanomesh
as a Scaffold for Nanocatalysts,
Nanomagnets and Functional Surfaces

Specific Targeted Research Project (STREP)

Priority 3 – NMP

Publishable final activity report

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Project coordinator name: Prof. Jürg Osterwalder
Project coordinator organization name: Universität Zürich, Switzerland

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1. Project execution

In the recent past substantial efforts have been devoted to define mechanisms that lead to self-assembly of regular nanostructures at surfaces, including the exploitation of regular arrays of misfit dislocations, long-range adsorbate-adsorbate interactions mediated by metallic surface states, or short-range adsorbate-adsorbate interactions based on hydrogen bonds. Very recently, a new type of self-assembly mechanism has been found in a purely inorganic system. It leads to a surprising new nanostructured material based on a layer of hexagonal boron nitride (*h*-BN) on a Rh(111) surface [1]. A highly regular mesh forms by self-assembly, with a 3.2 nm periodicity and a 2 nm hole size (Fig.1, left). In this discovery paper, a model with two layers of mesh was proposed based on scanning tunneling microscopy images and electron spectroscopy data. The two layers are offset in such a way as to expose a minimum metal surface area. The structure covers the surface uniformly after high-temperature exposure of the clean rhodium surface to borazine $(HBNH)_3$. Hole formation is likely driven by the lattice mismatch of the film and the rhodium substrate. This regular nanostructure has remarkable properties and can serve as a template to organize molecules, as is exemplified by the decoration of the mesh by C_{60} molecules (Fig.1, right).

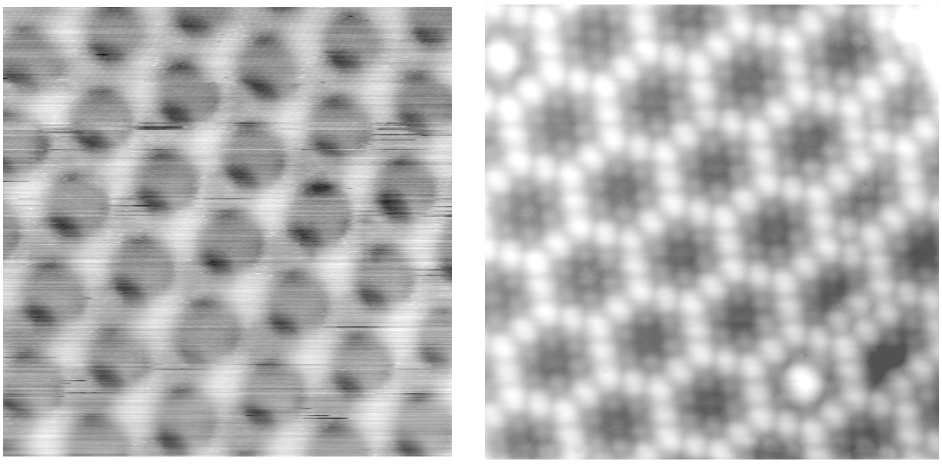

Fig. 1: *(left) Scanning tunneling microscopy image of boron nitride nanomesh formed by self-assembly on a Rh(111) surface. The mesh periodicity is 3.2 nm, the holes are 2 nm in diameter. – (right) Same nanomesh, here decorated by a monolayer of* C_{60} *molecules.*

The main objectives of the *NanoMesh* project were to understand the self-assembly processes leading to this highly interesting and non-trivial nanostructure, to find routes for controlling the mesh parameters and for mass production, and to demonstrate its prospects for future applications as a sturdy oxygen- and carbon-free template for the production of nanocatalysts, nanomagnets and functionalized surfaces. Rather than taking a broad approach on self-assembly in general, the *NanoMesh* project thus focused on this particular *h*-BN material. It brought together leading specialists in Europe with unique expertise in synthetic chemistry as well as novel experimental and theoretical techniques to investigate the processes leading to the self-assembly of the nanomesh in situ, and to explore new combinations of chemical precursors and substrates in order to control the mesh size and shape. It also included the expertise for fabricating self-assembling hydrogen-bonded molecular networks in order to try to achieve higher hierarchies of self-assembly on top of the nanomesh, leading to regular structures that bridge the nanoscopic and the mesoscopic scale, and to demonstrate the design of functionalized surfaces for sensing and biological applications. An industrial partner has investigated the nanomeshes as potential substrates for electronic devices, specifically for spintronic and quantum computing applications.

