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TNT2018 Keynotes / Invited Contributions

2D materials and perovskite solar cells: toward a reliable and scalable PV technology

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The possibility to produce 2D materials in the form of inks recently allowed their application for the emerging photovoltaic technologies, based on printing deposition techniques and roll2roll production processes. Recently, the use of graphene and 2D materials has been extensive exploited in perovskite photovoltaics, mainly as dopant or interlayer, with the aim to improve device efficiency and long term stability. As a matter of fact, several works claimed the beneficial role of graphene derivatives in enhancing the charge injection/collection when used in cell electrodes.[1] From our side, we demonstrated that the use of graphene flakes as dopant for the mesoscopic TiO_2 photoelectrode has the double role in improving both device power conversion efficiency (PCE) and stability under prolonged light soaking condition.[2] Time and temperature resolved photoluminescence (PL) spectroscopy revealed a strong morphological improvement in perovskite crystals wrapped into the graphene-based mesoporous TiO_2 layer.[3] At the same time, TOF-SIMS and measurements and transient absorption spectroscopy (TAS) pointed out the beneficial role of graphene in preventing iodine penetration within the mesoporous layer by retarding the smaller perovskite crystals degradation at $mTiO_2$/perovskite interface during the aging tests.[4] The interface engineering strategy based on 2D materials has been even implemented at the counter electrode side by underlining the beneficial role of MoS_2 and its derivatives when used as interlayer at perovskite/spiro-OMeTAD interface.[5] Finally, the proposed 2D engineered structure allowed to efficiently scale-up the perovskite fabrication process from small area devices to large area modules.[6] Remarkably, 2D material engineered modules showed averaged PCE above 13% on 108 cm^2 active area by demonstrating the crucial role of interface engineering in improving the reliability and in pushing the next commercialization of the emerging perovskite technology.

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NanoMechanics: new insights into helium superfluidity and thermal transport in 2D

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Mechanical resonators based on carbon nanotubes, graphene, and semiconductor monolayers are truly exceptional sensors of mass and force [1-3]. We are taking advantage of these sensing capabilities to study physical phenomena in extreme regimes that have not been explored thus far, because conventional measurement methods lack sensitivity. In a first experiment, we demonstrate the formation of superfluid helium monolayers and multilayers on a carbon nanotube. We observe layer-by-layer growth with discontinuities in both the number of adsorbed atoms and the velocity of the third sound, pointing to the hitherto unobserved layering first-order phase transition. In a second experiment, I will discuss a novel approach to measure the thermal properties of low-dimensional materials in an unprecedented way, down to cryogenics temperature, and with a device that is simple to fabricate. We measure the temperature dependence of the thermal conductivity and the specific heat capacity of a transition metal dichalcogenide (TMD) monolayer, something that has never been achieved thus far with a single nanoscale object.

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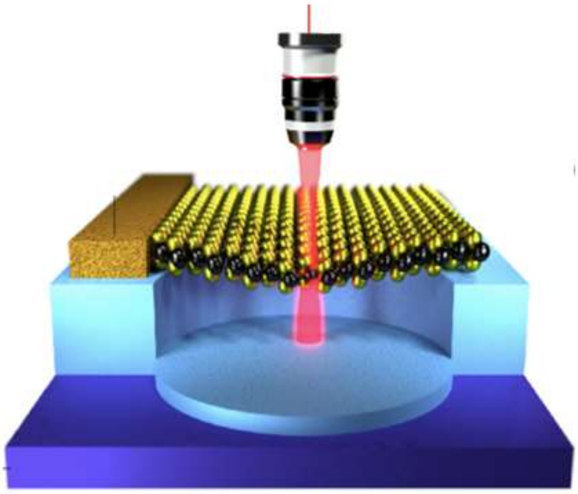

Figure 1. Schematic of an optomechanical drum based on a transition metal dichalcogenide monolayer

Super-selective nanomedicines

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We have also advanced our ability to deliver drugs combining the high selectivity of active molecules with molecularly engineered carriers equipped with the necessary attributes to navigate biological environments. A critical element of such a nanomedicinal effort is the introduction of ligands that enable targeting and selectivity to guide carriers across biological barriers. This is now allowing to extend drug discovery to target biological macromolecules that are not accessible via simple passive diffusion such as the inside of cells or the central nervous system. However, tight control on the selectivity of drugs and nanomedicines' interaction with biological systems is paramount for the development of targeted therapies. The large number of synthetically tuneable parameters makes it difficult to identify optimal design "sweet spots" without rational guiding principles. Here I address this problem combining super-selectivity theory (SST) with analytical models from soft matter and polymer physics into a unified theoretical framework. Starting from an archetypal system, a polymer-stabilized nanoparticle functionalised with targeting ligands, we use our model to identify the most selective combination of parameters in terms of particle size, brush polymerisation degree and grafting density, as well as tether length, binding affinity and ligands number. I further discuss how to combine multivalent interactions into multiplexed systems which act holistically as a function of the density of more than one receptor type, so as to achieve binding only when multiple receptors are expressed above a threshold density. I christen this as ”phenotypic” targeting and I propose its use for drugging unique cell populations enabling personalised therapies. I will show few examples of phenotypic targeting in both blood brain barrier crossing, cancer targeting and immune cell recognition. Finally I will combine phenotypic targeting with chemotaxis in all effect amplifying molecular interaction to create organotropic diffusion profile. I will show this with a fully synthetic, organic, nanoscopic system that ex- hibits attractive chemotaxis driven by enzymatic conversion of glucose. I will finally demonstrate that the chemotactic behaviour of these nano- swimmers, in combination with LRP-1 (low-density lipoprotein receptor–related protein 1) targeting, enables a fourfold increase in penetration to the brain compared to non-chemotactic systems.

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Germanium mid-infrared plasmonics for sensing

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Silicon photonics is an expanding market with an increasing number of applications being demonstrated each year [1]. Plasmonics has not yet made its way to the microelectronic industry, mostly because of the lack of compatibility of typical plasmonic materials like gold and silver with silicon CMOS foundry processes [2]. In this context, we have undertaken the development of heavily-doped germanium thin films as novel plasmonic materials, directly grown on silicon wafers with CMOS compatible processes [3]. Here, we review the Ge components that have been developed in the course of the project GEMINI ('Germanium mid-infrared plasmonics for sensing').

Plasmonic nanoantennas have been realized by electron-beam lithography and reactive ion etching in an inductively-coupled plasma with high selectivity for Ge over Si, starting from heavily-doped Ge films (electron density 10^{19}-10^{20} cm^{-3}) grown by low-energy plasma-enhanced chemical vapor deposition [3]. Their resonances have been predicted by simulations, confirmed by experimental infrared spectra, exploited for molecular sensing [4] and, more recently, for nonlinear frequency conversion [5]. Other nanoantenna designs have been explored, such as suspended Ge membranes with narrow slits, acting as resonant slot antennas in the mid-infrared [6]. Finally, ultrafast optical activation of undoped Ge antennas by femtosecond laser pulses has been demonstrated [7]. Ridge waveguides and rib waveguides have also been developed using similar fabrication processes on insulating Ge wafers to minimize free carrier losses. Propagation losses at mid-infrared wavelengths from 6 to 11 μm were determined to be in the range 1 to 10 dB/cm. A novel near-field diagnostic tool based on an atomic-force microscope and a tunable quantum cascade laser has been developed to image guided mode propagation on-chip in the mid infrared by measuring the local photoexpansion signal on a polymer block positioned at the end of each waveguide.

