

@nanonewsletter

No. 26 /// December 2012

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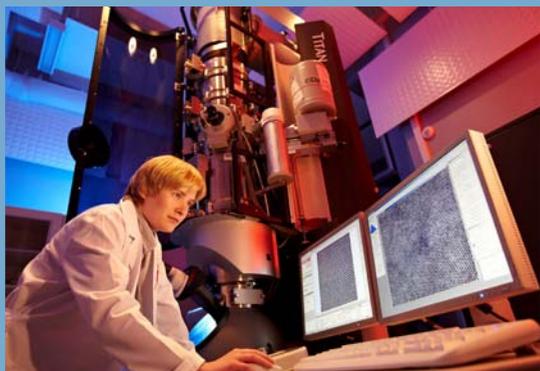


- * Single bond mechanochemistry at Silicon surfaces
- * Ethane bridged Zn-Porphyrin dimmers for tert-butylamine detection using magneto-optic surface plasmon resonance gas sensing
- * Preparation of complexes of Tobacco mosaic virus and magnetic nanoparticles and investigation of their behavior in an oscillating magnetic field

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dear readers,

Dear Readers,

Merry Christmas & Happy New Year 2013 from all the Phantoms Foundation team.



The AtMol Integrated Project (EU/ICT/FET) will establish comprehensive process flow for fabricating a molecular chip, i.e. a molecular processing unit comprising a single molecule connected to external mesoscopic electrodes with atomic scale precision and preserving the integrity of the gates down to the atomic level after the encapsulation. This E-nano Newsletter issue contains an article providing new insights on single bond mechanochemistry at silicon surfaces.

In 2011, the nanoICT project (EU/ICT/FET Coordination Action) launched its second call for exchange visits for PhD students and research personnel. The first outcome reports were published in issues 22, 23 & 25 and this edition contains two new articles providing insights in relevant fields for nanoICT.

On the scientific policy side, several Campus of International Excellence have been launched recently in Spain to promote research & technology transfer, new educational programs, etc. In this newsletter, the strategic goals of the Campus of International Excellence - CEI Euskampus - are described in detail.

We would like to thank all the authors who contributed to this issue as well as the European Commission for the financial support (ICT/FET FP7 AtMol No. 270028).

> **Dr. Antonio Correia** Editor - Phantoms Foundation

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Issue No. 27: January 31, 2013

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Direct 4-contact nanoprobing of an Au-capped Ni/NiO nanowire



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A. Sweetman¹, S. Jarvis¹, A. Stannard¹,
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1. Single atom extraction

The primary objective of the four year, eleven partner Atomic Scale and Single Molecule Logic Gate Technologies (AtMol) ICT project – namely, the fabrication of a molecular chip whose logic functions are derived from a *single* molecule – necessitates the imaging and control of matter at the single atom and single molecule levels [1]. Since the pioneering experiments of Don Eigler and his colleagues at IBM Almaden over twenty years ago [2], the scanning tunnelling microscope (STM) has been used to selectively position and modify individual adsorbates on a variety of substrates. Arguably the most elegant example of STM manipulation in recent years has been the assembly, and subsequent finely tuned distortion, of an artificial graphene lattice formed by CO molecules on a Cu(111) surface [3]. In a ground-breaking demonstration of the capabilities of state-of-the-art STM, Manoharan and co-workers used the tip of the tunnelling microscope to produce the precise amount of lattice distortion required to mimic the presence of very high magnetic fields (up to 60 T).

Manipulation modes other than lateral displacement of adsorbates are also, of course, possible. Earlier this year, and

building on their previous work on the electronic transport properties of atomic wires, Simmons and co-workers reported the fabrication of a single atom transistor [4]. This work is of particular relevance to the AtMol project as it exploited the hydrogen depassivation technique pioneered by Lyding et al. in the mid-nineties [5] to fabricate the devices with atomic scale precision. As reported in the previous eNano Newsletter (#25), the AtMol consortium, through the efforts of Marek Szymonski's research group at Jagiellonian University in Krakow, has fabricated pre-defined patterns of single dangling bonds (DBs) on the hydrogen-passivated Ge(100) surface via this H-desorption process (which is driven by vibrational heating arising from inelastic scattering of tunnelling electrons.)

Although the same fundamental patterning tool as that employed by Simmons et al. was used to generate the DB patterns on H:Ge(100) - i.e. extraction of H atoms using the tip of an STM - the strategy for device design and implementation differs dramatically. A concept at the core of the AtMol project is the quantum Hamiltonian computing (QHC) approach pioneered by Joachim et al. [6]¹. This represents a radically different and entirely non-classical approach to carrying out logic operations at the atomic or molecule scale where the logic operation is embedded in the Hamiltonian describing the electronic properties of a molecule or pattern of DBs (which, depending on the degree of

¹ QHC is not to be confused with quantum computing. In the QHC approach phase evolution on the time scale of the processing is not exploited and so decoherence is not an issue.

coupling between the bonds, can be thought of as a large ‘molecule’).

2. Mechanical atom manipulation

STM is of course not the only scanning probe technique available for precise control of atoms and molecules at surfaces. There has been a very rapid growth of interest in non-contact atomic force microscopy (NC-AFM) of late, due both to the introduction of the qPlus sensor geometry by Franz Giessibl (University of Regensburg) and a variety of exciting experiments which have not only demonstrated that extremely high resolution is possible using the technique [7] but that the force required to laterally displace single adsorbed atoms can be determined [8]. (“Non-contact” AFM is perhaps something of a misnomer as an increasing number of experiments are carried out in the Pauli exclusion regime of the tip-sample interaction potential, where the tip-sample separation is below the equilibrium bond length for the interacting atoms. “Dynamic force microscopy” is perhaps a more apt description. Nonetheless, the NC-AFM moniker is widely used and so, in the interests of consistency, will also be employed here).

We have recently shown [9] that the qPlus variant of NC-AFM can be used to controllably switch silicon dimers at the Si(100) surface between two stable (buckled) states, using mechanical force alone to modify the intradimer bond angle (see Fig. 1). This type of force-driven manipulation of single bonds bears many of the hallmarks of the mechanochemistry strategy proposed by Drexler a couple of decades ago [10], for which he was subsequently heavily criticised. Today, however, mechanochemistry is a nascent sub-field of scanning probe microscopy - and, more broadly, nanoscience - and within the AtMol consortium it is actively being pursued as a means to manipulate

surfaces and adsorbates which complements, and in principle has the potential to supersede, the tunnel current/field driven approaches generally used in STM manipulation.

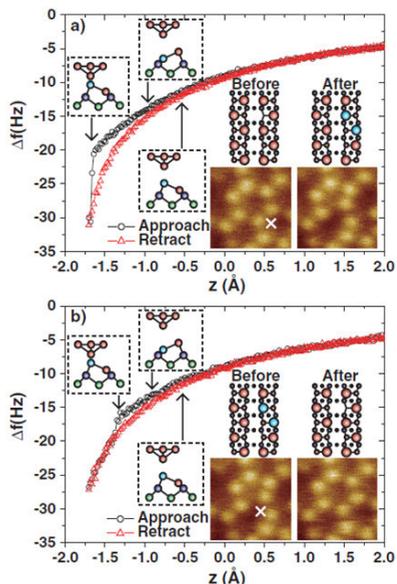


Fig. 1 > Flipping silicon dimers using chemomechanical force alone. Examples of dimer flipping showing frequency shift vs tip-sample separation curves (and corresponding before and after NC-AFM images) for (a) the creation, and (b) the removal (lower) of a two-phason state. Taken from Ref. 9./

As with any scanning probe technique, the tip state plays a crucial role in image formation, spectroscopy, and manipulation. In NC-AFM, however, the physicochemical properties and the geometry of the tip are significantly more influential than in STM due to the mixture of short-range (chemical) and long-range (van der Waals, electrostatic) forces which underpins any NC-AFM experiment. Gaining control over tip structure is therefore essential in order to understand not only the physics of image formation but to exploit the highly local nature of the

probe-sample interaction for atomic and molecular manipulation.