The *NanoMesh* consortium consisted of 9 partners (8 academic and 1 industrial) from 4 EU member states and 1 associated country. The project provided the critical mass of resources and the required synthetic, experimental and theoretical expertise by including the following leading European research groups:

- **Universität Zürich**, Physik-Institut, Surface Physics Group, Zürich (Switzerland), abbrev. UZH – coordinator
- **University of Nottingham**, School of Physics and Astronomy, Nanoscience Group, Nottingham (UK), abbrev. UNOTT-PH
- **University of Nottingham**, School of Chemistry, Supramolecular Chemistry Group, Nottingham (UK), abbrev. UNOTT-CH
- **Technische Universität Wien**, Institut für Materialchemie, Computational Chemistry Group, Vienna (Austria), abbrev. TUW
- **Leiden University**, Institut of Physics, Interface Physics Group, Leiden (The Netherlands), abbrev. ULEI
- **Justus-Liebig-Universität**, Physikalisch-Chemisches Institut, Surface Chemistry and Model Catalysis Group, Giessen (Germany), abbrev. JLU
- **Universität des Saarlandes**, Anorganische Chemie, Molecular Precursors Group, Saarbrücken (Germany), abbrev. USAAR
- **Universität Augsburg**, Physik-Institut, Thin Film Growth Group, Augsburg (Germany), abbrev. UA
- **Hitachi Cambridge Laboratory**, Pre-Production Device Development Team, Cambridge (UK), abbrev. HCL

The key scientific issues of the project were efficiently tackled in three work packages, as illustrated in Fig. 2. Specifically, the self-assembly processes of the *h*-BN nanomesh were studied in situ using complementary analytical and theoretical techniques. In parallel, new paths to nanomesh synthesis were be explored, using various alternative precursors and substrates, including low-cost metallic thin films. In parallel, promising applications of the nanomesh were evaluated and partly demonstrated, centered around **nanocatalysis** and **nanomagnetism**, as well as **functional surfaces**. The size of the mesh units, as well as its ruggedness, make the nanomesh a prime candidate for a self-assembling scaffold material for future nanotechnologies. For this reason most of the consortium partners will continue working with this template surface also beyond the end of the project period with alternative funding.

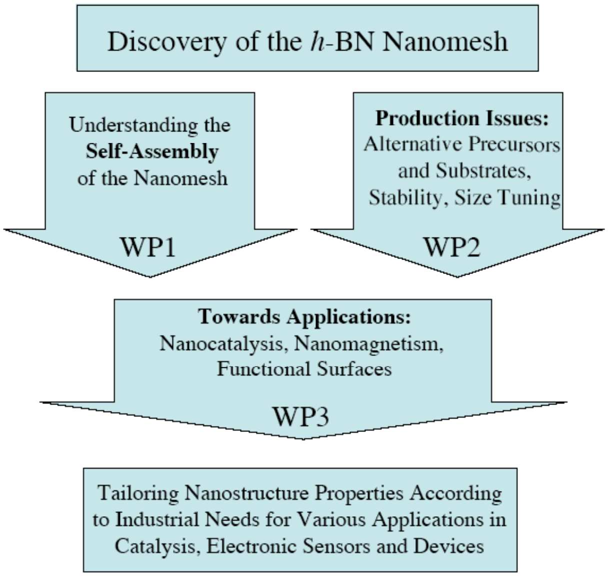

Fig. 2: *Mission and work packages of the NanoMesh project.*

The objectives of NanoMesh were addressed in a multi-disciplinary way, using state-of-the-art chemical synthesis methods for new high-purity boron nitride precursors and a variety of organic molecules for nanomesh functionalisation, highly optimized molecular-beam epitaxy (MBE) and pulsed-laser deposition (PLD) methods for thin film growth of various transition metal substrates, a wide variety of novel and standard surface science and materials science techniques, such as scanning tunneling microscopy (STM) (including a very fast high-temperature version), x-ray photoelectron spectroscopy and diffraction (XPS, XPD), angle-resolved photoemission (ARPES), surface x-ray diffraction (SXRD), low-energy electron diffraction (LEED) including also spot-profile analysis (SPA-LEED), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and finally very powerful theoretical tools such as density functional theory (DFT) and molecular dynamics simulations.

At the end of this three-year project (that had been granted a cost-neutral extension of three months) one can look back on a manifold of scientific results that provide a clear understanding of the nanomesh structure and a good understanding of the precursor decay and self-assembly mechanisms (WP1). Alternative precursors and substrates that could in principle be used for large-scale production of nanomesh films have been identified and successfully tested (WP2). The trapping functionality of the nanomesh pores for organic molecules to form vast molecular arrays has been fully established and is understood, while the functionality as a periodic template for the nucleation of monodisperse metallic clusters for catalytic or magnetic applications is less evident and needs more work (WP3). In the following paragraphs a few highlights of the project are briefly summarized.

At the outset of the project, it was believed that the structure of the h-BN nanomesh on Rh(111) consists of an atomic bilayer. After the first year we reported that alternative structures were being considered, one of which consisted of a single, buckled h-BN monolayer [2]. Detailed theoretical work [3] and further experiments [4] have definitely settled the issue in favour of the latter structure. An important element in the final proof has come from low-temperature STM observations which provide full atomic resolution over the entire unit cell and show full continuity in the atomic configuration, without steps and a phase shift at the rims of the pores as expected in the bilayer model. The DFT calculations show that the bilayer model is indeed energetically very costly compared to a strongly corrugated single layer with two distinctly different regions in the unit cell. There is a relatively sharp transition from low regions (pores) to high regions (wires), where it is the local translational position of the overlayer with respect to the Rh atoms of the substrate that determines whether the layer is locally high or low (Fig. 3). Most importantly, these calculations could also reconcile the experimentally observed splitting of the boron nitride electron energy bands with the corrugated single layer model, which was previously believed to be a strong argument for the bilayer model.

