POSTER B1

LASER ABLATION: AN EASY ROUTE TO OBTAIN GOLD AND SILVER NANOMATERIALS

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Gold and silver nanoparticles (AuNP and AgNP) have a very important role in nanotechnolgy and nanoscience, due to their physical, chemical and biochemical properties. We produced colloidal solution of Au and Ag nanoparticles in a fast and inexpensive way by laser ablation of the bulk metals in a liquid buffer using the 1064 nm line of a Q -switched Nd – YAG laser. On one hand these solutions are stable without any external chemical reagent, so nanoparticles can be obtained free in solution. On the other hand we succesfully performed the laser ablation synthesis (LAS) in water and in organic solvents, so it is possible to functionalize these particles during as well as after the LAS, simply solubilizing the ligands in the appropriate solvent.[1,2] Furthermore we found that in toluene, LAS of AuNP produces a graphite – gold nanocomposite. The graphitic matrix determined the quenching of the characteristic surface plasmon absorption (SPA) of the AuNP, that can be restored by the matrix removal.[3]

The characterization of AuNP and AgNP solutions is easily achieved by UV – vis spectroscopy using the Mie Theory to fit the SPA. For free particles in solution we conveniently fitted the SPA with the Mie Model for compact spheres and the Gans model for spheroids. We verified that one can account for the isolated nanoparticles fraction using the Mie model for simple spheres and for the aggregated nanoparticles fraction using the Gans model for spheroids.[2] In the case of the graphite – AuNP composite we reproduced the SPA quenching using the Mie model extension for core@shell particles.[3] HRTEM images confirmed the results obtained with the UV-vis spectroscopy.

Finally we were able to obtain a certain control on the average size and aggregation of nanoparticles by laser treatment at 532 nm of AuNP solution.

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POSTER B2

PREPARATION of NANOSCALE PITS on CeO_2(111)

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Ceria (CeO_2) is a material largely used in catalysis because of its performance as an oxygen buffer and as a support enhancing noble metal activity (Three Way Catalysts, production of H_2). Both properties are related to the possibility of cerium to change its oxidation state (+3, +4). A previous joint STM-DFT study (1) has demonstrated that the formation of oxygen vacancies on CeO_2(111) is governed by the localization of excess electrons. One of the major problems working with CeO_2 single crystals is that they gradually change their catalytic properties. In our study we faced this problem, which is partly related to contamination, and finally found a new recipe for sample preparation that yields large and clean terraces, and can be routinely repeated without changing the characteristics of the material. With this preparation method we were also able to create a new kind of defects on the surface: one-trilayer deep, nanoscale pits that expose steps and microfacets with different orientations. We investigated the reactivity of this new model system, exposing both oxygen vacancies and pits, to different gases, starting from atomic oxygen.

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POSTER B3

Ordered Patterning of Nanometric Rings of Single Molecule Magnets on Polymers by Lithographic Control of De-mixing

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We report on a new patterning process, which takes place as a result of de-mixing of a binary polymer/solute mixture [1]. An efficient, low-cost alternative approach for ordering nano-sized rings of so called single molecule magnets (SMM) is thus provided. Here we exploit for the first time the self-organizing process in which SMM patterned film evolves in a spatially correlated pattern of nano-rings[2]. Eventually, the anisotropic patterning of the film guides the ring coalescence to form parallel lines with nanometric width.

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POSTER B4

Electron-Stimulated Emission of Na Atoms from NaCl Nanocubes

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Emission of neutral cations/anions from solid akali halides can in principle be provoked by donating/subtracting electrons to the surface of alkali halide crystals, but generally constitutes a very endo-energetic process. The amount of energy required is expected to decrease for atoms located in less favorable positions, such as at surface steps and kinks, where the local coordination is smaller. The most favorable case of all should be represented by corner atoms of alkali halides cubes, where ionic binding is the weakest. We carried out first principles density funct ional calculations and simulations of magic-size neutral and charged NaCl nanocubes, to ascertain the stability and extractibility of neutralized corner ions. We find that detachment of neutral Na atoms upon donation of an excess electron is possible for a very modest energetic cost of the order of 0.6 eV, in line with early experimental observations. The atomic and electronic structure of the resulting Na+ vacancy is analysed in detail.

POSTER B5

Maya wall paintings: nanoscience for restoration

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Nanotechnology have been used for the restoration and consolidation of wall paintings in the Maya archaeological site of Calakmul in Mexico. The sub-tropical climate in Calakmul discourages from using polymers because they degrade fast. Nanosized $Ca(OH)_2$ particles instead of synthetic polymers provided excellent results in conferring renewed features to degraded painted surfaces. It is well known that alkaline water solutions can not be used since $Ca(OH)_2$ is not soluble enough to get a meaningful consolidation effect. Nanoparticles dispersed in organic media allow conservators to perform consolidation by using materials totally compatible with the inorganic substrate. Nanotechnology provided a reliable alternative to worldwide used chemicals that under normal condition of storage are destinated, even though with variable kinetics, to deteriorate and lose their chemical and mechanical features.

POSTER B6

Colloidal binary oxide nanocrystals with an anatase rod-like TiO_2 section and a size-tunable magnetic domain.

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The chemical synthesis as well as the morphological, structural, and magnetic characterization of colloidal binary oxide nanocrystals comprising a rod-like anatase TiO_2 section and a maghemite domain fused together in a unique particle will be presented. The heterostructures are obtained by preferential heterogeneous nucleation of iron oxide onto the lateral facets of preformed TiO2 nanorods (about 3 nm in diameter and 20 nm in length) in suitable surfactant mixtures. By properly adjusting the reaction conditions, it is possible to achieve high yields (up to 90%) of organic-soluble hybrid nanocrystals in which the mean size of the magnetic domain can be systematically tuned from ~4 to ~15 nm. A possible formation mechanism of such binary nanocrystals will be proposed on the basis of the experimental evidence. The technologic al potential of such highly asymmetrical semiconductor photocatalyst - magnetic oxide hybrid nanostructures will be also discussed.

