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The scattering of surface electrons by the edges of graphene islands grown on Ni(111) has been investigated by combining local tunneling spectroscopy and ab initio electronic structure calculations. We find clear signatures of spin- and edge-dependent electron scattering of the Shockley bands of Ni. Our results suggest the possibility of 2D lateral spin filtering for graphene layers, similar to that occurring across the interface.

The scattering of electrons at the interface between graphene and metal contacts determines the charge and spin injection efficiency into graphene and, consequently, it is a fundamental issue for the performance of graphene-based devices. Weakly interacting metal contacts simply dope the Dirac bands. The interface with more reactive metals, however, is usually characterized by significant electronic reconstruction, which defines a complex scenario for scattering. The graphene-Ni interface represents an interesting case where the interaction with the ferromagnetic substrate opens hybridization gaps and induces magnetic moments. Consequently, graphene is predicted to behave as a perfect spin filter in contact with a magnetic Ni electrode.

In this work, we have performed a combined experimental and theoretical study of the electronic properties of graphene nanoslides with well-defined edge geometry grown on a Ni(111) substrate. The strong interaction between C and Ni atoms induces a significant energy mismatch of the surface bands inside and outside graphene, quenching the transmission through the graphene edge. This effect, together with the different coupling to bulk states of majority and minority Ni bands, leads to a spin-dependent scattering of the Shockley bands of Ni. We further demonstrate that the edge scattering is strongly structure dependent, with asymmetries in the reflection amplitude of up to 30% for reconstructed and non-reconstructed zig-zag edges.

Our results elucidate the complex scattering properties of graphene-metal interfaces and are important for the control of electron transport and quantum confinement in lateral graphene junctions with spin-polarized electrodes.

Unraveling the complex scattering properties of graphene/metal interfaces
Co nanodot arrays grown on a GdAu$_2$ template: Substrate/nanodot antiferromagnetic coupling

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Nano Letters 14, 2917 (2014)

Controlling anisotropy and exchange coupling in patterned magnetic nanostructures is key to develop advanced magnetic storage and spintronic devices. We report on the antiferromagnetic interaction between a Co nanodot array and its supporting GdAu$_2$ nanotemplate that induces large anisotropy values in individual Co nanodots. In clear contrast with nonmagnetic Au substrates, GdAu$_2$ triggers an earlier switch from out-of-plane anisotropy in atomic high dots to in-plane when the dot height becomes biatomic.

Playing with nanomagnets at the interface: the role of rare earth atoms

One of the biggest challenges in magnetic storage and spintronics is to fabricate arrays of magnetic nanodots. On the one side, the objective is to achieve the densest network made of independent magnetic nanoelements, and on the other side the objective is to develop functional interfaces for spintronics. Here, we address the characterization of a periodic Co nanodot array self-assembled on a ferromagnetic (FM) nanotemplate of GdAu$_2$. This article deals with the fundamental question about the nature of the anisotropy and magnetic coupling across the interface between the nanostructures and the template.

Substrate/nanodots antiferromagnetic coupling

We focus the present study on arrays of independent Co nanodots on a monolayer thick GdAu$_2$ surface compound, where two different types of dots are observed being one or two atomic layer (AL) heights (see Figure 2A). The magnetic response of the Co nanodot array is shown in Figure 2 through element-specific X-ray magnetic circular dichroism (XMCD) analysis taken at the DEIMOS beamline. The shape of the XMCD asymmetry spectra is inverted with respect to the Gd atoms of the substrate indicating antiferromagnetic (AFM) coupling. Magnetization loops taken on the Co$_{L3}$ and the Gd$_{M5}$ absorption edges confirmed the AFM interaction and evidence a strong coupling. This is certified by our full-potential linearized augmented plane waves (FLAPW) calculations within the density functional theory (DFT) that probe the exchange coupling between Co dots and substrate induces significant changes on the Co anisotropy, leading to a switch from out-of-plane for monoatomic high dots to in-plane easy axis direction in biatomic high Co dots. Given the variety of the rare earth-noble metal moiré templates, the present study opens up a new route to explore similar magnetic nanodot arrays on different RE-Au$_2$ surfaces.

Figure 1. (a) Self-organized Co nanodots on GdAu$_2$(0.6ML). The inset shows the GdAu$_2$ template. (b) Histogram with nanodot height distribution. The inset displays one and two AL height nanodots together with a more minima.

Figure 2. XAS measurements of 0.6ML Co/GdAu$_2$ measured at 3K with an applied magnetic field of 6T and $\theta=60^\circ$ incidence from: (a) Co at the $L_3$ and (b) Gd at the $M_5$ absorption edges. (c,d) XMCD asymmetry signals as a function of applied field for 0.6 and 0.75ML Co on GdAu$_2$, respectively.

Figure 3. XMCD element specific magnetization curves measured at the Gd M$_5$ absorption edge from Co free and Co covered GdAu$_2$ layers (T=3K) at (a) in-plane, and (b) out-of-plane geometry, respectively. The clean substrate loops exhibit FM Gd with large uniaxial, in-plane anisotropy.