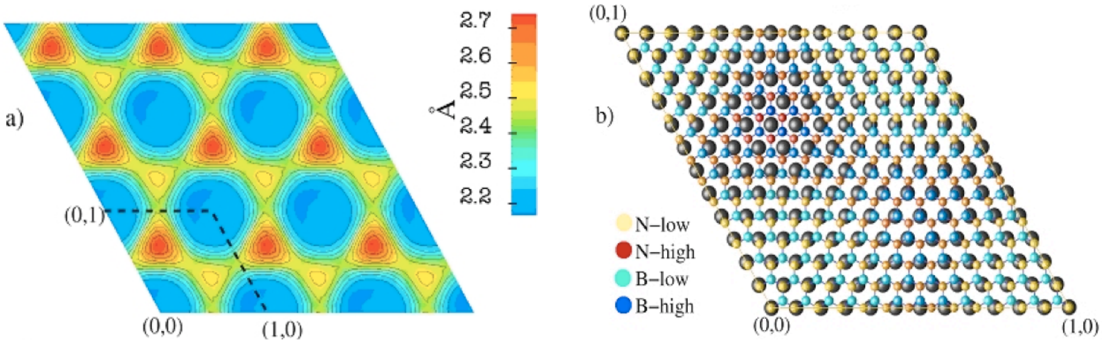

Fig. 3: *Structure of h-BN on Rh(111) surface (from TUW [3]).*

left: Map of the z coordinate of N atoms.
right: Ball and stick model including top Rh layer.

The revised structure model had pronounced consequences for several other scientific issues of this project. From the point of view of the self-assembly mechanism of the nanomesh, completely different scenarios apply for a bilayer model or a single layer model. At this stage we cannot claim to have reached a truly complete understanding of the formation of the nanomesh overlayer. Nevertheless, we have enough evidence from theory and experiment to propose a simple scenario. The combination of DFT calculations and STM observations suggests that intact borazine molecules can readily adsorb on the Rh(111) surface, even at room temperature. When these molecules 'meet', they can form B-N bonds between them, while releasing hydrogen. In principle, the entire *h*-BN overlayer can be formed in this way. However, for an optimally ordered overlayer with a large coherence length, a high two-dimensional mobility is a prerequisite. It is this high mobility that is provided by the high temperature, which forms an essential element in the optimized 'recipe' for the deposition of a well-ordered nanomesh overlayer on Rh(111) and other surfaces. The formation of the nanomesh structure proceeds via a nucleation-and-growth mechanism, in which the BN-density is locally maximized. For illustration the STM image of Fig. 4 shows a Rh(111) surface partially covered by nanomesh islands surrounded by regions of unresolved structure and composition. This sample was obtained by exposing a Rh(111) surface to borazine while kept at room temperature and subsequent annealing at 1100K. Under normal deposition conditions, i.e. at high temperature, the continued borazine supply serves to fill the entire surface with this preferred, high-density nanomesh structure.

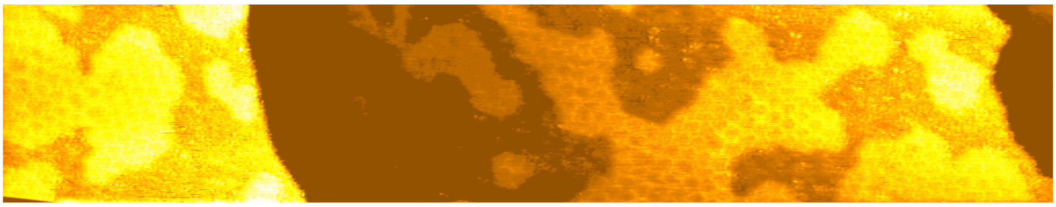

Fig. 4: *STM image (200 nm x 38 nm) of the Rh(111) surface, after a 30 s flash to 1100 K, following a room-temperature exposure to 60 L of borazine. Ordered nanomesh patches are visible. The regions in between display a disordered, lower-density overlayer (from ULEI).*

From our search for alternative precursor molecules for the formation of the h-BN nanomesh, it appears that the formation of complete and well ordered boron nitride layers is favoured by molecules that contain the $(BN)_3$-ring unit like borazine, trichloroborazine or trimethylborazine, and borazine has still remained the precursor of choice within the consortium. This is due to the fact that the purity of the material could be improved way beyond what is commercially available, and because it could always be supplied in sufficient quantities. Moreover, it produced the most perfect films of reproducible quality, aided also by a Peltier-cooled glass vial device for borazine evaporation that is currently commercialized by one of the partner groups. However, a surprising nanomesh reformation process could be established that suggests that an alternative pathway to nanomesh formation may exist, completely different from high-temperature exposure to borazine-like molecules. As illustrated in Fig. 5, a well ordered nanomesh sample is transformed into a disordered boron-oxide film by exposure to oxygen gas at low pressure and moderate temperatures. Exposure of this phase to ammonia and subsequent annealing appears to reform at least part of the original nanomesh structure and composition, as indicated by the reappearance of the superstructure spots in LEED (left panel of Fig. 5) and the partial recovery of the nitrogen and boron XPS signals at the correct binding energies (three colored panels in Fig. 5).