POSTER B7

MODELING INTERACTION OF CO_2 WITH Ni (110) SURFACE

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It has been experimentally observed [1] that a Cu/Ni catalyst is 40 times more active than pure Cu in the synthesis of methanol.
The reasons for that are still obscure, but, surprisingly, there is a lack of knowledge concerning even more basic questions related to the synthesis, such as the identification of the most stable CO_2 configurations on Ni surface and an accurate description at the nanoscale.
A few experimental studies give only some indications concerning possible adsorption site and symmetry.
We use first-principles density functional theory identify the more likely possible adsorption sites for CO_2 on Ni(110), which is the best candidate for CO_2 adsorption, and corresponding configurations and energies.
Though similar geometries are obtained by different exchange-correlation functionals, it is found that the adsorption energies are very sensitive to the functionals. Other properties as electronic and magnetic properties are also discussed and compared among different selected configurations. Electron transfers from surface to CO_2 is found to have in any case an important role in the adsorption. Preliminar investigations concerning hydrogenation of adsorbed CO_2 are also presented.

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POSTER B8

Spin Noise Fluctuations from Paramagnetic Molecular Adsorbates on Surfaces

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The measurement of spin noise in nuclei was pioneered on bulk samples more than 2 decades ago. An ensemble of spins can produce a coherent signal at the frequency of a static magnetic field without the application of an external rf driving field. A key point on these measurements is the detection of a signal blurred into noise. The issue of sensitivity and detachability of the signal into noise becomes more striking if the spin noise arises from the statistical fluctuations of the magnetization of a single spin center. In this paper we report on the verification of recent results on the detection of spin noise from paramagnetic molecules of BDPA by Durkan and coworkers. We also present the detection of the fluctuations of the magnetization on a second paramagnetic specie, DPPH deposited on Au(111) surfaces.Special emphasis is devoted to the preparation and characterization of the sample. ESR spectra from ultrathin films of DPPH and BDPA grown on Au(111) reveals that the paramagnetic molecules preserve their magnetism on the surface and that their spin dynamics is similar to that of molecules in solution. These data and a thourough analysis of the signal recovery apparatus help to understand the low statistical recurrence of the spin noise in the data set . A thourough description of the experimental apparatus is also reported.

POSTER B9
EMCD: Electron Energy Loss Magnetic Chiral Dichroism

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Circular dichroism is the dependence of the absorption cross section on the helicity of the incident X-rays; XMCD (X-ray Magnetic Circular Dichroism) is a powerful technique to analyse magnetic properties in ferro-magnetic or paramagnetic compounds like orbital and spin magnetization, magnetic ordering and strong electronic correlation. XMCD experiments carried out in synchrotron facilities have a strong sensitivity to the specimen surface and up to 30nm of lateral spatial resolution.

Transmission electron microscopy is a powerful tool to investigate the chemistry, the crystal structure and the electronic structure of solids with sub-Angstrom spatial resolution. The similarity between Electron Energy Loss Spectroscopy (EELS) and X-Rays Absorption Spectroscopy (XAS) is well known [1], but it was also believed that the measurement of circular dichroic effects in the TEM would have required spin polarized electrons. A recent theoretical work [2] suggested that it is possible to realize in a TEM scattering conditions equivalent to absorption of circular polarized photons in XMCD experiments. In order to do so, it is necessary to prepare in the TEM the incident electron beam as a superposition of two plane waves with a relative phase shift of $\pi/2$. The first direct comparison between EMCD measurements (shown in fig.1) so obtained in a TEM and XMCD experiments in the synchrotron was recently achieved [3] on Fe thin film deposited on GaAs substrate specifically prepared for this purpose. GaAs(001) substrates were prepared and thinned until electron transparency at the center for the electron microscopy of TASC laboratory in Trieste. Then a thin layer of crystalline Fe was epitaxially grown at Ape beamline at the ELETTRA synchrotron in Trieste. The crystal quality and the magnetic properties of the specimens were analysed together with XMCD experiments. EMCD experiments were performed to elucidate some of the unknown aspects of this new approach to the study of the magnetic properties of the materials.

Here we present the state of the art in EMCD experiments showing some interesting synergies between XMCD and EMCD.

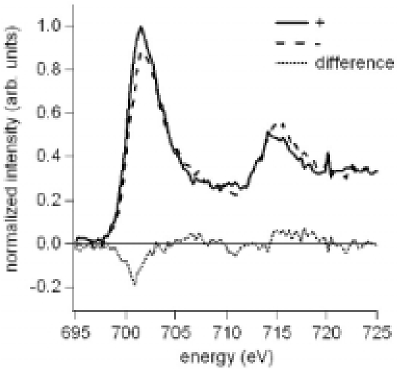

Fig.1. EELS spectra measured at the Fe $L_{2,3}$ edge, shifting the detector in the two position "+" and "-", that reverses the sign of the phase shift. Dotted line ("difference") is the dichroic signal.

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POSTER B10

Manipulation and imaging of coexisting photo induced oxygen ordered phases

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We have manipulated oxygen ordering in the La_2CuO_{4+y} (y=0.08) single crystal with a T_c=38 K by synchrotron radiation illumination dose and the texture has been identified by x-ray diffraction imaging. We have studied the growth dynamics of the three dimensional (3D) ordered phases at different temperatures under x-ray illumination. The critical temperature T_0~334 K of the order-disorder transition for the Q_2 phase has been determined. We have found that the illumination of the sample with a continuous polarized synchrotron radiation x-ray flux stimulates the oxygen ordering kinetics. The photoinduced ordering process shows a threshold characteristic of cooperative phenomena and its kinetics shows a temperature dependence that is controlled by the activation energy E_A=100 meV.