In conclusion, we developed the components for a chip-scale plasmonic platform technology using Ge on Si in the mid infrared. Envisioned applications include mid infrared spectroscopic sensors for healthcare, security and environmental monitoring. The research leading to these results has received funding from the European Union's Seventh Framework Programme under grant agreement no. 613055.

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Figures

Figure 1. Scanning electron microscope images of Ge antennas supporting localized plasmon resonances (left) and of a Ge waveguide (right).

Nanosensors for Life science applications

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Our research center of excellence IDUN combines research in nanosensors/centrifugal microfluidics and microfabricated devices for oral drug delivery. This allows us to explore the synergy between sensor development and search for new pharmaceutical delivery tools and materials. Our developed nanosensors get access to unique polymers and biomolecules and are able to characterize, among others, small volumes of materials and molecules, which are today not possible to analyze by any standard technologies. We will show examples of recent findings and results within drug/polymer characterization, diagnostics and process monitoring.

As part of our sensor integration we explore optics and mechanics from a DVD player. By rotating a polymer disc with integrated microfluidic channels it is possible to manipulate liquid samples such as blood – performing crucial operations like separation, valving and mixing. We integrate sensor elements such as cantilevers, nanoparticles, resonating strings and surface enhanced Raman scattering (SERS) substrates [1] with centrifugal microfluidics. The sensors are read out by a DVD pick-up head, which can perform transmission/absorption measurements and can detect nm deflections. Also, electrodes are integrated on a disc platform, facilitating electrochemical measurements.

By monitoring the resonance frequency shift of micrometer sized strings or cantilevers coated with thin layers of polymers, it was possible to monitor phase transitions using only ng of material. These systems also allowed us to monitor degradation of biomaterials used in the fabrication of the microcontainers [2]. Strings are inherently sensitive to temperature changes. The resonant frequency detunes as a function of temperature. This effect has been used to perform photothermal IR spectra on samples deposited on resonating strings and resonating filters. This has been used to study the amorphous and crystalline forms of indomethacin [3]. Centrifugal microfluidics and SERS has been used for the characterization of biofermentation products (drug compounds) in complex sample matrices [4].

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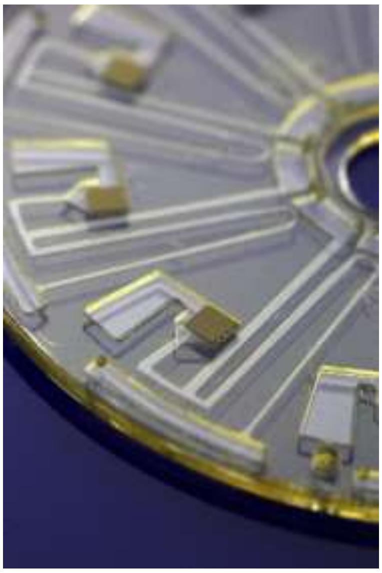

Figure 1. Example of nanopillar SERS substrate integrated into a centrifugal microfluidic system.

2D materials for energy

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Graphene and other 2D crystals are emerging as promising materials[1-5] to improve the performance of existing devices or enable new ones.[1-5] A key requirement for energy applications is the development of industrial-scale, reliable, inexpensive production processes,[2] while providing a balance between ease of fabrication and final material quality.

Solution-processing[2,6] is a simple and cost-effective pathway to fabricate various 2D crystal-based (opto)electronic and energy devices, presenting huge integration flexibility compared to conventional methods. Here, I will present an overview of graphene and other 2D crystals for energy applications, starting from solution processing of the raw bulk materials,[2] the fabrication of large area electrodes[3] and their integration in the final devices.[7-15]

We acknowledge financial support from the European Union's Horizon 2020 Graphene Flagship.

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Edge engineering in graphene devices

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Graphene’s ability to support ballistic transport of electrons is behind some of the most exciting new scientific discoveries as well as a key aspect of graphene’s possible use for next-generation electronics and sensors. In ballistic devices, however, the edges play a dominant role, and the difficulty in defining edges with sufficiently small amounts of disorder has been a serious challenge for more than a decade, and one of the main reasons for the slow progress in creating high-performance nanoscale graphene devices. In this talk I will overview three recent examples of how engineering of graphene edges can influence the transport properties in exciting ways: suppression of quantum Hall effect in low-disorder nanoconstrictions, ferroelectric molecular switching and gate-edge electrostatics, and ultra-dense lithographic superlattices with magneto-tunable bandgaps.

Contacting graphene:
First principles transport simulations

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Devices based on stacked van der Waals heterostructures of two-dimensional (2D) materials are promising candidates for future atomically thin, flexible electronics. Graphene can play the important role of a 2D electrode material due to its excellent semi-metallic electronic conduction. However, we still need to understand and control the behavior of the graphene electrodes for contacting other 2D materials. The same is the case for the metal-graphene contacts used to contact graphene in the first place.

A key advantage of graphene electrodes is the precise control of the carrier density by external gates. Atomistic first principles transport calculations, which can take voltage biases, currents, and gate potentials into account, can yield important insights into the behavior of devices.
I will in the talk illustrate this point by presenting examples of transport calculations based on Density Functional Theory combined with non-equilibrium Green's functions (DFT-NEGF) [1], or the Boltzmann equation [2].

The examples include the role of the gate and stacking order for the contact resistance between graphene and MoS_2 (see Fig. 1)[3], a gate-induced flexural electron-phonon scattering mechanism in graphene[4], how phonon-scattering in point-contacts to graphene can reveal the electronic coupling between graphene and substrate[5], and finally, the dependence of contact resistance on the metal used for contacting graphene at the edge [6]

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Figures

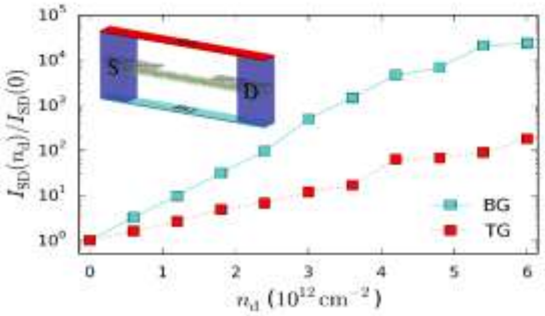

Figure 1. Calculated source-drain current as a function of gate-induced carriers in a graphene-contacted MoS2 channel for gate at top or bottom (insert). From Ref. [3].