3. Probing the probe

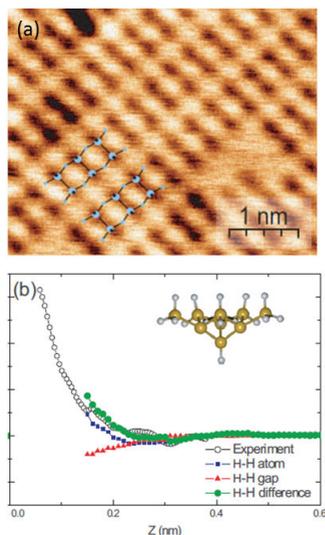


Fig. 2 > (a) A non-contact atomic force microscope image of the H:Si(100) surface taken with a qPlus sensor. The contrast is inverted such that the dark features in the image are associated with the H atoms passivating the silicon dimers. (b) A comparison of experimental and theoretical force-distance curves. Best agreement is reached when a H-passivated tip is used for the theoretical simulations. Taken from Ref. 11./

Given that, as described above, depassivation of Si(100) via hydrogen atom removal using an STM tip plays a central role in the AtMol project, we have recently focused both experimentally and theoretically on the interaction of NC-AFM tips with the H:Si(100) surface. Fig. 2(a) is a constant frequency shift NC-AFM image of H:Si(100)-(2x1) where the minima (i.e. dark spots) in the image correspond to the positions of the hydrogen atoms (see the ball-and-stick model in the inset) [11]. Thus, the image contrast is inverted compared to that we

might expect. A comparison, Fig. 2(b), of experimentally measured force-distance curves with their theoretical counterparts calculated using density functional theory (DFT) shows that the contrast inversion arises from the termination of the tip with hydrogen, resulting in a passivated, non-reactive apex. We stress that image inversion of this type is extremely common in our NC-AFM measurements of H:Si(100), most likely due to the (reactive) silicon termination of our tips [9] promoting a transfer of H from the surface to the probe. For more detailed information on the experimental and theoretical protocols please see Refs. 12 and 15. Similar regular observations of image contrast have been made by Such et al. during NC-AFM of hydrogen-passivated Ge(100) [12].

There then arises the question of the influence of the hydrogen termination of the probe on not just its imaging characteristics but on its propensity for atomic manipulation. More specifically, is hydrogen extraction from H:Si(100) possible using a H-passivated tip? If not, which particular type of tip apex is required in order to extract (or deposit) a hydrogen atom? We have addressed these questions using a series of DFT calculations involving two ‘archetypal’ H-terminated tip geometries which were studied in terms of their ability to transfer a H atom to a Si(100)-c(4x2) surface (Fig. 3 and Ref. 13). The key message resulting from these calculations is that even relatively minor modifications in the structure of the tip apex can have a major influence on the ability of NC-AFM to modify a surface at the atomic level.

With a tip apex which adopts a (111)-like symmetry, i.e. the terminating atom is back-bonded to three nearest neighbours in a so-called H₃ geometry (see Fig. 3), the H atom at the tip stubbornly refuses to transfer to the underlying Si(100) surface. Instead, the binding geometry of

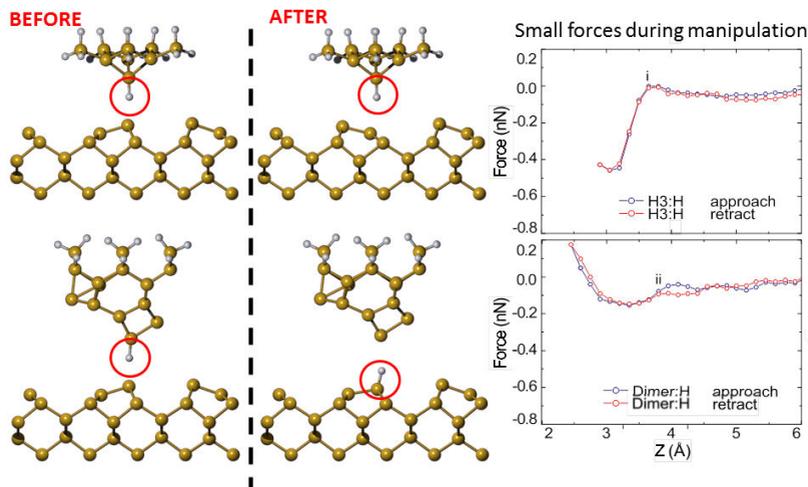


Fig. 3 > Importance of the tip apex geometry in determining which manipulation processes are possible in NC-AFM. The uppermost “before” and “after” geometries show that for a ‘H₃’-type H-terminated tip, hydrogen transfer to a Si(100)-c(4x2) surface is not possible. With a dimersized tip, however, H transfer is energetically favourable (as shown in the lowermost “before” and “after” images). The corresponding force distance curves are shown on the right. See Ref. 13 for more details./

the H atom at the tip is sufficiently stable - that is, the tip is sufficiently well-passivated - that it can be used to push (rather than pull, as is the case in Fig. 1) a silicon dimer from one buckled configuration to the other stable conformation. On the other hand, when a somewhat less rigid dimer-terminated tip is chosen, H atom transfer becomes possible. The short range chemical forces involved in the transfer are, however, remarkably small (~ 100 pN), as compared to the dimer flipping events shown in Fig. 1. Thus, a tip that gives good atomic resolution images of the H:Si(100) surface may well not be appropriate for the deposition or extraction of H - not only is an atomically sharp tip necessary but the bonding geometry of the atom terminating the apex has to be appropriate for the atomic manipulation task at hand.

4. Orienting a single molecule probe

Atomic precision mechanochemistry with NC-AFM therefore necessitates much greater control over the precise structure of the tip apex than is required for STM-actuated manipulation of atoms (which typically involves inelastic tunnelling-mediated dynamics). This begs the question as to how the structure of the tip can be monitored directly during scanning probe - and, in particular, NC-AFM - experiments. Guillaume Schull, Richard Berndt and co-workers have carried out a series of elegant experiments [14] where they have used single adatoms on metal surfaces to ascertain the orientation of a C₆₀ molecule which they have transferred to the end of an STM tip. Each adatom (and its associated atomic orbital) has a smaller effective radius of curvature than the molecule terminating the tip and so it

acts as an imaging centre, providing direct real space images of the apex of the STM probe.

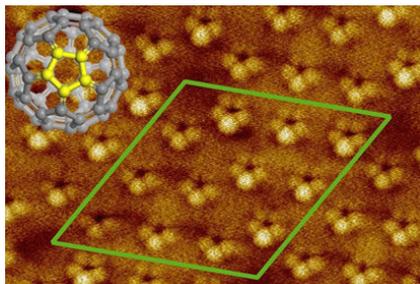


Fig. 4 > NC-AFM image of the Si(111)-(7x7) surface taken with a C₆₀-terminated tip. In this case the molecule is oriented so that a pentagonal face is facing the surface (albeit with a small tilt). Note difference in contrast between faulted and unfaulted halves of the unit cell. See Ref. 16 for more details./

We recently extended this ‘inverse imaging’ technique to NC-AFM, exploiting the dangling bond orbitals of the adatoms of the Si(111)-(7x7) surface as mini-tips (as first demonstrated by Giessibl et al. [15]) and thereby enabling atomic resolution imaging of a C₆₀ molecule terminating a qPlus sensor (Fig. 4 and Ref. 16). (Although Temirov et al. [17] have pioneered a technique they have coined scanning hydrogen tunnelling microscopy (SHTM) which enables atomic resolution imaging of the structure of adsorbed molecules, in general STM is sensitive only to molecular orbital density and therefore lacks the ability to resolve the atomic ‘framework’ of molecules).

While a variety of different molecular orientations have been resolved in our experiments, in Fig. 4 we show only an image of the ‘iconic’ pentagonal face of C₆₀. This image is noteworthy from a number of perspectives. First, the image was acquired in the attractive regime of the tip-sample interaction potential -

operation within the Pauli exclusion regime is not necessary to attain atomic resolution. This can be understood in the context of the reactive nature of the C₆₀-terminated tip with regard to the underlying Si adatoms. (Jelinek et al. [18] have similarly highlighted the central role played by tip reactivity in NC-AFM imaging of carbon nanostructures.)

Second, the precise orientation of the molecule at the end of the tip (in terms of rotation and tilt) can be determined directly from the NC-AFM image. For geometries where the molecule is adsorbed such that a double- or single-bond is facing the surface it is not possible to unequivocally distinguish between these possibilities using NC-AFM alone, for the reasons discussed in Ref. 16. In that case a comparison of the STM data with Hueckel molecular orbital calculations [19] is also required to ascertain the precise molecular orientation.

Finally, the termination of the tip with C₆₀ lends a hydrophobic functionality to the probe. This of course is of particular benefit when investigating other adsorbed molecular species as it potentially provides a route towards rudimentary chemical specificity. Of arguably more interest, however, is the possibility of terminating the probe with a molecule capable of rather more site-specific interactions such as hydrogen-bonding. This is something we are actively pursuing at the moment.

