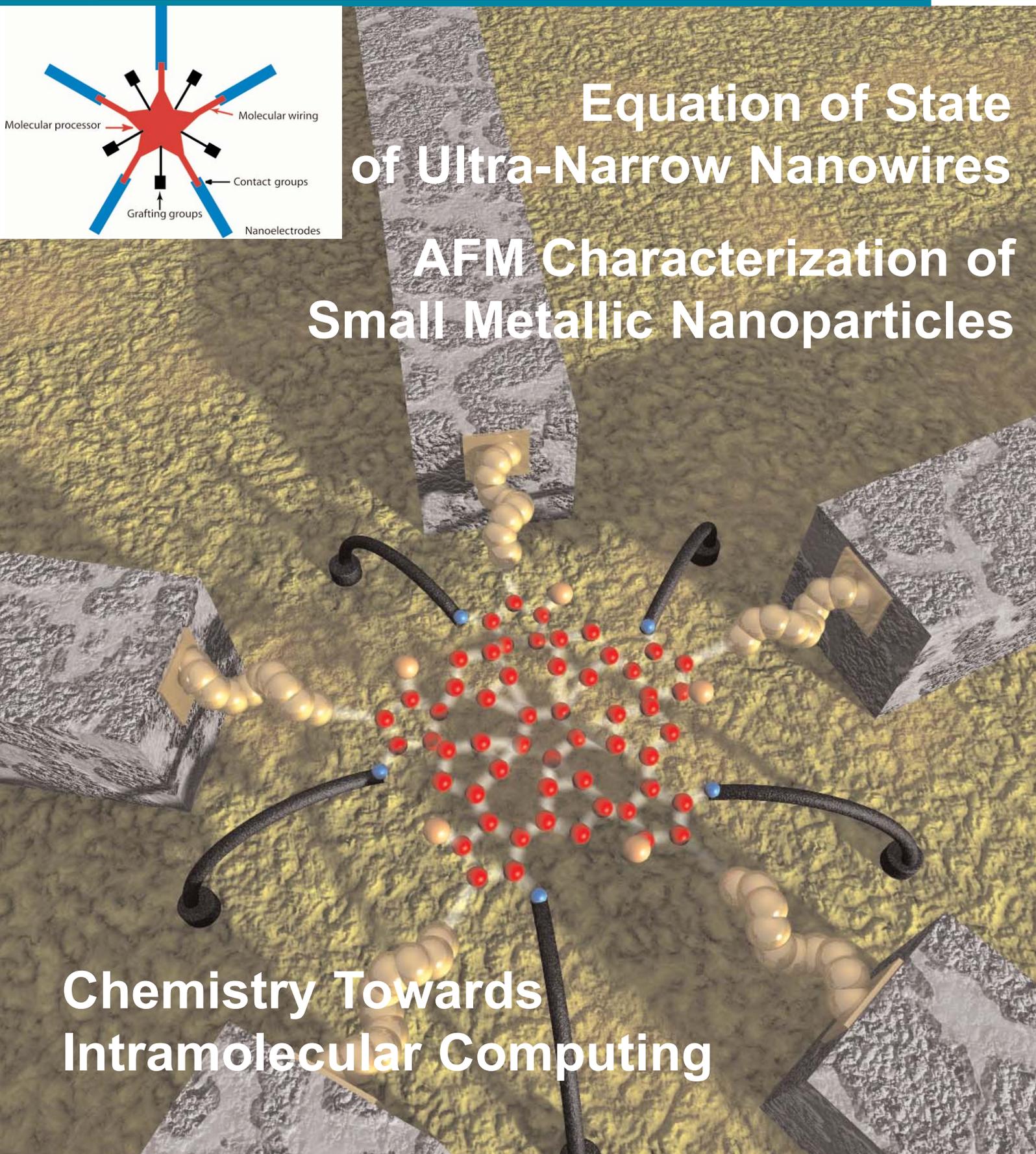


## Equation of State of Ultra-Narrow Nanowires

## AFM Characterization of Small Metallic Nanoparticles

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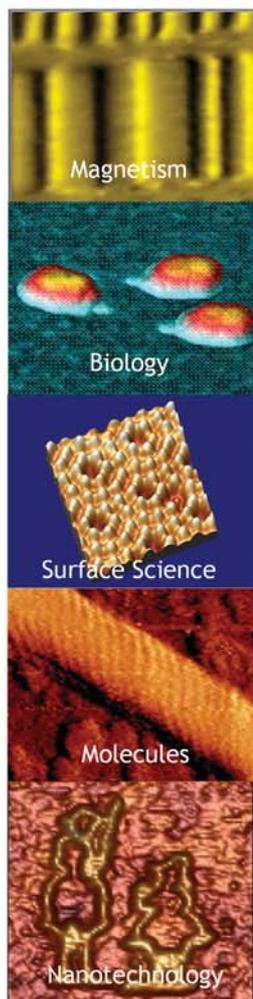
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Modelling behaviour of possible emerging nanodevices is becoming more and more important and should allow to: (i) Visualise what happens inside a device (ii) Optimise the devices under study (iii) Improve understanding of device properties (physical, chemical, etc.).

This E-Nano Newsletter issue provides insights on these issues through a research article on "Equation of state on ultra narrow nanowires" and the description of a new WEB-based initiative led by 4 Spanish Institutions and called "Modelling for Nanotechnology" (M4Nano).

M4Nano principal aim will be to help maintaining a systematic flow of information among research groups and therefore avoid that research efforts in Nanomodelling remain fragmented in Europe and more specifically in Spain.

A new section - "Research/Training" - is also presented in this issue to provide detailed information to researchers using new techniques (AFM, etc.) close to their resolution limits on how to use these and therefore avoid artefacts.

We would like to thank all the authors who contributed to this issue as well as the European Union (IST/FET/NANO) for its close collaboration.

**Dr. Antonio Correia**

*E nano newsletter* Editor  
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### Deadline for manuscript submission:

Issue n°05: August 15, 2006  
Issue n°06: November 15, 2006

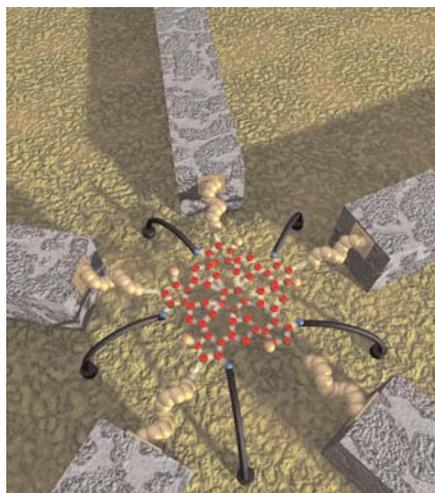
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*E nano newsletter* n°4  
May 2006

Published by  
**PHANTOMS Foundation** (Spain)

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## Equation of State of ultra-narrow nanowires: A benchmark for the Embedded Atom Method.

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### Summary

Two different interatomic potentials within the Embedded Atom Method (EAM) have been used to study several properties of selected bulk and surface structures, as well as crystalline (ordered) nanowire configurations for Al and Ni based systems. The reliability of these potentials has been studied in order to describe optimized geometries and cohesive energies. We have found that the description of low atomic coordination systems is strongly dependent on the kind of EAM parameterization. In particular we have analyzed the differences appearing in the nanowire equation of state, the relation between the cohesive energy and the nanowire radius.

### 1. Introduction

The unquestionable potential of Nanotechnology is based on the combination of preexisting and new methodologies of synthesis, fabrication and characterization of materials, systems or devices at the nanometer scale (1-100 nm), designed to exploit the novel features derived from their nanometric dimensions. These features are intimately associated to the properties of the chemical atomic bonding as well as to the specific shape and size of a particular nano-object [1]. Therefore, the study of the favorable configurations appearing in nanometric systems as well as their evolution under modification of external parameters is of capital interest. An accurate modeling of nanoscale systems allows huge savings in expensive fabrication and characterization procedures. Nowadays, two different computational approaches are the most widely used to describe nanosystems. The most powerful approach is based on ab-initio computational techniques [2] able to accurately determine stable and evolving configurations of a given set of atoms, taking into account the electronic wavefunctions (i.e suitably describing the electronic structure, chemical bonding and internal forces). Nevertheless, shortcomings in both computing resources and programming methods determine that standard ab-initio calculations be usually restricted to systems containing few hundreds atoms. Since a cube with  $10^3$  nm<sup>3</sup> typically contains of the order of  $10^5$  atoms it is clear that its computational description requires alternative methods to effectively describe the atomic interactions with lower computational cost. Following this strategy, the Embedded Atom Method (EAM) [3] represents an effective approach that is designed to efficiently optimize systems formed with millions of atoms and determine their time evolution upon modification of external parameters using classical Molecular Dynamics simulations (MD) or Monte Carlo methods [2].

In general, EAM interatomic potentials [3-5] are designed to accurately describe a set of bulk system properties (i.e. configurations with large atomic coordination number,  $N_C$ ) obtained in experiments or through accurate ab-initio computations. In some specific cases, EAM potentials include information corresponding to some low  $N_C$  situations. Therefore, it is not obvious that

a given interatomic potential (mainly optimized for bulk-like systems) will be able to describe the energetic and forces of low coordination situations (small clusters, ultra narrow wires, adsorbed species, etc). This possible lack of transferability, from high to low atomic coordination situations, represents a serious trouble when predicting stable atomic configurations and their dynamical behavior at the nanoscale. The predictive power of EAM potentials has been studied for several atomic species [3-8], however, their effectiveness for describing low  $N_C$  structures has not been extensively considered. In this work we present a study on several low  $N_C$  systems taking into account two standard and widely used EAM interatomic potentials. In particular we have focused on two metallic species, aluminum and nickel, due to their interest in nanoelectronics, magnetoresistive devices, magnetic storage and catalysis [1].

### 2. Computational details

The EAM approach provides a realistic description of the structural energy  $E$  of a metallic system through the expression:

$$E = \frac{1}{2} \sum_i \sum_{j \neq i} \phi(R_{ij}) + \sum_i F_i(\rho_i) \quad (1)$$

where  $\phi(R_{ij})$  is a pair repulsive term given by  $\phi(R_{ij}) = Z^2(R_{ij})/R_{ij}$ , where the function  $Z(R_{ij})$  corresponds to an effective ionic charge that depends on the interatomic distance  $R_{ij}$  between atoms  $i$  and  $j$ . The function  $F_i(\rho_i)$  corresponds to the required energy to embed an atom of type  $i$  into the background electron density  $\rho_i$  at site  $i$ .  $F_i(\rho_i)$  represents the cornerstone of the EAM methodology and is so-called the "embedding function". The electron density background acting on atom  $i$  is due to the electronic clouds associated to the neighboring atoms, and is expressed as  $\rho_i = \sum_{j \neq i} \kappa_j(R_{ij})$ , where the function  $\kappa_j(r)$  is the electron density of the atom  $j$ . The function  $F_i(\rho_i)$  depends on a large number of parameters chosen to reproduce specific properties of a given system. In the present study we have used two different parameterizations of the embedding function. On one hand, we have considered the approach proposed by Mishin *et al.* [6] (labeled as MFMP approach in this work) for Al and Ni, where the numerical embedding function was built by fitting almost 30 experimental and ab-initio data. This parameterization has been successfully used to find minimum cross section histograms of breaking Al ad Ni nanowires with MD techniques [9-11].

On the other hand, we have used the Sutton-Chen (SC) [4] approach in which the total energy is given by the following expression:

$$E = \varepsilon \left\{ \frac{1}{2} \sum_{ij} \left( \frac{a}{R_{ij}} \right)^n - c \sum_i \sqrt{\sum_{j \neq i} \left( \frac{a}{R_{ij}} \right)^m} \right\} \quad (2)$$

where  $\varepsilon$ ,  $c$ ,  $a$ ,  $m$  and  $n$ , are numerical values obtained from the fit of Eq. (2) to ab-initio results for the most stable bulk configurations. This approach has been used, for instance, to describe the geometry of ultra-narrow metallic nanowires [12,13]. For Al, we have used the set of parameters  $\varepsilon = 3,3147 \cdot 10^{-2}$  eV,  $c = 16,399$ ,  $a = 4.05$  Å,  $m = 6$  and  $n = 7$ , whereas for Ni,  $\varepsilon = 1.577 \cdot 10^{-2}$  eV,  $c = 39,7478$ ,  $a = 3,52$  Å,  $m = 6$  and  $n = 9$  [12]. In both parameterizations, atomic forces are calculated as the derivative of the potential energy with respect to the relative distance between atoms. Since the SC parameterization is analytical, it is of easy implementation in a computer algorithm. However, the low number of parameters appearing in the SC expression provides, *a priori*, a poorer description of non-bulk configurations.

The optimization of atomic configurations is carried out through standard total energy minimization procedures based on conjugate gradients (CG) optimization methods. Studied systems are described by a periodic supercell (a parallelepiped for 3D cases, or square or triangular supercells for 2D cases) containing several atoms (ranging from 1 to 100). In general, the analysis of 3D or 2D structures supercells is done including the fewest amount of atoms required to generate the crystalline structure. However, we have performed several tests using longer supercells to verify that the optimization results did not depend on the supercell lattice constant. Within our procedure, the supercell lattice constants are additional varying parameters of the CG procedure. For instance, during the optimization procedure of metallic nanowires, the atomic positions as well as the supercell length  $L_z$  have been simultaneously modified until reaching convergence. For some particular cases, we have confirmed that optimized structures represent minima of Eqs. (1) or (2) by subjecting them to subsequent MD simulated annealing processes at low temperatures (in the range 0K-4K) without noticeable changes.

In this work we have focused on different situations where MFMP and SC parameterizations have been used to illustrate the discrepancies between both approaches (mainly appearing for low coordination systems). In the next sections we will address a comparative study for several optimised 1, 2 or 3-dimensional (1D, 2D, 3D) crystalline systems, we will describe the surface energy and relaxations of interlayer spacing for different surfaces, and finally we will determine the equation of state of Al and Ni crystalline (ordered) nanowires.