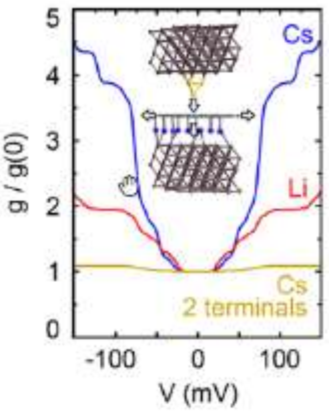

Figure 2. Calculated conductance (normalized to zero bias) as a function of voltage in a STM setup (insert). The sample is Cs or Li intercalated graphene on Ir(111). The sharp increase probes the inelastic phonon signals and reveal the electronic coupling between graphene and substrate. From Ref. [5].

Wearable Human Motion Detectable Sensors based on Graphene and 2D Material Composites

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Wearable strain-pressure sensors with high sensitivity and flexibility have attracted a great deal of attention for their broad range of applications such as healthcare monitoring and human motion detection. Sensing with continuous measurement of physiological parameters is an effective way to monitor personal health. For human friendly comfortable health monitoring systems, sensor integrated or mounted wearable systems are required. In addition, wearable and flexible sensors which are able to be integrated into clothes should be comfortable and do not affect people's everyday life and activities. In order to be applicable in real life, a wearable strain-pressure sensor should be able to accurately detect subtle body signals from external stimuli in an extensive sensing range from pulse signals to knee joint bending.

In this talk, a wearable and flexible physical sensor (pressure and strain) based on rGO (Reduced Graphene Oxide)-SWCNT composite coated fabrics for the motion glove is introduced. Sensing performance and reliability at different points such as fingertip, finger joint and wrist, are presented. The signal has good reproducibility in response to pressing, bending and stretching. Water tolerance of fabric-based sensors are also evaluated. This sensor can be applicable for personalized physiological monitoring and prosthetic hand.
In addition, a MoS2/graphene porous network (GPN) infiltrated Ecoflex hybrid nanostructure as a flexible strain-pressure sensor is also introduced. Drowsiness detection in response to motion signals such as eye blinking and neck bending is presented. This sensor will be used to calibrate any posture during exercise or to prevent fatal accidents caused by driving while drowsy.

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Figures

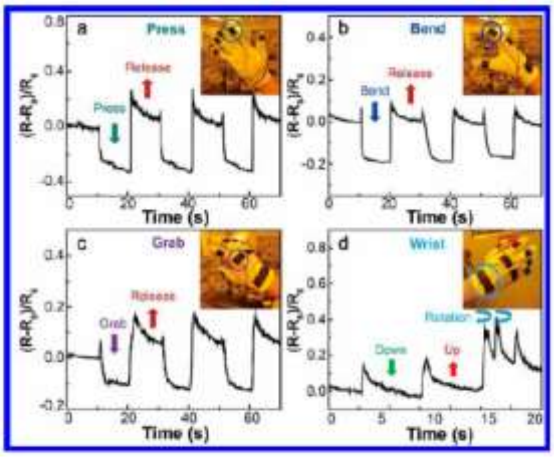

Figure 1. Relative resistance changes with various movements of the motion glove containing the rGO-SWCNT fabric-based sensors, such as (a) pressing, (b) bending, (c) grabbing, and (d) up, down, and rotation of the wrist.

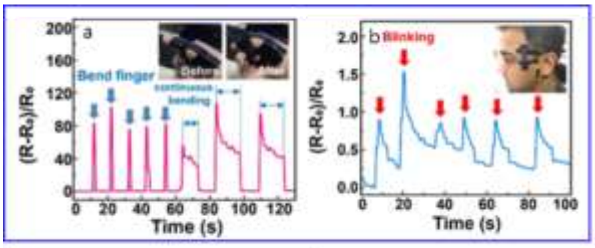

Figure 2. Relative resistance response of the MoS2/GPN/Ecoflex sensors corresponding to various motion signals such as (a) finger bending and (b) eye blinking.

Acknowledgments

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Characterizing plasmons at the nanoscale by first-principle simulations

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First principle methods such as time-dependent density functional theory are becoming increasingly popular in the investigation of surface plasmons localized on metallic nanoparticles and non-conventional plasmonic materials such as graphene nanoflakes. Besides revealing the dependence of the plasmon excitations on the microscopic details of the systems (atomistic geometry, role of surfactants and of the environment, etc.), such methods can also address basic questions such as the fundamental (quantum) nature of the plasmonic excitations themselves. In fact, nanoparticles are composed of electrons and nuclei like ordinary molecules. Therefore, it should be possible to understand their excited states, including plasmons, in terms of the same elementary electron-hole excitations routinely used to interpret molecular excited states, and to find the microscopic features that distinguish plasmonic from non-plasmonic excitations. In this talk I will present possible approaches to address this important problem, and the related results obtained so far by our group [1-3].

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Sensing towards the quantum limit: The convergence of molecular detection and artificial perceptrons

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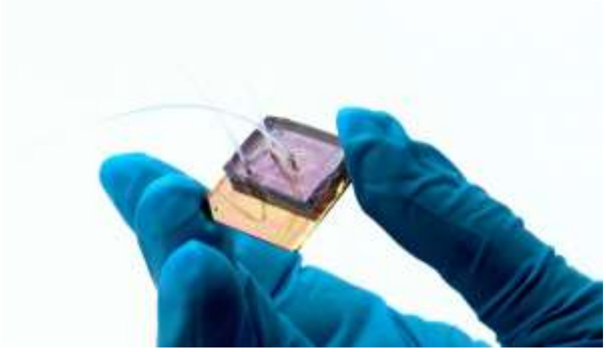
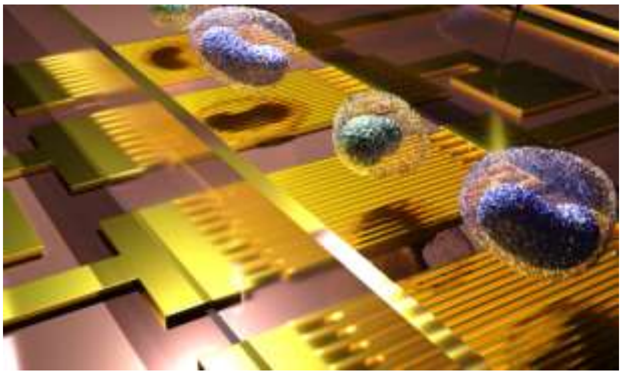
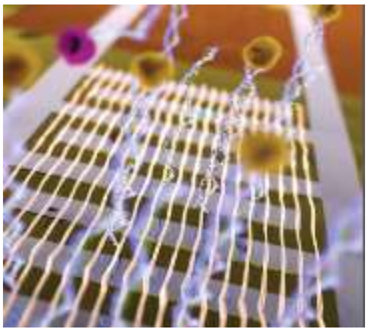
The explosion in the number of newly available functional nanomaterials capable to sensitively change their conductance in the proximity of charged analytes in parallel with the advances in nanofabrication and nanoimaging techniques have made available and cost-efficient a realm of novel strategies to exponentially increase the selectivity and sensitivity boundaries of the electrical detection of nanoobjects. Highly personalized diseases diagnostics and ubiquitous environmental monitoring are only two possible applications which could address a number of societal challenges ahead related to human life in a strongly globalized world. Nanoparticles, nanowires, 2D materials are dominated by quantum effects and employing them as active elements in transducers for novel devices opens up enormous perspectives for innovative sensor systems. Such devices bear the potential not only to outperform conventional sensor technology with respect to speed, sensitivity, long time stability and signal reliability but even to define completely new application fields in platforms that are cost efficient, flexible and portable. After an introduction of the fundamental sensing mechanisms of nanomaterials-based devices, I will present the innovative design and fabrication strategies for our sensor elements. The close interaction of simulation and experiment allows us to elaborate tailored, but also transferable, technological functionalization strategies for different analytes to cover a wide range of application scenarios. In a strongly interdisciplinary approach, we face the need for sophisticated integration and packaging solutions of the sensors into versatile lab-on-a-chip systems. Integrating the latter in microfluidic setups to provide large numbers of different assays just-in-time directs our technology in direction of highly automatized analytic procedures. The results of our research prove the vast potential of our sensing approach but also show the enormous space for further fundamental developments to boost the concept of nanomaterials-based sensor technology to a powerful and smart analytic tool capable of multiplexed studies, providing and evaluating rich and robust statistical output data. Recent results on artificial neuron behavior in our sensor devices will help shedding new light on the role of nanoarchitectures for a true neuromorphic computing.