POSTER B11

Epoxidation of ethylene on Ag(100) surface: a first principles study

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The interaction of ethylene with Ag surfaces has been studied extensively, mainly because silver displays unique catalytic properties in the ethylene epoxidation reaction, which is one of the most important selective oxidation processes based on heterogeneous catalysis on a metal surface.

In our recent density functional theory (DFT) study [1] two distinct ethylene adsorption modes on oxygenated Ag(100) were considered: weakly - bonded ethylene and ethylene oxametallacycle (OMC). The OMC has been recently proposed [2] as an intermediate in both selective partial oxidation to ethylene epoxide (EO) and non selective total combustion to CO_2 pathways.

In particular, OMC can react to form either i) EO or ii) acetaldehyde (Ac), the latter being the path to the undesired total combustion. Therefore one would like to enhance the first reaction while hindering the second.

Motivated by these considerations, we investigate the two reactions on Ag(100) using DFT, focusing on the dependence of surface reactivity on surface imperfections, such as step edges, and on the amount of adsorbed oxygen. We find that the formation of OMC on Ag(100) from gas-phase ethylene is an activated process, the reaction barrier being around 0.3 eV. The reaction barriers for the formation of EO and Ac are around 0.8 eV. With an increasing coverage of adsorbed on-surface oxygen, the reaction barriers for the formation of EO and Ac are substantially reduced, while this has only small e_ects on the OMC formation. The formation of OMC, EO, and Ac is hindered at step-edges, when the coverage of on-surface oxygen is large. The calculations of the transition states (TS) for the formation of EO and Ac have enabled us to identify the most important structural characteristics of the TS for the two reactions. Such an identification is valuable in the design of improved catalysts that will enhance the formation of EO, while hindering the formation of Ac.

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POSTER B12

WATER-SOLUBLE GOLD NANOPARTICLES: AN ESR INVESTIGATION OVER PROPERTIES OF THE MONOLAYER

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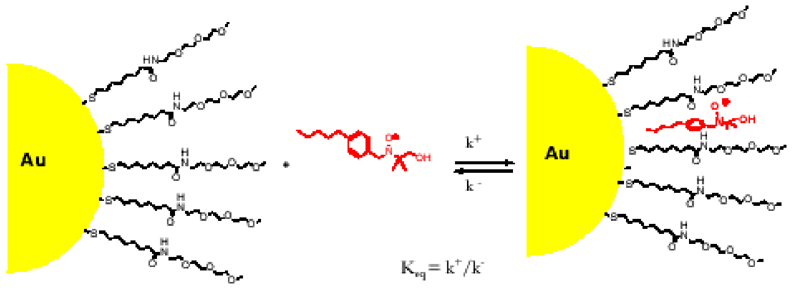
The passivating monolayer of gold nanoparticles (MPCs = Monolayer Protected Clusters) can be considered a membrane mimetic system and, because of specific orientation and low mobility of thiols, we can define precisely radial subregions of different polarity inside the monolayer. For instance, water-soluble gold nanoparticles like MPCC8- TEG are made of a metallic core covered with a monolayer of amphiphilic thiols (HS-C8-TEG) comprising a hydrophobic aliphatic portion close to gold surface and a polyoxoethylenic chain like hydrophilic unit who imparts the solubility in water [1]. Gold nanoparticles with different size of the core can be obtained tuning reaction’s conditions.

In order to investigate interactions between organic molecules and the monolayer of MPC-C8-TEG we have used ESR spectroscopy [2]. This technique allows us to distinguish a radical probe in the monolayer from a radical probe in solution and this is possible because of the time scale of EPR.

We have synthesized and characterized MPC-C8-TEG with three different size of the core and ESR measurements have been carried out in order to study the complexation equilibrium of a radical probe within the monolayer and its dependence on the nanoparticle core diameter. The equilibrium of appropriate radicals in water and in the monolayer have been studied by ESR measurements.



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POSTER B13

NEW CATALYSTS CONTAINING GOLD NANOPARTICLES

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Over the last few years many studies have concerned the use of gold nanoparticles supported on inorganic matrices as catalysts for oxidative processes: the interest in these materials finds its origins in the catalytic activity of gold when dispersed in nanometric particles, contrary to the behaviour of metallic gold as bulk.

There are many factors which determine the activity of these catalysts: for instance, size of the nanoparticles, kind and porosity of the support, specific interactions between metal and support, etc. In particular, materials containing metallic particles smaller than 2 nm and with an inorganic matrix of basic oxides like Fe_2O_3, MgO, CeO_2, seem to have the best catalytic activity.

Some years ago a methodology for the synthesis of nanoparticles passivated by an organic monolayer which stabilizes the gold cluster (MPC Monolayer Protected Cluster) avoiding particles aggregation has been reported [1] thiols are often used for the monolayer because they bind to the metal surface in a very effective way, determining the properties of the nanoparticles like solubility and possibility of insert functional groups [4]. We have applied this synthetic methodology to the synthesis of new catalysts with gold nanoparticles of appropriate size dispersed in a porous support. The results obtained as the catalytic activity of these catalysts will be discussed.

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POSTER B14

Relativistic DFT calculation of carbon, alkali atoms and nanoclusters. Quasi-particle time-dependent DFT theory for superconducting clusters

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There are presented the results of the density-functional (DF) and relativistic perturbation theory (PT) with the DF zeroth approximation [1,2] calculations for the electron structure and spectra of the carbon, alkali atoms clusters in neutral form and also single-, double-charged ones. It has been studied the contributions of the correlation and relativistic corrections into the calculated characteristics, which are to be important. We have carried out the DFT calculation for single buckminsterfullerene (C60) system. The levels spectrum has been obtained and compared with other calculations results (SCF LCAO, DFT etc.) The HOMO-LUMO gap is~2,4 eV. The problem of the Coulomb barriers in dissociation of doubly charged clusters has been also considered. A powerful motivation for cluster study is provided by known aspects relating with the high temperature superconductivity in the solid carbon clusters (K3C60 and Rb3C60), the potential relevance to alkali doped buckminsterfullerene superconductivity being emphasised as an important direction for future work. Early it was developed the Lagrange quasiparticle theory for super conducting multi-electron fermi-systems and time-dependent DF theory for super conductors [2]. We have presented the results of the numeral solution for set of the time-dependent Bogoliubov-de Gennes equations (c.f.[3]), which include exchange-correlation effects for the K_3C_{60} and Rb_3C_{60} systems.