### 3. Periodic 3D , 2D and 1D systems

We have determined [8] the cohesive energy per atom  $E_c$ , and the nearest neighbour distance  $d_{nn}$  for several Al and Ni configurations. Optimized 3D geometries were: face-centered-cubic (FCC;  $N_c=12$ ), body-centered-cubic (BCC;  $N_c=8$ ) simple cubic (SC;  $N_c=6$ ), and diamond ( $N_c=4$ ). In addition, 2D-hexagonal ( $N_c=6$ ), 2D-square ( $N_c=4$ ), 1D-linear chain ( $N_c=2$ ) and dimer ( $N_c=1$ ) low coordination geometries have been included to test the interatomic potentials under more demanding conditions. In Fig. 1 we show the absolute differences in  $E_c$  and  $d_{nn}$  between MFMP and SC methods. As expected, both parameterizations are very similar when describing high coordination situations ( $N_c \geq 6$ ). However the results differ for decreasing  $N_c$  values. It seems that MFMP approach shows better agreement with experimental or theoretical values of  $d_{nn}$  even for the lowest coordination situations (1D atomic chain and dimer). On the contrary, it seems that the SC approach provides better cohesive energies for both Al and Ni in low coordination situations. We have also found a strong dependence of the elastic properties on the EAM parameterization [8]. A first conclusion of this analysis reveals that MFMP and SC approximations provide different results for low atomic coordination number systems.

### 4. Surface relaxations

Surfaces represent an exigent benchmark to test the accuracy of the two chosen EAM parameterizations since surface atomic coordination naturally differs from that of bulk. For this study we have defined a thick metallic slab with more than 30 atomic layers (in order to avoid size effects due to the presence of two surfaces). In Table 1 we summarize the surface energies ( $\gamma$ ) and interlayer relaxations ( $\Delta d_{i,i+1}$ ) for three Al and Ni surfaces ((111), (110) and (100)), obtained using MFMP and SC approaches. In general, the MFMP approach provides a better description of surface energies (for both Al and Ni) than that of the SC parameterization. In fact, we have estimated a surface energy average error (with respect to experimental or ab-initio data) larger than 20% for the SC approach and of the order of 10% for the MFMP one. Concerning the surface interlayer relaxation, another important conclusion is that both EAM schemes do not provide agreement with experimental nor ab-initio results. Both EAM approaches did not predict the main relaxation  $\Delta d_{12}$  between the first and second surface atomic planes. For the Ni case, the SC approach describes the quantity  $\Delta d_{12}$  with less error than the MFMP parameterization. However, for Al, both parameterizations provide unreliable results.

### 5. Equation of state of ordered metallic nanowires

Metallic nanowires with atomic size diameters are examples of low coordination systems with interesting properties (as ballistic transport or quantized conductance). These properties make them good candidates to be used in future nanometric electronic devices [18]. In addition, these systems are of fundamental interest since it has been found both theoretically [19,20] and experimentally [21] that, in some situations, free standing narrow metallic nanowires lose their bulk-like crystalline ordering by forming helical or non-crystalline (weird or amorphous) structures. Since the nanowire reconstruction depends on small energy differences, and different EAM parameterizations provide different cohesive and surface energies, it is clear that EAM interatomic potentials should be carefully handled to study the properties of these physical systems.

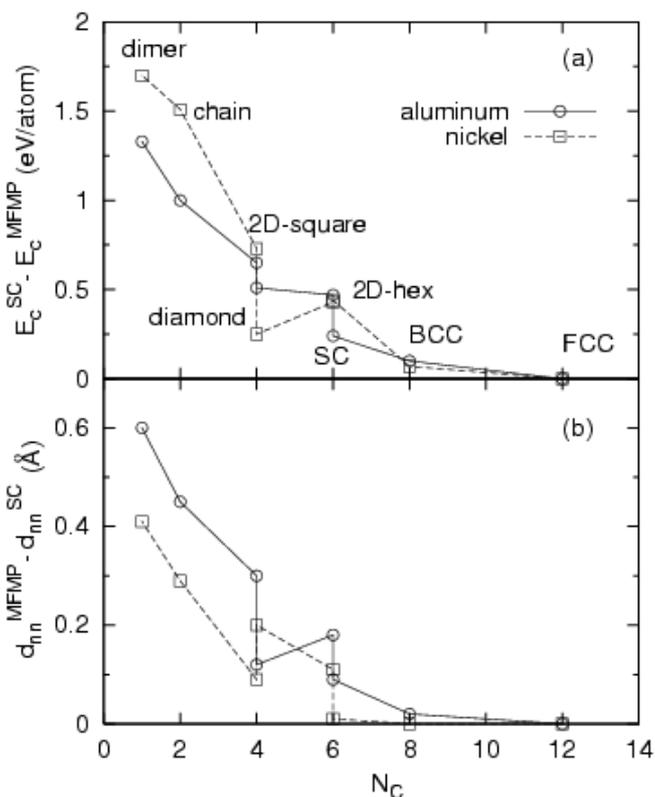


Figure 1. Difference between MFMP and SC values of (a) cohesive energy per atom  $\Delta E_c$  and (b) nearest-neighbor distance  $\Delta d_{nn}$  for different Al (circles) and Ni (squares) structures as a function of the coordination number  $N_c$

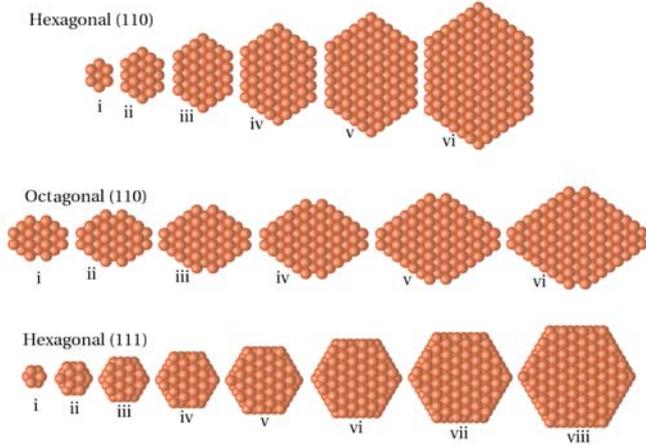


Figure 2. Nanowire cross-sections of different nanowire configurations families: hexagonal (110) (upper row), denoted as HEX-110; octagonal (110) (middle row), denoted as OCT-111, and hexagonal (111) (lower row), denoted as HEX-111. Depicted configurations represent the initial set of non-relaxed configurations.

In order to test the predictability of both EAM (SC and MFMP) approaches we have studied three different families of trial ordered nanowires (shown in Figure 2). Nanowires were generated defining their longitudinal crystallographic direction (ijk) and their geometric shape (hexagonal or octagonal). In particular, the three families we have studied are denoted as HEX-110, OCT-110 and HEX-111. During the optimisation procedure we determine the nanowire cohesive energy, the atomic coordinates and the supercell length  $L_{opt}$ . We have found that proposed geometries are stable in the limit  $T=0K$  and present a well defined minimum of energy with respect the modification of atomic positions. In some specific cases we have repeated the optimisation procedure for the same cross-section shape but using different nanowire lengths, obtaining the same results. Obtained quantities allow us to calculate the optimised linear density  $\rho_L = N_a/L_{opt}$  (where  $N_a$  is the number of atoms in the supercell) and the projected cross-section  $A_{CS}$  (assuming that each atom is a sphere with the bulk atomic radius). In order to characterize the nanowire size we define an effective nanowire radius  $R$  using the relation  $A_{CS} = \pi R^2$ . Figure 3 shows the dependence of the cohesive energy on the nanowire radius, noticing remarkable deviations from bulk behavior as  $R$  decreases.

In order to illustrate the deviations of cohesive energy from the bulk value we plot the cohesive energy per atom as a function of the inverse of  $R$  (see Figure 4). This dependence obeys the following crystalline nanowire equation of state[19]:

$$E_c(R) = -E_{bulk} + \frac{2\Omega_c}{R}\bar{\gamma} + \frac{\Omega_c}{\pi R^2}N_e\bar{\mu} \quad (3)$$

where  $E_{bulk}$  is the bulk cohesive energy,  $\Omega_c$  is the average atomic volume in the nanowire,  $\bar{\gamma}$  is the average surface energy,  $N_e$  is the number of edges ( $N_e=6$  and  $8$  for hexagonal and octagonal wires, respectively) and  $\bar{\mu}$  is the average edge energy per unit length. The quantity  $\bar{\gamma}$  is calculated using  $\bar{\gamma} = \sum_{(ijk)} \alpha_{(ijk)} \gamma_{(ijk)}$  where  $\alpha_{(ijk)}$  represents the fraction of exposed area relative to (ijk) facets with surface energy  $\gamma_{(ijk)}$ . The average edge energy is  $\bar{\mu} = \sum_{(ijk)-(i'j'k')} \beta_{(ijk)-(i'j'k')} \mu_{(ijk)-(i'j'k')}$  where  $\beta_{(ijk)-(i'j'k')}$  is the fraction of (ijk)-(i'j'k') edges with edge energy per unit length equal to  $\mu_{(ijk)-(i'j'k')}$ . We have fitted those curves of Figure 4 to a second order polynomial expansion using  $1/R$  as independent variable, and using Eq.

(3) we calculate the coefficients  $\bar{\gamma}$  and  $\bar{\mu}$ , (summarized in Table 2). For Al, we have found that the MFMP scheme provides larger  $\bar{\gamma}$  values (of the order of 45%) than those found with the SC one. For Ni, both EAM parameterizations provide similar  $\bar{\gamma}$  values (differences below 10%). However, the differences between MFMP and SC are rather large when analyzing  $\bar{\mu}$ . We have found that  $\bar{\mu}$  values calculated under the SC approach are approximately (and in average) 40 and 60 meV/Å below the corresponding MFMP values, for Al and Ni respectively. In some situations the calculated edge energy under the SC approach is negative, indicating that the edges are rather unstable. On the contrary the MFMP approximation always provide positive values of  $\bar{\mu}$ .

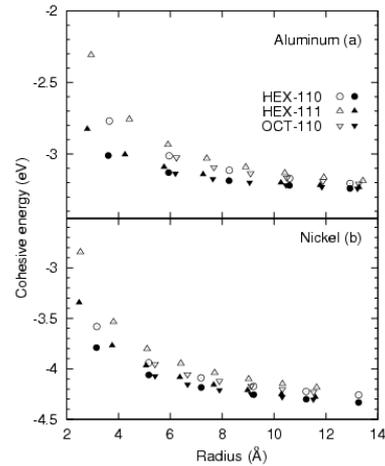


Figure 3. Cohesive energy per atom ( $E_c$ ) versus the nanowire radius ( $R$ ) of three different nanowire families for aluminum (a) and nickel (b). Three nanowire families have been considered (see Figure 1): HEX-110 (dots), HEX-111 (up-triangles) and OCT-110 (down-triangles). Open and full symbols denote results obtained with Mishin et al. (MFPM, Ref. 6) and Sutton-Chen (SC, Ref. 4) EAM parameterizations, respectively.

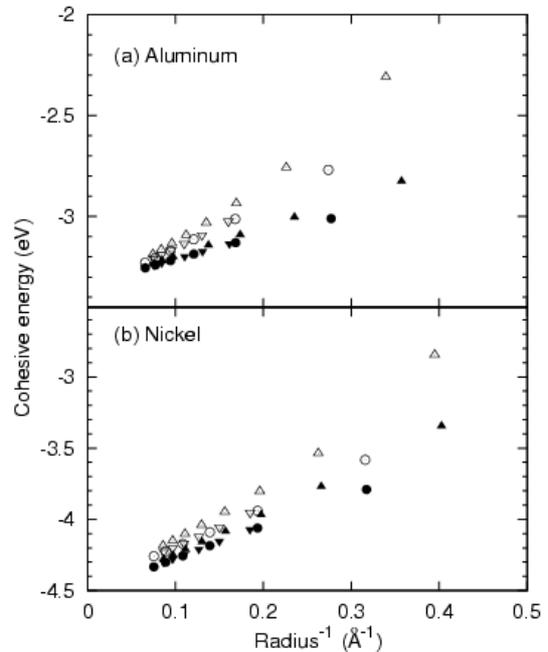


Figure 4. Cohesive energy per atom ( $E_c$ ) versus the inverse of the nanowire radius ( $R^{-1}$ ) of three different nanowire families for aluminum (a) and nickel (b). Three nanowire families have been considered (see Figure 1): HEX-110 (dots), HEX-111 (up-triangles) and OCT-110 (down-triangles). Open and full symbols denote results obtained with Mishin et al. (MFPM, Ref. 6) and Sutton-Chen (SC, Ref. 4) EAM parameterizations, respectively.

## Research

For comparison, previous studies on octagonal (110) Al nanowires using a different EAM approach [19] reported values  $\bar{\gamma} = 57.5 \text{ meV}/\text{\AA}^2$  and  $\bar{\mu} = 35 \text{ meV}/\text{\AA}$ , which are very similar to the MFMP results for our (110) nanowires families (both hexagonal and octagonal). Therefore, it seems that the predictive capacity of SC EAM parameterization to describe the equation of state is rather low. For Ni, the surface components are similar but strong discrepancies when predicting edge energies. This large differences found in the edge energy term are closely related with the discrepancies found in Figure 1, where cohesive energies in crystalline systems showed larger differences as the coordination number decreased.

### 6. Conclusions

EAM interatomic potentials represent a standard approach to describe atomic interactions in systems with high atomic coordination. However, depending on the type of EAM parameterization, different values of important physical properties (cohesive energy, nearest neighbor distance) are obtained for low atomic coordination systems since usually EAM schemes are designed to reproduce bulk or surface properties (i.e. high atomic coordination situations). This inaccuracy has important implications when modeling the static configuration and the dynamical behavior of physical systems with a significant fraction of atoms with low coordination, such as nanowires or clusters with radius of the order of few atomic radii.

In the present work we have considered two different EAM parameterizations (MFMP and SC) in order to disclose their differences when describing structural properties of ultra narrow Al and Ni nanowires. In particular we have focused on three nanowires families with different cross-section shapes. Using standard optimization procedures to obtain atomic configurations we have analyzed the dependence of the cohesive energy per atom with the nanowire radius  $R$ , determining the equation of state corresponding to each nanowires family. The dependence of such equation on the  $1/R$  terms allowed us to extract relevant information as the average surface energy or the average edge energy. We have found noticeable differences between MFMP and SC for both quantities, providing evidence that in the low atomic coordination limit (surface and edge atoms) the use of EAM potentials must be done very cautiously. These differences should extend to the study of dynamical processes appearing in breaking nanowires simulations where local situations with  $N_c \leq 4$  are rather likely at the latest stages of the nanowire breakage, or the structural transformation from ordered (crystalline) to helical/weird structures in ultra-narrow metallic nanowires. In addition, the differences among EAM schemes will limit their use for the study of stress-strain relations in metallic nanowires or their phonon spectrum properties. Comparative studies on both problems are in progress.