Magnetic anisotropy energy

The magnetic anisotropy was probed using different sample geometries with respect to the magnetic field and to the photon propagation vector. We found a reduction of the strong in-plane anisotropy of the GdAu$_2$ substrate after Co dot adsorption (see Figure 3). Such a situation occurs if the dots reveal an out-of-plane anisotropy. This is again ratified by the DFT calculations. Clean GdAu$_2$ layers have magnetic anisotropy energy (MAE) of 2.7meV per unit cell and show an in-plane easy-axis of magnetization. Moreover, the magnetic anisotropy of Co grown on GdAu$_2$ layers is found to be strongly dependent on Co coverage. Up to 1 AL thick Co dots the easy axis is perpendicular to the surface. In contrast, for more than 2 AL the easy-axis changes to in-plane. The magnetization curves of Figure 3 suggest that upon adsorption of 1 AL Co nanodots, a local out-of-plane anisotropy reorientation takes place in the underlying GdAu$_2$ alloy.

In conclusion, experiment and theory demonstrate the strong AFM coupling between Co and Gd. The electronic interaction between Co dots and substrate induces significant changes on the Co anisotropy, leading to a switch from out-of-plane for monatomic high dots to in-plane easy axis direction in biatomic high Co dots. Given the variety of the rare earth-noble metal moiré templates, the present study opens up a new route to explore similar magnetic nanodot arrays on different RE-Au$_2$ surfaces.

Electronic friction dominates hydrogen hot-atom relaxation on Pd(100)

M. Blanco-Rey, J. I. Juaristi, R. Díez Muñho, H. F. Busnengo, G. J. Kroes and M. Alducin


The performance of a material under realistic working conditions is highly dependent on the way it interacts with its environment. For this reason, the study of solid surfaces at the atomic scale is one of the most active fields of research in materials science. One of the current challenges is the modelling of the interaction dynamics between gas-phase atoms or molecules and a surface. The so-called ab-initio theoretical methods have contributed many advances in this field over the last few decades.

An important question is how energy is dissipated during the interaction time, i.e. how the gas species exchanges energy with the surface. This issue may have implications for the chemical properties of the surface or for its durability, in the case the surface is to be used as a catalyst or a coating. Even in apparently simple cases, such as an atom interacting with a metal, it is difficult to describe the gas/solid interaction processes, since many parameters come into play: chemical reactivity of the surface, momentum of the approaching species, surface temperature, etc.

Researchers of the DIPC and the CFM have investigated by means of ab-initio simulations the fate of a H₂ molecule that dissociates upon impact on a Pd surface. The energy contained in the molecular bond (a few eV) is liberated and, as shown by the simulations, the resulting H atoms initially acquire considerable propagation velocity on the surface. These “hot” H atoms slow down by transferring their kinetic energy to the Pd substrate using two channels: motion of the Pd nuclei via H-Pd collisions and electronic excitations of the metal surface charge. It was thought so far that the former channel was dominant for H on Pd, but this investigation has determined that the electronic channel can in fact decelerate the hot atoms at a five times larger rate, as shown in the Figure.

This finding could not have been accomplished without improving the existing theoretical methods with the inclusion of electronic excitations. These are accounted for “on-the-fly” at each point of the trajectory followed by the hot atom as a friction force that opposes its movement. The strength of this force depends on the charge density of the metal at each position, which is known as the LDFA approach. This technique has been denoted with the acronym AIMDEF (ab-initio molecular dynamics with electronic friction).

It is worth noting that this result for hot H atoms on Pd is compatible with the experimental observation of chemicurrents, i.e. electric currents that originate during adsorption, dissociation and recombination of a molecule on a metal. Chemicurrents may be used as sensors of chemical processes, and the deceleration rates found by AIMDEF can help calibrate them. In addition, AIMDEF demonstrates that energy dissipation happens gradually during the hot species propagation on the surface, rather than instantaneously. The simulations also yield the distances travelled by the hot atoms (see Figure) before stopping. Thus, it can be predicted whether the transient species can jump into and recombine with other species on the surface. Since the travelled distances cannot be inferred from the energy dissipation rate values alone, AIMDEF comes in as a valuable tool to characterise the chemical activity of the surface, too.
Self-assembly of bicomponent molecular monolayers: Adsorption height changes and their consequences


Surprising changes in the adsorption heights of molecules within donor-acceptor monolayer blends are found to have a measurable effect on the system’s interface dipole.

Charge carrier injection in organic optoelectronic devices depends on the electronic properties of metal-organic interfaces, which are, therefore, of utmost importance for device efficiency. Such properties are strongly affected by the detailed interfacial structure defined by the molecular orientation with respect to the substrate, the lateral distribution, and the molecule-substrate distance. The latter, in particular, plays a central role in the interfacial energy level alignment due to its interrelation with the interface dipole.

The most precise technique to determine the molecule-substrate distance experimentally is normal incidence x-ray standing waves (XSW). In this work we go beyond the common characterization of single-component layers, using XSW for the first time to determine molecule-substrate distances in donor-acceptor molecular blends, which hold particular interest for many organic devices.

We focus on the characterization of donor-acceptor blends comprising copper-phthalocyanines (CuPc, donor) and perfluoropentacene (PFP, acceptor). The lateral order of the 2D blends and the molecule-substrate distances have been assessed using scanning tunneling microscopy (STM) and XSW, respectively. Electronic properties have been investigated by photoemission. STM measurements show that codepositing CuPc and PFP on Ag(111) and Cu(111) leads to the self-assembly of ordered molecular layers in which molecules adopt a flat-lying configuration. As shown in Figure 1, donor-acceptor contact is maximized in the layers, thereby optimizing C-H···F intermolecular hydrogen bonds.

