IPCMS News
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◆ *Unique oscillations of Dirac Monopoles and Strings in Artificial Spin Ice*

Artificial spin ices are systems of tiny nanopatterned magnets arranged in a regular array. A key property of spin ices is that they are usually "frustrated", which means that the magnetization is not arranged in a minimum-energy state for all nanomagnets. By means of such frustrations, artificial spin ices effectively exhibit mesoscopic versions of elusive magnetic monopoles, which were predicted by the Nobel laureate Paul Dirac in 1931.

The micromagnetic finite-element algorithm based on Graphical Processing Units developed by Riccardo Hertel (IPCMS Strasbourg) and members from his former group makes it possible to investigate large-scale problems with high accuracy. This enabled a team of scientists from the IPCMS in Strasbourg (France), the Argonne National Laboratory (USA), and the Jülich Research Center (Germany) to demonstrate that artificial spin ices exhibit specific oscillations, which represent a signature of peculiar defects in the spin ice.

The team demonstrated that the magnets near such spin ice monopoles, and in strings of defects connecting them, oscillate at very specific frequencies. Owing to this peculiar ringing, it is predicted that monopoles and their connecting strings in a spin-ice array can be detected and quantified experimentally. In terms of possible applications, the signature opens the possibility of using such strings for information storage and computing devices based on magnonic devices. ■

S. Gliga, A. Kákay, R. Hertel, and O. G. Heinonen, *Phys. Rev. Lett.*, **110**, 117205 (2013).
The Beat that Tells of Spin-Ice Monopoles, D. Ucko, Physics – Spotlighting Exceptional Research, http://physics.aps.org/synopsis-for/10.1103/PhysRevLett.110.117205.

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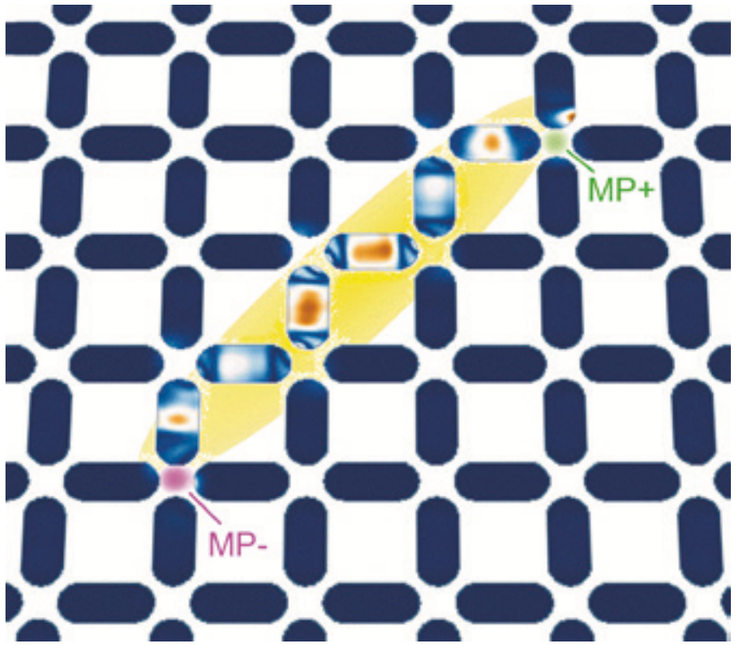

◀ *In an artificial spin ice lattice, two monopole defects (denoted as MP- and MP+ according to their magnetostatic charge) are connected by a Dirac string (highlighted in yellow). After a short external perturbation, the nanomagnets along the string oscillate at a specific frequency, giving rise to a collective mode that extends from one Dirac monopole to the other. The spectral analysis of the oscillation modes of a spin ice lattice – a standard measurement in experiments on the dynamics of magnetic nanostructures – could therefore be sufficient to detect and to quantify monopole defects in an array. Moreover, by inserting or removing such frustrated regions, the dynamic properties of the ensemble can be altered, thereby opening new perspectives for programmable and non-volatile logic devices based on spin wave excitations.*