### Acknowledgements:

We thank P. García-Mochales, A. Hasmy and E. Medina for their helpful advice. This work has been partially supported by the Spanish DGICYT (MEC) through Project BFM2003-01167-FISI.

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Tables:

		Aluminum			Nickel		
		MFMP	SC	E-AI	MFMP	SC	E-AI
(111)	$\gamma$ (mJ/m <sup>2</sup> )	870.57	1100.44	980 [14]	1629.64	1367.27	2280 [14]
	$\Delta d_{1,2}$ (%)	0.02	-4.75	1.0 [15]	-1.28	-1.92	-0.9 [17]
	$\Delta d_{2,3}$ (%)	-0.29	0.53	0 [15]	-0.11	-0.04	0 [17]
	$\Delta d_{3,4}$ (%)	-0.02	-0.03	0 [15]	-0.01	-0.00	0 [17]
(110)	$\gamma$ (mJ/m <sup>2</sup> )	1006.10	1134.52	980 [14]	2049.25	1572.65	2280 [14]
	$\Delta d_{1,2}$ (%)	-1.51	-17.91	-6.8 [16]	-1.71	-7.56	-10.3 [17]
	$\Delta d_{2,3}$ (%)	1.55	4.00	3.5 [16]	-1.06	0.94	3.2 [17]
	$\Delta d_{3,4}$ (%)	-2.13	1.65	-2 [16]	-0.56	-0.85	0 [17]
(100)	$\gamma$ (mJ/m <sup>2</sup> )	943.64	1066.44	980 [14]	1877.74	1480.01	2280 [14]
	$\Delta d_{1,2}$ (%)	-0.56	-7.14	1.2 [16]	-1.09	-2.77	-3.6 [17]
	$\Delta d_{2,3}$ (%)	-0.92	-0.65	0.2 [16]	-1.15	-0.24	1.4 [17]
	$\Delta d_{3,4}$ (%)	0.01	-0.03	-0.1 [16]	0.01	-0.03	0.3 [17]

**Table 1.** Surface energy  $\gamma$  and interplanar relaxation between consecutive planes  $\Delta d_{i,i+2}$  (expressed as percentage of the bulk interplanar distance) for (111), (110), and (100) faces of aluminum and nickel, and obtained using Mishin et al. (MFMP, Ref. 6) and Sutton-Chen (SC, Ref. 4) parameterizations. The subscript  $i=1,2,3$  refers to the first, second and third atomic layer, respectively. Column E-AI refers to experimental or ab-initio data (references in brackets).

		Aluminum		Nickel	
		MFMP	SC	MFMP	SC
HEX-110	$\bar{\gamma}$ (meV/Å <sup>2</sup> )	57.98	40.37	112.39	111.87
	$\bar{\mu}$ (meV/Å)	25.92	-17.09	44.48	-23.99
OCT-110	$\bar{\gamma}$ (meV/Å <sup>2</sup> )	55.92	40.01	109.01	103.69
	$\bar{\mu}$ (meV/Å)	26.69	-12.54	49.46	10.35
HEX-111	$\bar{\gamma}$ (meV/Å <sup>2</sup> )	65.63	42.89	130.83	121.79
	$\bar{\mu}$ (meV/Å)	59.08	2.80	105.55	25.44

**Table 2.** Average surface energy ( $\bar{\gamma}$ ) and average edge energy per unit length ( $\bar{\mu}$ ) obtained from the nanowire equations of state (see Eq. (3)) used to fit data shown in Figure 4

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# TNT2006

## Trends in NanoTechnology

September 04 - 08 , 2006 Grenoble (France)

MINATEC and Trends in Nanotechnology Conference series will join forces to organise 2006 event in Grenoble (France)

In response to the growing awareness of the importance of nanotechnology, many workshops, symposia, and conferences are being organised worldwide to discuss the latest advances and future tendencies of this field. Among those, the "Trends in Nanotechnology" conference series has become, undoubtedly, a key meeting in Europe.

This high-level scientific meeting series aims, therefore, to present a broad range of current research in Nanoscience and Nanotechnology as well as related policies (European Commission, etc.) or other kind of initiatives (iNANO, IEEE, GDR-E, etc.). TNT events have demonstrated that they are particularly effective in transmitting information and establishing contacts among workers in this field. Graduate students fortunate to attend such events quickly learn the importance of interdisciplinary skills, thereby becoming more effective in their future research.

TNT2006 is being launched following the overwhelming success of earlier Nanotechnology Conferences. The TNT2006 edition will be organised out of Spain for the first time - Grenoble (France) - to emphasise the importance at the European level of the launch of the Centre of Innovation in Micro and Nanotechnology, MINATEC. This centre, to be inaugurated in June 2006, came into existence at the instigation of CEA-LETI Grenoble and Institut National Polytechnique Grenoble and its ambition is to become Europe's top centre for innovation and expertise in micro & nanotechnology. TNT2006 "Trends in Nanotechnology" (04-08 September, 2006) will be held in the brand new congress facilities of the Micro & Nanotechnology House within the MINATEC complex.

The TNT2006 structure will keep the fundamental features of the previous editions, providing a unique opportunity for broad interaction. TNT2006 will be organised by the following institutions: **Phantoms Foundation, Universidad de Oviedo, Universidad Autónoma de Madrid, Universidad Carlos III de Madrid, Universidad Complutense de Madrid, Donostia International Physics Center, NIMS, University of Purdue, Georgia Tech, CEA-LETI-DRFMC and MINATEC.**

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Trends in NanoTechnology

## AFM characterization of small metallic nanoparticles

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In this work, we present a detailed method to observe small metallic nanoparticles (size below 5 nm) with standard AFM equipment for users with a basic experience in AFM. We show that if the particles are well dispersed in a solution before deposition onto a substrate it is possible to image them individually by means of AFM. The particle size can also be measured from the images, considering the particle height, while the width is largely distorted by the tip geometry. Although AFM observations can not substitute HREM studies, they can be complementary as AFM allows observation of aggregation states, difficult to image by HREM, and the possibility of characterise the size of the protecting shell.

### 1. INTRODUCTION

Nanoparticles (NPs) exhibit physical properties that are different from bulk materials and result largely dependent on their size and structure, mainly because of two reasons: (i) As the size of these system reaches the typical lengths of some phenomena, it is expected that the response of the system depends on the boundary conditions (which are no longer periodic, but determined by the particle size), and therefore, to be different from bulk material. (ii) Because of the large ratio of surface to volume atoms in NPs, the surface energy becomes important when compared with volume energy and therefore, the equilibrium situation for NPs can be different from that of bulk materials.

Thus, it is essential a good structural characterization of the NPs in order to understand their properties and the size effects. Nowadays the most powerful tool to analyse those structures is the Transmission Electron Microscopy (TEM) [1]. In particular, High Resolution Electron Microscopy (HREM) provides accurate data about the size, shape and crystallography of the NP, which can not be achieved by any other technique [2], [3], [4]. However, HREM measurements are carried out in UHV and some structures can be modified during the measurements. In the case of small NP (size below 5 nm) which are usually unstable, the energetic electron beam can also promote precipitation or particle growing during the measurement. Furthermore, information about the aggregation

state and dispersion features on different substrates cannot be obtained from TEM studies. At this stage, Scanning Probe Microscopies (SPM) can be very useful as they are generally non-invasive techniques, do not require elaborated sample preparation and measurements can be performed onto a large variety of substrates [5]. Obviously, SPM that give information mainly about the NP surface can not substitute a HREM analysis, but they can be complementary in order to check if the preparation and measurement processes modify the size of the nanoparticles. Another interesting possibility with the SPM is to observe directly the tendency of the NPs to aggregate, or form ensembles, when deposited on different substrates. Nevertheless, for both techniques it will be doubts regarding the knowledge of the aggregation state for the same nanoparticles in colloidal solution, because in both cases a drop of solution is dropped onto a substrate and then leaved for drying. Among the different SPM techniques, Scanning Tunnelling Microscopy (STM) provides the best resolution [6]. However, this technique is limited by the electrical properties of the sample, as it is necessary a good conductivity to reach tunnel current. The Atomic Force Microscopy (AFM) is one of the most widely used SPM for the observation of nanostructures, since this technique does not need specific sample preparation. Although AFM analysis of nanostructures with size of tens of nanometers is well established [7], [8], [9], [10]. the observation of small NP (below 5 nm

size) is not straightforward [11] because the size of the NPs is about the limit of the technique resolution. Furthermore, when the particles are dispersed in a solution, and must be deposited onto a substrate to image them, the interaction with the tip can move the NPs, giving rise to the so-called "sweeping" effect [12], [13]. In this case, it is necessary to carry on the analysis very carefully and looking for the best conditions in order to obtain proper information about the particle size. AFM experts can achieve atomic resolution and they are able even to manipulate single atoms [14]. However, AFM is becoming no more an "experts technique" but a general tool used by people working on nanostructures. In this work, we present a detailed method to observe small nanoparticles with a standard AFM and discuss the information that can be obtained from the measurements that can be carried out by persons with a basic experience in AFM.

### 2. EXPERIMENTAL

#### 2.1 Materials

Samples analysed were nanoparticles of Pd, Au and Ag with sizes in the 1 to 5 nm range, and capped with different chemical species. Palladium NPs were obtained by a redox-controlled size-selective method using tetralkylammoniumsalts as surfactants [15]. In this work a solution of Pd(NO<sub>3</sub>)<sub>2</sub> was used as palladium precursor in an excess of tetrabutylammonium acetate. Gold NPs protected with tetralkylammonium salts were obtained by the chemical reduction of the precursor salt (HAuCl<sub>4</sub>) using sodium borohydride as reducing agent in the presence of tetraoctylammonium bromide as surfactant (i). Thiol-derivatised gold and silver NPs were prepared by chemical synthesis following the Brust method [16]. Sodium borohydride was used as reducing agent and dodecanethiol as the thiol linker molecule. More details about the preparation of those samples has been described elsewhere [2], [3], [17], [18]

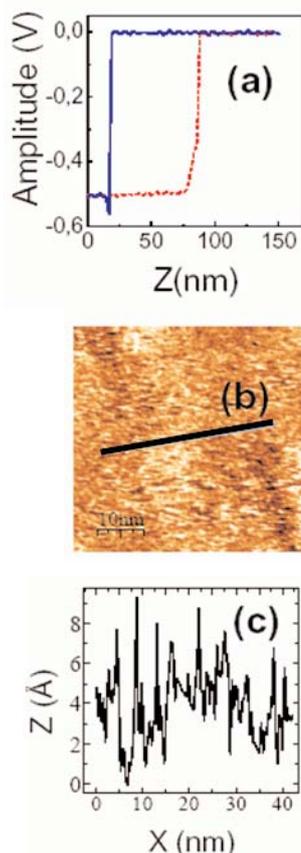


FIG. 1. (a) AFM Photodiode signal vs vertical displacement of the tip. Dashed red line corresponds to the downward movement (tip approaching to the sample) whereas solid blue line corresponds to upward movement. (b) Image of a cleaved mica surface obtained in the conditions described in the text. The height profile along the line is shown in (c). (Carabias et al.)

2.2 Method

The observations on mica using tapping mode were carried out with a Standard Cervantes AFM microscope from Nanotec. AFM probes were rectangular SiN Olympus cantilevers with pyramidal tips and resonance frequency of 77 kHz.

The size of Pd and Au NPs were also measured by HREM microscopy in order to compare them with AFM results. Colloidal solutions of sample were dropped onto carbon coated copper grids. After drying, the samples were analysed in a Philips CM200 TEM microscope working at 200 kVolts. Particle size distribution histograms were obtained by analysing several pictures with an automatic image analyser.

2.2.1 Substrate and measurement conditions.

In order to observe the NPs with the AFM two conditions must be achieved. First, the roughness of the substrate must be about one order of magnitude below the particle size, that is, ~0.3 nm. The second is that the resolution of the measurement must be within the same order of magnitude.

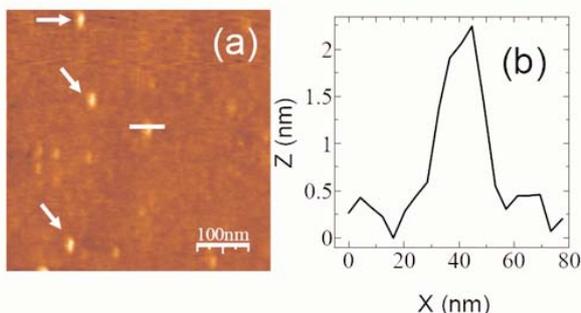


FIG. 2. (a) AFM image of Pd nanoparticles protected by tetrabutylammonium salts onto mica substrate. The arrows indicate individual NPs. (b) Height profile along the line indicated in the figure. (Carabias et al.)

Several substrates can be used for image the NPs, as mica, highly-oriented pyrolytic graphite (HOPG), quartz and others [6],[19]. Actually, the results of the measurements may depend on the substrate used because of substrate-NPs interactions. In this work a slide of commercial mica was used as substrate. It is easy to obtain large very plain surfaces in mica by cleavage. However, those surfaces degrade easily in a few days when working in air because of pollution deposition and air moisture. Thus, clean surfaces were obtained cleaving the slide immediately before sample deposition and measurements. To cleave clean surfaces, adhesive tape was fixed to the surface of the mica slide and subsequently was retired by a firm and straight movement.

The resolution of the measurement can be increased maximizing the signal to noise (S/N) ratio. The observation of NP was performed in the so-called "tapping mode" that measures the modification of the tip oscillation amplitude due to the tip-sample interactions. We worked at constant amplitude: the system moves the tip up and down to maintain constant the tip oscillation amplitude. The vertical movement required to satisfy this condition while scanning the sample reproduces its topography. The "contact mode" is forbidden when the NPs are not strongly fixed or embedded in the substrate, because the tip mass is several orders of magnitude larger than NPs, so the lateral force should move the particles along the surface [12], [13].

In order to determine the best imaging conditions we measured amplitude vs distance, obtaining the curve shown in Fig. 1(a).