5. Automated Optimisation: Evolving the Probe

A significant amount of a scanning probe microscopist’s working time is spent coercing the tip into a state that yields atomic resolution. For NC-AFM in particular, a wide variety of different image types, each showing atomic resolution, are possible depending on the

precise structure of the apex of the probe. The same is true to a lesser extent for scanning tunnelling microscopy. Thus, not only is atomic resolution required but a very specific type/class of image is generally sought (corresponding to that where the tip is providing an accurate representation of the surface structure).

The component at the very heart of scanning probe microscopy - the probe itself - therefore represents a major bottleneck in both the imaging and manipulation processes. Over the past three years we have explored the possibility of both automating the tip preparation process and, more importantly, of establishing the possibility of 'dialling in' a particular state of the probe. In essence, our long term objective is the development of algorithms and protocols to enable the addition of two buttons to the graphical user interface of an ultrahigh vacuum scanning probe microscope controller: "Auto-Optimize Tip" and "Generate Tip State X" (where Tip State X is selected from a library of possibilities).

Our first steps towards realising these extremely challenging goals are shown in Fig. 5 (taken from Ref. 20). Here we chose the 'archetypal' tip-sample system for STM studies: a PtIr tip scanning a graphite sample. We select as a target image type either the trigonal or honeycomb structure of the graphite lattice (both types of structure are commonly observed in STM images of the highly oriented pyrolytic graphite (HOPG) surface). Our strategy for tip optimisation comprises two distinct algorithms. We first start with simple rules-based protocols very similar to those used by a human operator in deciding the quality of an STM tip. When the image quality passes a certain threshold (determined by a number of different metrics, as described in Ref. 20)

the rule-based algorithm is superseded by an evolutionary algorithm which mutates the scan parameters, compares the fitness of the image against the target, and makes a selection in parameter space based on the fitness. The gradual evolution of the fitness of the STM image is shown in Fig. 5. Note that no human operator involvement, other than the placement of the tip and sample in the microscope at the start of the experiment, was required.

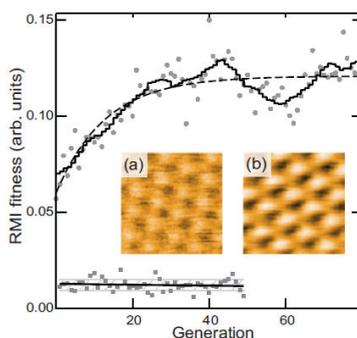


Fig. 5 > Automated probe microscopy via evolutionary strategies at the atomic scale. The figure shows the gradual increase in fitness of STM images of a graphite sample due to scan parameters selected via an evolutionary algorithm. Random selection (lower graph) produces no change in fitness. From Ref. 20./

Our future goals with regard to automated probe control include computer-controlled selection of the orientation of a tip-adsorbed molecule (such as the C_{60} molecule described in the previous section) and, of key importance for the AtMol project, the automatic generation of dangling bond patterns on H:Si(100).

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AtMol Events

Ecole de Physique des Houches AtMol Winter School

Quantum resources for single molecule-machines

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Unit 01: Back interconnects nanofabrication process

Coordinator: P2 – CEA Grenoble (France)

- Controlling on-surface polymerization by hierarchical and substrate-directed growth; *Nature Chemistry* 4, 215 (2012).
- Polymerization on stepped surfaces: Alignment of polymers and identification of catalytic sites; *Angew. Chem. Int. Ed.* 51, 5096 (2012).
- Voltage-dependent conductance of a single graphene nanoribbon; *Nature Nanotechnology* 7, 713 (2012).

Unit 2: Molecule logic gate chemistry & design

Coordinator: P1 – CEMES/CNRS (France)

- Electronic and magnetic properties of molecule-metal interfaces: Transition-metal phthalocyanines adsorbed on Ag(100); *Physical Review B* 85, 155437 (2012).
- Spin doping of individual molecules by using single atom manipulation; *Nano Letters* 12, 3609 (2012).
- Energetics and stability of dangling-bond silicon wires on H passivated Si(100); *Journal of Physics Condensed Matter* 24, 445005 (2012).
- Gold for the generation and control of fluxional barbaralyl cations; *Angew. Chem. Int. Ed.* (2012).
- Methylterylene isomers; *Tetrahedron* 68, 9371-9375 (2012).

Unit 3: LT-UHV-STM, NC-AFM atomic scale construction & simple testing

Coordinator: P6 – Fritz-Haber-Institut / Max-Planck-Gesellschaft (Germany)

- Electronic properties of STM-constructed dangling-bond dimer lines on a Ge(001)-(2×1):H surface; *Physical Review B* 86, 125307 (2012).
- Role of orbital overlap in atomic manipulation; *Physical Review B* 85, 235305 (2012).
- Identifying passivated dynamic force microscopy tips on H:Si(100); *Applied Physics Letters* 100, 233120 (2012).
- Precise orientation of a single C₆₀ molecule on the tip of a Scanning Probe Microscope; *Physical Review Letters* 108, 268302 (2012).

Unit 05: Management, dissemination and training activities

Coordinators: P1 – CEMES/CNRS (France) /

P3 – Phantoms Foundation (Spain)

- AtMol International Workshop 2012 Berlin-Germany Abstracts Book: "Imaging and manipulating molecular orbitals"
- E-Nano Newsletter 25, 5 (2012): "Towards atomic-scale logic gates construction on a Ge(001)-(2x1):H surface"
- E-Nano Newsletter 25, 12 (2012): "Hierarchical linking of individual molecules into complex structures"



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Deadline: January 20, 2013

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"Graphene nanopores for single-DNA analysis"

Contact person:

c.dekker@tudelft.nl

(Delft University of Technology, Netherlands)

Deadline: January 25, 2013

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Contact person:

appliedsciences@cranfield.ac.uk

(Cranfield University, United Kingdom)

Deadline: January 25, 2013

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(IMDEA, Spain)

Deadline: January 31, 2013

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"Optical frequency combs for optical communications"

Contact Person:

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(Chalmers University of Technology, Sweden)

Deadline: January 31, 2013

• **Postdoctoral position:**

"Synaptic Molecular Electronics"

Contact Person:

dominique.vuillaume@iemn.univ-lille1.fr

(CNRS, France)

Deadline: January 31, 2013

• **PhD position:**

"Polymer-Carbon Nanotubes Active Systems for Photovoltaics"

Contact Person:

manager-nano-bio@ehu.es

(University of the Basque Country

UPV/EHU, Spain)

Deadline: February 13, 2013

• **Postdoctoral position:**

"Femtosecond optical manipulation of antiferromagnetic materials"

Contact Person:

simon.wall@icfo.eu

(ICFO, Spain)

Deadline: February 28, 2013

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Contact Person:

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Ethane bridged Zn-Porphyrin dimmers for tert-butylamine detection using magneto-optic surface plasmon resonance gas sensing

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Abstract

Thin film of ethane bridged Zn-Porphyrin dimers is deposited via Langmuir-Schäfer (LS) technique over Au/Co/Au transducers properly realized on glass substrates. They have been tested as sensing layers in the novel Magneto-Optical Surface Plasmon Resonance (MO-SPR) sensor for monitoring the controlled adsorption of molecules of a volatile compound such as tert-butylamine vapours. The sensing performance of the organic layer onto the novel MO-SPR transducer sensor has been evaluated.

Introduction and motivation

Chemical sensors are mainly composed of two main elements: the sensing layer, interacting directly with the analyte to be detected and the transducer, necessary to convert the detection of molecules in the environment into a detectable signal. In a typical SPR sensor a metallic thin films properly deposited onto glass substrates represent the transducer,

namely the layer necessary to excite surface plasmons at the interface Au/air and to monitor the changes in the refractive index at this interface because of the changes in the resonance condition.

In fact, Surface Plasmon Polaritons (SPPs) are essentially transversal electromagnetic waves bound to a metal-insulator interface (i.e. materials with dielectric constants of opposite signs) that can be excited on thin metal films for example through gratings or prism couplers. When excited, such collective oscillations of conduction electrons create regions of enhanced electromagnetic (EM) fields in the direct proximity of the metal surface that are highly sensitive to the local changes of refractive index occurring at the surface of the thin metal film, which in turn provides a capability for a label-free form of analytical detection [1]. As a result, this technique is widespread to monitor the binding of biomolecules to the Au or Ag surface, as well as to monitor interactions between biomolecules of different nature in the nanomolar to picomolar range in real time. Applications of this technology can be found in biology, medical diagnostics, environmental monitoring and food safety [2-6].