The steady supply of single-crystal Rh(111) or Ru(0001) films has been a prerequisite for enabling several surface science groups in the consortium to carry out a large number of different experiments with nanomesh samples, that would have been too costly (in time and money) when using commercial single crystals. Within the first year already, nanomesh samples could be prepared on Rh(111) films that were grown on sapphire (0001) platelets.

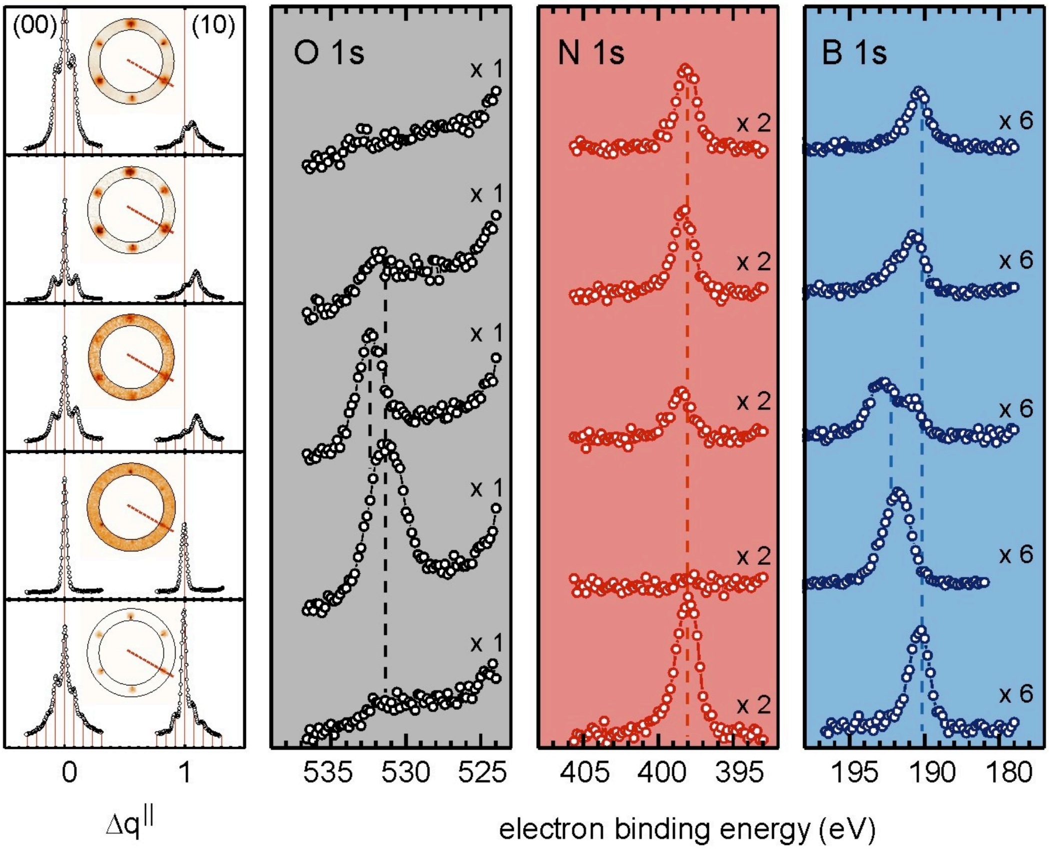

Fig. 5: *Intensity plots of the LEED profiles along two different directions and XPS data of the reaction sequence (O1s, N1s, and B1s detail spectra)*
bottom to top: step 1 to 5 as described in the text:

1) *BN nanomesh prepared by CVD of borazine*
2) *Oxidation of the BN film and formation of an unstructured boron-oxygen film*
3) *Addition of ammonia: beginning of the BN reformation, XPS indicate the presence of B-N-O-(H)- on the surface*
4) *Further addition of ammonia. Oxygen content is decreased, BN formation visible in LEED profile*
5) *Annealing of the film leads to full elimination of oxygen and reformation of the original BN superstructure*

These first films contained twin crystal orientations. In the second year, first samples were grown on metal films grown on Si(111) with intermediate YSZ oxide buffer layer. The third year brought an optimization of such Si(111) supported films on 4” wafers, with no twins, and with a uniform crystallinity and thickness as illustrated in Fig. 6. This result constitutes a first step, and maybe the most difficult step, towards the large-scale production of nanomesh films. A last missing step would be to design a dedicated vacuum chamber with a wafer heating stage and a borazine inlet. Unfortunately, this last step had not been within the scope of the project (financially and timewise), and the production of nanomesh covered film samples proved to be the time-limiting factor for many applications-oriented studies within the consortium, especially for the industrial partner. The preparation of each sample occupies the non-dedicated UHV chamber in one of the surface science partner laboratory for one full day and requires about half a work day of a well trained person. On the other hand, the nanomesh, once prepared, proved to be remarkably stable, both in air and even in water and some organic solvents. This made convenient sample transfer between vacuum chambers possible.