Figures







3D plasmonic nanostructures for biology and medicine

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In this talk we will show our last achievements and future perspectives of distinct class of plasmonic devices devoted to biological and medical applications. Among them, we will introduce the concept of meta-electrodes, namely a nanostructured surface that can work as electrode, a broad band plasmonic antenna, and optimal cellular interface (see Figure 1). We show that meta-electrodes combined with commercial CMOS technology enable high quality intracellular electrical signals on the large network scale. The developed platform may enable significant advances in the investigation of the neuronal code, development of artificial retinas and low-cost in-vitro platforms devoted to the pharmacological screening of drugs. Also, we will present an artificial hyperbolic meta-particle that enables a tailoring of both ohmic and radiative channel in the visible and near-infrared spectral ranges. We show that the radiative channel can be completely decoupled from the ohmic one thus enabling to create a system that is almost purely radiative or absorptive. Many interesting applications can be foreseen including thermal emission manipulation, photoacoustic imaging, controlled drug delivery and hyperthermia.

Figures

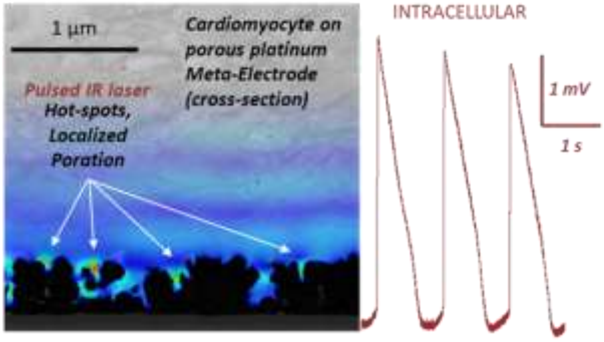

Figure 1. SEM cross-section of human cardiomyocyte on the porous CMOS-MEA and intracellular action potentials recorded on the network scale.

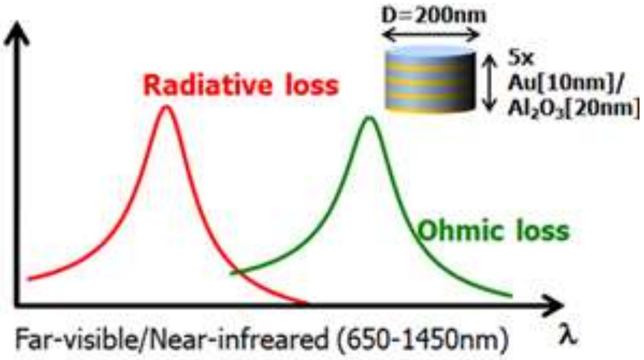

Figure 2. Tailoring radiative and ohmic channels in hyperbolic nanostructured metaparticles.

Immune cells and graphene: interactions and potentiality

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Before any successful translational application of nanomaterials in medicine, a critical step is represented by the assessment of their impact on the complexity of the immune system and immune cells [1]. We present our results on carbon nanomaterials, in particular on graphene, and their interactions with the blood immune cells [2-9]. We here discuss different scenarios of interest where the immune response can have a key role in the carbo nanomaterials applications: from cancer therapy, to space biology, to immunotherapy, to bone regeneration. We discuss how an immune design of graphene and other nanomaterials can facilitate their translation into the everyday clinical practice. Indeed, the understanding of the interactions between nanoparticles and immune cells is hindered by the scant implementation of high throughput technologies in nanotechnology. A novel tool for flow cytometry analysis has been developed, gaining leverage with the precision of mass spectrometry. The combination of the two techniques, Single-cell mass cytometry, provides the measurement of more than 40 simultaneous cellular parameters at a single-cell resolution with over 100 available detection channels. As suggested by Goldberg (Cell 2015), we propose, for the first time in the context of nanotechnology, a new analytical strategy taking advantage of this powerful method, able to deconvolve the immunological impact of nanomaterials, at the single-cell level [2]. The analytical pipeline we recently reported encompass the immunological characterization of the most studied nanomaterial in the last years: graphene. Mass cytometry enables us to describe the immune cell interactions of thin graphene oxide (GO) flakes and GO functionalized by amino groups ($GONH_2$) on 15 cellular populations corresponding to 200 nodes of distinct but logically interconnected cell sub-populations. Together we performed whole-transcriptomic analysis for functional and molecular characterization on human T-cells and monocytes as a representative for the adaptive and innate responses. Our results emphasize the importance of the functionalization on enhancing the biocompatibility of GO-based nanomaterials. Notably, only the functionalized $GONH_2$ was able to induce a specific monocytoid dendritic cell and monocyte activation skewed toward a T helper 1/M1 response. The positive impact of $GONH_2$ on specific immune cells could serve as a starting point for the development of new nanoscale platforms in medicine as novel immunotherapy, vaccine carrier, or nanoadjuvant tools.
Our recent study[2] paves the way for the future use of single-cell mass cytometry for a deep characterization of immune responses to any nanomaterials useful for biomedical applications.

Moreover, we will present our results on graphene-based tools in the context of osteoimmunology and their applications for bone loss-related diseases.

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Minibands for Dirac electrons in moiré superlattices

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When graphene lattice is aligned with the hBN lattice, a long-wavelength periodic moiré pattern forms due to a weak incommensurability of the two lattice structures, leading to a long-range superlattice affecting properties of electrons in graphene, including formation of miniband spectra for Dirac electrons [1-3] and reappearance of magnetic minibands [4,5] at the rational values of magnetic field flux through the supercell area (in units of φ0=h/e), also known as Hofstadter butterfly [6].