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Summary

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Editorial

The present issue of IPCMS news focuses on representative achievements at the forefront of nanoscience published in 2013 by IPCMS researchers. These contributions underscore the impact and the novelty of efforts encompassing atomic-scale observations, nanoparticles synthesis, supramolecular organization and molecular devices. In the example provided by the team of S. Bégin-Colin, microwave irradiation is employed to enhance the assembling reaction of iron oxide nanoparticles on a self-assembled monolayer. A fascinating route for controlling architecture of single molecule magnets in liquid crystal host enable the discovery of new correlations between structural morphologies and magnetic properties (paper by E. Terrazzi, G. Rogez, J.-L. Gallani and B. Donnio). As shown by J.-F. Dayen and coworkers, the construction of "smart" electrical interconnects in molecular devices proved instrumental in achieving a spectacular increase in the device sensitivity, the process being driven by substantial "co-tunneling". Theory can play a fundamental role in the understanding of systems made of tiny nanopatterned magnets in regular arrays ("artificial spin ice"). This has been exemplified in the contribution by R. Hertel. Atomic scale resolution, obtained by M. Boero and coworkers on a computer model based on density functional theory provided insight into the etching mechanism of graphene. The authors were able to identify new reaction pathways for etching via an oxygen plasma. Finally, the TEM (transmission electron microscopy) facility of IPCMS has allowed the observation of a so far unknown phase of silica consisting of disordered layers obtained by nucleation and growing on a metal surface (contribution by the team of F. Banhart).

As an example of the role played by IPCMS researchers in the international scene, we highlight the on-going framework of collaboration with the Ewha Womans University of Seoul (South Korea). Within this context, four IPCMS researchers (Stefan Haacke, Carlo Massobrio, Loic Mager, Sébastien Le Roux) have attended, as invited speakers, the 2013 ICAMD meeting of the Korean Physical Society (see picture) held in the beautiful resort of the Jeju island, one hour flight south of Seoul. To strengthen the links between IPCMS and Ewha Womans University, a Korea delegation of about 50 people will be attending the Winter School on "Advanced Functional Materials and Characterization" to be held at IPCMS during the last week of January 2014.

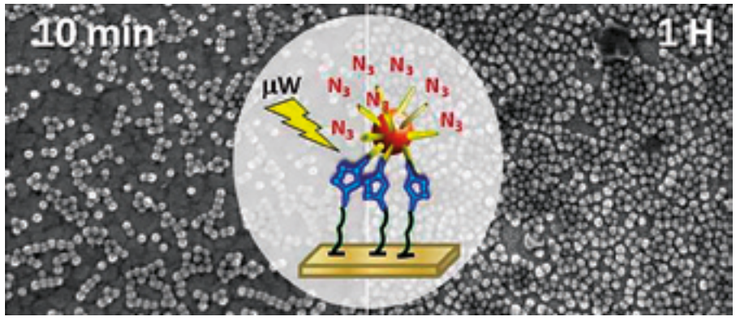
Stefan Haacke, *Director*

Awards to IPCMS researchers

IPCMS researchers have been awarded important distinctions in 2013. Guillaume Schull (CNRS researcher) was the recipient of the CNRS bronze medal for his outstanding studies in the area of electron transport through molecules via STM. Silvia Zanettini, PhD student in the team of Bernard Doudin, was awarded the prestigious "Fondation l'Oréal France–Unesco" for her research on organic electronics. Guido Pupillo, professor at the University of Strasbourg, was the recipient of the price "Fondation Université de Strasbourg-Cercle Gutenberg" targeted to a young researcher having achieved important results in challenging areas of research.
The Swiss Chemical Society has recognized, through the Sandmayer Price, the research work of Stéphane Bellemin-Laponnaz in partnership with academic and industrial teams.