This curve represents the oscillation amplitude of the tip as a function of the tip-sample (in this case the tip-substrate) distance. Actually, the y axis does not represent the oscillations amplitude but the signal detected at the photodiode which is proportional to that value. According to Fig. 1(a), we could obtain good resolution working in the range 0.5 to 0.1 eV. However, we observed that working at very low values implies that the tip is closer to the sample and therefore, the risk of crashing or sample modification (movement of the NPs because of the tip-sample interaction) increases. On the contrary, large values reduce the resolution of the images. Hence, in our experience, the best working condition are intermediate values as, in this case, 0.3 eV. Working with these parameters we obtained the image shown in Fig. 1(b) for a mica substrate. As the profile in Fig. 1(c) shows, the roughness is about ~0.4 nm, low enough to observe NPs with few nanometers size.

2.2.2 Sample preparation

In order to observe individual NPs, they must be dispersed in liquid solvents. For those NPs capped with polar molecules the solvent was ethanol while toluene or tetrahydrofuran was used for NPs capped with non polar species. Approximately 1 to 10 mg of the sample were dissolved in 50 ml of the appropriate solvent. The solution has to be colourless in order to achieve a good dispersion of the NPs, which is essential to obtain the AFM images. These solutions containing the nanoparticles were sonicated for at least five minutes. Immediately after the sonication one or two drops of these solutions were deposited onto cleaved mica and they were allowed to evaporate under ambient conditions for one hour.

3. RESULTS

3.1 Observation of individual NPs

Figure 2 shows the Pd nanoparticles protected by tetrabutylammonium salts. Although TEM studies [3] revealed that the particle metallic cores were approximately spherical with average size about 2.4 nm, in the AFM images the particles width is fairly larger than their height. Actually, the average height obtained from the AFM measurements is similar to that obtained from HREM studies, whereas the average width is about 25 nm.

These results can be understood considering that AFM measures the interaction between the tip and the sample, and keep a constant distance between them. The tips have some thickness at the end, which is in the order of tens of nanometers. Thus, as it is explained in Fig. 3, the profile of the tip lateral displacement when scanning over a NP will be at least its width, that is clearly larger than the NP size. On the contrary, the maximum height of the tip matches quite well the size of the NPs. Therefore, when measuring small NPs with the AFM, all the information related to the particle size must be obtained from the height curves.

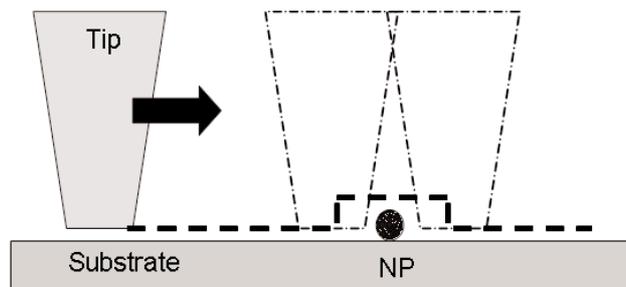


FIG. 3. Profile of the AFM tip displacement when scanning over the NP. The width of the NP measured by the AFM is at least the tip width at its end. (Carabias et al.)

Formally, it should be possible to get information about the particle size from their width, considering that the image is the convolution of the NPs and the tip. However, the tip geometry is difficult to characterise and can be modified during operation because of occasional crash with the sample, so it is better to analyse the NPs height to obtain information about their size.

A more detailed comparison analysis of the information obtained by AFM and TEM can be performed comparing the size histograms obtained by both methods. Figures 4(a) and 4(b) show AFM images obtained from thiol capped Au NPs. Once again, we found that the width of the NPs is always larger than 20 nm, while the height is in the 1 to 5 nm range. The size histogram corresponding to the height presented in Fig. 4(d) results almost identical to that obtained by TEM [2]. This confirms the fact that measuring the height of the NPs we obtain appropriate results about the NPs diameter.

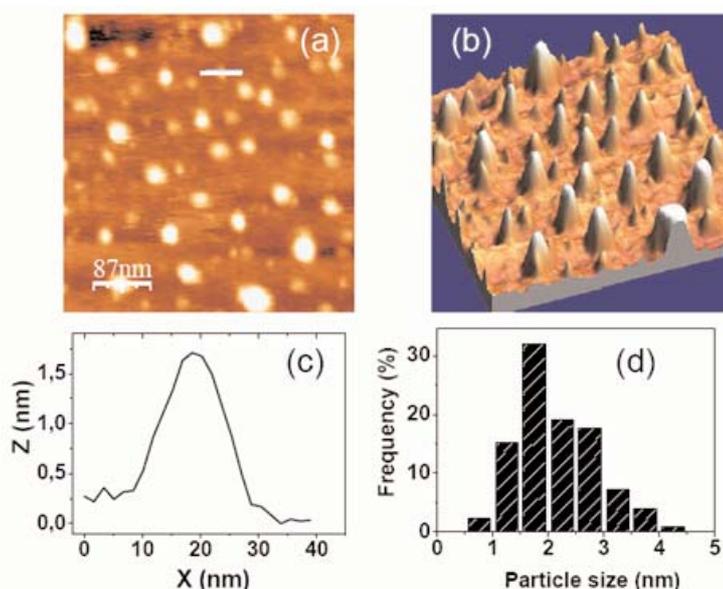


FIG. 4. (a) AFM image from Au thiol-capped NPs and (b) the 3D representation. (c) Height profile along the line indicated in (a). (d) Particle size histogram obtained from the height of the NPs. (Carabias et al.)

In general, SPM microscopies yield to larger sizes than TEM measurements. This is because TEM images the metallic core of the NP, whereas the SPM measures the whole NP and capping shell system. Actually, the difference between SPM and TEM has been used to measure the capping shell size<sup>6</sup>. However, in the case of AFM tapping mode, if the capping system is soft, it is compressed under the pressure applied by the tip, and the measurement do not give a real value of the NP+shell size [19]. To this purpose, a less invasive technique is needed. This is the case of the no-contact mode [9], in which the reduction of oscillation amplitude is due only to shifts in the resonant frequency because of atomic Van der Valls forces.

Another remarkable feature we observed was that the NPs seemed to grow with time. In average, for each day after the sample preparation, the particle height increased about ~4 nm per day during the five days after deposition. This effect is probably due to the deposition on the NPs surface of some chemical species present in the air. Such effect will be dependent on the capping species and the environment, but it is worthy to bear it in mind in order to avoid mistakes in the measurement of particle size. Hence, it is important to perform the measurements just immediately after the sample preparation.

### 3.2 Observation of aggregates

As stated above, one of the advantages of AFM is that it allows the observation of some features as possible aggregation states of the particles onto different substrates. In Fig.5, we observe AFM images from alkylammonium protected Au NPs, which were less dispersed (increasing their concentration on the solvent or reducing sonication time). The NPs tend to form rings when they are deposited onto the mica substrate. In this case, it is possible to observe the individual NPs as well as the agglomerates. The agglomerate rings are about 1 micron size, and the particles are likely to join the ring, although some of them appear also inside the ring. In these images it is also possible to observe individual NPs distributed onto the substrate.

However, if the NP have a strong tendency to aggregate, it may not be possible to observe them individually. As an example, Fig. 6a shows thiol-capped silver NP. Optical measurements confirmed that NPs were spherical and smaller than 10 nm size. From the AFM images, the particle height (Fig. 6b and 6c) is between 2 and 2.6 nm with a maximum in 2.3 nm, whereas the width is above 100 nm (Fig. 6d). This width is too big to consider that they are individually isolated and, in this case it can not be due to the tip geometry. Taking into account these points, it seems that NPs are laterally aggregated. The aggregation is so strong that AFM resolution is not enough to distinguish individual NPs. The aggregation is probably originated during the NP deposition process onto the substrate or during the fabrication process. These results also point out that the AFM observation of NP is not exempt of certain problems. If the measurements are not carried out carefully nor they are repeatable, it can lead to mistakes in the structural characterization of the NP. In particular, the only observation of NPs with AFM, without other techniques can yield to false particle sizes.

## 4. CONCLUSIONS

In summary, we showed that it is possible to observe small NPs (size 1-5 nm) with a standard AFM. To this purpose, the substrate and measurement conditions must be optimised, since we are close to the resolution limit of the technique. Information about NP geometry must be obtained from their height, while the width is largely distorted by the tip geometry. AFM imaging of NP results complementary to TEM measurements and allows studying the aggregation of NPs. However, the only analysis of the NPs using AFM, without other techniques may lead to large mistakes if the particles are aggregated.

### Acknowledgements

The authors thank A. Gil and P. Ares from Nanotec for the continuous technical support and valuable advice about the AFM equipment. Authors thank I. Rosa for her help in the preparation of the nanoparticles. Financial support from the MCyT and Junta de Andalucía is also acknowledged.

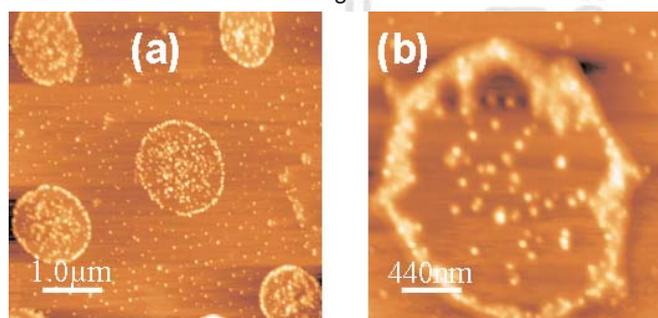


FIG. 5. AFM images from Au NPs protected by ammonium salts showing aggregation rings. (Carabias et al.)

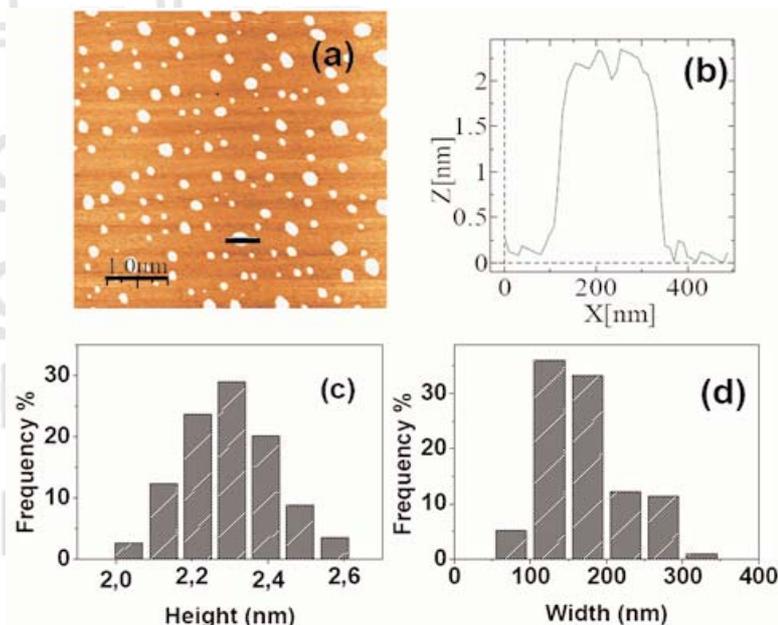


FIG. 6. (a) AFM image from Ag thiol-capped NPs and (b) the height profile along the line in the figure. (c) and (d) represent the height and width histograms respectively (obtained from several images). (Carabias et al.)

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Networking is vital to any scientist and even more so for persons working in the inter-disciplinary field of Nanotechnology and in particular Nanomodelling. To fulfil this necessity, **M4nano** will provide a comprehensive guide -“who’s who”- of groups working in Modelling at the nanoscale listing their accomplishments, background, infrastructures, projects and publications. In this way, **M4Nano** completes the aim of both raising awareness of scientists in Nanotechnology modelling issues and aiding them in developing beneficial collaborations and employment opportunities.

Emerging research areas such as Molecular Electronics, Biotechnology, Nanophotonics, Nanofluidics or Quantum Computing could lead in the mid-term future to possible elements of nano-based devices. Modelling behaviour of these possible nanodevices is therefore becoming more and more important and should allow to: (i) Visualise what happens inside a device (ii) Optimise the devices under study (iii) Improve understanding of device properties (physical, chemical, etc.).

**M4nano** in close collaboration with other European Research Institutions deeply involved in “modelling at the nanoscale” will develop tools such as a user’s database, a forum to stimulate discussions about the future of Nanocomputing, a source of documents (courses, seminars, etc.) on modelling issues, etc. and in the mid-term future implement a computational HUB, repository of simulation codes useful for modelling and design of nanoscale electronic devices .

Information spreading will also be enhanced using mailing list alerts, press releases and flyers. Collaborations with similar initiatives such as the **NanoHub** (USA) or **Icode** (Italy) will also be set-up.



For more Information contact:  
**Dr. Antonio Correia** ([antonio@phantomsnet.net](mailto:antonio@phantomsnet.net))

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**NANO News - <http://www.phantomsnet.net/Resources/news.php>****Carbon nanotubes target OLED anodes (May 22, 2006)**

<http://www.nanotechweb.org/articles/news/5/5/13/1>

Researchers in Canada claim to have demonstrated organic light-emitting diodes (OLEDs) based on carbon nanotube anodes that are 70% as efficient as comparable indium tin oxide (ITO) devices.

*Keywords: Nanotubes*

**Carbon nanotube membrane filters fast (May 18, 2006)**

<http://www.nanotechweb.org/articles/news/5/5/11/1>

Researchers at Lawrence Livermore National Laboratory and the University of California, Berkeley (US), have experimentally demonstrated the predicted fast transport of water and gases through membranes containing carbon nanotube pores.

*Keywords: Nanotubes / Energy*

**ATDF and UT Launch Advanced Processing and Prototyping Center to Help Bring Nanoelectronics to the Marketplace (May 15, 2006)**

<http://www.atdf.com/news/releases/20060515.htm>

ATDF and The University of Texas at Austin (UT), have joined forces to create the Advanced Processing and Prototyping Center (AP2C), a highly specialized R&D program designed to speed leading-edge nanoelectronic technology to the marketplace.

*Keywords: Nanoelectronics / Scientific Policy*

**Carbon nanotubes hottest topic in physics (May 08, 2006)**

<http://www.nanotechweb.org/articles/news/5/5/5/1>

Carbon nanotubes are the hottest topic in physics, according to a new way of ranking the popularity of different scientific fields. Nanowires are second, followed by quantum dots, fullerenes, giant magnetoresistance, M-theory and quantum computation.