Here, we show that the miniband in long-period moiré superlattices (mSL) in graphene/hBN heterostructures affect their transport measurements up to the room temperature. In relation to the low-field behavior, we find that the overall temperature dependence of resistivity displays the opening in a new scattering process: the umklapp electron-electron scattering in which two electrons coherently transfer the mSL Bragg momentum to the crystal [7]. The formation magnetic minbands and their manifestation in magneto-oscillation of the diagonal conductivity tensor persist up to the room temperature [8], too, with full hierarchy of features that are attributed to the rational flux values φ=(p/q)φ0, with p=1, 2 and up to 3 (and 7<q<1), now, observed [9] at the intermediate range of 50K<T<200K.

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Quantum simulators in hybrid nanocircuits

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Digital quantum simulators are among the most appealing applications of a quantum computer [1]. In principle, any model that can be mapped onto a spin-type Hamiltonian can be encoded in a digital quantum simulator. Then, its time evolution can be solved exactly, thus overcoming the unavoidable exponential scaling of computational resources that is inherent to quantum manybody physics.

Here I will review our recent theoretical proposal for a universal, scalable, and integrated quantum computing platform based on tunable nonlinear electromechanical nano-oscillators. In particular, I will describe a minimal architecture where qubits could be encoded in the anharmonic vibrational modes of nanomechanical resonators coupled to a superconducting nanocircuitry [2], see Fig. 1.

Practical realizations of such qubits will be discussed, based on engineered nano-electromechanical systems such as suspended nanotubes, 2D nanomembranes (such as, e.g., graphene sheets), or cantilevers.

An effective scheme to induce large single-phonon nonlinearities in nano-electromechanical devices will be explicitly discussed, and the quantum simulation of a few targeted models will be shown by solving the dynamical evolution in this ideal quantum hardware [2].

Finally, I will show how we challenged our proposed simulator with an actually existing one, i.e. the IBM-Q quantum computer freely available for cloud quantum computation [3].

Such a state-of-art implementation of an actual quantum computer, which employs purely superconducting qubits (the 'transmons') in a microwave nanocircuit (schematically represented in Fig. 2), is actually able to perform a digital quantum simulation of a few targeted models of interest in condensed matter physics. Nevertheless, encoding the qubits in mechanical degrees of freedom would allow to outperform the current implementations both in terms of fidelity as well as scalability of the quantum simulation.

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Figures

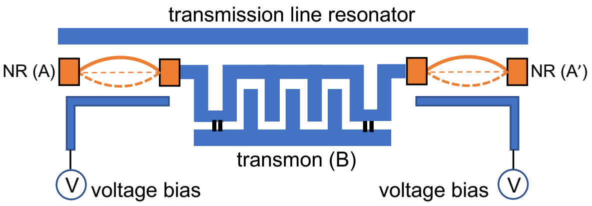

Figure 1. Schematic building block of an electromechanical quantum simulator within a superconducting nanocircuit: qubits are encoded in A, A' anharmonic oscillators, while B is used as a mediator of their effective interaction. Tunability is ensured by electrical control through external voltage pulses.

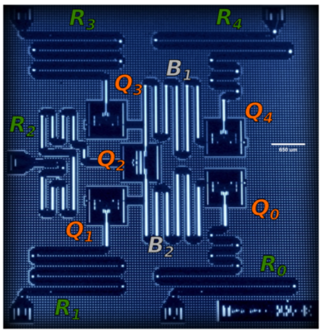

Figure 2. Picture of the ibmqx4 hardware with 5 qubits, which we employed for quantum simulation testing.

Transistors and memories based on 2D materials for integrated circuits dedicated to machine learning

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In this talk we will discuss the challenges, opportunities, and the performance potential of atomistic engineering of electron devices exploiting the fundamental properties of 2D material heterostructures, with a particular attention to computer architectures for machine learning applications.

The "materials-on-demand paradigm" based on the 2D materials is a modern evolution of what in the 1980s was called "band-gap engineering" or "band-structure engineering", *i.e.*, the artificial modification of band edge profiles using heterostructures made possible by epitaxial growth of III-V and II-VI material systems.

Lateral and vertical heterostructures of 2D materials could represent a revolutionary and enabling technology to device engineering providing the possibility to engineer a transistor at the atomistic scale.

We show that field-effect transistors based on lateral heterostructures of 2D materials [1][2] and floating-gate non-volatile memories [3] based on vertical heterostructures of 2D materials for the gate stack and lateral heterostructures for the channel (as shown in Fig. 1) can represent a viable option for an integrated circuit technology dedicated to machine learning applications.

We evaluate the expected performance of the two type of devices on the basis of accepted figures of merit (Figure 2). [2][4]

The possibility of fabricating the two types of devices on the same platform and in close vicinity, can enable the fabrication of logic-in-memory architectures for deep neural networks with promising performance in terms of inferences per unit energy.

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Figures

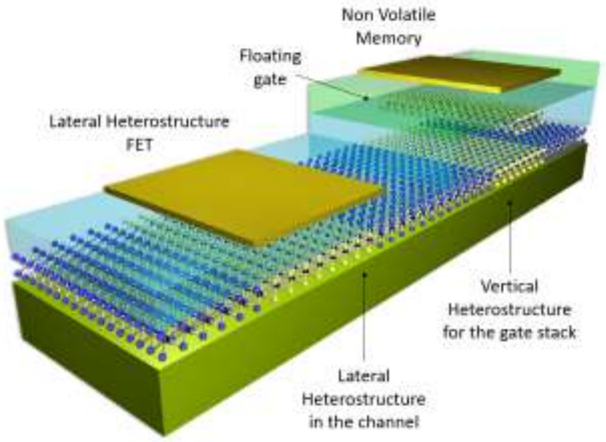

Figure 1. Illustration of the lateral heterostructure FET and of the floating-gate non-volatile memory base on lateral and vertical heterostructures of 2D materials.

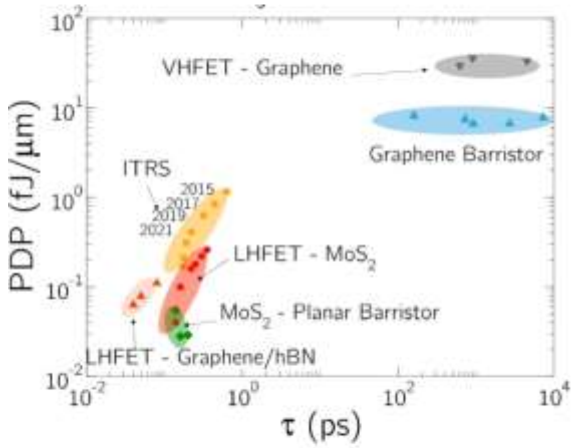

Figure 2. Power delay product (PDP) and delay time (t) of different FET structures based on heterostructures of 2D materials compared with the expectations of the International Technology Roadmap for Semiconductors (2015 edition)

Guided Bloch long-range surface plasmon polaritons

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Light confinement near the surface of a photonic structure is appealing for the realization of optical sensors, in which one relies on the interaction between the electromagnetic field and an adlayer forming on the surface as analyte binds thereon. In this respect, surface plasmon polaritons (SPPs) are probably the most studied and utilized. Yet, despite their success, the use of SPPs is somewhat limited by propagation losses associated with the absorption of light in the metal. An approach to mitigate this problem makes use of symmetric structures based on a thin metal layer to support long-range SPPs (LRSPPs) [1]. The existence of the LRSPP requires that the SPPs at the upper and lower surfaces of a thin metal layer propagate at similar speeds, namely they must have similar effective indices. This condition is automatically satisfied when one works with symmetric structures, but this can be a serious constraint for some applications.