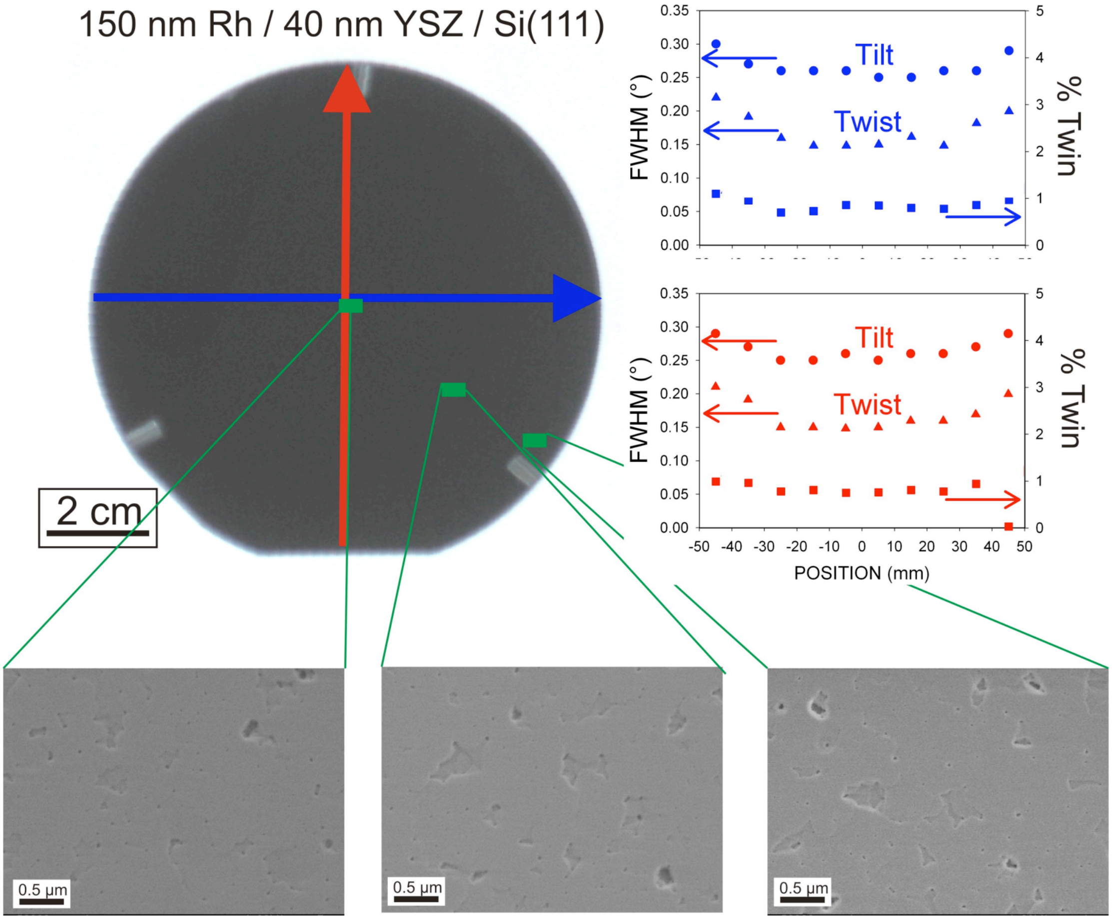

Fig. 6: *4-inch Rh/YSZ/Si(111): SEM images of the Rh surface at different positions and mosaicity values along the two indicated directions.*

In terms of chemical functionalisation, the pore edges appear in the single layer model less likely as potential sites for covalent functionalisation of the mesh, because they no longer represent steps that are maybe saturated by hydrogen. From a topographical point of view, the nanomesh is simply a corrugated layer with the pores lying some 0.6 Å closer to the Rh surface than the wire regions. One might thus wonder whether this corrugation is sufficient to produce the template functionality advertised in the proposal. It is therefore extremely important that several results obtained within the project confirm the strong templating action, especially for the trapping of molecules and partly for the formation of monodisperse cluster arrays. The efficient trapping of molecules within nanomesh pores has been demonstrated for the case of naphthalocyanine [4], a flat molecule with a diameter slightly smaller than a pore diameter (Fig. 7). This trapping is surprisingly strong, as evidenced by time-lapse series of STM images and by thermal desorption spectroscopy, and can thus be used to form vast arrays of well-separated individual molecules arranged in a hexagonal pattern.