*Keywords: Nanotubes / Nanotechnologies*

**Philips and Dutch University of Groningen demonstrate a breakthrough in fabricating molecular electronics (May 04, 2006)**

<http://www.research.philips.com/newscenter/archive/2006/060504-molelec.html>

Scientists from Philips Research and the University of Groningen (the Netherlands) have for the first time fabricated arrays of molecular diodes on standard substrates with high yields. The molecular diodes are as thin as one molecule (1.5 nm), and suitable for integration into standard plastic electronics circuits.

*Keywords: Molecular Electronics / Nanoelectronics*

**IBM Researchers Demonstrate New Method for Rapid Molecule Sorting and Delivery (May 01, 2006)**

[http://domino.watson.ibm.com/comm/pr.nsf/pages/news.20060501\\_afm.html](http://domino.watson.ibm.com/comm/pr.nsf/pages/news.20060501_afm.html)

IBM researchers have demonstrated a new nanoscale method that both rapidly separates very small numbers of molecules and also delivers them precisely onto surfaces with unprecedented control. When fully developed, the new technique has the potential to improve such diverse applications as medical lab tests and future nanoelectronic circuit manufacturing.

*Keywords: Nanoelectronics / Nanoprobes / Nanomedicine*

**Checking up on nanotube behaviour (April 28, 2006)**

<http://www.nanotechweb.org/articles/news/5/4/15/1>

Researchers at Columbia University and Brookhaven National Laboratory, both in the US, have used electron diffraction and Rayleigh scattering spectroscopy to determine the properties of individual single-walled carbon nanotubes. The team confirmed that nanotubes exhibit two behaviours predicted by the single-particle tight-binding model of electronic structure.

*Keywords: Nanotubes*

**Fujitsu makes a big push in nanotechnology (April 13, 2006)**

<http://www.nanotechweb.org/articles/feature/5/4/1/1>

Japanese IT and communications giant Fujitsu is investing considerable sums in nanotechnology research.

*Keywords: Nanophotonics & Nano-Optoelectronics, Nanotubes, Scientific Policy*

**Nanogenerator to Power Nanoscale Devices (April 13, 2006)**

<http://www.gatech.edu/news-room/release.php?id=932>

Researchers have developed a new technique for powering nanometer-scale devices without the need for bulky energy sources such as batteries.

*Keywords: Nanosensors & Nanodevices*

**Graphene Provides Foundation for New Electronics (April 13, 2006)**

<http://www.gatech.edu/news-room/release.php?id=931>

Ultra-thin sheets of graphite allow fabrication of devices that handle electrons as waves.

*Keywords: Nanoelectronics*

**FET launches a public consultation on future directions of research for FP7 (April 09, 2006)**

<http://cordis.europa.eu/ist/fet/id.htm>

The Commission is preparing the 7th Framework Programme for RTD (FP7), the EU's chief instrument for funding scientific research and technological development over the period 2007 to 2013.

*Keywords: Scientific Policy*

**NANO Conferences - <http://www.phantomsnet.net/Resources/cc.php>**

**(June 2006)**

**Ultimate Lithography and Nanofabrication for Electronic and Life Science (LITHO2006)**

June 25-30, 2006 - Marseille (France)

<http://www.lithoconf.com>

*NanoPhotonics & Nano-Optoelectronics, NanoBiotechnology, NanoFabrication*

**MIGAS'06 - Emerging silicon devices for the end of the roadmap**

June 25-30, 2006 - Autrans/Grenoble (France)

<http://www.migas.inpg.fr/>

*Nanoelectronics, Nanotechnologies*

**International Workshop on Nanostructured materials (NANOMAT2006)**

June 21-23, 2006 - Resort Dedeman Antalya (Turkey)

<http://www.metucenter.metu.edu.tr/nano2006/>

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**VIII International Workshop on Non-Crystalline Solids**

June 20-23, 2006 - Oviedo (Spain)

[http://www.nanomagnetism.org/iwnacs\\_2006/](http://www.nanomagnetism.org/iwnacs_2006/)

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**NanoBio-Europe'06**

June 14-16, 2006 - Grenoble (France)

<http://www.minatec.com/nanobio2006/>

*NanoBiotechnology, NanoMedicine*

**(July 2006)**

**ICN&T 2006 - International Conference on NanoScience and Technology (NANO9 meets STM'06)**

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<http://www.icnt2006.ch/>

*Molecular Electronics, NanoBiotechnology, NanoMedicine*

**Summer School on "Metal Clusters and Surfaces"**

July 03-06, 2006 - Tirrenia-Pisa (Italy)

<http://h2.ipcf.cnr.it/alex/SchoolMCS/school.html>

*NanoMaterials, NanoPatterning*

**(August 2006)**

**ESONN2006 - European School on Nanosciences and Nanotechnologies**

August 27 - September 16, 2006 - Grenoble (France)

<http://www.esonn.inpg.fr/>

*Nanotechnologies*

**Second: Psi-k/NanoQuanta School + Workshop Proposal**

August 27 - September 11, 2006 - Benasque Center for Physics (Spain)

<http://benasque.ecm.ub.es/2006tddft/2006tddft.htm>*Theory & Modeling***CANEUS2006. MNT for Aerospace Applications**

August 27-September 01, 2006 - Toulouse (France)

<http://www.caneus.org/CANEUS06>*NEMS & MEMS, NanoMaterials, NanoSensors & NanoDevices***XV International Materials Research Congress.**

August 20-24, 2006 - Cancún (México)

<http://www.imrc2006.buap.mx>*NanoMaterials***(September 2006)****WS-19 Physical and Chemical properties of Nanoclusters**

September 25-27, 2006 - Avila (Spain)

<http://www.icmm.csic.es/aseva/docs/ws-19%20circular.pdf>*NanoMaterials***V Spanish Conference of Forces and Tunnel 2006**

September 20-22, 2006 - Murcia (Spain)

<http://www.imm.cnm.csic.es/FYT06/>*NanoProbes, Theory & Modeling***International conference on Micro- and Nano- Engineering (MNE2006)**

September 17-20, 2006 - Barcelona (Spain)

<http://www.mne06.org>*NEMS & MEMS***ESONN2006 - European School on Nanosciences and Nanotechnologies**

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September 11-15, 2006 - Granada (Spain)

<http://ergodic.ugr.es/cp/>*NanoBiotechnology, Theory & Modeling***Trends in Nanotechnology (TNT2006)**

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<http://www.tnt2006.org>*Nanoelectronics, NanoMaterials, NanoBiotechnology***NANO2006 Workshop. 'Perspectives in Nanoscience and Nanotechnology'.**

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### PhD and Postdoctoral fellowships in single molecule Biophysics

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Applications should be submitted by e-mail to: Prof. M.F. Garcia-Parajo ([Hmgarcia@pcb.uv.es](mailto:Hmgarcia@pcb.uv.es))  
BioNanophotonics group, Laboratory of Nano-BioEngineering, Barcelona Scientific Park (PCB), Josep Samitier 1-5, 08028 Barcelona, Spain;  
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### Post doctoral position in 2D polymerization

The Nano-Femto Laboratory (NFL) at INRS is seeking postdocl candidates to strengthen a multidisciplinary team of scientists based at INRS-EMT ([www.emt.inrs.ca](http://www.emt.inrs.ca)) and McGill University (Prof. Dimitrii Perepichka), to investigate the synthesis of 2 D conjugated polymers.

The main research area of this team focuses on molecular self-assembly at surfaces investigated by Scanning Tunneling Microscopy both in Ultra High Vacuum and in solution. The synthesis of 2D polymers will be carried out using various approaches, including electrochemical and catalytic.

PhD level candidates are sought with expertise in, though not limited to, one or more of the following areas: Scanning Tunneling Microscopy in solution and/or in UHV and surface science techniques including XPS and IR; experience with synchrotron based techniques may also be useful

The starting salary is 35,000 CA\$ per year and the position is awarded for one year, renewable. This project is supported by the Petroleum Research Fund of the American Chemical Society and by the US Air Force Office of Scientific Research.

To apply and for further information please send a cover letter with your research interests and a CV with the names and contact details of at least 3 referees to:

Professor **Federico Rosei**, ([rosei@emt.inrs.ca](mailto:rosei@emt.inrs.ca)) Canada Research Chair in Nanostructured Organic and Inorganic Materials  
INRS-EMT, 1650 blv. Lionel Boulet, Varennes, QC J3X 1S2, Canada.

### Post doctoral position in nanostructured biomaterials

The Nano-Femto Laboratory (NFL) at INRS is seeking postdoctoral candidates to strengthen a multidisciplinary team of scientists based at INRS-Energy-Materials-Telecommunications ([www.emt.inrs.ca](http://www.emt.inrs.ca)), University of Montreal (Professor Antonio Nanci) and McGill University (Professor Dimitrii Perepichka), exploiting nanotechnology approaches in tissue regeneration and biomaterials.

The present research areas of this team are the following: molecular self-assembly and nanoscale templating at surfaces investigated by Scanning Tunneling Microscopy, Nanoscale modification and characterization of biocompatible materials for orthopaedic implants (mostly Ti-based alloys) as well as Calcified tissue formation in vitro.

PhD level candidates are sought with expertise in, though not limited to, one or more of the following areas: biocompatible materials, surface modification from a materials point of view, surface characterization from a materials point of view (including STM, AFM, SEM, XRD, XPS, IR)

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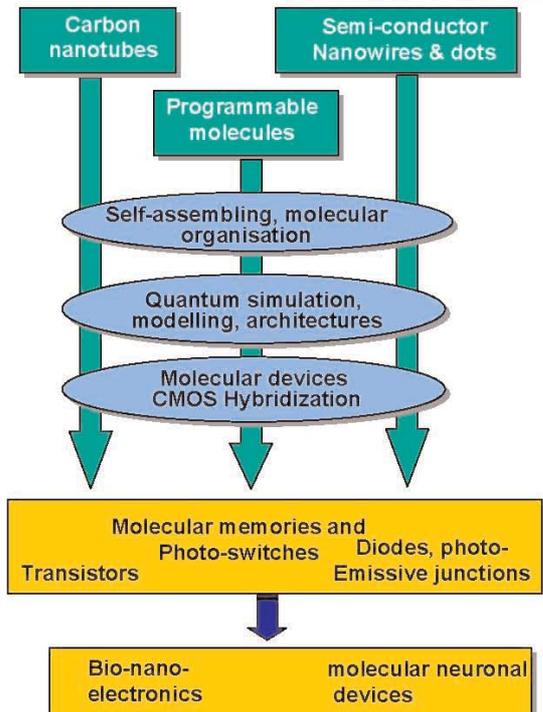
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Women are actively encouraged to apply.

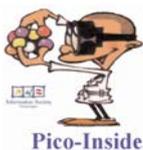


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## Chemistry towards intramolecular computing

### Introduction

A. Gourdon

NanoSciences Group, CEMES-CNRS 29 rue J. Marvig, P.O. 94347, F-31055 Toulouse Cedex 04, France

The objective of the Pico-inside project is the exploration of the fundamental and technological aspects towards intramolecular computing. In its final design (figure 1), the envisioned device, working at room-temperature, will comprise a large molecular circuit fixed on an insulator and connected to several nano-electrodes in ultra-clean environment, in a perfectly controlled geometry on a planar insulating substrate. Each term of this proposition is nowadays highly prospective and will obviously require extensive studies. By consequence carefully designed molecules perfectly adapted to the experiments towards these aims will have to be imagined and synthesized.

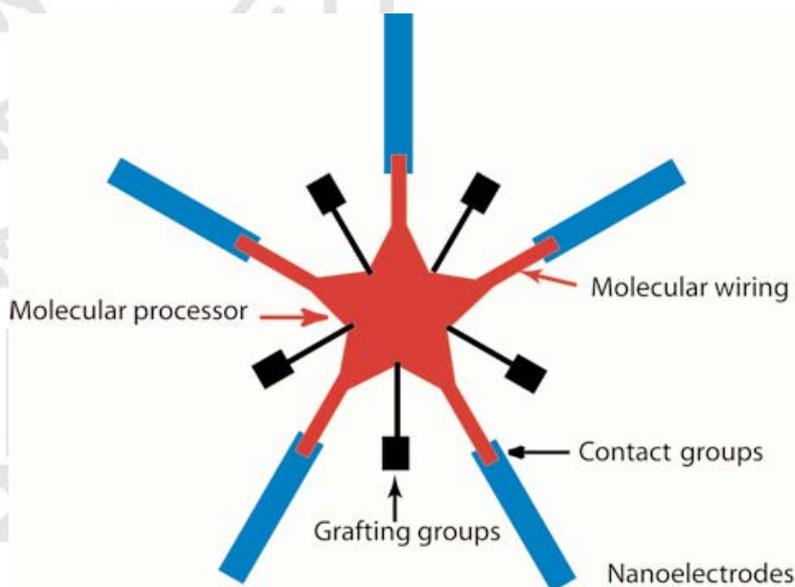


Figure 1. Schematic view of a monomolecular computing device.

On the way to this complex design, the Pico-Inside consortium will focus on simpler model systems, smaller molecules connected to two to three electrodes, with the objective to understand the fundamental laws at this scale and to propose theories and technological solutions. Let's now address some of the key problems to be solved:

#### a) Planar experiment

Clearly the design schematized in figure 1 implies to work on planar insulating surfaces. But so far most conductance measurements and switching experiments on a single or a few molecules have been done in a "vertical" geometry with the molecule more or less perpendicular to the metallic surface (Fig. 2a) and addressed by a STM tip or in a "suspended" geometry with the studied molecule between two meso-scale electrodes in break junctions (Fig. 2b), holes, cross-bars...