A few years ago, Konopsky showed that a one-dimensional photonic crystal (1DPC) structure can be used on one side of a thin metal layer to mimic the optical properties of the material on the other side [2]. Inspired by this approach and motivated by the use of LRSPP waveguides for biosensing, we propose and realized metal stripes on a SiO2/Ta2O5 1DPC (see Fig. 1 and 2) as waveguides supporting fully guided Bloch LRSPP [3].

The measured propagation losses of the Bloch LRSPP are between 12 and 12.8 dB/mm at 1349 nm, thus in good agreement with the theoretical values, which are expected to be between 11 and 12 dB/mm, depending on the working wavelength.

These results provide a significant advantage in terms of material flexibility for the substrate and further the attraction of metal stripe waveguides and LRSPPs for biosensing applications.

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Figures

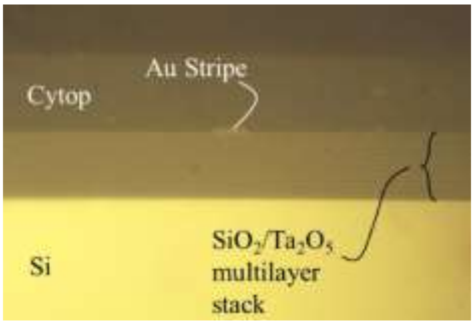

Figure 1. Microscope image of a polished end facet, revealing individual layers of the multilayer stack, the Au stripe, and Cytop upper cladding

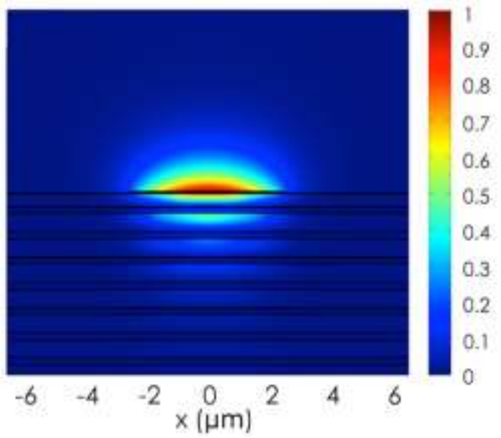

Figure 2. Calculated Field intensity for the Bloch LRSPP on an Au stripe on a 1DPC with a Cytop upper cladding.

Halide Perovskites Nanocrystals: Synthesis, Transformations and their Application in Devices

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Halide perovskite semiconductors can merge the highly efficient operational principles of conventional inorganic semiconductors with the low-temperature solution processability of emerging organic and hybrid materials, offering a promising route towards cheaply generating electricity as well as light. Perovskites not only show exceptional primary optoelectronic properties such as a direct bandgap, small exciton binding energy, low carrier recombination rates, ambipolar transport, and tunability of the bandgap covering a wavelength range from the near-infrared to the ultraviolet, but they are also very attractive for their ease of processability for mass production (e.g. printing from solution) and for the large availability of their chemical components. Following a surge of interest in this class of materials, research on halide perovskite nanocrystals as well has gathered momentum in the last three years. In such a narrow time span, several properties/features of halide perovskite nanocrystals were investigated, among them electroluminescence, lasing, anion-exchange, as well as control of size and shape such that nanocrystals in the quantum confinement regime were recently reported. The present talk will highlight the research activities of our group on halide perovskite and perovskite-related nanocrystals, with emphasis on synthesis, as well as structural, chemical, and surface transformations, and their applications in various types of devices.[1-3]

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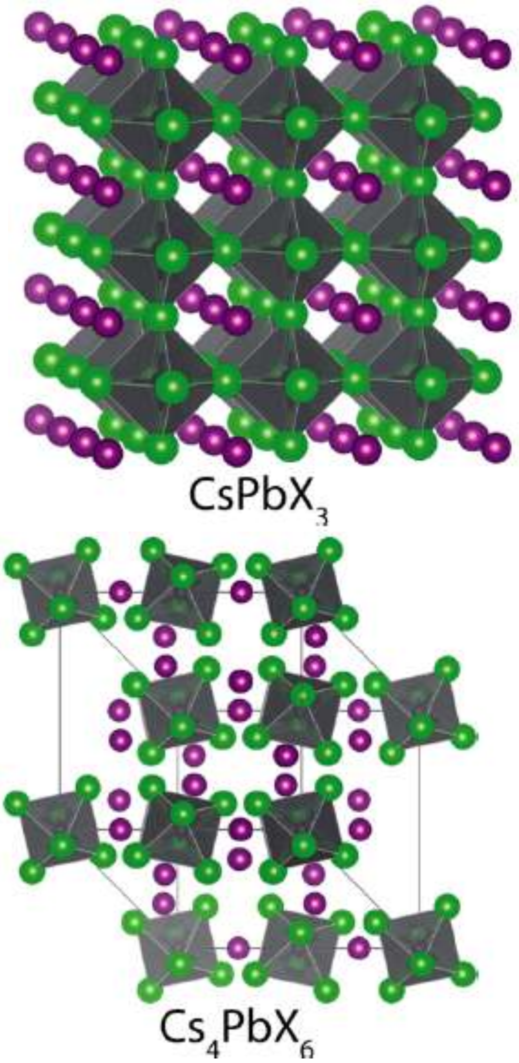

Figure 1. Crystal structure of $CsPbBr_3$ (top) and Cs_4PbBr_6 (bottom).

Engineering of Nanoporous Anodic Alumina as a Versatile Platform for Biomedical Applications

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Nanoporous anodic alumina (NAA) is a nanostructured material suitable for developing complex and cost-effective biomedical applications like selective molecular separation, chemical/biological sensing, cell adhesion and culture, and drug delivery [1-2].

NAA is obtained by the electrochemical etching of aluminum and presents a self-ordered hexagonal pore distribution of parallel cylindrical nanopores with diameters between 10 and 300 nm [1-2]. Its geometric characteristics such as diameter, length and separation distance is controlled by the anodization conditions (voltage and time of anodization, temperature, and electrolyte) [3-4].

Chemical resistance, thermal stability, and intrinsic photoluminescence are some of the outstanding properties of NAA [5]. Its highly effective surface area (hundreds of m^2/cm^3) makes of NAA an interesting platform for sensing and loading and releasing of active agents.

In this abstract we present the use of NAA for developing advanced drug delivery systems and complex gated materials for biosensing applications [6]. In these systems, the NAA nanopores are used as nanocontainers of drugs or molecules that are released in a controlled way under selective external conditions. NAA is also engineered to produce one-dimensional photonic crystals (1D-PC) with an enhanced optical response. Low-cost NAA 1D-PC biosensors were developed for the detection of substances of interest for the health and the environment like bacteria, proteins or drugs.