Various approaches have been proposed to enhance the sensitivity of such technique [7-12]. Among them a MOSPR sensor, based on the interrelation of magneto-optic effects and SPR has been proposed recently [13]. This sensor is

based on the use as transducer films of multilayers of noble (such as Au [14] or Ag [15]) and ferromagnetic metals (such as Co [14,15] or Fe[16]) with magnetoplasmonic (MP) effects. As reported in literature [17,18] a great enhancement of MO Kerr signal can be recorded when the surface plasmon resonance is achieved. That enhancement strongly depends on the excitation conditions of the SPP and therefore on the refractive index of the dielectric in contact with the metal layer, thus providing the sensing principle of the MO-SPR device. This is why the MP multilayer structure combining noble metal and ferromagnets layers realized with a proper thickness, is chosen as transducing component in a MO-SPR sensor.

As gas sensing layer in this novel configuration both inorganic and organic materials deposited in thin film form can be chosen. It is worth mentioning, the reported enhancement of gas sensing capabilities for a MO-SPR sensor with respect to a standard SPR sensor using a porous TiO₂ film as sensing layer [19].

The aim of this work is to propose a novel combination of materials based on ZnPP macromolecules thin films to act as the sensing element in MO-SPR gas sensors for amine vapour detection. Amine detection is of commercial interest because of toxicity and potential health hazard in production of dyes, emulsifiers, stabilizers and corrosion inhibitors.

Porphyryns are conjugated macrocycles widely studied for gas sensing because, for their particular structure, the simultaneous presence of various interaction mechanisms is expected to take place between individual porphyryns and analyte molecules, in addition to unavoidable van der Waals forces. In particular, supramolecular assemblies of metalloporphyryns have got great

attention from the scientific community because their increased sensitivity performances when exposed to volatile molecules [20-23]. Moreover these materials can be prepared in thin film form using different chemical deposition techniques like casting, spin coating, Langmuir-Blodgett. In particular, in our case, the horizontal lifting or Langmuir-Schaefer technique (a modification of the Langmuir-Blodgett technique) was suitable to be adopted thanks to the thin film deposition methodology in which the sensing multilayers can be deposited avoiding to dip the transducer in the water.

The suitability of the proposed porphyrin for use as chemical gas sensor is investigated by analyzing the sensing performances of the proposed organic thin films in the MO-SPR sensing configuration upon exposure to different concentration of amine vapors. The results of this preliminary study will be used to guide the choice of proper analytes for the proposed sensor in view of a possible industrial application.

Experimental details

A scheme and the details of that experimental setup with test chamber for gas sensing are shown in reference [19]. Briefly, MO-SPR measurements were performed in a home-made experimental set-up using Kretschmann's prism. Surface plasmon excitation was achieved by focusing a p-polarized light beam of a He-Ne monochromatic laser source ($\lambda = 632.8$ nm) onto the prism/sample interface. The reflected light is detected by a Si photodiode. To explore the modulation of the surface plasmon wavevector by an external magnetic field, an electromagnet was placed in transversal configuration, producing a magnetic field that lies in the plane of the magnetic layer and perpendicular to the incidence plane,

which changes its magnetization between the saturation states by using a magnetic field of 30 Oe and frequency of 800 Hz. A lock-in amplifier extract the component of the modulated signal at the specific reference frequency rejecting noise. The variation of the reflectance signal upon the modulation of the direction of the magnetic field in the transversal configuration can be thus recorded: $\Delta R = R(+M) - R(-M)$.

As discussed above, the MP structure used as a transducer layer in the MO-SPR sensor consist of sandwiches of Au/Co/Au layers (namely, 15 nm Au/6 nm Co/25 nm Au) properly deposited onto Corning glass substrates dc magnetron sputtering at room temperature in an ultrahigh-vacuum chamber with a base pressure of 10^{-9} mbar, after a flash evaporation of Ti layer.

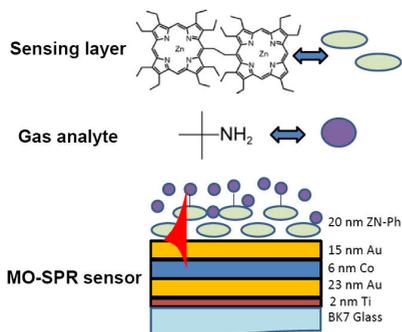


Fig. 1 > Sketches of the molecular structure for both the ethane bridged Zn-porphyrin dimer (ZPD) as sensing layer and the tert-butylamine as gas analyte. Besides, a scheme of the ZPD functionalized MO-SPR sensor detecting the organic vapours is shown at the bottom of the figure./

This film of Ethane Bridged Zinc-Porphyrin Dimers (ZPDs) was used as sensing layers (see figure 1) properly deposited onto the MP multilayer structure. This ZPD thin film is a

prospective candidate for amine sensing since ligand-to-metal coordination interactions between amine groups and the ZPD are expected.

Langmuir–Schäfer (LS) technique has been used to transfer a multilayer of ZPD run by run over the Au/Co/Au substrate. The surface layer containing the organic chemicals was transferred from the water surface by the LS deposition technique by lowering the MP multilayer horizontally until contact with the floating film. During the transfer the floating film surface pressure was kept to 15 mN/m. Six runs (about 20 nm thick) have been transferred onto the transducer to perform sensing test (a scheme is shown in figure 1).

The analytes chosen in our investigation are vapors of a tert-butylamine, one of the four isomeric amines of butane used as an intermediate in the preparation of rubber accelerators, pesticides, pharmaceuticals, dyes and other organic compounds. The MO-SPR sensor response of the ZPD-functionalized Au/Co/Au multilayers was measured for different tert-butylamine concentrations, evaluating sensitivity, stability, reproducibility and recovery of the process.

Results and discussion

Angular measurements of the reflectivity and transverse MO Kerr effect (TMOKE) signal have been carried out using the Kretschmann configuration for a given wavelength $\lambda=632$ nm as it is explained in references [15,16,19]. Two representative reflectivity versus incidence angle measurements with a dry-air flux and a flux of tert-butylamine vapours diluted in dry-air, which leads to a VOC concentration of $1.43 \cdot 10^5$ parts-per-million (ppm) inside the gas chamber, are shown in the figure 2 (a). The SPP excitation manifests itself as a minimum on the

reflectivity at a specific angle of incidence (around $\theta_{\min}=55^\circ$ and $\theta_{\min}=58^\circ$ for the dry-air and tert-butylamine curves respectively) above the critical angle for total internal reflection (around 42° in both cases). The angle for SPP excitation corresponds to the matching between the in-plane component of the wavevector of the incident light and that of the SPP. As it is well known, the SPP wavevector (k_{SPP}) and the optical constants of the metal and insulator regions where that SPP is excited can be related in the next equation:

$$k_{SPP} = k_0 \frac{n_m n_d}{\sqrt{n_m^2 + n_d^2}} \quad (1)$$

where k_0 is the wavevector of the incident light in vacuum, n_m and n_d are the effective refractive index of the metal and insulator media close to the interface of the SPP excitation, respectively. It explains the angular shift towards higher angles of the θ_{\min} , when the organic molecules reach the surface of the sample.

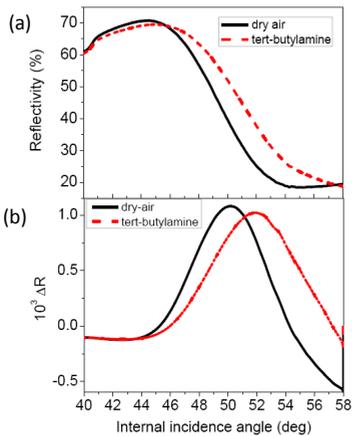


Fig. 2 > Angular measurements of the Reflectivity (a) and TMOKE signal (b) under Kretschmann configuration which allows SPP excitation for the ZPD functionalized MO-SPR sensor with dry-air (black continuous lines) and tert-butylamine vapours (red dashed lines) inside the gas chamber./

As is reported in previous works [13,14,15,19] a magnetic field applied in the plane of a Au/Co/Au multilayer film with a cobalt thickness of a few nanometers and perpendicular to the SPP propagation direction induces a modification of the SPP wavevector while keeping its transverse magnetic (TM) character, this modification being the physical origin of the magnetic field induced variation of the reflectivity (ΔR). Therefore this TMOKE signal exhibits a maximum value around the angular region of the SPP excitation for both measurements with dry-air flux and tert-butylamine flux (see figure 2 (b)). That enhancement of the TMOKE signal is due to the different distribution of the electromagnetic field inside the Au/Co/Au multilayer structure. For the angular positions corresponding to total reflection where the plasmon is not yet excited, the corresponding EM field distribution decreases exponentially from the glass incident light side. However, for angular positions where the SPP has been excited, the EM field gradually increases as the light gets deeper into the structure, reaching as expected a maximum value at the dielectric–Au interface, where the SPP is located [24]. This implies that the EM field is drastically enhanced at the MO-active layer region, being responsible for the enhancement of the magneto-optical signal. As can be expected the presence of the organic vapours onto the surface modifies the dielectric environment, and as a consequence, gives rise to the mentioned angular shift of the maximum of ΔR for the tert-butylamine curve. It is important to remark that the value of the maximum of the TMOKE signal for the tert-butylamine curve is very similar to that observed before the arrival of those VOC vapours. It indicates the preservation of the Co layer: the top Au layer avoids possible oxidation problems with those gases.