Regarding the adsorption heights of CuPc and PFP we find that, as compared with single-component layers, the PFP-substrate distance increases by ~0.3 Å in the blends. Instead, CuPc shows only negligible changes. Figure 2 shows a schematic of adsorption heights of CuPc and PFP in single component and mixed layers, evidencing how PFP’s surprising adsorption height change further increases the height difference between neighboring molecular species in the blend. The changes in adsorption height found in the mixed layer are expected to lead to variations in the interface electronic properties. Indeed, work function measurements on the mixed layers show that PFP’s contribution to the interface dipole is reduced by about 40% with respect to what would be expected from its configuration in the single-component layer. We argue that the increased molecule-substrate distance of PFP found in the mixture translates into a reduced Pauli repulsion, thereby decreasing the effective interface dipole. We hereby provide a direct measure of the effect of a molecule’s adsorption height on vacuum level shifts and, in turn, interfacial energy level alignment.
Chemical control of electrical contact to sp² carbon atoms

T. Frederiksen, G. Foti, F. Scheurer, V. Speisser and G. Schull

Research carried out at UPV/EHU, DIPC and CNRS advances the understanding of electric contacts in future carbon-based nanoelectronics.

Carbon-based nanostructures such as nanotubes, graphene sheets, and nanoribbons are unique building blocks showing versatile nanomechanical and nanoelectronic properties. These materials which are ordered in the nanoscale — that is, in the dimension of a millionth of millimetre — are promising candidates to envision applications in nanoscale devices, ranging from energy conversion to nano-electronic transistors. A good connection between carbon-based materials and external metallic leads is of major importance in nano-device performance, an aspect where an important step has been surmounted by researchers from UPV/EHU, DIPC and CNRS by studying contacts of carbon nanostructures with atoms of different chemical nature.

The chemical nature of contacting leads is of major importance as it affects the electronic properties and the geometry of the contact. The impact of these two aspects on the transport properties are entangled and this group studied these two parameters for contacts shrunk to the limit of individual atoms as for large structures it is challenging to address them separately.

In close collaboration, the researchers used a prototype carbon-based molecule made of 60 carbon atoms arranged in a sphere that can be viewed as a graphene sheet rolled into a tiny ball. The experimental team in Strasbourg led by Guillaume Schull attached this molecule to the apex of an extremely tiny metal needle of a scanning tunnelling microscope (STM). The molecule-terminated needle was then cautiously approached to individual metallic atoms of different chemical nature up to the formation of a robust connection. By simultaneously measuring the electrical current passing through these connections, they could deduce which of the individual metallic atom is injecting charges to the carbon-made molecule with the greatest efficiency.

Large-scale computer simulations performed by the theoretical team in San Sebastian led by Thomas Frederiksen, Ikerbasque Research Professor at the DIPC, revealed a fascinating and unexpected aspect of these extremely tiny connections: their electric and mechanical properties are in fact representative for much larger carbon-based materials.

These results, published in the prestigious journal Nature Communications, set the bases to find extremely efficient contacts in the near future. The study paves the way to probe a great number of different metallic species (as well as tiny alloys made of two or three different metallic atoms), allowing for a systematic classification of their abilities to inject electrons into emerging carbon-based electronic devices.

Artistic view of an electric connection between a C₆₀ molecule (attached to the tip of a STM) and a single metallic adatom (gray ball). The researchers were able to quantify how the current depends on the chemical nature of the contacting adatom.

Individual metal adatoms contacted with a C₆₀-functionalized STM tip. (a) STM image (7.0 × 6.2 nm²) of different metal adatoms on Cu(111) acquired with a C₆₀ tip at a sample voltage V = 1.7 V. (b–d) Close-up views (1.4 × 1.4 nm²) of Cu₆₀, Au₁ and Fe₁ images with a C₆₀ tip for tunnelling conditions corresponding to the initial parameter of the traces in (b). (e) Sketch of the C₆₀ tip where z = 0 corresponds to contact with the flat surface. (f) Experimental conductance traces G(E) in units of the conductance quantum G₀ = 2e²/h. Black crosses mark the contact points defined as the intersection of the contact and transition regimes such as indicated by the dashed grey lines in panel (f) for the bare surface data.
Time-resolved random laser spectroscopy of inhomogeneously broadened systems

J. Fernández, S. García-Revilla, L. D. Carros, E. Pecoraro, M. A. Arriandiaga and R. Balda
Laser and Photonics Rev. 8, No. 3, L32-36 (2014)

The understanding of energy transfer processes in biological systems occurring among optical centers which exhibit inhomogeneously broadened spectral bands is of paramount importance to determine time constants and spatial distribution of energy flow. In this work a new time resolved-spectroscopy based on the random laser generation of the optical probes is reported. This new spectroscopy may resolve not only the spectral features of the system but also provide a high speed picture of the energy transfer and excited state relaxation of efficient interacting chromophore pairs embedded in inhomogeneous scattering structures.

It is well known that in fluorescence, much of the molecular information content is available only by time-resolved measurements. Frequently, macromolecules can exist in more than a single conformation, and the decay time of a bound probe may reveal the presence of different conformational states. Moreover, in the presence of energy transfer, the intensity decays map out the rate of the process and may provide information about the excited-state dynamics of both donors and acceptors. Among time-resolved spectroscopies, fluorescence line-narrowing is one of the most suitable for studying interline energy transfer in inhomogeneous broadened systems. The measurements are made at low temperature, where kT is much less than the chromophore spectral width. In spite of this, the theoretical grounds of such spectroscopy can be applied to the dynamics of the room temperature excited state of an inhomogeneously broadened transition when the excited state is followed by its own random laser emission produced by multiple light scattering. The random laser process selects only a small subset of emitting centres which gives the well known narrowed spectral emission.