The main draw-backs of these experimental set-ups (a and b) are first the impossibility to connect the molecule to more than 2 electrodes, but also their blind character: no control the number of molecules, no access to the molecule conformation, to the precise molecule-electrode contact geometries etc... But we now know that these parameters are crucial and that they rule all conductance and switching experiments. As a consequence, to tackle this problem one has to get a precise image of the molecule and its environment during or just before the measurement. Accordingly it is required to work in planar configuration, ie with set-ups in which the electrode-molecule direction is more or less parallel to the STM or AFM scanning plane so that it gives access to all physical and chemical parameters during the experiments. These constraints have led the Pico-Inside partners to focus on three experimental geometries (c to e) shown on figure 2 for which different types of molecules have to be designed:

-STM on metallic or semi-conducting surfaces (Fig 2c) using specifically designed molecules in which the active part is lifted above the substrate by molecular spacers to reduce as much as possible the metal-molecular wire electronic coupling. This is the lander concept. It has been largely explored in the European project BUN and most parameters describing the properties of these molecules have been explored: adsorption, mobility, conductance, surface restructuring etc..[1]

But this concept is a sort of trick which allows the study of molecular devices by STM on metals but is limited to a reduced number of experiments and further advances in this domain require now to work on insulating substrates

-Non-contact AFM on bulk insulators (Fig. 2d). This is the most exploratory system since even though the properties of large organic molecules on metallic surfaces have been extensively studied in the past decades [2], much less is known on molecules on insulators. This situation can be explained by several factors like (a) the less advanced development and the difficulty of NC-AFM techniques when compared with STM, but this situation is improving rapidly, (b) the lack of complete understanding of the image formation mechanism and of precise simulation tools, and (c) a more fundamental difficulty: the high mobility of organic molecules on some insulating surfaces, an even worth problem for isolated molecules. For points b and c, the solutions will arise from extensive collaborations between theoreticians, chemists and microscopists. Indeed, the complete understanding of the NC-AFM image contrast for isolated soft organic molecules, the manipulation control at sub-molecular level will necessitate series of experiments on well identified families of molecules on different substrates. The use of NC-AFM in this domain will only be effective once these parameters are fully mastered.

-STM on insulating layers/metal (Fig 2e). This intermediate solution permits to exploit all STM possibilities (imaging at atomic scale, manipulation, spectroscopy) but with reducing the molecule-surface electronic coupling by use of thin layers of insulators (salts or oxides) on metals. Several experiments in the frame of the European project CHIC (Consortium for Hamiltonian Intramolecular Computing) have shown that it was possible to image and manipulate planar polyaromatic compounds like pentacene [3] on two monolayers of sodium chloride on copper. The electronic decoupling between the molecule and the copper surface is high enough to allow an imaging of the "free molecule

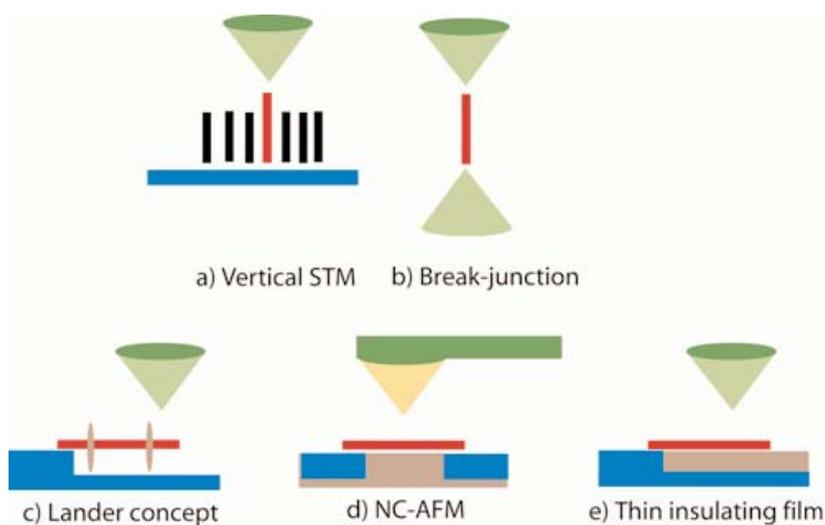


Fig 2: Experimental set-ups to measure molecular conductances and switching. The molecule is in red, the metallic substrates in blue, the tip in green and the insulators in brown. In a) and b) the molecule is parallel to the tunnel current which prevents any determination of the molecular conformation and electrode-contact geometry. The set-ups c) to d) are named planar in the text. They allow full submolecular imaging, atomic and molecular manipulation.

frontier orbitals" without too much broadening. This breakthrough opens numerous possibilities like the study of molecular devices in action for instance. Several other experiments on phthalocyanine on ultrathin alumina film grown on NiAl(110) surface have also shown the potential of this geometry for the study of electronic properties of single molecules [4]. The major foreseen difficulty will be to fabricate planar, monolayer or buried, nanoelectrodes to address these molecules [5].

b) Processing unit. Despite the theoretical design of a complete realistic molecular processor still remains a long term objective, many preliminary experiments will have to be carried out on smaller systems and simpler functions to test the validity of recently described new concepts such as Hamiltonian computing explored in the IST-FET programme (<http://www.cemes.fr/chic/>). For instance we will first focus on 3 terminal planar polyaromatic devices such as described by A. M. Echavarren in the part 1: Design of New Polyarene Scaffolds (see below)

c) Molecular wiring. Although this molecular wiring is a part of the central unit, the conception of efficient high conductance branches will probably be necessary for practical reasons to maintain the nanoelectrodes at a large enough distance which will also avoid inter-electrode crosstalk. Electronic addressing of the core "molecular processor" will be done by molecular wiring which implies studies of high conductance molecular systems like the polyacenes or polyrylenes ribbons. One solution currently explored in the Pico-Inside project is the use of (hetero)helices. This point will be discussed in the part 2: BLABLA

d) Contacting groups. These molecular wires or ribbons will be addressed by nanoelectrodes and the quality of the contact is a problem tackled by the Pico-inside project since we know that reproducible addressing requires 0.05 nm precision. Two components of this problem will be studied: first, the type of molecule-electrode chemical

bonding remains an open question. It is now known that the creation of a strong chemical bond between the molecule and the electrode can be detrimental to the contact conductance by localization of the involved orbitals. One solution could be the use of large physisorbed polyaromatic ribbons as suggested above. Second the precise positioning of the molecular wire with respect to the nanoelectrode atoms, possible by STM molecular manipulation for scientific exploration, will have to be replaced by self-position in large scale fabrications. One possible solution could be the development of molecular moulding which will be discussed in part 3: Molecular moulding . It could allow the fabrication in UHV of nanoscale electrodes directly contacting their molecular mould.

e) Immobilisation on the insulating surface. The high mobility of organic molecules on perfect insulating surfaces at room temperature may require the addition of anchoring groups to maintain the molecular processor in a fixed place at room temperature and reduce intramolecular movements.

One possible solution currently being explored is to change the surface geometry by creation of single defects or nanopits in which one or a few molecules can be trapped as described by Socoliuc et al. [6]. The main advantage of this approach is that it readily provides highly charged centres for the nucleation of a 2D ordered molecular island. The disadvantage is that the molecules are then in a trench, surrounded by strong electric dipoles and that it will be difficult to contact them unless 2D metallic nanoelectrodes could also be formed inside the pitches. But the most general solution will be to use the molecule surface interactions by equipping the molecules with various grafting arms depending on the type of substrate (ionic, oxide, diamond). The main benefit here is that these equipments

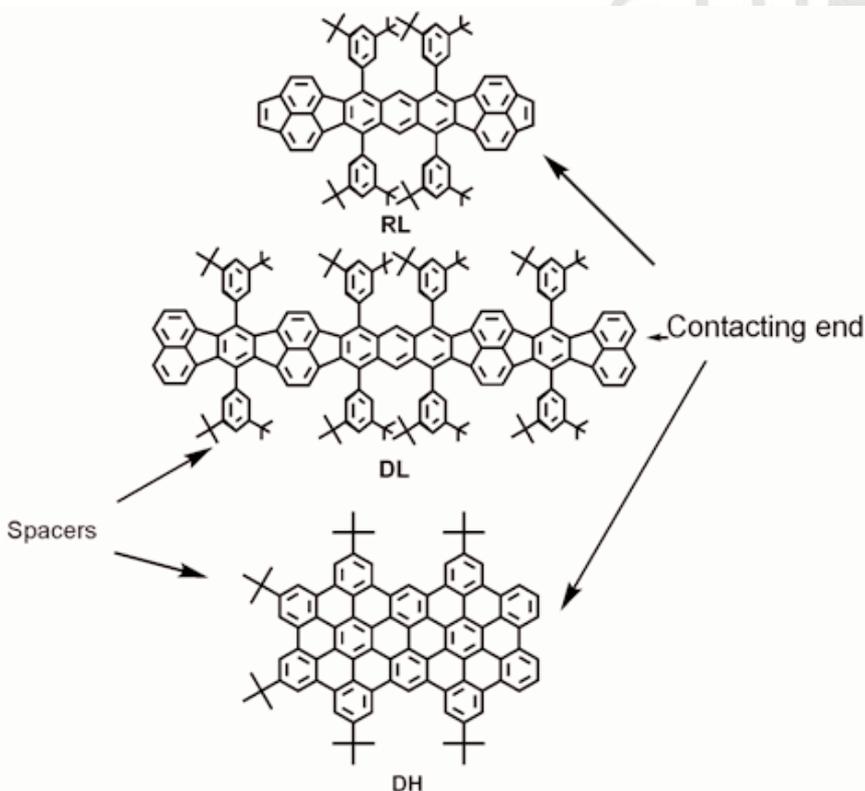


Figure 3. Examples of molecular landers. The molecules comprise an active part (the central polyaromatic hydrocarbon), 4 to 8 spacers, and one or two contacting ends.

can be external branches with little electronic coupling with the active core of the molecule. Of course the central part will also be in interaction with the surface but it is foreseen that, in the case of polyaromatic hydrocarbons, this molecule-surface interaction will be significantly weaker than chemisorbed groups or highly polar arms. Therefore experiments on the mobility of series of molecules on various substrates can be decoupled from those on the "molecular processor" which simplifies the design of molecular benchmarks.

f) Ultra-clean environment. Using a single molecule in a perfectly controlled way obviously necessitates working in ultra-clean environment. So far, a large majority of the conductance experiments described in the literature have been carried out between ductile gold electrodes (or tips) on self-assembled monolayers of organic thiols obtained by dipping electrodes in organic solutions. Most of the time, the molecule being studied is inserted in the self-assembled monolayer by chemical substitution of one or some alkyl thiols. Obviously these chains prone to substitution are the mobile ones, those bonded to defects, step-edges, grain boundaries for instance and not those nicely packing on the flat parts of the surface. And the inserted studied molecule is then loosely bonded to the substrate and it has been shown that this bond-formation/bond-breaking mechanism was the cause of most blinking or switching observations. Furthermore most measurements are done in air at room temperature or in low vacuum, environment for which even partially hydrophobic surfaces are covered with several nanometers of water. Many other potential

problems have also been identified like the SAM reorganisation under applied potential, the formation of metallic filaments between electrodes etc., etc.. In these conditions it is exceedingly difficult to extract significant, unquestionable laws from poorly reproducible experiments.

Therefore, one of the specifications of the Pico-Inside project is to carry out experiments in UHV on ultra-clean surfaces and of course this point transfers several constraints on the chemical design.

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The general purpose of this workshop is to gather researchers interested in the design and fabrication of nano-devices and micro-devices for electronics and life science. The association of researchers working in theory, design/modelling, on miniaturisation (top-down, bottom-up and coupling of both processes) and biology will be an opportunity for fruitful discussions.

### Keynotes

- |   |   |
|---|---|
| <b>Jouni Ahopelto</b> VTT (Finland)                       | <b>Nikolaj Moll</b> IBM Research (Switzerland)            |
| <b>Helmut Bechtel</b> Philips Technologie GmbH (Germany)  | <b>Francesc Perez-Murano</b> CSIC-CBM-IMB(Spain)          |
| <b>Leslie Carpenter</b> Dow Corning Corporation (Ireland) | <b>Dietmar Pum</b> Center for Nanobiotechnology (Austria) |
| <b>Anne Charrier</b> CRMCN - CNRS (France)                | <b>Freimut Reuther</b> Micro Resist Technology (Germany)  |
| <b>Stephen Y. Chou</b> Princeton University (USA)         | <b>Viatcheslav Safarov</b> CRMCN - CNRS (France)          |
| <b>Gabriel Crean</b> Tyndall National Institute (Ireland) | <b>Helmut Schiff</b> Paul Scherrer Institut (Switzerland) |
| <b>Paolo Facci</b> S3-INFM-CNR (Italy)                    | <b>Mark Welland</b> IRC / Cambridge University (UK)       |
| <b>Alexander Latyshev</b> RAS (Russia)                    | <b>Heiko Wolf</b> IBM Research GmbH (Switzerland)         |
| <b>Gilbert Lecarpentier</b> SUSS MicroTec AG (Germany)    | <b>Cornelis Wouter Hagen</b> TU Delft (The Netherlands)   |
| <b>David Mendels</b> NPL Management Ltd (UK)              |   |

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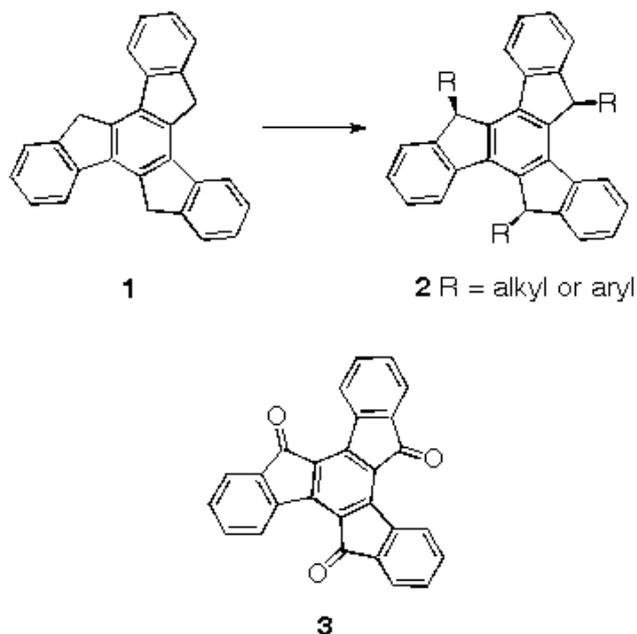
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## 1. Design of New Polyarene Scaffolds

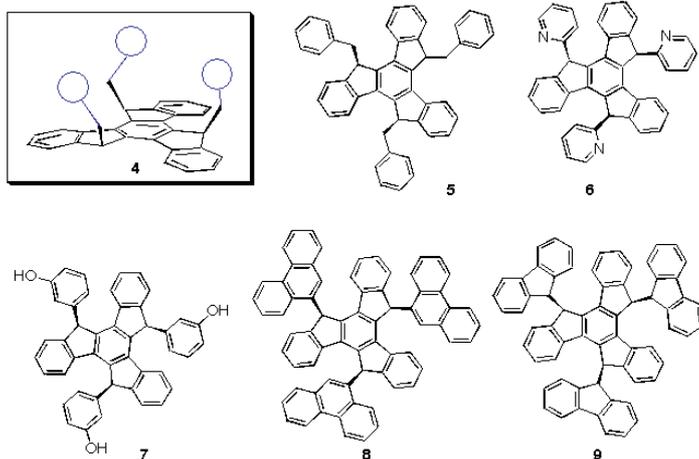
A. M. Echavarren

Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 Tarragona (Spain) (aechavarren@iciq.es)