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POSTER B15

Light diffraction on modulations of nano-structured solid surface relief and low threshold IR multi-photon molecular dissociation on surface

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It well known that the light diffraction on relief of surface can make a significant influence on dynamics of laser induced reactions, which are taken a place near the relief with spatial modulated profile [1,2]. In this paper we present new approach to modelling the optimal scheme for isotopic selective low threshold IR multi-photon dissociation of molecules near surface with periodic relief. Besides, there are considered possible improvements of so called “Stells” technology. It is carried out modelling the optimal scheme for isotopic selective low threshold IR multi-photon dissociation of molecules near nano-structured surface with given relief. The physical system is molecular gas SiH4 (SF6, UF6), that is resonantly excited by the CO2 laser radiation near surface of the periodic Cu lattice and nano-structured Si. A definition of the local electromagnetic fields and their increasing near surface, contribution of the surface relief parameters (form, depth etc) are quantitatively taken into account within non-linear analytic theory of diffraction of the limited 2D and 3D light beams on surface with arbitrary discrete Fourier spectrum of relief [1]. A majority of tasks, connected with action of powerful laser fields on molecular gases, are more less adequately described by multi-level models, that leads to necessity of consideration of the high dimension differential equations systems or the Focker-Plank differential equations in the partial derivatives for density of molecules with vibration-rotation energy x and operators, describing the RT relaxation and action of external radiation (including the surface electromagnetic wave) [1]. New multi-level model for optimization of excitement of the molecular gas and definition of the optimal form for laser pulse to reach the maximal effectiveness of laser action in process is based on differential equation of the Focker-Plank type and optimal governing theory [2-4]. Numerical testing of optimized model for molecules of SiH_4 , UF_6 is carried out. The obtained results are used for proposition of a new laser isotope separation scheme with application to problem of the U isotopes separation.

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POSTER B16

Role of surface peroxo and superoxo species on the oxygen buffering of oxide supports

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The high performance of ceria (CeO_2) as an oxygen buffer and active support for noble metals in catalysis relies on an efficient supply of lattice oxygen at surface reaction sites, which is governed by the formation of oxygen vacancies [1] and by the high mobility of oxygen adspecies [2]. Among these, superoxo and peroxo species have been shown to be strongly involved into many important catalytic reactions, like CO oxidation or water-gas shift. The mechanisms for vacancy formation and adsorbate diffusion are studied from first-principles with density functional theory calculations by comparing reducible (ceria) and non-reducible (zirconia, ZrO2) supports, modeled as oxidized and reduced (111) surfaces. The dissociative adsorption of molecular oxygen results in characteristic peroxo surface groups: upon adsorption, the O ad-atom and a surface O^{2-} ion become electronically equivalent. The resulting O_2^{2-} peroxo group is tilted by $\sim 64^0$ with respect to the surface normal, can freely rotate if the support is CeO2 while rotation requires an activation energy of 0.6 eV in the case of ZrO2. The calculated energy barrier for diffusion of the O adatom to the nearest surface O site is however similar for the two substrates, 1.4 and 1.6 eV, for CeO2 and ZrO2 respectively. The same groups are formed upon O_2 adsorption on the reduced surfaces, while O adatoms display a strong tendency towards vacancy sealing. Preliminary results on the stability and mobility of superoxo ad-species suggest their higher reactivity and will be discussed in the context of recent spectroscopic measurements [3].

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POSTER B17

PEEM with chemical and magnetic sensitivity at the nanometer length scale

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The instrumentation for synchrotron based photoemission electron microscopy (XPEEM) has recently undergone significant improvements. The spectroscopic photoemission and low energy electron microscope (SPELEEM) operational at the “Nanospectroscopy” beamline at ELETTRA combines structural and spectroscopic analysis methods in a single instrument, exploiting the inherent chemical sensitivity of X-rays and complementary methods such as LEEM and micro-LEED. One of the key features of this microscope is the high photon flux made available by the micro-spot illumination, which allows imaging of nanostructures well into the sub-micron range. The SPELEEM reaches an energy resolution of 0.2 eV and a lateral resolution of few tens of nanometers in XPEEM. In this work, we report some of the recent work on magnetic and chemical imaging, illustrating the capabilities of the SPELEEM. The following examples will be illustrated: (i) magnetic imaging of patterned nanostructures by X-ray Magnetic Circular Dichroism Photo Emission Microscopy, (ii) chemical imaging of dynamical reorganization of Au-Rh thin films occurring during reaction conditions; (iii) direct correlation of quantum electron confinement with the surface reactivity of ultra-thin Mg films during oxidation.

POSTER B18

Highly-Ordered arrays of Terbium double-decker single molecular magnets on surfaces

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The technological applications of single molecular magnets (SMMs) for quantum computing and information storage media rely on the capability to address each individual molecular magnet in a two-dimensional array. The formation of a highly-regular arrangement of SMMs is to date a major scientific and technological challange. It has been shown that a new class of SMMs, Tb-Bis(Phthalycyanato)Terbium(III), displaying strong magnetic anisotropy and high blocking temperature, can be assembled into long-range ordered twodimensional arrays on Cu(111). The structural, electronic, and magnetic properties of these nanostructures has been studied by combining low-temperature scanning tunneling microspy (STM) and spectroscopy (STS) with density functional theory calculations (DFT). The SMM monolayer displays a characteristic and unusual bias debendent STM imaging: it can be observed only when specific orbitals are accessible for the tunneling electrons, as predicted by DFT calculations.