◆ Fast Assembling of Magnetic Iron Oxide Nanoparticles by Microwave-Assisted Copper(I) Catalyzed Alkyne Azide Cycloaddition (CuAAC)

Two dimensional (2D) nanoparticles (NP) assemblies have become very attractive due to their original collective properties, which can be modulated as a function of the nanostructure. Beyond precise control on nanostructure and easy way to perform, fast assembling processes are highly desirable to develop efficient and popular strategies to prepare systems with tunable collective properties. In this article, we report on the highly efficient and fast 2D assembling of iron oxide nanoparticles on a self-assembled monolayer (SAM) of organic molecules by the microwave (MW)-assisted copper(I) catalyzed alkyne azide cycloaddition (CuAAC) click reaction. Microwave irradiation favors a dramatic enhancement of the assembling reaction, which was completed with maximum density in NPs within one hour, much faster than the conventional CuAAC click reactions that require up to 48 h. Moreover, the MW-assisted click reaction presents the great advantage to preserve specific reactions between alkyne and azide groups at SAM and NP surfaces, respectively, and also to avoid undesired reactions. MW-assisted click reaction is reported for the first time to control the assembling of nanoparticles on surfaces. ■



▲ *SEM micrographs after performing the assembling MW CuAAC "click" reaction of azide terminated NPs on alkyne-terminated SAM for 10 min and 1 hour.*

D. Toulemon, B. P. Pichon, C. Leuvrey, S. Zafeiratos, V. Papaefthimiou, X. Cattoën, S. Bégin-Colin, *Chemistry of Materials,* 2013, **25**, 2849-2854.

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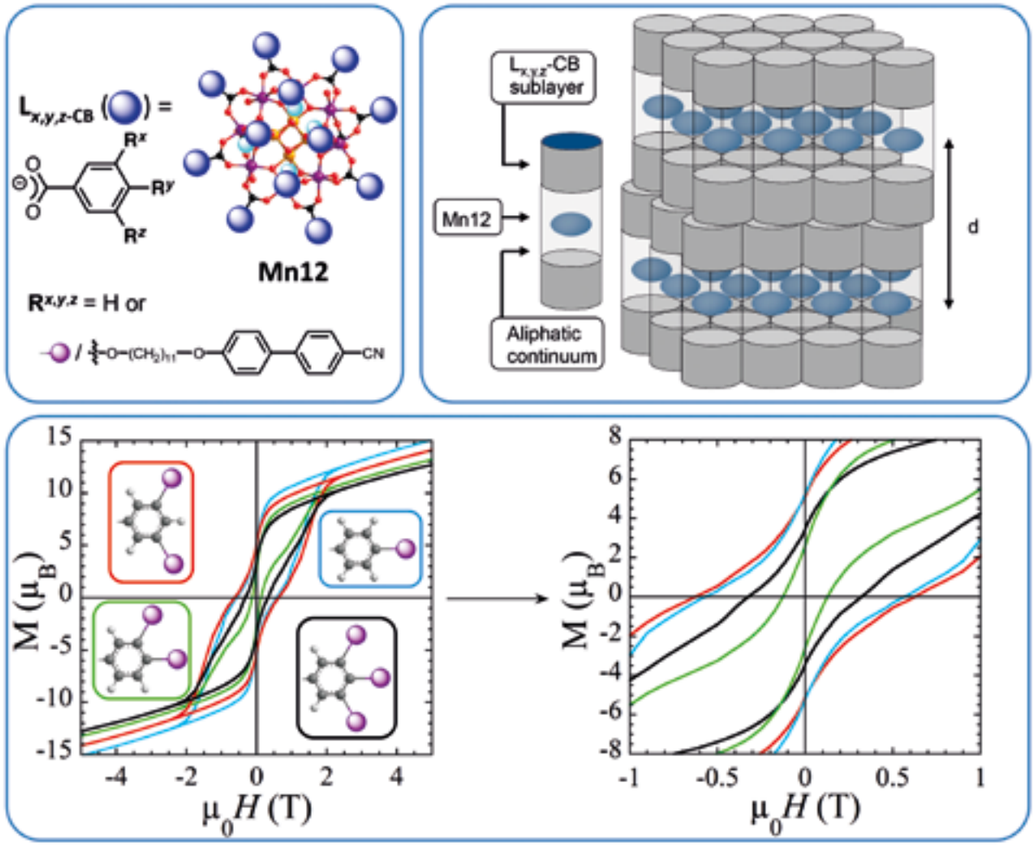
◆ Supramolecular organization of manganese single molecule magnets