NAA also can be applied for reproducing 3D cellular microenvironments and understanding the complex cellular interactions and behaviors. The effect of the geometry and functionalization of NAA on cell adhesion and morphology of human aortic endothelial cells is investigated.

Finally, we propose NAA for the production of particles for biological applications. We present the successful fabrication, characterization, and functionalization of NAA particles [7]. We evaluate the simplified process of linking a protein/antibody to the NAA particles and demonstrate their biocompatibility by analyzing the cell viability and cytotoxicity.

Acknowledgements: The Spanish Ministry of Economy and Competitiveness TEC2015-71324-R, the Catalan authority AGAUR 2017SGR1527, and the ICREA Academia Award.

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Figures

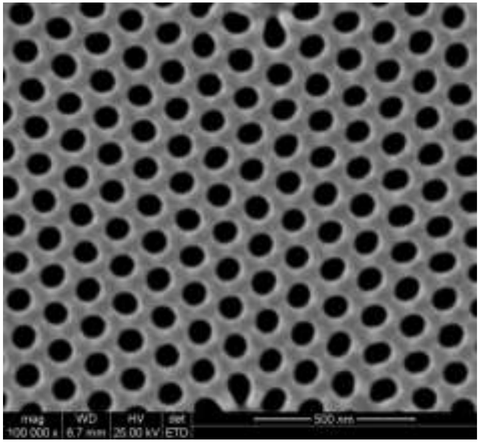

Figure 1. Top view of nanoporous anodic alumina.

Graphene Technology: synthesis, characterization and technological device integration

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Graphene fascinating properties hold promises for a great technological impact [1]. Nevertheless, to allow for a real exploiting of their extraordinary properties, a complete control of the fabrication steps of graphene-based devices is mandatory. In this contribution we will show an integrated approach for the integration of graphene membranes in state-of-the-art technological processes and for the exploitation of their properties in an applicative framework.

Our approach starts from the careful control of the synthesis parameters of the CVD growth of graphene membranes, as well as of their structural and functional properties. It moves then to the definition of tailored transfer processes leading to the integration of graphene membranes in a wide class of functional substrates (technological surfaces, glass, plastic and polymeric flexible substrates), as well as of their surface functionalization, to provide the control of physical and chemical properties over large area, typically mandatory in the devices fabrication processes. [2-5]. Final step is the definition of the complete set of technological processing steps needed to achieve a full integrability of the membranes within the processes of fabrication of micromachined devices.

Examples concerning design and fabrication of micromachined sensing device or concerning the integration of graphene membranes as transparent conductive electrodes in thin film solar cells or in light emitting devices will be provided [6-8].

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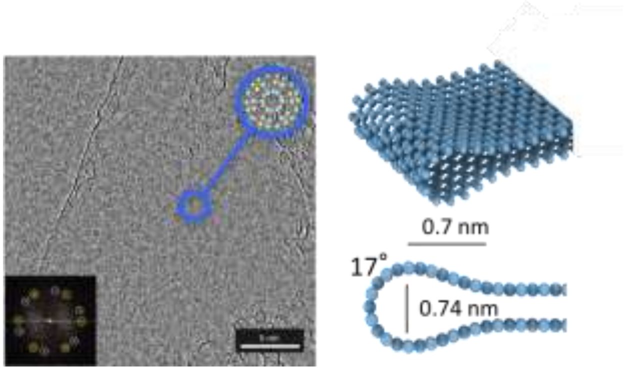

Figure 1. CVD grown graphene membrane 3D/strain reconstruction with sub-nanometric lateral resolution

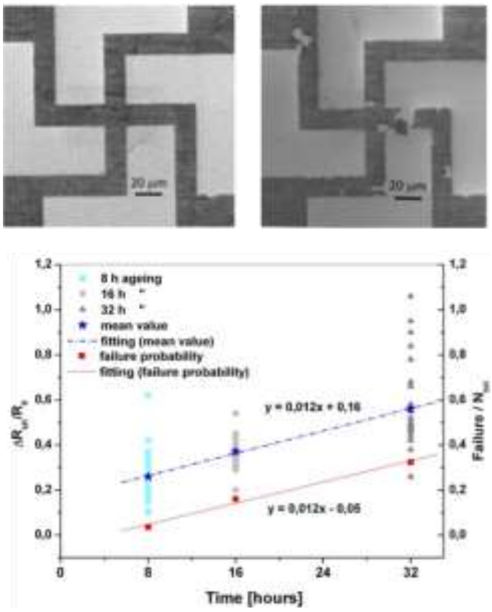

Figure 2. Reliability-driven graphene integration in Si Technology

Soft Actuators based on Graphene and 2D Materials

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Abstract

Ionic soft actuators, which exhibit large mechanical deformations under low electrical stimuli, have been attracting attention in recent years with the advent of soft and wearable electronics. However, a key challenge for making high-performance ionic soft actuators with large bending deformation and fast actuation speed is to develop a stretchable and flexible electrode having high electrical conductivity and electrochemical capacitance. Here, we newly report a functionally antagonistic hybrid electrode with hollow tubular graphene meshes and nitrogen-doped crumpled graphene for superior ionic soft actuators. Three-dimensionally (3D) networked and hollow tubular graphene meshes, which are grown from Nickel mesh platforms by a chemical vapor deposition method, provide high electrical conductivity and mechanically resilient functionality on whole electrode domain. On the contrary, nitrogen-doped wrinkled graphene supplies ultrahigh capacitance and stretchability, which are indispensably required for improving electrochemical activity and actuation speed in ionic soft actuators. Present results show that the functionally antagonistic hybrid electrode greatly enhances the actuation performances of ionic soft actuators, resulting in much larger bending deformation up to 620 % and 10 times faster rise time and much lower phase delay in a broad range of input frequencies. This outstanding enhancement in ionic soft actuators mostly attributes to exceptional properties and synergistic effects between hollow tubular graphene mesh and nitrogen-doped crumpled graphene, which have functionally antagonistic roles in charge transfer and charge injection, respectively.[1]

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Figures

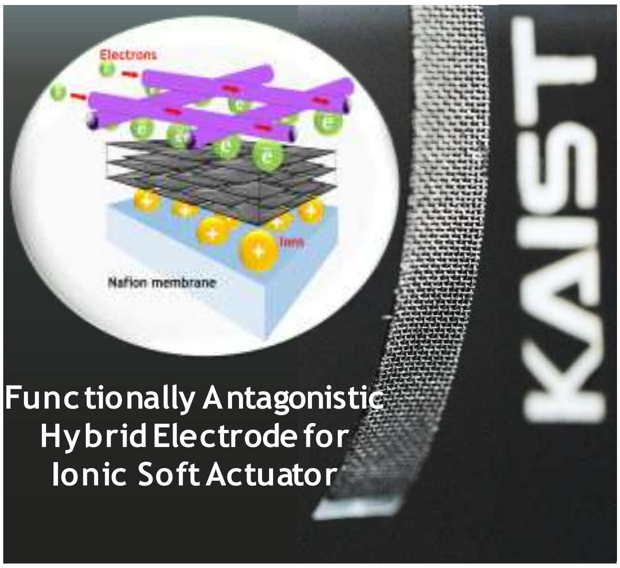

Figure 1. Functionally antagonistic hybrid electrode based on graphene mesh and nitrogen-doped graphene.