The coupling between the SMM and the metallic substrate is predicted to be weak, suggesting that the magnetic anisotropy and slow relaxation behavior of the free SMM are retained upon surface adsorption, and therefore opening the way for their technological exploitation in molecular devices.

POSTER B19

Building Gas/Metal-Surface Interactions One Metal Atom at a Time

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The currently available density functionals cannot describe the dispersion component of the interaction energy present in weakly-bound complexes. Moreover, the exchange energy is often incorrect in these functionals. Examples of problematic cases for DFT include van der Waals-bound rare-gas dimers and other molecules, hydrogen-bonded complexes, and larger systems such as ones composed of physisorbed rare gases (or even weakly chemisorbed molecules) on metal surfaces. Thus, more accurate ab initio methods (e.g., the coupled-cluster theory or the symmetry-adapted perturbation theory of intermolecular interactions) are used for treating the interactions in the smaller weakly-bound systems. However, these methods are not applicable to larger systems (e.g., the complexes formed by physisorption) due to their prohibitive scaling with system size. For this reason, DFT continues to be used. In this talk, I will show the insufficiency of DFT for the physisorption example of Xe/Cu(111) and for smaller rare-gas/metal cluster complexes, as compared to accurate ab initio calculations. The talk will conclude with some preliminary results using a blend of "corrected" DFT coupled with a damped-dispersion interaction.

POSTER B20

Van der Waals Cofficients in Density Functional Theory: a Simple Approximation for the Polarizability

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Long range interactions appear and play crucial roles in many systems, including soft matter, van der Waals complexes, biomolecules, etc. Density Functional Theory(DFT) within Local Density and Generalized Gradient Approximations for exchange-correlation energy is known to fail in describing properly van der Waals interaction, while approach from the exact Adiabatic Connection Formula of this quantity is computationally impracticable, except for few simple systems. We show in this report that a simple, computationally fast procedure to calculate van der Waals coefficients in DFT framework with reliable result can be developed from a simple approximation for the kinetic energy functional. Results of calculations applied to atomic and molecular systems strongly support the validity of the method in capturing essential part of long range correlations. This result may give useful information for constructing an exchange-correlation functional which includes van der Waals energies.

POSTER B21

Carbon nanotubes as metal cluster support for nanostructured catalysts

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Recently the deposition of transition metals (Rh, Pt) on single-walled and multi-walled C nanotubes has lead to unconventional catalysts, whose activity has been tested in numerous heterogeneous reactions, also important for environmental chemistry. In this field, a particular relevance pertains to the conversion of nitrogen oxides, which are among the most harmful environmental pollutants.

We have studied the catalytic behavior of Rh decorated single-walled Carbon nanotubes (SWCNTs) by exposing this system kept at about 200 K to NO_2 and to NO, and by using high resolution photoemission spectroscopy to follow the thermal reactions of the chemical species residing at the surface.

A commercial *bucky paper* made of SWCNTs (average diameter 1.2 nm) bundles was introduced into the ultra-high vacuum experimental chamber of the SuperESCA beamline at the ELETTRA synchrotron light laboratory (Trieste, Italy) and cleaned by repeated annealing cycles up to 1800 K. Rh was evaporated on the *bucky paper* kept at 220 K and a standard procedure (oxygen treatments at 800-1000 K and hydrogen reduction at 400-700 K) was then carried out to achieve atomically clean Rh.

The $Rh3d_{5/2}$ surface core level shift of 440±20 meV gave the evidence that the Rh atoms evaporated onto the SWCNTs predominantly arrange into ordered nanocrystallites exhibiting a surface termination close to the (111) oriented crystal. The addition of Rh slightly perturbs the nanotube electronic structure, as reported by the valence band and C1s core level spectra.

After NO_2 up-take at 200 K, the thermal evolution of the NO_x adspecies indicate for the Rh nanocrystallites a catalytic behavior similar to the low index Rh surfaces. In the case of NO adsorption, the molecules that at 273 K adsorb intact on the single crystal Rh(111) surface undergo to a partial dissociation on the nanotube supported Rh nanocrystals. This result possesses a strong appeal for the development of nanostructured catalysts as the enormous specific surface of the Rh clusters supported on nanotube bundles can be exploited to reduce the amount of the precious active metal in the catalyst, still maintaining a high catalytic efficiency.

Moreover, the modification of the C1s and $Rh3d_{5/2}$ core level spectra throughout the whole experiment allowed us to detect the formation of the metal-SWCNTs contact and to reveal the effect that the bonds between oxidizing species and Rh have on the electronic structure of the metal-SWCNTs interface. We found that the oxidation of the metal/nanotubes contact, caused by the chemisorption of the oxidising species on Rh, corresponds to modify the barrier at the metal-nanotube contact simulating the occurrence of hole doping of the C nanotubes.

POSTER 22

New directions in the synthesis of ZrO_2 CVD precursors

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The working on the synthesis of precursors for metal-organic chemical vapor deposition (MOCVD) requires the solving of two major problems limiting the usefulness of these compounds: a lack of either volatility or chemical stability. Quite good example to illustrate these problems is the synthesis of ZrO_2 precursors used in CVD method.

Zirconium dioxide is a very important material for a number of modern thin-film devices. It should be mentioned about oxygen-conductive membranes for use in fuel cells, oxygen sensors, optical and high-temperature thermal barrier coatings or ferroelectrics. According to previous reports the following Zr(IV) complexes: β-dikenonato - $Zr(thd)_4$ – tetrakis(tetramethylheptanedionato)zirconium, alkoxo - $Zr(OR)_4$, (where R = Et, Pr^i, Bu^t) or fluoroalkoxo-complexes $Zr(hfip)_4$ (hfip = $OCH(CF_3)_2$ are commonly used as ZrO_2 precursors in CVD methods. The first one is fairly air-stable due to their high coordination stauration, but has to be heated to quite high temperatures in order to achieve a vapor pressure sufficient for CVD. The next mentioned complexes show excellent volatility, but also extreme hydrolisis sensitivity, which renders handling and long-term storage problematic. Consequently, there is ongoing research for alternatives to these two precursors' families.