In this paper, scientists from DIPC explore the potentialities of random lasing as a spectral probe of molecular relaxation in high concentrated Rhodamine B-doped d-U(600) organic-inorganic diureasil hybrid powders. The analysis of the random laser emission, which was detected by using a streak camera, shows that the energy transfer between Rhodamine B monomers and dimers is at the origin of random laser emission of dimer species and can be formally interpreted as spectral migration in a similar way to fluorescence line-narrowing in inhomogeneously broadened systems. It is worth noticing that in spite of the overlapping between the emission bands of monomers and dimers, the frequency selection introduced by the random laser process allows to discriminate from both groups of emitters. Moreover, the subnanosecond nature of the random lasing buildup time allows for a real time tracking of the transfer process between them.

This new random lasing-based spectroscopy can, in principle, be applied to any kind of efficient interacting chromophores pairs and could efficiently help to understand the spectro-temporal dynamics of ultratrace energy transfer processes occurring at cellular level, when engineered efficient chromophore markers are used as sensors. The results open a new door for the application of random laser emission in complex systems and provide a new tool for high resolution studies of spectro-temporal energy transfer processes at room temperature.

Photograph of the random laser emission of a high concentrated Rhodamine B-doped diureasil powder.

A new random laser based spectroscopy is reported.
Polymer chain dynamics: Evidence of nonexponential mode relaxation using thermally stimulated depolarization current techniques

S. Arrese-Igor, A. Alegría, and J. Colmenero

Actual theories for macromolecular chain dynamics assume exponential relaxation for the different chain modes while molecular dynamics simulations usually show deviations from the exponential behavior. In this work thermally stimulated depolarization current technique was used to show that on approaching the range of the kinetic glass transition the slowest (p=1) chain mode significantly deviates from an exponential decay.

Fluctuations of the end-to-end vector of a polymer chain are at the basis of the viscoelastic properties having thus great impact on the processing and final application of macromolecular systems in general. Although molecular dynamics simulations usually show deviations from the exponential behavior, actual theories for macromolecular chain dynamics assume exponential relaxation for the different chain modes, i.e., the spatial and time correlations of the random forces acting on a polymer segment are neglected. Testing the question from an experimental point of view however has remained elusive due to difficulties in recording the response of a single mode rather than the global response (addition of several modes).

In this work the authors have developed an experimental procedure to isolate the slowest chain mode (p=1) relaxation by means of thermally stimulated depolarization current (TSDC) technique. It has been shown that on approaching the range of the kinetic glass transition (T_g) the relaxation p=1 mode significantly deviates from an exponential decay, i.e., from the behavior assumed by Rouse and tube-reptation theories. The effect is found to be more pronounced the closer the timescale of the p=1 chain mode and that of the local density fluctuations (α-relaxation) leading to the glass transition process. The observed behavior is consistent with an scenario where exponentiality for the chain modes would be lost as a consequence of breaking the condition of time uncorrelation for the forces acting on a chain segment due to the slowing down of the local density fluctuations. Moreover, the phenomenology observed for homopolymers close to the glass transition resembles that observed for the chain dynamics of the fast component in blends with high dynamic asymmetry when approaching the glass transition of the slow component, and suggests a general interpretation for both contexts.

Parameter β describing the non-exponential character of the mode relaxation as a function of the ratio between the timescales of the slowest (p=1) chain mode and the relevant density fluctuations in the system (the α-relaxation in the case of homopolymers and the α-relaxation of the slow component in the blends): Linear polyisoprenes of different molecular weights by TSDC (black squares); linear polyethyleneoxide by MDS (downside triangles); 20% linear polyethyleneoxide -fast component- blended with higher T_g polymethylmethacrylate -slow component- by MDS.

The exponential character of the slowest chain mode relaxation is lost as a consequence of breaking the condition of time uncorrelation for the forces acting on a chain segment due to the slowing down of the local density fluctuations.
Determining the polarization state of an extreme ultraviolet free-electron laser beam using atomic circular dichroism

Nature Communications 5, 3648 (2014)

Two-color photoionization of an atom is a powerful and straightforward tool to determine the sign of the helicity and the magnitude of circular polarization of any XUV or indeed X-ray FEL beam with high accuracy. Moreover, this study confirms the theoretical prediction of CD in the two-color multi-photon ionization of atoms.

Ultrafast extreme ultraviolet and X-ray free-electron lasers are set to revolutionize many domains such as bio-photonics and materials science. These short-wavelength FELs enable investigation of non-linear phenomena and femtosecond time-resolved spectroscopy. In addition, X-ray FELs have enabled imaging experiments aiming to determine the structure of a single biomolecule.

Nearly all short-wavelength FEL experiments to date have been carried out with linearly polarized light. As far as we know, only one experiment was performed with circularly polarized light but at the expense of a strong reduction in intensity. This limitation was overcome only recently thanks to FEL FERMI, designed specifically to produce circularly polarized extremely intense XUV radiation.

In this work, characterization of the polarization properties of the FEL beam was carried out by analyzing the sidebands in the photoelectron spectrum and compared with theory (Figure 2):

- Maximal electron emission observed at 90° is in agreement with theoretical results.
- The angular distribution with two sidebands (caused by a two-photon process) is much narrower than that of the 1s photoline (mostly from a one-photon process).
- Dichroism of opposite sign for the main line and the sidebands is observed both for experiment and theory.

The observation of the CD demonstrates unequivocally that chirality is introduced into the (initially unpolarized atomic) system by the circularly polarized ionizing XUV radiation. The overlap with an NIR-dressing field of the same or the opposite helicity causes different probabilities for the transfer of electrons from the main line to the sidebands, i.e., for the free-free transitions.