Single molecule magnets (SMM) may be considered for the construction of future integrated nanodevices, provided some degree of ordering is imparted to these molecules.[1] Combining such nano-objects with liquid-crystalline orderings to control their assembly and address them individually is a promising strategy. Liquid crystals (LC) are outstanding examples of soft, molecular self-assemblies that exquisitely combine order and fluidity, within components self-organizing into a wide diversity of mobile and long-range ordered periodic structures. These are intrinsically defect-tolerant since positioning errors are corrected automatically during the process of self-assembly. In this study,[2] we have explored the influence on the supramolecular orderings and magnetic properties



▲ *Molecular structure of the LC-hybridized Mn12 clusters, their self-organization within a smectic phase, and their magnetization versus applied field curves, as a function of the ligand substitution pattern.*

of the peripheral modifications of a set of four mixed-valent $[Mn^{III}_8Mn^{IV}_4O_{12}(L_{x,y,z\text{-}CB})_{16}(H_2O)_4]$ SMM, bearing different liquid-crystalline cyanobiphenyl ligands, ($L_{x,y,z\text{-}CB}$), i.e. number and symmetry of the substitution pattern.

All hybridized clusters self-organize at room-temperature into the same type bilayer smectic phase, the polymetallic cores are further organized according to a short-range 2D lattice with hexagonal and/or square symmetry. Whilst no obvious mesophase structural difference emerged, the compactness of the arrangement, as deduced by the cross-sectional area per anisotropic group, is strongly dependent on the number of pending mesogens, the substitution (and symmetry) pattern, and the two connecting sites around the cluster (i.e., axial versus equatorial positions). All these parameters influence the packing constraints and degree of distortion of the clusters. The mesomorphous hybridized dodecamanganese complexes still possess the SMM property of their archetypical Mn12 parent. They exhibit blocking of the magnetization at about 2.6 K. Magnetization hysteresis cycles reveal coercive fields varying between 0.13 and 0.6 T, depending on the surface ligands topology. The hybrids reveal intricate correlations between the structural features (i.e. compactness, symmetry of the ligands substitution patterns) with respect to the relative proportion of slow- and fast-relaxing species (SR/FR) and the absolute values of the coercive fields. The occurrence of SR species is higher in symmetrical compounds, and the compounds that have the lowest coercivity are those which cores are forced to tilt out of the median plane of the smectic layers by the pressure effects.
Along with the photosensitivity of LC Mn12 derivatives,[3] that allows addressing the magnetic state of the molecule using a combination of light and magnetic field, we showed how the use of anisotropic promesogenic ligands can provide a means for finely tuning the molecular geometry and the magnetic properties without fundamental alteration. ■

[1] G. Rogez, B. Donnio, E. Terazzi, J.-L. Gallani, J. P. Kappler, J. P. Bucher, M. Drillon *Adv. Mater.* **2009** 21 4323-4333.

[2] E. Terazzi, G. Rogez, J.-L. Gallani, B. Donnio J. *J. Am. Chem. Soc.* **2013** 135 2708-2722.

[3] B. Donnio, E. Rivière, E. Terazzi, E. Voirin, C. Aronica, G. Chastanet, D. Luneau, G. Rogez, F. Scheurer, L. Joly, J.-P. Kappler, J.-L. Gallani *Sol. State Sci.* **2010** 12 1307-1313.
E. Rivière, B. Donnio, E. Voirin, G. Rogez, J.-P. Kappler, J.-L. Gallani J. *Mater. Chem.* **2010** 20 7165-7168.