The high reactivity (lability) of the metal-alkoxide bond makes them useful starting compounds for a variety of species (ie species with different types of ligands) such as $Zr(OR)_{n-x}L_x$ (where L = β-dik or OOCR'). Our works are focused in synthesis and application of carboxylate and perfluorocarboxylate derivatives of Zr(IV) alkoxides. Carboxylates are generally non volatile, althought volatility was observed with bulky R' groups such as tertiobutyl as for instance for bismuth. We decided to choose to our synthesis the acids, which posses tertiobutyl or pseudo - tertiobutyl group, such as: HOOCR', where R' = Bu^t, $C(CH_3)_2Et$, CH_2Bu^t and Zr(IV) alkoxides, $Zr(OR)_4$ (R = Pr^i, $C(CH_3)_2Et$. In molar ratio alkoxide:acid = 1:2, we have obtained multinuclear oxo-carboxylates Zr(IV). In the other synthesis we have based upon perfluorocarboxylic acids – HOOCR", where R" = CF_3, C_2F_5, C_3F_7, obtaining perfluorocarboxylate derivatives - $[Zr_6O_4(OH)_4(OPr^i)_4(OOCR")_8]$. The structure and chemical constitution of above mentioned compounds were determined by X-ray single diffraction method and spectral analyses (IR, ^{13}C NMR). Volatility and thermal stability all obtained compounds were determined using thermal analysis, integrated variable temperature IR (VT-IR) spectroscopy and mass spectrometry. On the base of led analyses, we chose some of obtained complexes, which show the best volatility, to CVD experiments, treating them as precursors of zirconium dioxide. Thin ZrO_2 layers were obtained using horizontal thermal inducted CVD reactor and deposited at 730-753 K on Si(111), under the pressure 1,5-2,5 mbar and argon atmosphere. The films were characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The morphology of obtained films was studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Moreover, studies on the conductivity and photoluminescence properties of ZrO_2 layers have been carried out.

POSTER B23

Synthesis and Characterisation of Ferrite Nanoparticles for Hyperthermic Applications

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In the last few decades magnetic nanoparticles had a large impact in biomedicine. The first application in this field was as contrast agents in magnetic resonance imaging (MRI). Just as an example, the diagnosis of lymphatic metastasis has improved from 60% to 94% with the use of nanoparticles. Nowadays, their interest extends onto many other areas, including drug targeting, diagnostics, immunoassays, molecular biology, DNA purification, cell separation and purification, and hyperthermia therapy.

In this widespread scenario we started a project aimed to design new biocompatible materials based on magnetic nanoparticles allowing a two-fold anticancer action, i.e. capable of combining the therapeutic effect based on targeted drug-delivery with hyperthermia for the treatment of widespread diseases. Moreover in designing these new systems, the possession of enhanced relaxometric properties will be also pursed, in order to track the path and the deposition of the carriers inside human body and inside tumoral cells by MR imaging. The final goal is that of assembling a final product composed of a magnetic core, a biocompatible shell, and one or more biologically active molecules (drug, antibody, enzyme, etc.) anchored to the surface. Thanks to the presence of the nanometric magnetic particles, hyperthermia can be generated by simple application of a controlled alternating magnetic field. Hyperthermia alone can selectively induce cytolysis of tumour cells, which are in this respect more sensitive than normal cells, by heating to temperature up to 45 °C, or just enhance drug action or tissue regeneration by heating to temperatures below 41 °C.

In this contribution we present the synthesis and the investigation of the static and dynamic magnetic properties of highly monodisperse cobalt ferrite and magnetite nanoparticles with average size of few nanometers embedded in different chemical environments. Particles were synthesised by the polyol technique and their surfaces were then coated by properly designed grafting molecules. The structural properties were characterised by XRD, DLS and TEM. The characterisation of the physical properties was mainly focused to establish the correlation between synthetic parameters, structural features (size, crystallinity, composition, particle concentration) and magnetic properties with particular attention to those determining the hyperthermic behaviour. The understanding of such relations allows to attain the capability of tailoring the properties of the nanomaterials and to select the best promising products for the proposed biomedical applications.

POSTER B24

Initial Stages of the Hydroxylation Reaction of O/Ag(110)

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Water interaction at surfaces is a topic of particular interest from the fundamental as well as from the applicative point of view, as demonstrated by the extensive research in this field [1]. In particular hydroxylation of metal substrates occurs in several catalytic reactions in the heterogeneous phase, acting e.g. as an intermediate in the oxidation of hydrogen to water on Pt surfaces [2]. As an electronegative adsorbate it can affect also electrochemical processes. On the other hand, being a fundamental component of the atmosphere water corrosion is an important phenomenon for all those devices working in air.

We present here a low temperature STM investigation of the H_2O interaction with O/Ag(110) at a crystal temperature T=250 K. In accord with previous crystallographic studies [3,4] we find that oxygen gives rise to added O-Ag rows in the <001> direction with (nx1) periodicity (n=2,…,8 depending on coverage) and that the OH generated in the reaction orders into a (1xm) superstructure consisting of OH rows running along the <1-10> direction. m=n/2 for even n, while domains of different periodicity coexist for odd n [5]. We find hydroxyls to be imaged dark by STM at all voltages and to sit in the valleys between the Ag rows. Ag adatoms are imaged bright. Most of them have disappeared after hydroxylation, most probably ending at the step edges. Some of them are however still present, especially in the initial stages of the hydroxylation process. When these Ag-adatom sit between still intact O-Ag rows they cluster into zig-zag shaped structures with a periodicity of two lattice spacing, consisting most probably of Ag atoms at the sides of an O-Ag row. On the contrary, when they are found in OH covered domains, they dispose themselves along the OH rows forming linear arrays with a periodicity of two lattice spacings.