The degree of circular polarization is obtained by comparing the CD determined from the experimental and the simulated theoretical electron spectra at emission angles of (90±4)°, where theory predicts maximal CD:

- Measured amplitude of the CD is 0.04±0.004 at the high-energy sideband (25.2–26.1 eV).
- \( \text{Pcirc} = 0.95\pm0.05 \) for the XUV radiation.

CD measurement is in excellent agreement with theory and Pcirc with predictions. The method is therefore an important metrological tool for the determination of the degree of circular polarization, which is otherwise difficult to measure at the high power levels used here. Moreover, the sign of the dichroism is directly related to the relative helicity of both the NIR and XUV fields; the negative dichroism indicates that the FEL beam was in a state of left-handed circular polarization.

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Quantum dots (QDs) are semiconductor nanocrystals that present very fascinating properties like high extinction coefficients, a tunable bandgap with size, carrier multiplication and also hot carrier extraction. When QDs are placed on a thin film and then photoexcited, the generated holes and electrons are extracted at two different electrodes to generate current. One of the main problems of this cell is that electron and holes can recombine before reaching the electrodes. This creates short-circuits, lowers the diffusion length of the film and reduces the device performance. To circumvent these problems, it is paramount to increase electron-hole mobility.

In this work, we have collaborated with the optoelectronic group at TU Delft in the Netherlands to combine theoretical calculations based on Density Functional Theory (DFT) with experiments. Ligand exchange is a much-used method to increase the conductivity of colloidal QD films by replacing long insulating ligands on QD surfaces with shorter ones. Here we show that while some ligands indeed replace the original ones as expected, others may be used to controllably remove the native ligands and induce epitaxial necking of specific crystal facets. In particular, with our DFT calculations, we have demonstrated that amines strip lead oleate from the (100) surfaces of PbSe QDs. This leads to necking of QDs and results in cubic superlattices of epitaxially connected QDs. The number of amine head-groups as well as the carbon chain length of linear diamines is shown to control the extent of necking. DFT calculations show that the removal of Pb(oleate)2 from (100) surfaces is exothermic for all amines, but the driving force increases as monoamines < long diamines < short diamines < tetramines. The neck formation and cubic ordering results in a higher optical absorption cross section and higher charge carrier mobilities, thereby showing that the use of the proper multidentate amine molecules is a powerful tool to create supercrystals of epitaxially connected PbSe QDs with controlled electronic coupling.

In summary, our DFT calculations have been used as a powerful tool to identify organic ligands that ultimately led to a 5-fold increase in conductivity of PbSe QD films.

Currently, silicon-based single-junction solar cell devices available in the market have a reasonable efficiency of 15% but they suffer of high production cost. To increase the efficiency and lower the costs, a new generation of solar devices based on nanomaterials is being developed. Quantum dots solar cells (QDSC) are among these most promising new photovoltaic cells and in just few years they passed from efficiencies below 1% to almost 10%.

In this work, we have collaborated with the optoelectronic group at TU Delft in the Netherlands to combine theoretical calculations based on Density Functional Theory (DFT) with experiments. Ligand exchange is a much-used method to increase the conductivity of colloidal QD films by replacing long insulating ligands on QD surfaces with shorter ones. Here we show that while some ligands indeed replace the original ones as expected, others may be used to controllably remove the native ligands and induce epitaxial necking of specific crystal facets. In particular, with our DFT calculations, we have demonstrated that amines strip lead oleate from the (100) surfaces of PbSe QDs. This leads to necking of QDs and results in cubic superlattices of epitaxially connected QDs. The number of amine head-groups as well as the carbon chain length of linear diamines is shown to control the extent of necking. DFT calculations show that the removal of Pb(oleate)2 from (100) surfaces is exothermic for all amines, but the driving force increases as monoamines < long diamines < short diamines < tetramines. The neck formation and cubic ordering results in a higher optical absorption cross section and higher charge carrier mobilities, thereby showing that the use of the proper multidentate amine molecules is a powerful tool to create supercrystals of epitaxially connected PbSe QDs with controlled electronic coupling.

In summary, our DFT calculations have been used as a powerful tool to identify organic ligands that ultimately led to a 5-fold increase in conductivity of PbSe QD films.
Complex chiral colloids and surfaces via high-index off-cut silicon

Nano Letters 14, 2934 (2014)

Highly symmetric surface cavities are commonly obtained on masked silicon wafers through selective exposure of circular and polygonal areas to alkaline solutions. The cavities arise because the silicon (111) atomic planes are etched slowly, compared to any other crystallographic orientation. We apply this traditional etching technique to nonstandard, high-index, off-cut silicon (137) wafers, resulting in the generation of highly complex, nanoscale, chiral cavities that would otherwise be difficult to produce. By using such cavities as templates where metals such as Ag or Au can be deposited, the study demonstrates the production of chiral gold surfaces and nanoparticles of a specific handedness. When the nanoparticles are dispersed in liquids, gold colloids exhibiting record molar circular dichroism at red wavelengths are obtained.

An object, such as a molecule or nanoparticle, is chiral if it does not contain any plane of symmetry. In other words, its mirror image cannot be superimposed onto it. For optically active chiral molecules and nanoparticles, the absorption of light is different for left and right circularly polarized light (LCP and RCP, respectively). Indeed, circular dichroism (CD) refers to the difference in their absorption \( \Delta \varepsilon \equiv \varepsilon_L - \varepsilon_R \), which is wavelength dependent. By sending equal amounts of LCP and RCP light to a sample and recording \( \Delta \varepsilon \) at different wavelengths a unique, particle-dependent CD spectrum is obtained.