The character of this trapping potential appeared to be quite unique and has been addressed in a study employing photoemission from adsorbed Xe atoms (PAX). In this technique the core level binding energies of Xe are sensitive to the local electrostatic potential just outside the surface, a quantity that might be termed the local work function. It was found that the nanomesh features a modulated potential energy landscape, with the pores having a potential some 300 meV lower (for negative charges) than the mesh wires. This experimental result immediately implies that the pore rims represent electric dipole rings. The conjecture is then that polarizable molecules get trapped inside the pores by dipole-dipole interaction [5].

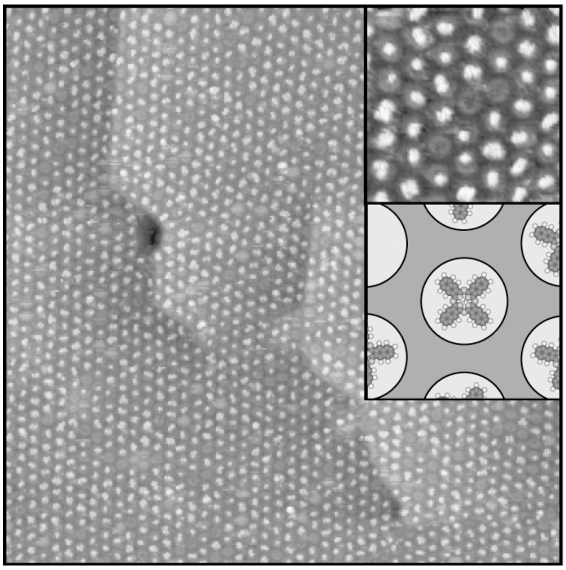

Fig. 7: *Site-selective adsorption of molecules in the nanomesh pores.*

<u>Main image</u>: STM image (120 x 120 nm^2, I = 0.3nA, U = 1.3V) showing a nearly complete monolayer [2] of Nc molecules on the nanomesh. The sample has been annealed at T = 550 K after the deposition of the molecules.

<u>Inset top</u>: high-resolution view, 19 x 19 nm^2
<u>Inset bottom</u>: schematic representation of the molecular structure of naphthalocyanine ($C_{48}H_{26}N_8$) plotted on top of a nanomesh pore.