In order to test the gas sensing capabilities of the ZPD-functionalized MO-SPR sensor, the signal of reflectance variation ΔR has been recorded at a fixed angle (the one which gives the maximum slope with dry-air flux) while amine vapours-dry air cycles have been performed at different tert-butylamine concentrations. Figure 3 (a) presents a dynamic response curve of the ΔR signal recorded sending into the test chamber different concentrations of analyte vapours mixed in dry-air and separated by a flux of bare dry-air for evaluating also the recovery of the sensor. The different concentration are obtained mixing dry air with analyte vapours at (2-20-40-80% respectively). The dynamic curve shows the stability of the signal and reversibility of the absorption and desorption processes in all concentration range. Reproducibility of the measurements is ensured by repeating the measurements for more cycles. However, the desorption processes is very slow with respect to adsorption process demonstrating the strength of interaction of the sensing layer with analyte vapours.

A calibration curve can be obtained by reporting the sensor response with respect to the concentration of the tested analyte vapours. The sensor response is calculated by considering the variation in the sensor signal with respect to the baseline signal recorded in dry air conditions normalized to the noise of the MO-SPR transducer (for more details see reference [19]). As shown in figure 3 (b) the sensor response exhibits a linear behavior in that concentration range (reaching concentration values of $1.4 \cdot 10^5$ ppm). Taking into account that the sensor is still behaving linearly at the highest tested concentration, we can deduce that the ZPD thin film is still not saturated of those vapour molecules. A linear fit of the experimental values has

been performed in order to obtain a sensitivity (η) of our ZPD functionalized MO-SPR sensor for this organic gas using the slope of the calibration curve. The sensitivity value allow us to extract the limit of detection defined as $LOD = 3 \sigma / \eta$ where η is the above mentioned sensitivity and σ the standard deviation of the measured parameters [25]. Thus an experimental limit of detection of 7.3×10^2 ppm has been calculated, which is similar to the values obtained for a porous TiO_2 MO-SPR sensor detecting alcohol vapours (methanol, ethanol and isopropanol, see reference [19]).

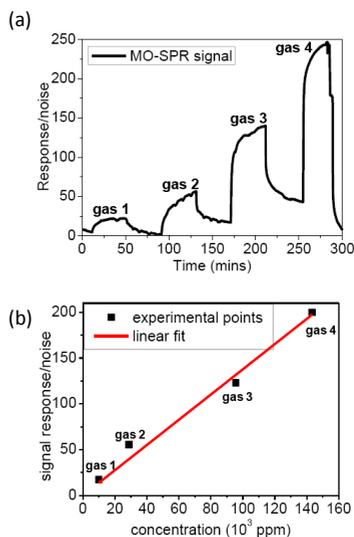


Fig. 3 > Sensorgram (a) and calibration curve (b) of the ZPD functionalized MO-SPR sensor for four different concentrations of VOC vapours. A linear fit is also presented for the tert-butylamine detection./

Further experimental tests are in progress in order to understand the role of the sensing layer morphological aspects and of the amine composition in the sensing activity of the proposed MOSPR sensor. A deep understanding of the parameters involved in the sensing activity will be a

key point for the optimization of this new and promising transducing technology.

Conclusions

We have studied the interesting capabilities of ethane bridged Zn-porphyrin dimmers (ZPD) for tert-butylamine detection using magneto-optic surface plasmon resonance as VOC sensors. In particular, the sensing performance for tert-butylamine vapour detection of six monolayers of ZPD deposited onto Au/Co/Au trilayer by LS technique has been successfully studied. Very promising sensing performances are demonstrated in term of stability, reproducibility, reversibility of the sensor and also a linear range of analyte concentration has been found. Further experiments with different aliphatic amines, such as n-butylamine, dibutylamine and tributylamine, are in progress in order to extend the performance of the proposed MO-SPR sensor.

Acknowledgments

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Preparation of complexes of Tobacco mosaic virus and magnetic nanoparticles and investigation of their behavior in an oscillating magnetic field

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Abstract

Targeted drug delivery presents one of the most promising applications of nanotechnology in medicine. In the following we report on the decoration of Tobacco mosaic virus with magnetic nanoparticles by a combination of genetic modification, chemical coupling and biochemical interactions. Furthermore first experiments were performed to describe the behavior of these complexes in an oscillating magnetic field. The work has been performed by an interdisciplinary group of physicists, chemists, biologists and biochemists at the University of Stuttgart, Germany and the CIC nanoGUNE in San Sebastian, Spain with financial support by the Phantoms Foundation.

Introduction

The potential of nanotechnology in future drug therapy lies in the development of multifunctional therapeutic agents that fulfill various functions. Such agents are expected to direct the drugs to the site of action, allow visualization of the drug-carrier in the body, release the cargo (drugs) upon an external stimulus and

eventually perform further tasks like hyperthermia to support the effect of the drug. Several drug delivery vehicles have been proposed such as liposomes, microspheres or synthetic polymers [1] but also magnetic nanoparticles [2]. Plant viral particles have several advantages over these systems. These viruses are non-pathogenic to humans, very stable and can be produced *in planta* and isolated with high yields [3]. Furthermore, viruses have evolved to carry cargos (nucleic acids) and they present on their surface a manifold of precisely arranged functional groups readily available for genetic modification [4, 5] and chemical conjugation [6]. Tobacco mosaic virus (TMV) is such a possible viral drug delivery vehicle. One viral particle consists of 2130 identical coat proteins, helically arranged on a single-stranded RNA molecule of 6390 nucleotides. This arrangement forms a tube-like particle of 18 nm in diameter with a central channel of 4 nm [7]. It has been shown before that the central channel of the particle can be filled with aqueous solutions [8]; in addition, possibilities to plug the ends of the tube exist [9] and are under further investigation. Furthermore, the surface of the virus has been modified to bind antibodies [10] or present antibody fragments (unpublished data) that might be used to target the virus particle with its cargo to a certain tissue. The release of the cargo, however, still presents a major challenge. The disassembly of the viral particle which would lead to the release of a potential drug can be performed *in vitro* by treatment with detergents, extreme pH values or temperature [11, 12]. *In planta*, the virion

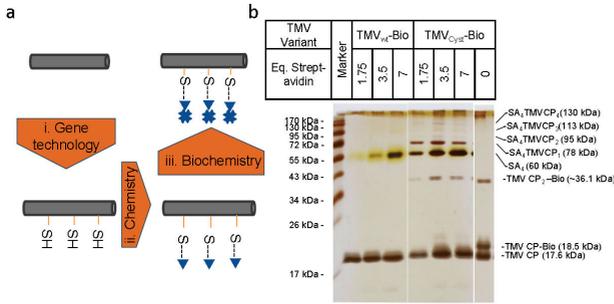


Fig. 1 > Modification of TMV nanorods with streptavidin. **a**: Schematic overview: i. Mutagenesis of a surface-exposed amino acid to cysteine, ii. Modification of this cysteine with a biotin molecule linked to maleimide and iii. Binding of streptavidin to a biotinylated TMV variant. **b**: Electrophoretic mobility shift assay of biotinylated TMV coat proteins incubated with different equivalents of streptavidin. As a control, wildtype TMV not capable of biotinylation was used./

disassembles via a complex mechanism including the detachment of loosely bound terminal protein monomers due to changes in pH and calcium concentration, followed by a subsequent co-translational disassembly aided by ribosomes [13]. As this mechanism is not possible outside cells, other means of disassembling viral particles serving as drug delivery vehicles need to be investigated. Triggered local heating would be a possibility to disassemble viral nanotubes as soon as they had been directed to the desired tissue. Such a local heating process can be achieved with magnetic nanoparticles subjected to an oscillating magnetic field, a strategy which is already used in cancer therapy (hyperthermia or thermoablation) [14] and drug delivery [2]. Here we report on the binding of superparamagnetic nanoparticles to TMV and subsequent treatment in an oscillating magnetic field, aiming at the disassembly of the viral particles.