In the infrared region, CD spectroscopy can be used for structural studies of small organic molecules, proteins and DNA. The ability to measure CD spectra at red wavelengths is expected to refine such structural studies. In addition, chiral structures can lead to interesting optical effects such as superchiral electromagnetic fields. More generally, chirality is a fundamental asymmetry found in nature and it should be possible to use it for the design of artificial optical surfaces and colloids.

In this collaboration between researchers at DIPC and in Switzerland, Germany and South Korea, it is demonstrated that off-cut silicon wafers can provide a versatile approach to fabricate high-quality chiral surfaces as well as chiral colloidal nanoparticles with complex shapes, difficult to obtain otherwise. The nanoparticles contain tips and binding pockets for exploration of enhanced detection of structural chirality. The obtained chiral colloids made from solid particles open possibilities in nonlinear optics, opto-fluidics, and photocatalysis.

We demonstrate that off-cut silicon wafers can provide a versatile approach to fabricate high-quality chiral surfaces as well as chiral colloidal nanoparticles with complex shapes.
Coherent ultrafast charge transfer in an organic photovoltaic blend

Science 344, 6187 (2014)

Silicon panel-based technology requires a very costly, contaminating manufacturing process, while organic photovoltaic (OPV) devices have been positioned as one of the most attractive alternatives as a source of solar energy.

This research has made a ground-breaking discovery because it is the first time that the quantum mechanisms that trigger the photovoltaic function of these devices have been deciphered. Angel Rubio, Professor of Condensed Matter Physics at the Faculty of Chemistry of the UPV/EHU-University of the Basque Country, director of the Nano-Bio Spectroscopy Group, and associate researcher of the Donostia International Physics Center (DIPC), has participated in the research conducted in this field in collaboration with various centres in Germany, Italy and France. The research has been published in the prestigious journal Science.

These organic devices use a photosensitive polymer linked to a carbon nanostructure that functions as a current collector. When light falls on the device, the polymer traps the particles of light and induces the ultrafast transmission of electrons to the nanostructure through an electron impulse in the order of femtoseconds (fs), in other words, 10^-15 seconds. Evidence was recently found to confirm this ultrafast transfer, but the research of Rubio and his team has gone a step further because it has succeeded in deciphering the elemental mechanism that unleashes the electron transfer between the polymer and the nanostructure. First principle theoretical simulations in a simplified model predicted that the coherent vibrations are the ones that dictate the periodic transfer of charge between the polymer and the fullerene.

The experimental group confirmed this prediction by studying the optical response of a common material comprising a polymer and a by-product of the fullerene (a conventional nanostructure with a spherical shape) by means of high-resolution temporal spectroscopy.

The results confirmed that the coupling of the vibrations of the polymer and the fullerene bring about the electron transfer in a coherent and ultrafast way (~23 fs), difficult to reconcile with incoherent processes that are manifested in slower transfers (100 fs). These studies demonstrate the critical role played by quantum coherence in organic photovoltaic devices.

The research offers a vision that is consistent with elemental quantum processes in organic photovoltaic devices and constitutes a significant step forward in this field.
Acoustic Surface Plasmons (ASP) originate from the excitation of a two-dimensional (2D) electron gas whenever it is effectively screened by an underlying 3D electron gas as, e.g., it occurs at the noble-metal surfaces. Contrary to sheet plasmons, characterized by a square-root like dependence on wavevector, ASPs have a linear soundlike dispersion and hence a frequency-independent group and phase velocities. These excitations are very promising for future applications in plasmonics since the speed and thus the wavelength of ASPs is three orders of magnitude lower than that of light, permitting us in principle to locate plasmonic excitations on the scale of a few nanometers. A hypothetical polychromatic ASP signal would indeed propagate without distortion, allowing for accurate signal processing.

The dispersion curves of ASP and light do, however, per se not cross at clean surfaces so a momentum source is needed to realize coupling of the ASP with photons; this can be realized by, e.g., a grating. However, the short wavelength of the ASP requires realization of this grating on the atomic scale. Nanostructuring, however, implies concomitant generation of atomic defects, so it is necessary to understand how defects and confinement in nanosized regions modify the ASP dispersion. Combining the energy loss spectroscopy-low energy electron diffraction (ELS-LEED) experiment and density-response calculations, we demonstrate here the existence of two plasmonic modes at the Au(111) surface both parallel and perpendicular to the steps, due to the splitting of the Shockley surface state (SSS) band existing of the bare Au(111) surface into separate subbands caused by the step potential as shown in Figure 1.

The measured plasmon peak positions are collected in Figure 2. Our data clearly indicate that two losses with sound-like dispersion are present, denoted by I and II in Figure 2a). Across the steps the data points level out at large $q_{\parallel}$. The branch with the steeper slope originates clearly from the ASP associated to the SSS of the (111) terraces, which has a very similar slope as on flat Au(111), while the lower branches have no counterpart on pristine Au(111).