The Ag-OH rows are unstable under the STM tip action above a critical voltage. It ranges from 350 mV, when the voltage pulse is applied at the end of a row, to 800 mV, when the current is injected at the middle of the rows. The voltage pulses scatter the OH groups around the surface. The damage propagates along the row where the voltage pulse is applied, leaving nearby rows unperturbed. The directionality of the destruction is indicative of a strong interaction among OH groups in the <1-10> direction. Noteworthy the critical voltage occurs close to the threshold of the excitation of the OH stretch which may thus be involved in the energy transfer to the adlayer.

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POSTER B25

XANES microscopy of phase separation in $Mg_{1-x}Sc_xB_2$

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MgB_2 has been the object of extensive research since the discovery of its superconductivity at elevated temperature ($T_c \approx 40$ K) in 2001 [1]. The system has a simple hexagonal structure P6/mmm , where the boron atoms form graphite-like sheets separated by magnesium layers. Therefore the MgB_2 crystalline structure is a heterostructure at the atomic limit made of superconducting layers (boron monolayers) intercalated by different layers (Mg hcp monolayers) playing only the role of spacers.

Chemical substitution for Mg and B is one of the approach used to get further inside to the superconductivity of MgB_2, due to the fact that the substitution provide a way to control and manipulate the electronic and structural parameters. In fact the introduction of hole or electron into MgB_2 through the replacement of divalent Mg by a metal atom, having lower (or higher) valence, change the charge density in the boron layers and the chemical potential is shifted downward (or upward) . Sc and Mg have nearly the same atomic radius, and the synthesis of $Mg_{1-x}Sc_xB_2$ could be very useful due to the fact that it can allow to study the band filling effect on the superconducting properties with a minimum effect on the structure parameters. With this motivation we have synthesized the new superconducting ternary system $Mg_{1-x}Sc_xB_2$ for $0.12<x<0.27$ [2], where the chemical substitution induces minor lattice variations since the ionic radius of Sc (1.620 Å) is only a little larger than that of mg (1.602 Å). We have found in the $Mg_{1-x}Sc_xB_2$ system a phase separation into a Sc-poor and Sc-rich region for $x>0.27$. Surprisingly this phase separated samples exhibit a critical temperature higher than the pure MgB_2.

We have explored the actual Sc distribution along the sample by micro-XRF, with a beam spot size below 1 micron, and we found Sc poor texture of 100 micron size embedded in a Sc-rich matrix. With micro-XANES we have studied the chemical state in the Sc-poor region, responsible of high T_c, and found that Sc does not enter in MgB_2 lattice. This results suggest that enhanced T_c could be due to the strain, which can be induced by the Sc impurities or by the Sc-rich matrix.

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POSTER B26

Indium migration through a nanotube forest: fingerprinting the diffusing species by combining DFT and XPS data

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Migration of In atoms along multi-walled nanotubes has recently been reported in the context of controllable material transport in nanostructures (Nature 428, 924, 2004). In the present work, we study the mass transport and bonding configuration of In atoms through a "forest" of aligned nanotubes by combining X-ray photoemission spectromicroscopy (XPS) with density functional theory calculations. The In 3d core level binding energies are excellent fingerprints for the In bonding to the C atoms of the nanotubes. The measured experimental

In 3d core level shifts with respect to the In metallic state are calculated in the final-state approximation via total energy differences in order to d etermine the possible bonding configurations of In atoms at the surface of the nanotubes. Due to the large external diameter of the nanotubes (150 nm), their surface is modelled as a graphene sheet. The adsorption geometry and the electronic structure of several possible binding configurations of In adatoms on graphene are fully characterized, identifying those yielding core-level shifts compatible with the experiment and therefore involved in the diffusion process.

POSTER B27

Ab initio studies of magnetism induced by vacancies in graphene

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Magnetic carbon has aroused a lot of interest in the last years, due to the underlying new basic physics, and the appealing range of possible applications of magnetism in these materials, which makes the understanding of its origins and stabilization mechanisms of extreme importance. Motivated by experimental results previously published by one of the present authors [1], ab initio calculations have been performed using the program SIESTA, in the framework of Density Functional Theory (DFT), using norm-conserving PBE-GGA pseudopotentials, spin polarization and a DZP basis set. Studies on small (4x4x1, 31-32 atoms) and large (8x8x1, 127-128 atoms) graphene supercells have been performed to assess magnetic moments induced by graphene with a single carbon atom vacancy (SAV-g) and the effects of adsorption of foreign species on the system. For SAV-g we find a magnetic moment of ~ 1:2 μB, and the appearance of a narrow peak on the DOS at the Fermi energy (EF). Atoms rearrange to form a pentagonal structure, opposite to which is located the magnetic center, on an atom with a dangling bond. The influence of the adsorption of atoms of foreign X species, where X = H;O;N, on small and large supercells of perfect graphene, (which we shall call X-SAV-g), and graphene with a Stone-Wales defect (SW-g), was also studied. Results for H adsorption agree with recent DFT calculations [2], showing no magnetism on perfect graphene and a small spin gap for SW-g. O induces no magnetic moment on either perfect or SW-g. While H/N adsorption onto the magnetic center induces a small quenching of the liquid spin on SAV-g, O causes it to completely vanish, all of these elements inducing a _nite DOS at E_F. Allowing for relaxation of cell vectors changes the results dramatically: a rather pronounced deviation from the original symmetry of a perfect cell is seen on both cell vectors and angles. Moreover, the magnetism of H-SAV-g completely disappears, while N-SAV-g displays the same magnetic moment as for the un-relaxed cell. Large un-relaxed cells of H-SAV-g display a much weaker magnetism; together with the result for the relaxed small cell, this suggests that the effect of mechanical tension is important for the magnetism in this system.
Calculations for relaxation of large cells of all mentioned systems are under way.