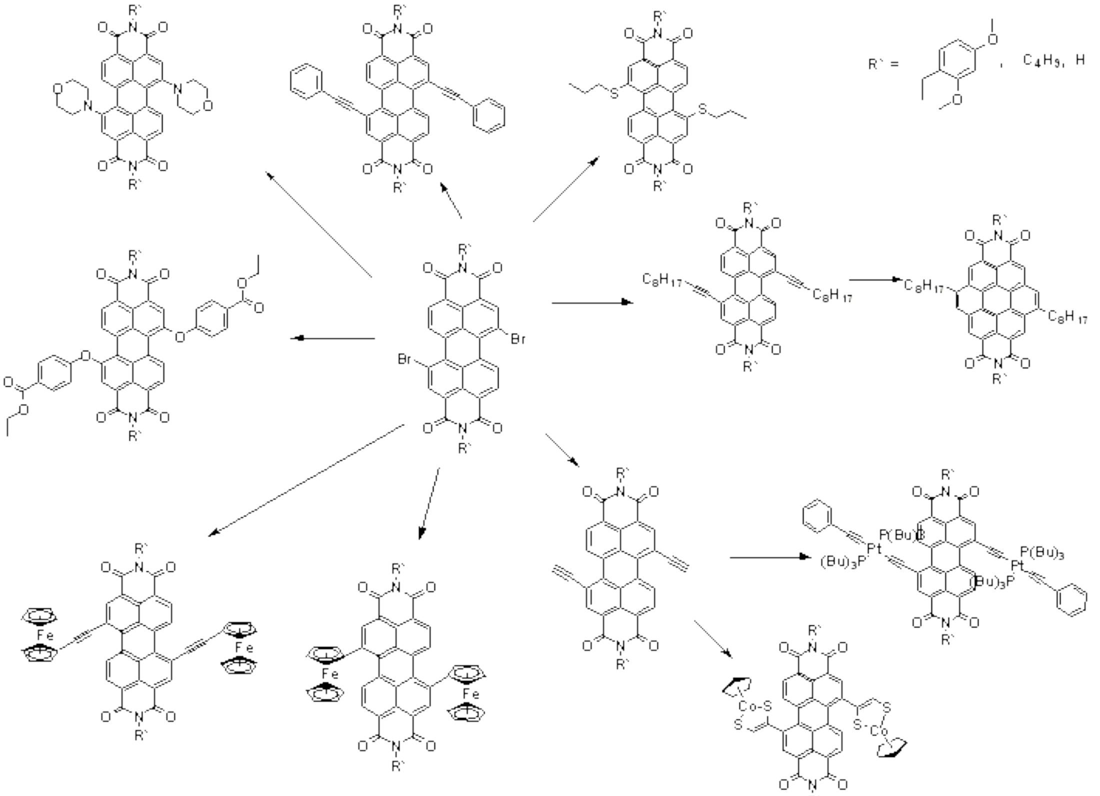

Fig. 8: *Representative examples of novel perylene based species.*

A large set of new molecules with specific functionalities, and with the ability to form supramolecular frameworks on top of the nanomesh, has been successfully synthesized. Among others, perylene based species have been targeted as such systems allow the introduction of chemical functionality as well as photoactive and redox active moieties. A range of molecules with a variety of chemical functionality and physical, electrochemical and optical properties are displayed in Fig. 8. It became apparent in the course of the project that there was a considerable “impedance mismatch” between the productivity of the synthetic chemistry groups and the time scale over which a careful adsorption study of such molecules on nanomeshes by cumbersome surface science techniques could be carried out. At the end of the project only a small subset of these molecules has actually been used in a study of supramolecular self-assembly, while most of them remain in the pipeline for further experiments to be carried out beyond the end of the project period.

Attempts have been made to replicate the formation of the hydrogen-bonded bimolecular perylene-3,4,9,10-tetracarboxylic diimide (PTCDI) - melamine network, previously demonstrated on an Ag terminated Si(111) surface, on the nanomesh [6]. Due to operational issues the nanomesh sample was transferred through air to a system where melamine was available for this experiment. The apparent influence of melamine, bonding PTCDI molecules into trimers, is visible on the right hand side of Fig. 9, where some trimer structures seem to be centered on nanomesh wires. On the left hand side of the same image, an island of hydrogen-bonded molecules can be recognized, with a periodicity similar to that of the underlying nanomesh. Attempts to prepare more extended hydrogen-bonded arrays, as observed on other surfaces, have not been successful. However, due to technical problems during the first two years of the projects, these studies have only just begun to be productive, and we expect considerable improvements in the order and variety of self-assembled supramolecular structures on the nanomesh, based on these types of functional molecules.

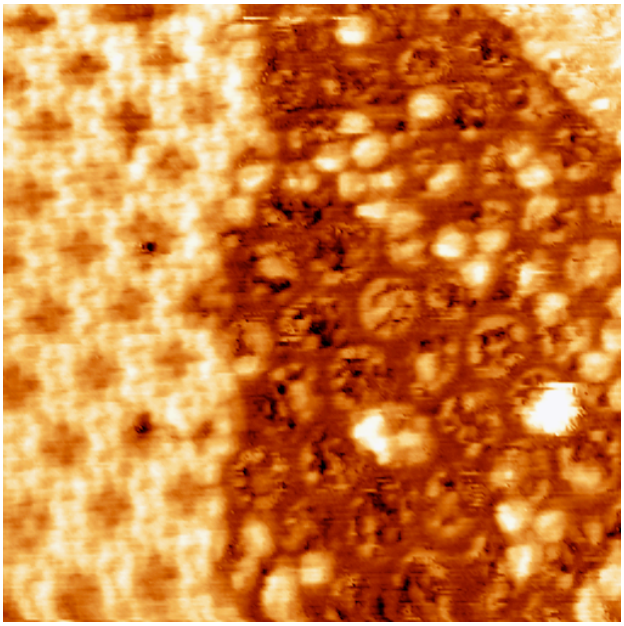

Fig. 9: *PTCDI and melamine on the nanomesh. 26 nm × 26 nm.*

The functionality of the nanomesh as an array of nucleation sites for metal cluster arrays could be demonstrated partially, but some limitations in the trapping capability for ultra-small clusters have yet to be overcome before dense periodic arrays of monodisperse clusters with diameters of about 2 nm can be produced. The STM images of Fig. 10 show, for the example of Au deposition on the nanomesh, that small clusters commensurate with the nanomesh pores are formed only at the lowest Au coverages, say 10% of a monolayer. At higher coverages, small clusters coalesce and form a conglomerate of drop-like clusters and flat islands, uninfluenced by the periodicity of the nanomesh. Similar studies with Co deposition on the nanomesh at low temperature, carried out in a lab outside the consortium, but in collaboration with one of the partners, indicated that Co atoms and even clusters up to Co_5 are still mobile at room temperature, i.e. they do not feel the nanomesh wires as a significant diffusion barrier. Therefore, additional steps have to be taken to enhance the cluster nucleation by the nanomesh pores, such as e.g. the deposition of Co via Co carbonyl molecules that deposit a critical cluster size in a single step. This approach is currently under investigation and will be pursued beyond the end of the project period.