These findings lead to the following remarkable physical scenario:
(a) Along the steps we observe two ASP modes with different group velocities determined by the maximal Fermi velocities of two partly occupied SSS subbands.
(b) The anisotropy introduced by the steps on Au(788) does not automatically lead to plasmon localization normal to the terraces, but the SSS subband formation is reflected by a splitting of the ASP also normal to the steps.
(c) The GW1 and GW2 subbands are still able to generate propagating plasmonic modes across the steps at wavelengths longer than the terrace width. The slightly different slopes of the modes parallel and normal to the steps reflect the anisotropy of the system.
(d) Across the steps signs of plasmon localization become visible when $q_{\parallel}$ exceeds the reciprocal lattice vector $G_0$ of the periodic step array, and get more and more dominant when multiples of $G_0$ can be transferred. Together with an increasing efficiency of momentum transfer at steps with decreasing plasmon wavelength this leads to nearly complete localization at the highest $q_{\parallel}$ of present measurements.
Superconductor-ferromagnetic insulator structures for thermoelectric devices


Large thermoelectric power from a combination of magnets and superconductors thermoelectric devices can cool materials by passing currents, or convert temperature differences into electric power. However, especially metallic structures have a very poor thermoelectric performance, and therefore most thermoelectric are made of semiconductors.

Last year Asier Ozaeta and F. Sebastian Bergeret from the Mesoscopic Physics Group at DIPC (Donostia-San Sebastian) in collaboration with researchers from the University of Jyväskylä and Aalto University (Finland), have shown how a proper combination of magnetic metals and superconductors could allow reaching very high thermoelectric conversion efficiency. The electronic structure of semiconductors and superconductors looks superficially similar, because both contain an ‘energy gap’, a region of energies forbidden for the electrons. The difference between the two is that doping semiconductors allows moving this energy gap with respect to the average electron energy. This is in contrast to superconductors, where the energy gap is symmetric with respect to positive and negative energies, and therefore the thermoelectric effect from positive energy electrons cancels the effect from the negative energy electrons. In the first work published in 2014, Ozaeta, Bergeret and the international research group showed how this symmetry can be broken within the superconductor with a spin-split density of states induced by the proximity of a ferromagnetic insulator (Figure 1). As a result, the system exhibits a very large thermoelectric effect. Because conventional superconductors require temperatures of the order of a few Kelvin, this mechanism cannot be used directly in consumer devices such as portable coolers or waste heat converters. However, it could be used in accurate signal detection, or a similar mechanism could be applied in semiconductors to improve their thermoelectric performance.

In a subsequent work, F. Sebastian Bergeret in collaboration with researchers from the Scuola Normale Superiore in Pisa (Italy), Cambridge University (UK) and the Massachusetts Institute of Technology (USA), demonstrated that the efficiency of such devices can be considerably improved if the superconductor-ferromagnetic insulator element is embedded in a superconducting loop. In such a case a very large Seebeck coefficient of the order of mV/K can be achieved, leading to a figure-of-merit (ZT) far exceeding the values of state-of-the-art thermoelectric materials (Figure 2).

One of the published works was chosen as an ‘Editor’s suggestion’ category in Physical Review Letters, recommending articles for wide range of people because of their clarity.
A new technique which uses light like a needle to thread long chains of metallic particles allows to modify their optical response and could help bring novel material concepts such as cloaking devices one step closer to reality.

A new method of building and manipulating materials using light, developed and analyzed by researchers at the University of Cambridge (UK) and Donostia International Physics Center (DIPC), could one day enable technologies that are often considered the realm of science fiction, such as invisibility cloaks and cloaking devices. Although cloaked starships won’t be a reality for quite some time, the technique which researchers have developed for constructing materials with building blocks a few billionths of a metre across can be used to control the way that light flies through them, and works on large chunks all at once. Details are published in the journal Nature Communications.

The technique developed by the Cambridge team involves using unfocused laser light as billions of electromagnetic needles, literally stitching gold nanoparticles together into long strings, directly in water for the first time. These strings can then be stacked into layers one on top of the other, similar to Lego bricks. The method makes it possible to produce materials in much higher quantities than can be made through current techniques. These nanoparticle strings show clear resonances in their response to light that can be tuned from the visible to the infrared, and might constitute the building blocks of novel metamaterials that show technologically relevant properties such as negative refraction index or broadband cloaking materials.

In order to make the strings, the researchers first used barrel-shaped molecules called cucurbiturils (CBs). The CBs act like miniature spacers, enabling a very high degree of control over the spacing between the nanoparticles, locking them in place. In order to connect them electrically, the researchers needed to build a bridge between the nanoparticles. Conventional welding techniques would not be effective, as they cause the particles to melt. The challenging aspect of this novel synthesis is to precisely control the bridge between nanoparticles as well as scaling up the process of particle linking. The key to controlling the bridges lies in the cucurbiturils: the precise spacing between the nanoparticles allows much more control over the process. When the laser is focused on the strings of particles in their CB scaffolds, it produces plasmons: ripples of electrons at the surfaces of conducting metals. These skipping electrons concentrate the light energy on atoms at the surface and join them to form bridges between the nanoparticles, acting as effective electromagnetic needles that physically sew these nanoblocks. Using ultrafast lasers results in billions of these bridges forming in rapid succession, threading the nanoparticles into long strings, which can be monitored in real time.

The active formation of strings of particles is unambiguously identified thanks to a peculiar optical fingerprint that characterizes “linked” particles: a mid-infrared plasmonic peak emerges in the optical spectrum as the threaded nanoparticles are formed, and both the position and width of this novel peak are tremendously sensitive to the geometrical details of the interparticle bridge formed. An excellent agreement between the optical fingerprints of the bridges experimentally created in Cambridge and those of the model bridges simulated at DIPC helps to understand the dynamics and morphology of the nanoparticle-string creation.