Results and discussion

As a general method to bind molecules or larger particles to the outer surface of TMV, we used the biotin-streptavidin

technology. Biotin immobilized on TMV serves as high-affinity anchor point for streptavidin (SA), a tetrameric protein. Streptavidin itself can be easily conjugated to other molecules or can be used as a coating of colloids or other nanoparticles, thereby connecting the biotinylated virus tubes with the SA-modified elements (Fig. 1a). In previous work, a TMV mutant has been created exposing

cysteine residues on its outer surface [15]. This mutant will be abbreviated as TMV_{Cyst} in contrast to TMV_{wt}, a variant which does not contain any exposed cysteine moieties. The thiol functions of exposed cysteines were used to couple biotin with the help of a maleimide-activated linker (EZ-Link Maleimide-PEG11-Biotin). Specific conjugation of biotin to TMV_{Cyst}, resulted in a reduced electrophoretic mobility of the respective viral coat protein (CP), due to an increase of its molecular weight by about 0.8 kDa which can be detected via SDS polyacrylamide gelelectrophoresis (Fig. 1b, lane 8). Furthermore, dimeric CP_{Cyst} (of about 36 kDa) were produced during the reaction as a side product by to a so far unknown mechanism. To test whether the biotin-coated viral particles were able to subsequently bind streptavidin, TMV_{wt} and TMV_{Cyst} were treated with biotinylation reagent, purified and incubated with different equivalents of SA. After denaturation of the modified viral nanotubes at 65 °C in the presence of sodium dodecyl sulfate (SDS, under conditions that leave the biotin-streptavidin bonds intact), samples were analyzed by SDS PAGE. In the case of

wildtype virus, two bands were visible for all equivalent ratios, one of which can be assigned to the tetrameric streptavidin (SA₄, expected molecular weight of 60 kDa) and the other to the free, unconjugated TMV CPs (expected molecular weight of 17.6 kDa; Fig. 1b, lanes 2-4). For modified, biotinylated TMV_{Cyst} (TMV_{Cyst}-Bio), the band corresponding to biotin-CP was shifted at all concentrations of SA used, and higher molecular weight aggregates of streptavidin with TMV CP_{Cyst} appeared (Fig. 1b, lanes 5-7). Although bands corresponding to SA₄ with two, three or even four CP monomers occurred at all concentrations, most prominent was the one representing a single streptavidin tetramer bound to one CP monomer. The dimeric CP was not able to bind to streptavidin, since this band was not shifted. In summary, we conclude that TMV_{Cyst} can be readily biotinylated (with an efficiency of about 30 % of the CP subunits, as determined by relative band intensity), and that the modified viral nanorods are able to bind SA. No biotinylation and thus no SA binding occurred with the wildtype version of TMV.

In the next experiment, TMV_{Cyst}-Bio was decorated with streptavidin-coated superparamagnetic nanoparticles (SA-μMACS[®]) obtained from Miltenyi (Bergisch-Gladbach, Germany) to obtain a complex of magnetic beads and biological carrier tubes. Solutions of TMV and SA-μMACS[®] were mixed at different ratios and incubated for several hours. With ratios below 10 ng TMV_{Cyst}-Bio per μl of the SA-μMACS[®] solution, no visible aggregation was observed, in contrast to strong aggregation with 33 to 333 ng TMV_{Cyst}-Bio per μl SA-μMACS[®]. At higher ratios, aggregate formation decreased again (Fig. 2a). This reflects the typical aggregation behavior of two interacting particles with multiple

interaction sites. At relatively low concentrations of TMV_{Cyst}-Bio, all biotinylated sites of the viral particle were saturated with streptavidin bound to the magnetic nanoparticles, resulting in TMV completely coated with magnetic nanoparticles (Fig. 2a and b), while with increasing TMV_{Cyst}-Bio concentrations large networks were formed. Further increase in the TMV_{Cyst}-Bio concentration led to structures of single magnetic nanoparticles surrounded by a large number of TMV rods. No aggregation was observed with non-biotinylated TMV_{Cyst} or with TMV_{wt} treated with biotinylation reagent, proving the specificity of the interaction. To visualize the aggregation more precisely, dynamic light scattering (DLS) measurements were performed (Fig. 2c). As the suspensions were polydisperse and occasionally heavily aggregated, the standard evaluation of size distributions was not attempted; the calculation result would not be reliable. We therefore referred to the correlation directly. With the addition of non-biotinylated TMV_{Cyst}, a slower decrease of the correlation coefficient was observed if compared to the solution containing magnetic particles only. This may be either due to the presence of TMV nanotubes, or due to some unspecific interaction between viral and magnetic particles, or both. If solutions of TMV_{Cyst} and TMV_{Cyst}-Bio incubated with SA-μMACS[®] were compared with respect to the correlogram, the correlation was slower for the preparation with the biotinylated virus compared to the non-biotinylated control (Fig. 2 center), confirming the formation of larger aggregates due to the specific interaction of the two kinds of nanoparticles by the biotin-streptavidin bonds. The difference in the dynamics of the solution between TMV_{Cyst} and TMV_{Cyst}-Bio was even larger when higher virus concentrations were incubated with the SA-μMACS[®] solution (Fig. 2c right).

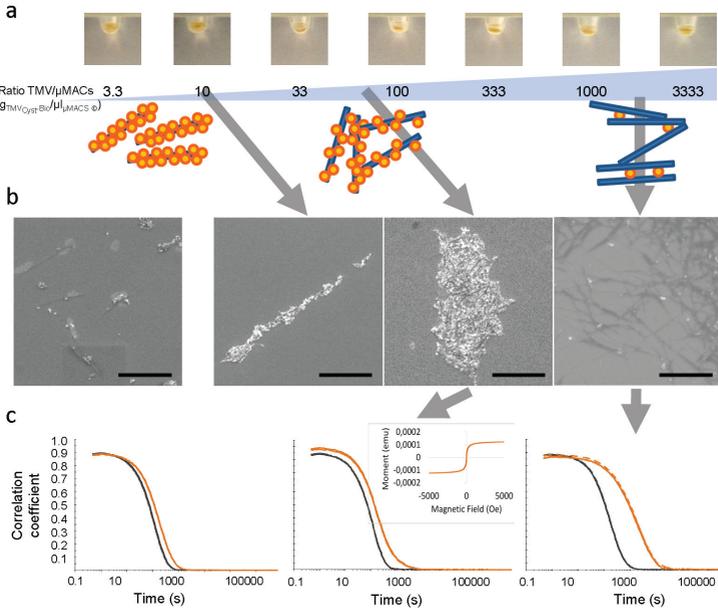


Fig. 2 > Aggregation behaviour of SA-coated μMACS with a biotinylated Tobacco mosaic virus variant. a) Photographs of SA-coated μMACS incubated with different amounts of biotinylated TMV as indicated. Below: Schemes demonstrating the expected constitution of the aggregates formed. b) ESEM images showing selected areas of samples of non-biotinylated TMV incubated with SA- μMACS with a ratio of 140 ng_{TMV}/μ_l μMACS (left) and of biotinylated TMV (right) incubated with SA- μMACS at different ratios (increasing concentrations from left to right: 10, 50, 2000 ng_{TMV}/μ_l μMACS). Bar = 1 μm. c) DLS correlograms (triplicates) of TMV-SA- μMACS aggregates at different ratios. Left: Unspecific binding of TMV_{wt}-Bio to SA- μMACS (Ratio of 3000 ng_{TMV}/μ_l μMACS , orange) compared to the signal of SA- μMACS without TMV (grey). Center: TMV_{Cyst} (grey) and TMV_{Cyst}-Bio (orange) incubated with SA- μMACS at a ratio of 30 ng_{TMV}/μ_l μMACS . The inset shows the hysteresis of TMV_{Cyst}-Bio (orange) incubated with SA- μMACS obtained by SQUID measurements (10μl sample). Right: TMV_{Cyst} (grey) and TMV_{Cyst}-Bio (orange) incubated with SA- μMACS at a ratio of 3000 ng_{TMV}/μ_l μMACS .