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◆ *Amplifying the sensitivity of Multifunctional molecular devices*

Metal Nanoparticles Networks are ideal model materials for studying the charge transport properties of Quantum Dots assemblies. Experiments performed at the macroscopic scale provide insight into properties at the nanoscale, revealing in particular the electronic properties of the molecular spacers between the nanoparticles. We designed electrical interconnects addressing sub-micron 'slices' of nanoparticles assemblies, typically 80 nm long, and several tens of microns wide. These provide access to electrical properties resulting from a finite number of interparticle tunneling events N, in the range 1-7, by design. The usual device resistance results from a sequential interparticles tunneling process, with a resulting device resistance proportional to $N.R_T$, where R_T is the interparticle resistance value. Metal nanoparticles can also behave as Coulomb Island where strong electron-electron repulsion prohibits sequential charge transfer. At sufficient low temperatures, a collective process can take place, where adding a charge to one nanoparticle requires a simultaneous charge leaving the island, leading to a "co-tunneling" process. The resulting device resistance becomes now proportional to R_T^N.

In a recent experiment [1], in collaboration with the KIT and the group of S.J van der Molen of Leiden University (The Netherlands), funded by a European NanoSciERA project, we used chemical exchange for chemically changing R_T by a factor around 50. This powerful experimental 'knob' provides an opportunity to reveal how collective process modifies the sample properties: at low temperatures, where co-tunneling becomes predominant, the device relative resistance value (ie. the device sensitivity) changes by 50^N, reaching 10^5 !

This study demonstrates the opportunity given by co-tunneling processes in nanoparticles networks to realise innovative amplifying devices in electrical transport, open to multiple physical or chemical excitations. Our aim is to explore changes of the molecular spacer resistance value by physical means, by using switchable molecules, with intrinsic electrical properties modified by external stimuli, for example magnetic or electric field, light, pressure... These devices could pave the way to creating multi-stimuli molecular devices with enhanced properties. ■

J.-F. Dayen, E. Devid, M.V. Kamalakar, D. Golubev, C. Guédon,V. Faramarzi, B. Doudin and S. J. van der Molen *Advanced Materials*, **25**: 400–404 (2013). doi: 10.1002/adma.201201550