Dr. Ventsislav Valev, the leading researcher within the team of Prof. J.J. Baumberg in Cambridge worked with researchers from the Department of Chemistry, the Department of Materials Science & Metallurgy, and researchers of the “Theory of Nanophotonics Group” at the Donostia International Physics Center on the project.

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Aromaticity in transition structures

P. v. Ragué Schleyer, J. I. Wu, F. P. Cossío and I. Fernández
Chemical Society Reviews 43, 4909-4921 (2014)

Aromaticity is an essential concept in chemistry and physics, employed to account for the unusual stability, reactivity, molecular structures, and other properties of many unsaturated organic compounds. This concept was later extended to systems with mobile electrons, as well as to transition structures. Although transition structures are inherently delocalized, not all exhibit aromaticity. We contrast examples of pericyclic reaction transition structures (where aromaticity is significant) with those for illustrative pseudo- and non-pericyclic reactions.

In 2014 Dr. I. Fernández and DIPC researcher Prof. F. P. Cossío were invited to coordinate as Editors a themed issue of Chemical Society Reviews (cf. I. Fernández, F. P. Cossío, Chem. Soc. Rev. 2014, 43, 4906-4908). The title of this issue was “Applied Computational Chemistry”, in line with the concept of “Applied Theoretical Chemistry” coined by Prof. Roald Hoffmann. This themed issue was hence focused on the application of computational/theoretical methods to problems of interest to a wide experimental audience.

This paper summarizes current computational methods for identifying aromatic transition structures, with special emphasis on magnetic criteria. It also illustrates representative examples of pericyclic, pseudo-pericyclic and non-pericyclic reactions involving aromaticity. In pericyclic transformation aromatic stabilization of the corresponding transition states is very important, whereas in pseudo- and non-pericyclic reactions aromaticity is less or not relevant. The tremendous development of computational chemistry during the past few decades provides chemists and physicists with a robust theoretical framework and very helpful tools to generalize the concept of aromaticity and its application to transition structures, which are not accessible for a direct experimental study. The computation-based discovery that aromatic transition states can participate in non-pericyclic reactions exemplifies the effectiveness of theoretical approaches for recognizing novel chemical transformations. Despite caveats that aromaticity is just a chemical bonding model without a quantifiable, precise meaning, it remains a highly popular and essential concept in chemistry and physics accounting for anomalous properties such as geometry, reactivity and magnetic behaviour. A detailed analysis of aromaticity in transition structures extends the applicability of this concept to “closed circuit” structures involved in the transformation of matter via cyclic molecular mechanisms.

Strong ferromagnetism at the surface of an antiferromagnet caused by buried magnetic moments

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Here we show that the Si-Rh-Si surface trilayer of the antiferromagnet EuRh₂Si₂ bears a surface state, which exhibits an unexpected and large spin splitting controllable by temperature. The splitting sets in below 32.5 K, well above the ordering temperature of the Eu 4f moments (24.5 K) in the bulk, indicating a larger ordering temperature in the topmost Eu layers. The driving force for the itinerant ferromagnetism at the surface is the aforementioned exchange interaction. Such a splitting may also be induced into states of functional surface layers deposited onto the surface of EuRh₂Si₂ or similarly ordered magnetic materials with metallic or semiconducting properties.

For a long time, rare-earth intermetallic materials have attracted considerable interest because of their exotic properties at low temperatures, which include complex magnetic phases, valence fluctuations, heavy-fermion states, Kondo behaviour and many others. EuRh₂Si₂ is apparently well-suited to give insight into the interplay between magnetic and electronic degrees of freedom. Its electronic structure is strongly correlated, involving massless and heavy quasiparticles, which are mutually interacting. Below the Neel temperature 24.5 K the Eu 4f moments in EuRh₂Si₂ order antiferromagnetically (AFM). Like in several other RERh₂Si₂ compounds, the magnetic structure of EuRh₂Si₂ is composed of ferromagnetic Eu layers in the ab planes stacking AFM along the c axis.

Here we report on strong ferromagnetic properties of the surface and subsurface region in the antiferromagnet EuRh₂Si₂, which are driven by the ordered local 4f moments of Eu. These properties are monitored by angle-resolved photoelectron spectroscopy and density functional theory calculations looking at the diamond-shaped surface state that exists around the M point of the surface Brillouin zone. This Shockley-type surface state is observed at the Si-terminated surface, and resides inside a large gap in the projected bulk band structure. The surface ferromagnetism is manifested by a huge splitting of this state due to the exchange interaction with the ordered local moments of the Eu atoms lying three atomic layers below the surface. The exchange splitting of the surface state, which may be described as a trapped two-dimensional electron gas within the top four layers, provides immediate information on the magnetism of the first buried Eu layer in EuRh₂Si₂ when followed, for instance, as a function of temperature.

In summary, we have given clear evidence for a large exchange coupling of a Si-derived Shockley surface state to the outermost Eu layer that is located four atomic layers below the surface of the antiferromagnetic compound EuRh₂Si₂. The resulting exchange splitting provides direct information on the temperature dependent magnetism in the Eu layer and reveals an ordering temperature of 4f moments close to the surface that is notably higher than the bulk TN. Our results suggest that the mechanism of formation of the surface ferromagnetism discovered in EuRh₂Si₂ can be extended to other antiferromagnetic metallic or semiconducting compounds where surface states exist in an energy gap at the Fermi level. These spin-split surface states may induce magnetization in functional surface layers of topological insulators or and Rashba-type surface systems deposited onto the antiferromagnetic material, thus opening an energy gap in the topological or Rashba-type surface states.