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POSTER B28

Needle-like ZnO nanostructure synthesized by organic-free hydrothermal process: A tip for AFM probe

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Abstract

Needle-like ZnO nanostructures were synthesized by an organic-free hydrothermal process. The hydrothermal synthesis was performed at very low pressure (~20 kPa) with duration of process only 10 min. The products were characterized by X-ray powder diffraction (XRD)and transmission electron microscopy (TEM).The XRD pattern indicated that the needle –like ZnO nanostructures were hexagonal. Morphology, diameter and length of needles were investigated. Finally, the mechanism for organic-free hydrothermal synthesis of the needle-like ZnO nanostructure is discussed.

POSTER B29

Structure and dynamics of CO_3/Ag(210) with subsurface oxygen

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The interaction of oxygen with Ag is widely investigated, both in theory and experiments due to the importance of Ag in many crucial industrial oxidation reacions, e.g., ethylene epoxidation. It has been known that defects, e.g., steps, kinks and other surface imperfections play a key role in surface chemistry. In high resolution electron energy loss spectroscopy (HREELs) experiments on O2 /Ag(210) [1], it was observed that O2 undergoes a complete dissociation on Ag(210) surface (comprising of one-atom wide (100) terraces and (110) faceted steps), contrary to the flat Ag(100) and Ag(110) surface. The authors observed two peaks at 32 and 40 meV corresponding to oxygen adsorption at (100) ter- races and (110) steps respectively. Additionally, a third peak at 56 meV was observed and it was proposed to be corresponding to a subsurface oxygen. Motivated by these experiments, Bonini et al. [2] performed ab initio calculations to understand the structure and dynamics of O/Ag(210) surface and the results obtained were in excellent agreement with the experiments.

Recently, in X-Ray photoelectron spectroscopy (XPS) and HREELs experiments by the same group (Rocca and coworkers), it was found that when O/Ag(210) surface was ex- posed to CO, the peak corresponding to subsurface oxygen shifted towards lower fre- quency and grew in intensity. There was an additional peak at 101 meV, which was as- signed to carbonate (CO_3) vibration. In the present work, we again use density functional theory (DFT) and density functional perturbation theory (DFPT) to study the structure and dynamics of oxygen adsorbed on Ag(210) surface in the presence of CO_3. We find that indeed CO3 stabilizes the subsurface oxygen. We also calculate the activation barriers for subsurface oxygen coming to the surface in the absence and presence of CO_3 using nudge elastic band theory [3]. In the phonon calculations, we find that CO_3 vibrates at a frequency which is in good agreement with that of the experiments. In agreement with experiments, we find that a high concentration of subsurface oxygen is stabilized by CO_3 and the vibrational frequency of 51.5 meV found in experiments is corresponding to the coupling between subsurface oxygens.

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POSTER B30

X-ray photoabsorption and total electron yield of Fe thin films at the $L_{2,3}$ edge

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Abstract: We have used x-ray absorption spectroscopy (XAS) to study photoabsorption and total photon yield spectra of Fe thin films in the range of the L edges. Energy dependent photoabsorption cross sections at the Fe $L_{2,3}$ edge measured in total-electron-yield (TEY) to determine the electron yield escape depth (l_e) and x-ray penetration length (l_x) .

POSTER B31

TITLE ?

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By employing ab initio density functional molecular dynamics, we find that the heat capacities for the pair of clusters Na_{55} and Na_{58} are dramatically different. Such a size sensitive behavior has not been observed in Sodium clusters. The calculated melting temperature for Na_{58} an electronic closed-shell system, is the highest, i.e. about 375 K, among sodium clusters studied. By analyzing the evolutionary trend in the ground state geometries of Na_{55} to Na_{62} we bring out unique feature of Na_{58} namely electronically driven spherical shape leading to rather large melting temperature.

POSTER B32

DIFFERENTIAL ADSORPTION OF GLOBULAR PROTEINS ONTO NANOPATTERNED POLYMER SURFACES

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The preferential adsorption of three model globular proteins, human lactoferrin (Lf), human serum albumin (HSA) and chicken egg lysozyme (Lys) onto nanostructured surfaces has been investigated. The nanopatterned polysiloxane surfaces consisted of 2D arrays of hydrophilic nanopores or nanorings (made of O_2-plasma treated polysiloxane) surrounded by hydrophobic polysiloxane matrix or the reverse. The pattern geometry and chemical contrast was modulated by using two different methods, one based on dewetting-driven self-assembly of colloidal masks followed by polymer deposition due to capillarity, the second method, based on spin coating of suitable colloidal and polymer solutions.

The characterization of the nanometric features of adsorbed proteins was performed by means of Atomic Force Microscopy (AFM), while the corresponding homogeneous surfaces were studied by Quartz Crystal Microbalance with Dissipation monitoring technique (QCM-D), for the adsorption kinetics and the determination of coverage and viscoelastic properties, and XPS, for chemical structure and coverage of the protein adlayers. HSA and Lf showed the opposite preferential adsorption behaviours, i.e., increased adsorption of Lf and HSA into the hydrophilic or hydrophobic areas of the nanopores, respectively. The driving chemical factors are related to the surface free energy properties as well as to the chemical termination of the different surfaces.

POSTER B33

HUMAN SERUM ALBUMIN NANO-CONTACT PRINTING BY PDMS REPLICAS OF COLLOIDAL ASSEMBLIES.

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Close-packed arrays of nano-pores were molded in PDMS from monolayers of carboxylated polystyrene colloids having a diameter of 489 nm. Hexagonal and random packing were obtained by spontaneous dewetting-driven processes and LB-driven vertical deposition from aqueous suspension on hydrophilic SiO_2 substrates. The random patterns were uniformly extended over the whole sample area (up to 2 cm^2), while the hexagonal order was obtained over tens of micrometers. The PDMS molds were used as stamps for the nano-imprinting of human serum albumin (HSA). Atomic Force Microscopy revealed that protein transfer on the substrates was successful, creating irregular honey-comb-like structures with features having typical height 5-7 nm.