These findings confirm the strong and specific binding of TMV_{Cyst}-Bio to the streptavidin-coated magnetic nanoparticles. The behavior of the magnetic nanoparticles bound to TMV_{Cyst}-Bio was also investigated via SQUID measurements. In the complex with TMV they showed no difference to the pure magnetic nanoparticles with only a very slight hysteresis (Fig. 2c, inset in the central diagram), which indicates that they remained superparamagnetic. No coupling of the magnetic moment due to the presence of TMV template could be observed.

After verifying the correct binding of TMV_{Cyst}-Bio to streptavidin-coated μMACS particles, we sought to investigate the behavior of these aggregates in an alternating magnetic field. Therefore non-biotinylated and biotinylated TMV_{Cyst} were incubated with the magnetic nanoparticles, before the solutions were split with one aliquot being exposed to an oscillating magnetic field prior to a DLS measurement, whereas the second aliquot was subjected to DLS measurement without magnetic treatment. The dynamics of the suspensions of pure μMACS and the

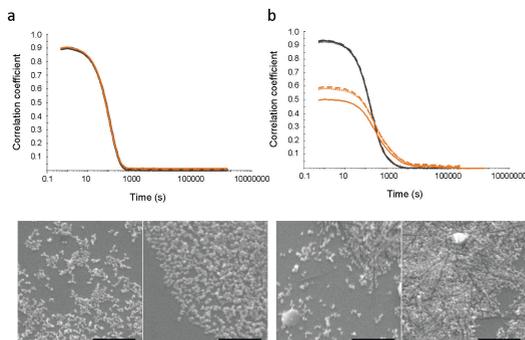


Fig. 3 > Behavior of TMV-SA- μ MACS[®] aggregates of 30 ng_{TMV}/ μ l _{μ MACS[®]} in an oscillating magnetic field ($H=1000$ Oe, $\nu=10000$ Hz, $U_{rel}=5$ V). a: TMV_{Cyst} (non-biotinylated, negative control); b: TMV_{Cyst-Bio} (biotinylated). Upper panel: Correlograms (triplicates) of the dynamic light scattering of the aggregates before (grey) and after (orange) exposure to the oscillating magnetic field. Lower panel: ESEM images before (left) and after (right) exposure to the oscillating magnetic field. Bar = 500 nm./

mixture with non-biotinylated TMV_{Cyst} were not affected by the alternating magnetic field (Fig. 3a, upper image). By contrast, with the mixture of biotinylated TMV with SA-coated magnetic nanoparticles, a change in the correlation was observed: The mixture treated by an oscillating magnetic field showed a significantly slower correlation than the untreated control (Fig. 3b, upper image). This indicates that the exposure of the as-prepared magnetic viral complexes with an alternating magnetic field led to further large-scale aggregation of the particles. The low initial value of the correlation coefficient of about 0.6 even suggests the formation of large sedimenting aggregates and such large complexes were visualized with ESEM (Fig. 2b). This could not be observed at higher relative TMV_{Cyst-Bio} concentrations. A possible interpretation of this finding is that the local heating of the magnetic nanoparticles bound to TMV_{Cyst-Bio} led to a partial disassembly of the virus tube and hence to the partial release of free RNA, which then led to aggregation due to

RNA-RNA interactions. However, further experiments are necessary to prove this hypothesis. As the frequency of the alternating magnetic field was, due to experimental limitations, one order of magnitude lower than the frequencies usually applied in thermoablation (100 kHz) [14], the true nature of the effect may become evident when such a high frequency is applied thereby amplifying the effect.

In conclusion, stable and well-dispersed hybrid bio-magneto-nanocomposites have been prepared by the conjugation of magnetic nanoparticles with TMV *via* a streptavidin-biotin linkage.

These composites were influenced by an alternating magnetic field which led to enhanced aggregation contrary to the expected disassembly to smaller non-aggregated particles. The underlying mechanism of this effect, however, remains to be elucidated.

Materials and Methods

Viral nanotubes were prepared from infected leaf material via standard procedure [3]. Biotinylation of TMV_{Cyst} has been performed by incubation of 20 equivalents of EZ-Link Maleimide-PEG11-Biotin (Thermo Pierce) in a solution of 4 μ g/ μ l virus in 1x PBS (phosphate buffered saline) for 24 h at 25 °C and under shaking at 500 rpm. The biotinylated virus was purified by PEG precipitation as described [16]. SDS PAGE was performed in 15 % polyacrylamide gels using a Laemmli buffer system [17]. Streptavidin was obtained from Sigma and streptavidin-coated magnetic nanoparticles (SA- μ MACS[®], 50 μ m magnetic core) from Miltenyi (Bergisch-Gladbach, Germany).

For binding of the magnetic nanoparticles to TMV, streptavidin-coated μ MACS[®] were mixed with virus solutions in 10 mM SPP (sodium-potassium phosphate) buffer pH 7.2 for several hours at different ratios. For preparative purposes, 50 μ l μ MACS[®] solution (as received from Miltenyi) was mixed with 0.5-500 μ g TMV depending on the intended final ratio in a total volume of 200 μ l. The oscillating magnetic field was produced in a home-made device based on yokes and wires, wound around the yokes in solenoid shape, to achieve a frequency of 10,000 Hz operated with a voltage of 5 V resulting in a magnetic field of 1000 Oe. DLS measurements were performed in a Nanosizer ZS (Malvern Instruments) with 70 μ l of undiluted sample. For ESEM imaging, the samples were washed twice by centrifugation at 10,000 g for 5 min (Eppendorf 5417C tabletop centrifuge) and resuspending the resulting pellets in Milli-Q water ($r=18.3$ M Ω *cm, < 10 ppb organics) to the original volume. Few micro liters were spotted onto a plasma-treated silicon wafer and examined under the ESEM (FEI Quanta 250). Magnetometry was performed with a Quantum Design MPMS SQUID-VSM at 300 K.

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The Euskampus Campus of International Excellence (**CEI Euskampus**) is a strategic project of the University of the Basque Country /Euskal Herriko Unibertsitatea (UPV/EHU), jointly promoted by Corporación Tecnológica Tecnalia and the Donostia International Physics Center (DIPC). The **CEI Euskampus** seeks to achieve international excellence and showcase the range of educational programmes, research and knowledge transfer in three main areas of specialisation: environmental technological and sustainable ecosystems, innovative processes and new materials, healthy ageing and quality of life. The Euskampus projects likewise includes broad university outreach and social responsibility objectives regarding the territory overall, which are backed by the public administrations and the main entities of the Basque Network for Science, Technology and Innovation.

CEI Euskampus aspires to be a:

- Driving force for the economic transformation process of the Basque

Country, by driving forward a model where education, research, innovation, internationalisation and attracting talent play an essential role in improving the competitiveness of the production structure.

- Technological, scientific and academic benchmark of the European Atlantic Corridor.
- Benchmark model for territorial development and in the search for solutions to the environmental, cultural and social challenges of the Basque Country.

Therefore, CEI Euskampus's strategic goals are to:

- Foster and implement first-rate research as a means to improve the Basque Innovation, Technology and Science System, thus becoming a driver for social wellbeing.
- Set up a collaboration framework among all the stakeholders involved in Euskampus with a multidisciplinary and cooperative approach to respond to the demands and needs of society.
- Increase the industrial competitiveness and economic growth of the Basque Country.
- Encourage creativity and the innovative spirits in business and academic activity to adapt to the changing social and economic situation.

CEI Euskampus seeks to consolidate academic areas with an international dimension that showcases a first-rate and modern public higher education

model abroad, consolidated by and linked to a broad array of entities and stakeholders that boost knowledge-transfer and research capacities. It thus contributes to the international promotion of the Basque Country as a talent, creativity, innovation, technology and science hub, thus turning into reality the slogan that inspired the Euskampus projects: “A University, a County, a Campus”.

One outcome to be highlighted from the consolidation of the international excellence dimension is the fact that the UPV/EHU is now on the prestigious Shanghai ranking of the 500 best universities in the world published annually, for the first time. The UPV/EHU appears in this ranking, ex aequo, between posts 301 and 400, and is consolidated as one of the seven best universities of Spain.

The UPV/EHU contribution in the economic and social modernisation of its territorial environment is another aspect that should be outlined. According to the impact study of its activity (IVIE, *the UPV/EHU as the driver for development of the Basque Country: social and economic contributions, 2012*), the existence of the UPV/EHU represents an additional outputs of nearly 2,000 million euros (20% up on 2007), income of 882 million euros (17.2% up on 2007) and provides nearly 20,000 jobs (18.7% up on 2007), representing 1.31% of the GDP and 1.89% of the employment rate of the Basque Country. Thanks to its activity, over a fifth of the growth of the last two decades of the Basque economy is directly and indirectly attributable to the contributions of the UPV/EHU.