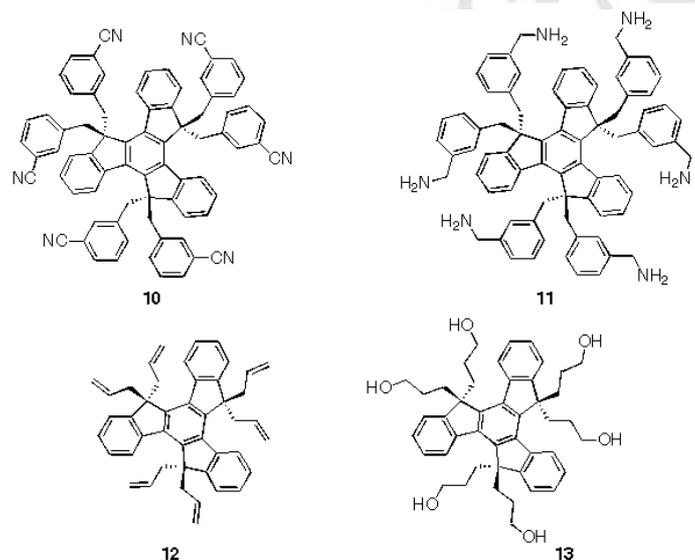
Truxene (**1**) and truxentrione (**3**) are readily available materials that can be prepared in the laboratory in large scale in a single step [1]. Truxene (**1**) has been used for the construction of larger polyarenes [2,3,4,5,6] and for the synthesis of new materials [7,8,9,10] we developed a synthesis of derivatives (**2**) by reaction of the trianion of (**1**) with a variety of alkylating agents followed by *anti* to *syn* isomerization with KO<sup>t</sup>Bu in *t*BuOH [11,12]. We have also reported that *syn*-5,10,15-triaryltruxenes (**2**) (R = aryl) can be obtained from truxentrione (**3**) by addition of aryllithium compounds, followed by reduction of the alcohols with Et<sub>3</sub>SiH and BF<sub>3</sub>, and *anti* to *syn* equilibration.



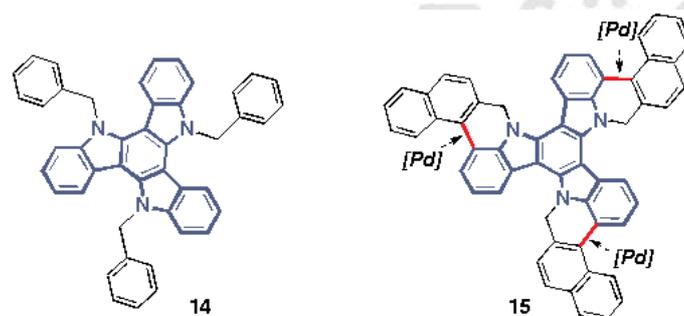
Truxene provides a unique platform for the preparation of derivatives (**4**) with an almost flat aromatic surface and three groups extending above that surface. In particular, tribenzyl derivatives such as (**5**), with a variety of functional groups at the peripheral phenyl groups, can be readily assembled in two steps from truxene in high yield. Similarly, derivatives (**6**)–(**9**) with aryl groups (even very bulky groups) directly attached to the truxene core have been prepared from truxene (**1**) or truxentrione (**3**).



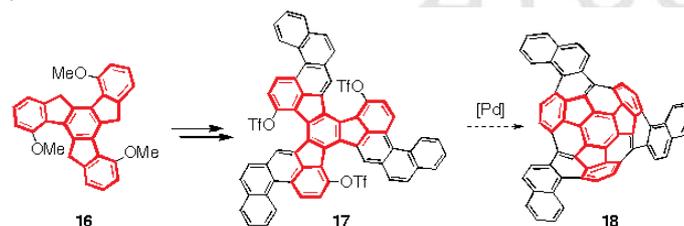
Substitution of the truxene core with up to six groups is also possible, leading to compounds such as (**10**)–(**13**) [14]



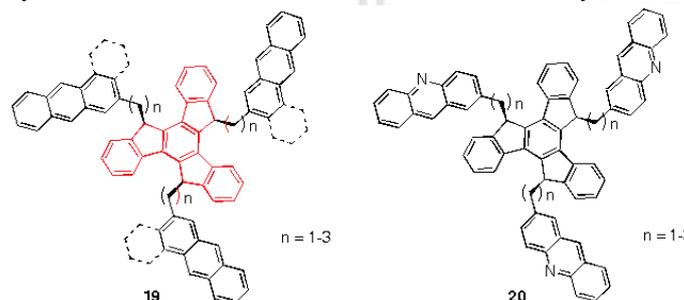
Triaza analogues (**14**) can be prepared from symmetrical triindole ("triazatruxene") by using simple *N*-alkylations as well as palladium-catalyzed reactions [15].



For the synthesis of polyarenes with the topology of the fullerenes, , , trimethoxy truxene **16** has been transformed into **17** (a "crushed fullerene") a potential precursor opened C<sub>60</sub> compounds such as **18**.



As one of the immediate goals of the PICOINSIDE project, we plan to prepare a series of new truxene derivatives with larger pendant polyarene groups **19** (i.e. anthracene, tetracene, tetraphene, or larger polyarenes). Hexasubstituted derivatives will also be prepared. Similarly, acridine derivatives **20** will be synthesized from 1-, 2-, 3-, or 4- acridinecarboxaldehydes.



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## 2. Helicenes as Intriguing Objects for Chemical and Physical Studies

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### Introduction

Helicenes are unique 3-D aromatic systems that are inherently chiral, chemically stable, soluble in common organic solvents and perfectly pi-conjugated materials.[1] They possess a helical arrangement as a result of the steric repulsion of terminal benzene rings (Figure 1). Starting from the systems comprising six fused benzene rings, they are configurationally stable even at elevated temperatures and can be separated into enantiomers. Due to the above mentioned facts, helicenes represent intriguing objects for studying novel chemical and physical properties.

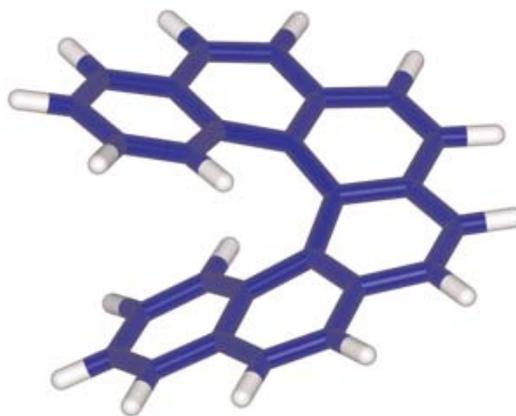


Figure 1. Hexahelicene.

### Synthesis

Even though helicenes were considered rather exotic compounds for the past decades, several methods for their preparation have emerged. Katz et al. [2] substantially improved Matin's photocyclisation procedure, [3] introducing bulky substituents to prevent a non-regioselective ring closure and, furthermore, using methyloxirane to preclude photoreduction of the double bonds in a starting material. However, other important drawbacks of the method have remained. It is not general and, even more seriously, high dilution conditions to suppress polymerisation of the starting material make it extremely laborious. The same author introduced an alternative approach to helicenes which is based on a Diels-Alder reaction of aromatic vinyl- or bisvinylethers with p-benzoquinone to afford helicenes having terminal quinone rings. [4] The simplicity of this method represents, on the other hand, a drawback - the variations of substituents on the terminal rings of a helicene skeleton are rather limited.

To make the synthesis of helical aromatics more practical, we have proposed a novel strategy for the preparation of helicenes and helicene-like compounds. We have already demonstrated that intramolecular [2+2+2] cyclisation of aromatic triynes in the presence of transition metal catalysts such as Ni0 or CoI complexes is a viable, efficient and highly flexible approach (Figure 2). [5] Using this methodology, we synthesised various helicene derivatives ranging from penta- to heptacyclic backbones, being partially hydrogenated or fully aromatised, consisting of carbocycles only or incorporating seven-membered heterocycles and bearing different functional groups at different positions. Currently we are paying our attention to azahelicenes, extended helicenes and the preparation of individual enantiomers (Figure 3).

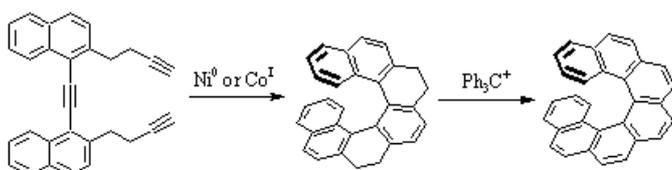


Figure 2. Helicenes via [2+2+2] cycloisomerisation.

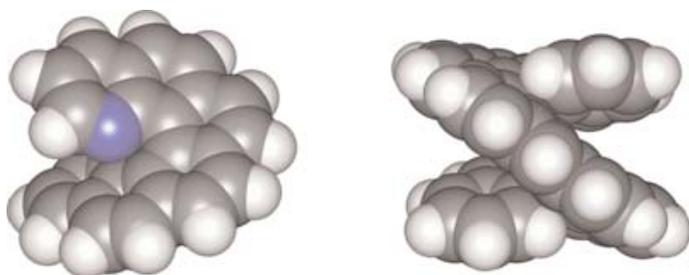


Figure 3. Helical aromatics of our interest.

### Highest Helicene Homologues

The world record in the realm of carbohelicenes belongs to Martin who prepared [14]helicene (Figure 4). [6] As far as heterohelicenes are concerned, the longest derivative had 15 thiophene/benzene rings combined together. [7] Recently, Vollhardt has published synthesis of [17]helicene that is comprised of alternating fused benzene and cyclobutane rings. [8]

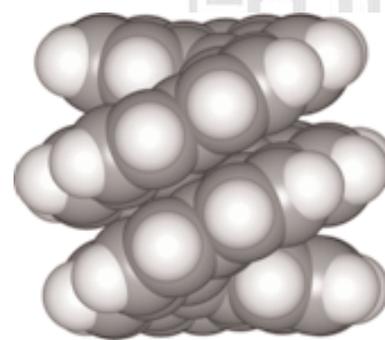


Figure 4. The highest [14]helicene prepared by Martin.

### Chemical & Physical Properties

Due to the unique structure of the helical aromatic scaffolds, interesting properties of helicene derivatives have been foreseen and demonstrated. One of the most astonishing attributes of helicene assemblies was described by Katz. [9] Properly substituted nonracemic helicenes, possessing both electron-rich inner rings and electron-deficient outer ones, can aggregate spontaneously to create columnar structures exhibiting enormous values of optical rotation and NLO properties. In Langmuir-Blodgett films, a parallel columns array can be observed directly by AFM. [10] Moreover, these columns are further organised into long micrometre-wide lamellar fibres being visible under an optical microscope. [11]

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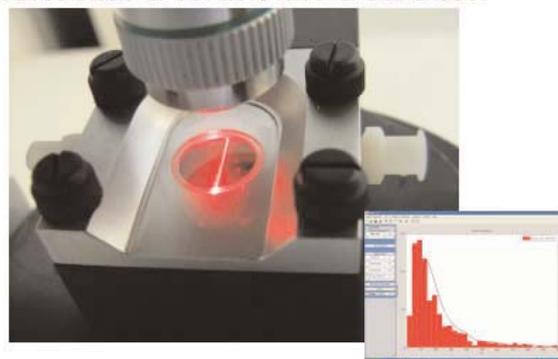
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However, there are other remarkable examples of the helicene utilisation in various branches of chemistry and physics. Nonracemic helicene diol was successfully used by Reetz in molecular recognition of chiral amines displaying enantioselective fluorescence quenching. [12] Another type of the unprecedented recognition of optical antipodes detected by NMR measurements was recorded by Katz. A helicene derivatising reagent served as a remote chirality sensor for chiral alcohols, amines and phenols. [13] In the study related to life science by Sugiyama and Tanaka, (P)-thio[7]helicene has been found to display structural selectivity in binding to the left-handed Z-form of DNA. [14]

Focusing on molecular machinery, there is an amazing application of a helicene structure by Kelly. In an artificial molecular motor, a helicene ratchet ensured the unidirectional rotary motion being fuelled by chemical energy of periodic bond making/bond breaking processes. [15]

As far as electron spectroscopy is concerned, excitation lifetime and quantum yields of fluorescence and triplet state formation at helicenes were investigated. [16] Sapir and Vander Donckt found out that the photophysical properties evolved steadily with the increasing number of ortho-fused benzene rings, which was in sharp contrast to what was found in a linear acene series. Studying the fluorescence maximum of helicenes, a red shift was observed with the increasing molecular size of helicenes. [17]

Finally, an electrochemical study of a series of helicenes was performed by Laarhoven, who measured values of polarographic half-wave potentials. [18]

#### Studying Helicene Monolayers on Metal Surfaces

Recently, helicenes have successfully been deposited on metallic surfaces creating monolayers whose intriguing properties were further studied. Taniguchi published a series of papers dealing with the both racemic and nonracemic thiaheterohelicene monolayer on Au(110) and Au(111) and utilising LEED and STM. [19] Ernst used the UHV near-edge X-ray absorption spectroscopy with linearly polarised synchrotron radiation to investigate orientation of nonracemic [6]helicene on a Ni(100) surface. He assigned the local adsorption geometry by measuring adsorption energy. [20] He also studied adsorption of [7]helicene by thermal MS and LEED under UHV conditions. In the saturated layers of racemate, the individual enantiomers were clustered into two different domains. [21] The measurements of the angle-scanned full-hemispherical X-ray photoelectron diffraction of nonracemic [7]helicene on Cu(111) and Cu(332) were also carried out. [22] Circular dichroism was recorded if emission was stimulated by circularly polarised synchrotron radiation as reported by Fecher on a helicene monolayer on Ni(111). [23]

#### Theoretical Studies

The unique helicene structure has steadily attracted the attention of theoretical chemists. Accordingly, theoretical papers dealing with different aspects of helicene molecules have appeared within the last decade. Paying attention to the conformational behaviour, Grimme and Peyerimhoff studied the relationship between the structure and racemisation barrier in the series of helicenes by means of semiempirical AM-1 and ab initio SCF methods. [24] Similarly, Haufe recalculated barriers to racemisation for helicenes finding an excellent agreement with the experimental results. He confirmed the fact that within the homologous series of carbohelicenes the barriers tend to converge to the value of about 45 kcal/mol. [25] Ab initio calculations were carried out by Schulman in the series of helicenes and their closest topological isomers, planar phenacenes. [26] Their comparison revealed only slight loss of aromatic character.