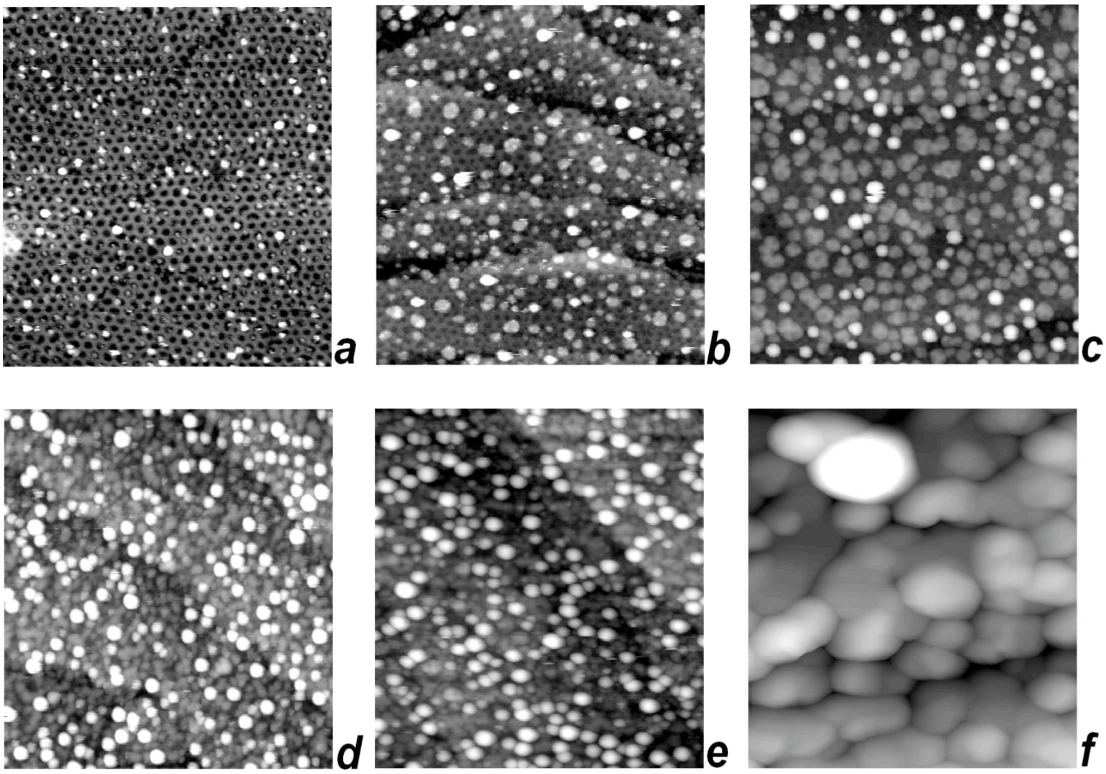

***Fig. 10**: STM images 86 nm × 86 nm of RT grown Au films on h-BN/Ru(0001): a) Au coverage Θ_{Au} = 0.1 ML, U_{sample} = 1.15 V, $I_{tunneling}$ = 0.6 nA; (b) 0.2 ML, 1.4 V, 1 pA; c) 0.3 ML, 1.0 V, 0.5 nA; d) 0.5 ML, -1.05 V, 5.5 nA; e) 1 ML, 2.0 V, 1 nA; f) 14 ML, -1.8 V, 1 nA.*

Unfortunately, attempts towards direct nanomesh-based electronic device applications by the industrial partner have been unfruitful. No viable concept for transferring the mesh periodicity to a semiconductor substrate could be found. The main problem arises due to the fairly thick Rh layer needed to grow the nanomesh, which is incompatible with any established device technology. Nevertheless, the extraordinary stability of the nanomesh in application-friendly environments (ambient, water, organic solvents) that was demonstrated in this project has generated interest in other application sectors not anticipated at the beginning of the proposal. Funding is currently sought for investigating the formation of ordered molecular arrays, and functional surfaces resulting from them, by simple dip coating techniques or through electrochemical means. Last but not least, boron nitride monolayers, and in particular the nanomesh, may become an important functional element in graphene-based technologies, as insulating layers of ultimate thinness and atomic definition, due to there near-perfect lattice match and related bonding properties.

References

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2. Dissemination and use

The dissemination of the results from the NanoMesh project has been continuously stepped up over the project period. Numerous presentations have been given at various national and international conferences, either as invited talks, contributed talks or posters, and a number of scientific papers have been published in or submitted to international peer-reviewed journals. Several are still in preparation. The NanoMesh Workshop held in Braunwald, Switzerland, from September 17-20, 2006, attracted a total of 52 scientists and brought lively discussions of these results and a series of talks on potentially relevant topics for future nanomesh applications (see http://www.nanomesh.ch/workshop). It represented a major dissemination event and was definitely a highlight of the project. The nanomesh as a highly interesting template surface has become well known within the nanoscience and surface science communities through this project. Further research involving the nanomesh will be pursued by some partners and by other international research groups, therefore the dissemination of the NanoMesh results will continue in the future. Finally, a “nanomesh” entry has been made in Wikipedia in order to share the knowledge also with the general public.