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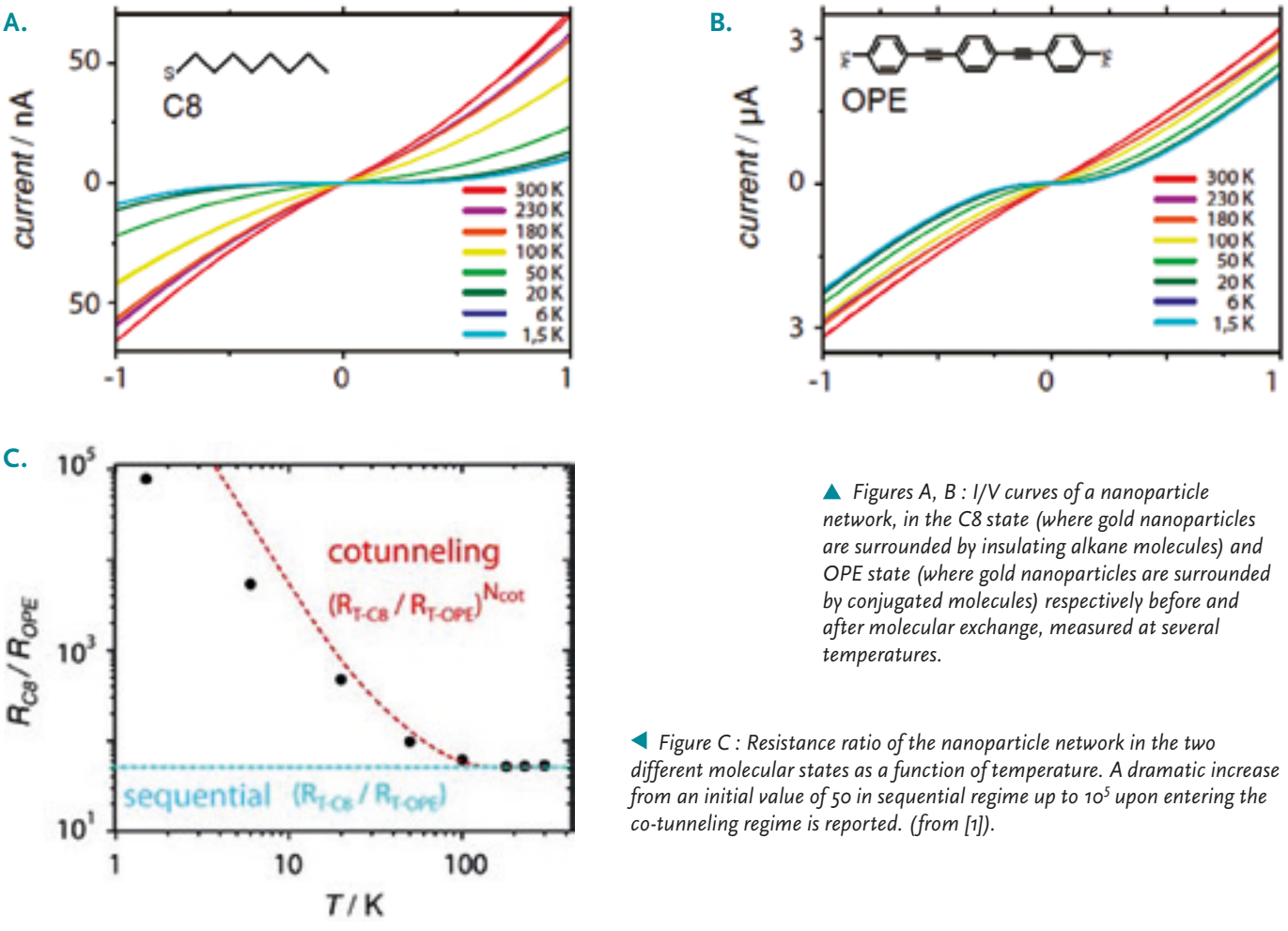


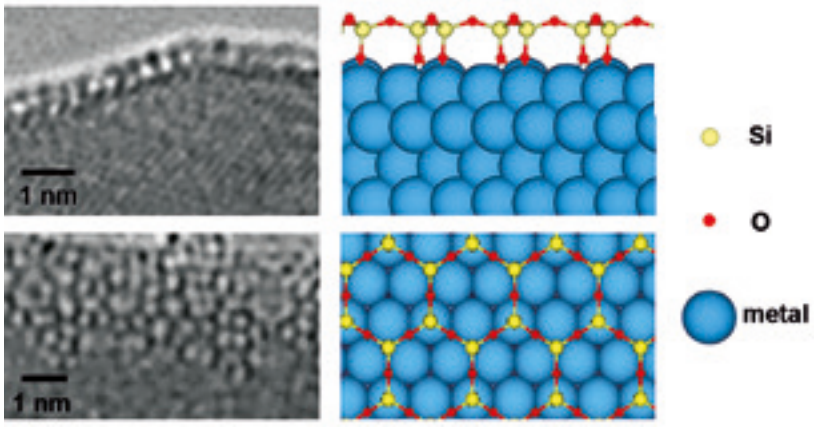
▲ *Figures A, B : I/V curves of a nanoparticle network, in the C8 state (where gold nanoparticles are surrounded by insulating alkane molecules) and OPE state (where gold nanoparticles are surrounded by conjugated molecules) respectively before and after molecular exchange, measured at several temperatures.*

◀ *Figure C : Resistance ratio of the nanoparticle network in the two different molecular states as a function of temperature. A dramatic increase from an initial value of 50 in sequential regime up to 10^5 upon entering the co-tunneling regime is reported. (from [1]).*