Not only structural and electronic properties of helicenes have been investigated by computational methods. Most interestingly, the I/V characteristics of helicenes was calculated and the ballistic electronic conductance was analysed. Accordingly, their intriguing semiconductivity and conductivity was foreseen by Treboux, [27] depending on the radius and the width of the helical aromatic ribbon. For a specific structure, which is still far from any practical synthesis, even metallic conductivity might be expected. Furthermore, helicenes were shown to exhibit large band gaps, which might diminish by a careful helicene structure modification.

Helicenes can also be viewed as tiny mechanical objects as their structure resembles a molecular spring. It was found out that the nanospring stiffness could be modulated by increasing/decreasing the electron density and length of helicenes. [28] The Hartree-Fock calculations by Lipkowitz using PM3 Hamiltonian revealed that tuning electron density of helicenes had only a small effect on the spring stiffness. Far more effective was to vary the length of the nanospring.

Finally, electronic spectra, optical and chiroptical properties of helicenes were studied in detail by computational methods. The electronic CD spectra were calculated by Ahlrichs for helicenes exploiting the adiabatic time-dependent DFT method as a prime tool for chiroptical property investigations. The agreement between the most important spectral features and interpretation was illustrated. [29] There are also other theoretical approaches to chiroptical spectroscopy published by Hansen. [30] Photoelectron spectra of helicenes did not exhibit a striking difference in comparison with the planar aromatics, as studied by Schmidt. [31] The hyper-Rayleigh scattering second-order NLO responses of helicenes and heterohelicenes were investigated by Botek employing the time-dependent Hartree-Fock approach and AM1 semi-empirical Hamiltonian. [32]

In conclusion, helicenes represent an attractive objective for further research as the area of their application is evidently underdeveloped. Due to the recent remarkable progress in their synthesis, various helicene derivatives have become available in a more effective way and, moreover, novel structures have emerged. It provides promising bases for discovering new properties and exploitations of helicenes.

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### 3. Molecular Moulding

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As recently described by Linderoth and Besenbacher in a previous issue of E-nano newsletter [1], the idea of molecular moulding has recently opened a new possibility for the fabrication of atomically defined nano-electrodes in UHV-environment. This concept is indeed a part of molecule induced surface restructuring. [2] in which the presence of molecules on bare metallic surfaces (Figure 1) can also induce interfacial roughening, stabilization of diffusing vacancies, creation of trenches [3, 4]

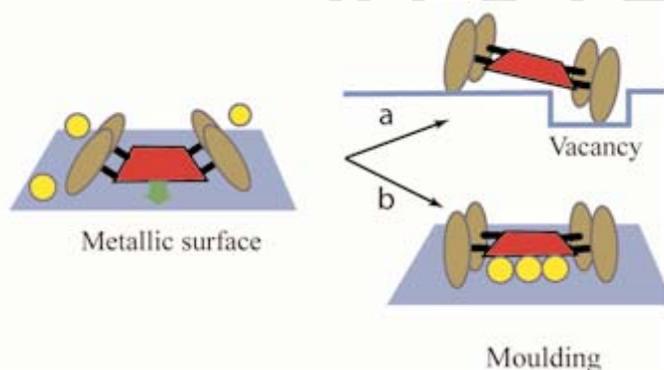


Figure 1: Mechanism of surface restructuring by lander molecules. The lander polyaromatic plateau is in Van der Waals interaction with the surface which induces severe strain energy. This strain can be released by (a) creating or stabilizing a trench or (b) by trapping mobile metal atoms (static moulding)). In both cases the polyaromatic plateau complexes the zero-valent metal atoms underneath.

The background idea is that suitable molecules able to create a niche between their polyaromatic part and the metal surface can trap and stabilize metal adatoms. The stabilization mechanism comprises: a) a distortion of molecule from its adsorption conformation to allow the entrance of the atoms b) which eventually reduces the molecule distortion induced by Van der Waals forces c) chemical complexation of isolated zero-valent metal atoms with the molecule aromatic pi-electrons. Of course the geometry of these metallic nano-islands is function of the molecular mould geometry as shown for different types of landers [5, 6] which opens the way to complex designs using suitable polyaromatic boards. This moulding can be considered as a static moulding since the molecule is fixed and the adatoms are mobile; but we also have recently described a dynamic moulding when, at low temperature, the metal adatoms are not mobile and the mould is displaced by STM manipulation to gather the atoms (molecular Hoover) [7].

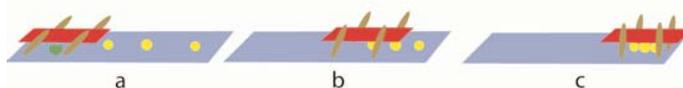


Figure 2. Dynamic moulding. In this case, a STM tip is used to move the lander above metal adatoms which are then trapped under the polyaromatic plateau and glide with the molecule toward the next adatom.

The beauty of this technique is the foreseen possibility to fully exploit the chemistry potential: versatility of chemical designs, softness-rigidity, self-assembly to create ab-initio metallic nanostructures.

We have recently shown that this concept could be used to fabricate a nanoelectrode using a molecular wire as a static mould and then use this nanoelectrode as a rail to manipulate the molecule up to a position where the polyaromatic wire extremity is in contact allowing the measurement of the electronic coupling between the molecular wire and its own electrode [8]. The main advantage here is that the atomically precise nanoelectrode is made in ultra-clean conditions and that this electrode exactly fits its "mother molecule". The figure 3 shows schematically this experiment:

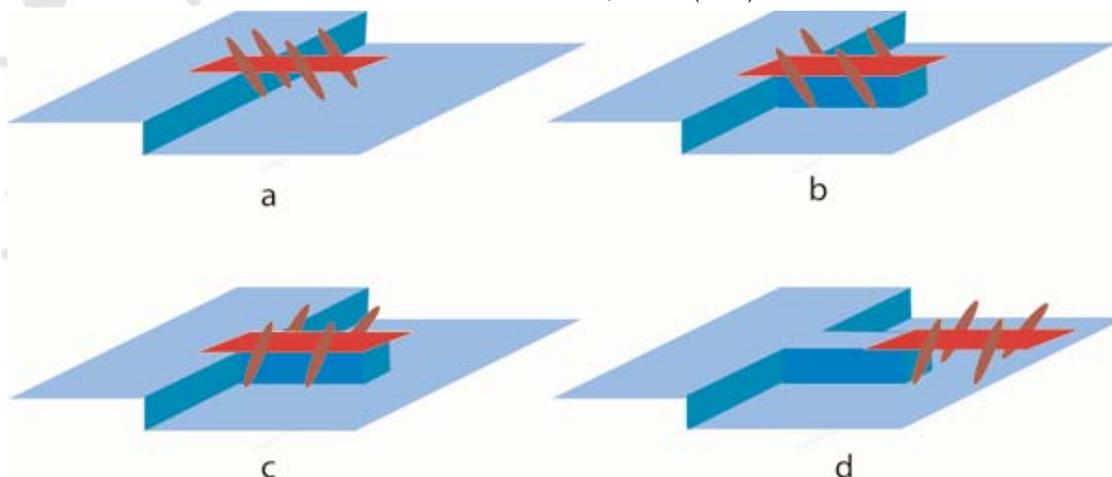


Figure 3. Contacting a single molecular wire by molecular moulding and STM manipulation. a) the lander (for instance RL; see Fig 1 in the introduction) is transferred on a metallic surface and the molecule decorates monoatomic step-edges by adsorption through its contacting end. b) then diffusion of mobile atoms underneath the plateau creates a nanoelectrode. c) the temperature is then decreased to stabilize the nanoelectrode and allow STM manipulation using it as a rail to push the molecule to the situation: d) where the molecular is in contact position, ready for measurement.

This clean contacting experiment will be used to probe different types of molecule-electrode chemisorption and physisorption using landers with a variety of contacting ends.

So far we have only described static and dynamic molecular moulding on metal surfaces but it would be of course much more useful to realize moulding of nano-scale electrodes or clusters on insulating surfaces. In a first step, the self-assembling properties of well-designed molecules could give a 2D molecular network (Fig 4a) with a design depending mainly on the molecules chemical structures. Then, diffusion of metal atoms (Fig 4b) at high enough temperature would give metallic nano-wires or nano-islands.

This concept could also be extended to "molecular masking". In this case the molecular assembly on the substrate leaves well defined bare spaces that can then be filled with metal atoms or molecules. This idea has already been described by Beton et al. [9] who prepared 2D open honeycomb networks by assembly of PTCDI and melamine. The templated network then acted as an array of 2D large pores which could accommodate in a second step small islands of fullerene molecules.

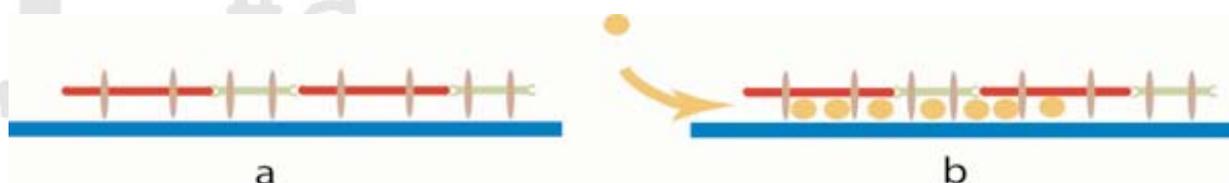


Figure 4. Concept of extended molecular moulding using molecular self-assembly.

Obviously these very attractive and promising new ways of fabricating metallic networks in UHV by a bottom-up approach will require extensive studies of fundamental processes: thermodynamics of self-assembly on insulators, mobility of metal atoms on these substrates, mechanism of trapping.

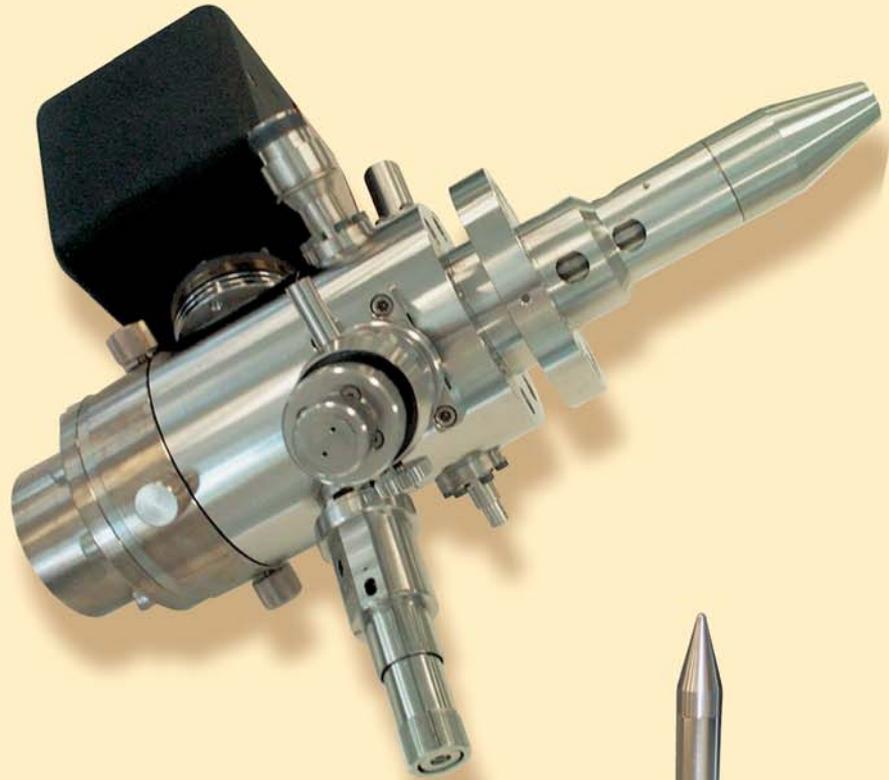
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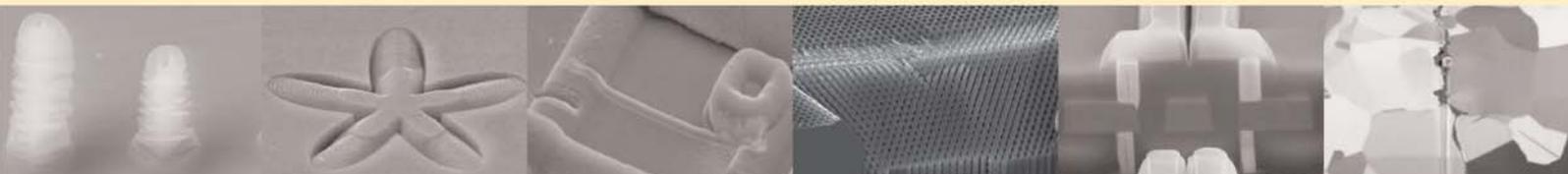
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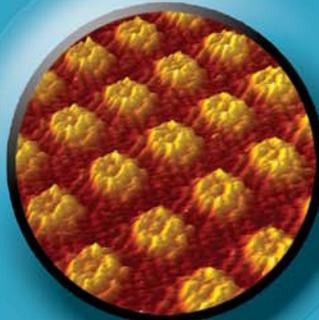
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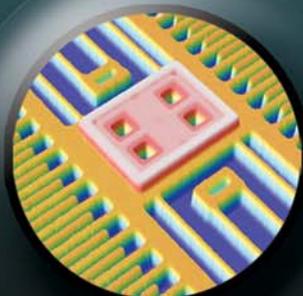
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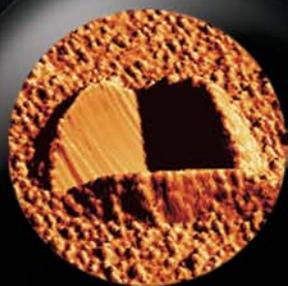
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