The majority of the envisaged policies have been implemented during the first development phases of the **CEI Euskampus Strategic Plan** (October 2010-September 2012). Amongst them

all, it is advisable to outline in a specific way some of them that are clearly strategic and that have been mainly implemented by means of the CEI project.

The strategic alliance: Euskampus Fundazioa

Right from the start, the Euskampus inter-institutional alliance has been based on the necessary private-public complementary work in science, technology, innovation and their application to the productive structure and to the benefit of society. It is the only case of public-private CEI alliance in Spain. Thus, the **CEI Euskampus** may respond to the different dimensions of excellence (academic, scientific, technological and innovation) by covering the whole value generation and knowledge chain.

Right from the outset, **CEI Euskampus** has been committed to continuity and to becoming a core element to achieve and develop key social and economic values in the Basque Country overall.



Thus, **Euskampus Fundazioa** was set up on 19 July 2011 and a private-public inter-institutional initiative. The legal standing of foundation was chosen as it is the one that best adapt to achieving the goals of the **CEI Euskampus** project. The UPV/EHU, DIPC and TECNALIA are the founding members of **Euskampus Fundazioa**. The Pôle de Recherche et d'Enseignement Supérieur Université de Bordeaux (PRES higher education and

research hub - Université de Bordeaux) is its European strategic partner. **Euskampus Fundazioa** seeks to design, coordinate and implement measures that, complementarily and in conjunction with the alliance members, consolidate and accelerate the process to modernise the University through the **CEI Euskampus** project.

Specialisation: Knowledge Hub Community (Cooperative innovation and research)

CEI Euskampus was designed as a Knowledge Hub Community in three areas of specialisation.

The breadth of existing research lines in the areas has led to **9 Knowledge Hubs** to be identified (table 1).

Euskampus Knowledge Hubs	CEI Euskampus Specialisation Area
Health and sustainability of the oceans The environment and agricultural innovation	Sustainable ecosystems and environmental technologies
Healthy food Mens sana (neurosciences)	Healthy ageing and quality of life
Simulation, modelling, computing and optimising Speaking and language technologies for global communication Manufacturing (Flexible, sustainable and smart manufacturing) Natural and cultural heritage of humanity Materials	Innovative processes and new materials

Table. 1 > 9 Hubs in the specialisation areas./

Apart from those 9 Hubs in the specialisation areas, two more Hubs are being designed from a more transversal and cross-disciplinary standpoint: one Hub focused on the Arts, Science and Creativity, and another one dealing with

the socioeconomy of the social transformations of this century.

A Knowledge Hub is an area for multi/disciplinary and systematic cooperation in order to design and implement policies in the sphere of training, research and transfer whose common denominator is the search for results and solutions aimed at tackling a social and global challenge from a technological/scientific perspective. Any partnership activity carried out within the framework of the Knowledge Hubs aims for excellence and the international recognition of the generated knowledge or the innovation produced.

This Knowledge Hub Community seeks to consolidate the natural leadership of the UPV&EHU in the full integration of the Basque Country in the Knowledge Society.

Master's and Doctorate School

The **UPV/EHU Master's and Doctorate School (EMD)** was opened in January 2012. The **EMD** is a UPV/EHU centre entrusted with coordinating and managing the doctorate programmes and interdisciplinary research training in all knowledge spheres developed by the UPV/EHU, along with coordinating and managing the official Master's Degrees, except those with professional attributions. A strategic target is to drive the excellence, visibility and internationalisation of the Master's and PhD courses, along with organising cross-current training activities in a multidisciplinary context, to bring the skills acquired during the doctorate in line with the real needs of society.

The EMD offer a total of 92 Master's and 71 PhD programmes, 32 of which hold the "citation of excellence" from the Ministry of Education. The UPV/EHU heads this excellence and quality ranking

nationwide and obtains the highest ratings, as it has holds the greatest number of citations of excellence for its post-graduate studies, on a competitive basis among all Spanish universities. Furthermore, the UPV/EHU also priorities foreign outreach initiatives and is a partner on Erasmus Mundus joint PhD and Master's programmes and, in 2008, set up a Latin American Master's and PhD Network together with 12 universities.

Cross-border Euroregional Campus

The Cross-border Euroregional Campus together with the PRES Université de Bordeaux is considered a core aspect both in the CEI Euskampus project and in the Bordeaux Excellence Initiative, recently recognised by the French government within its excellence programme. The Campus seeks to set up a cross-border network with an international impact, which will be the benchmark along the Atlantic corridor to generate knowledge and technological and scientific capacities throughout the knowledge value chain, from the idea until its conversion into a social benefit.

The Cross-Border Campus Strategic Action Plan 2012-2015 sets the following objectives:

- Providing students with greater job skills.
- Constructing a European leadership based on the synergies between the spheres of research excellence.
- Creating value based on crossed fertilisation of the knowledge transfer cultures.
- Promoting the image of a Euro-regional Excellence Campus.
- Driving collaboration by means of dissemination and internal promotion of the cross-border culture among academic staff, researchers and service and administration staff.

UPV/EHU Scientific Park

The setting up of the UPV/EHU Scientific Park, with a potential building surface area of 188,000 m², is part of a plan to create and expand new infrastructure to generate knowledge by facilitating innovation and its transfer to the Basque production fabric. This initiative is deemed to be strategic, not only for the UPV/EHU, but also for the socio-economic development of the province of Bizkaia and of the Basque Country overall. This is behind the involvement of the public institutions (Bizkaia Provincial Council and the Basque Government).

The UPV/EHU Scientific Parks seeks to become one international technology-scientific benchmark by creating a functional, flexible and innovative space where highly creative people, researchers and technologists, companies with capacity to exploit new initiatives, research groups that work on the frontier of knowledge interact with one another.

Work has begun on developing technological-scientific infrastructures within the UPV/EHU Scientific Park, which will be areas for innovation and research excellence, and they will incentivise university-company relations, along with marketing-orientated research. Amongst the infrastructures included the UPV/EHU Scientific Park Headquarters building, the Animal Biotechnology Centre, the Biophysics Unit (UPV/EHU-CSIC mixed centre), the Technological Platform Center I, and the European Spallation Source ESS Bilbao stand out.

Finally, the following chart (see table 2) illustrates the evolution of some of the key indicators of the CEI Euskampus Strategic Plan during this first stage (October 2012-September 2012), which once more make evident the consolidation of the project:

Area	Indicator	Initial Situation 31.12.09	Report date situation 31.12.11	% progress
Academic Improvement and ESHE adjustment	Number of UPV/EHU postgraduates and doctorates jointly carried out with Euskampus association	31	53	▲71%
Academic Improvement and ESHE adjustment	Number of Doctorates with "citation of excellence"	-	32	-
Academic Improvement and ESHE adjustment	Average number of international thesis in the last 3 years	50	62	▲24%
Scientific improvement and knowledge transfer	Number of scientific publications annually indexed	1.816	1.993	▲10%
Scientific improvement and knowledge transfer	Number of publications in first fourth-month period	916	1.093	▲19%
Scientific improvement and knowledge transfer	H Index	105	124	▲18%
Scientific improvement and knowledge transfer	Annual Average of coordinated European projects	45	78	▲73%
Scientific improvement and knowledge transfer	Annual average of national patents submitted	67	100	▲50%
Campus transformation towards the development of	% of degrees that include in their academic curricula the social responsibility	5%	46%	
Campus transformation towards the development of an integrated social model	Investigation groups working in the sustainability area	32	35	▲9%

Table 2 > Evolution of some of the key indicators of the CEI Euskampus Strategic Plan during the first stage (October 2012-September 2012)./

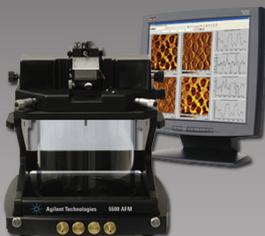


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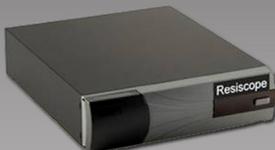
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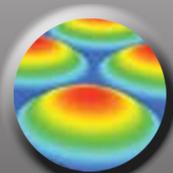
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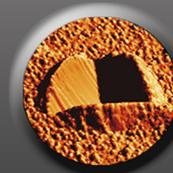
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