• Growth of a two-dimensional glass observed by in-situ electron microscopy

In 2012 it became known that a two-dimensional phase of silica may exist, consisting of a mono- or biatomic layer of SiO_2 in a hexagonal network. The structure resembles that of graphene in many respects; it forms a network with almost twice the lattice parameter of graphene and it shows exactly the same defect structures. The cellular arrangement and the high flexibility of the structure allow different bond angles, and so either a regular network of hexagons or a random arrangement of different polygons (pentagons, heptagons etc.). This allows the formation of a quasi-amorphous phase that can be considered as the first two-dimensional glass. Only two groups worldwide have hitherto observed this new phase of silica until it has been shown in an electron microscopy study at the IPCMS how this phase can be grown in a solid-state transformation of bulk silica on a catalytically active metal surface.

Thin metal layers (Fe, Co, Ru) on amorphous silica films were heated in a TEM stage and observed at the same time at high spatial resolution. Layers of the new silica phase were seen nucleating and growing on the metal surface. Depending on the epitaxial match with the substrate, a perfectly ordered hexagonal structure or a disordered vitreous phase were observed. Calculations show that the interplay between the gain in silica–metal interaction energy due to their epitaxial match and energy loss associated with the mechanical strain determine the structure. The new 2D silica phase is of considerable technical interest since it is the thinnest silica layer with atomically defined thickness. Applications as insulating layers in nanoelectronics or tunnel junctions could come in sight once the large-scale synthesis of 2D silica has been developed. The work has been carried out in collaboration with experts in density functional theory at the University of Helsinki. ■



▲ *Electron microscopy images (left) and models (right) of a monolayer 2D silica lattice on metal substrates. Top row: side-view; bottom row: top view. The top-view TEM image (bottom left) shows the 2D glass as a disordered arrangement of different polygons with defect structures that have also been observed in graphene.*

F. Ben Romdhane, T. Björkman, J. A. Rodríguez-Manzo, O. Cretu A. V. Krasheninnikov, F. Banhart, *ACS Nano*, 2013, **7**, 5175.

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• Atom-Scale Reaction Pathways and Free-Energy Landscapes in Oxygen Plasma Etching of Graphene

Our main target is to address open issues and to get an atomic-scale insight into the etching mechanism of graphene, with the aid of the most advanced computational tools. In view of the importance of graphene in forefront research and its potential applications in future nanoelectronics, tailoring and shaping this material represents still a challenge. In this respect, oxygen plasma etching provides a versatile tool to forge shapes and to pattern such a material. In this article we have identify a comprehensive reaction pathway (see figure), holding in all cases, consisting of a two-step mechanism passing always across a lactone formation. Furthermore we work out the free energy landscape and associated activation barriers for all the various stages of the etching, showing that CO_2 the only possible released product and supporting to the notion of layer-by-layer etching processes. This settles also a long-standing controversy about possible release of CO and provides a guideline in tuning the best possible oxygen plasma conditions. ■

K. Koizumi, M. Boero, Y. Shigeta, A. Oshiyama, *J. Phys. Chem.* Lett. **4**, 1592 (2013).

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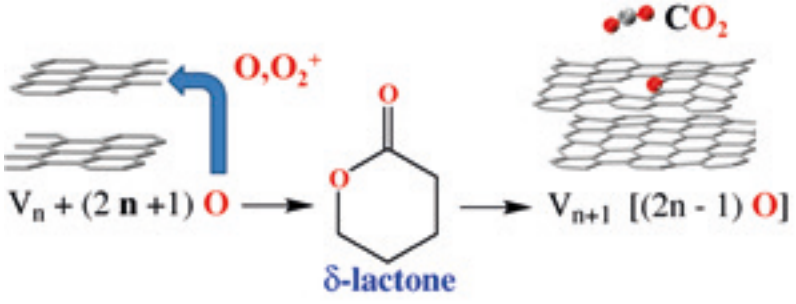

◀ *General reaction pathway for oxygen plasma etching of graphene. In each case n indicates the already etched C atoms on a general site V of a graphene sheet.*