Soft polymeric nanoconstructs for vascular drug delivery and tissue depots

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Abstract

Over the past 10 years, a plethora of multifunctional nanoconstructs has been proposed for the 'smart' delivery of therapeutic and imaging agents.

The Laboratory of Nanotechnology for Precision Medicine at IIT-GE synthesizes disease- and patient-specific particle-based nano-scale systems by finely tuning during the fabrication process the *4S parameters* of the nanoconstructs.
Specifically, our platforms present *sizes* ranging from a few tens of nanometers to a few microns; *shapes*, including spherical, cubical and discoidal; *surface* properties, with positive, negative, neutral coatings; and mostly mechanical *stiffness*, varying from that of cells to rigid, inorganic materials, such as iron oxide.

While the effects of size, shape, and surface properties on nanoparticels in vivo performance has been extensively investigated, only recently softness is emerging as a key parameter for modulating nanoparticles interaction with biological environment. In this lecture, the role of manipulating these 4S parameters will be fully elucidated.
Particularly, it will be emphasized how softer nano-constructs are able to evade immune system surveillance and uptake regardless of the size and shape, thus enhancing their accumulation within the diseases tissue.
Overall, our research approach based on the rational design of multifunctional nano-constructs is expected to inspire more efficient strategies for drug delivery and biomedical imaging.

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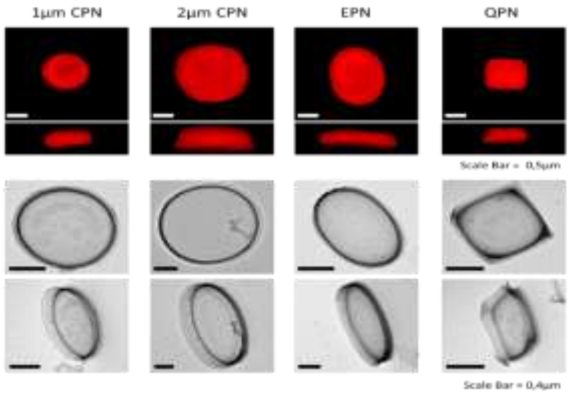

Figure 1. Different geometries and sizes of Discoidal Polymeric Nano-constructs

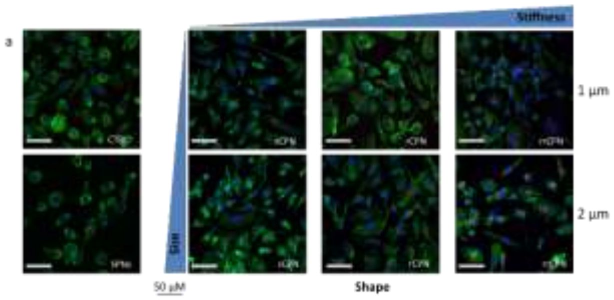

Figure 2. Discoidal Polymeric Nanoconstructs with different mechanical stiffness interacting with professional phagocytic cells.

Magnetic Nanocrystals and magnetic hyperthermia to tackle cancer

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The use of heat to reduce tumor mass is very ancient. Nowadays, there are several techniques that allow to precisely focalize the heat in very specific body regions resulting in treatments that are more efficient and minimize side effects. Magnetic Nanoparticles can act as heat mediators under external magnetic activation in the so-called magnetic hyperthermia. The field of magnetic hyperthermia has received a renewed interest since the colloidal syntheses by non-hydrolytic methods have revealed several merits over conventional wet chemical hydrolytic processes in terms of controlled size, size distribution and crystallinity. All these parameters together with nanoparticles solubility and state of aggregation can affect structural and magnetic properties of nanomaterials and thus their heat performance. I will first focus on our recent progress on ironbased nanoparticles as heat mediators. Then, I will show our ongoing studies aiming at correlating heat effects on cancer stem cells. I will also report about in vitro hyperthermia experiments on primary tumor cells to relate nanoparticle geometry to changes of magnetic hyperthermia performances in tumor cell. Finally, I will show our preliminary in vivo studies performed with the aim to combine magnetic hyperthermia and heat-mediated drug release.

Multifunctional neural interfaces with micro- and nano-structured tapered optical fibers

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There is widespread agreement that innovative new research tools are required to better understand the incredible structural and functional complexity of the brain. To this aim, optical techniques based on genetically encoded neural activity indicators and actuators have represented a revolution for experimental neuroscience, allowing to get a dynamic picture of the brain in action. Recently, a great amount of research has been devoted to obtain “multifunctional” devices, exploiting micro- and nano-structures to deliver and collect light from the brain, to record electrical activity from single or multiple cells and to locally release drugs [1-4].

After a review of the state-of-the-art in this field, this presentation will focus on the engineering and use of multimodal tapered optical fibers for interfacing with the brain. We will describe our approach to obtain minimally invasive multipoint optical control and monitoring of neural activity, based on a mode division multiplexing/demultiplexing approach. Exploiting micro and nanotechnologies to structure non-planar surfaces, tapered fibers also allow the integration of electrodes for extracellular readout of neural activity, representing an important complement to currently available technologies [5-7].

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Surprising charge transport in DNA

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Abstract (Calibri 11)

The DNA double-strand recognition, as well as the ability to manipulate its structure open a multitude of ways to make it useful for molecular electronics. Step by step we improve the synthesized constructs and the measurement methods of single DNA-based molecules. I will present new and surprising results on dsDNA molecules. I will present new DNA-based molecules and report on our measurements of their properties.

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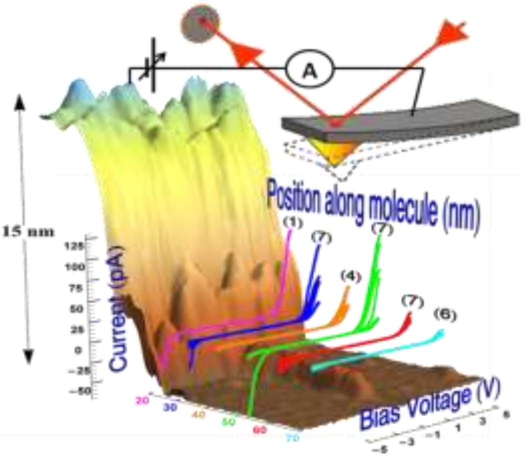

Figure 1. Three dimensional presentation of a G4-DNA molecule protruding from under a sharp metal border. The AFM tip and electrical circuit are illustrated. On top of the molecule appear current-voltage curves measured on ten different molecules.

Mechanics of 2D materials and related 3D composites

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Abstract

The rapid development of synthesis and characterization of graphene, other 2D materials and related 3D composites as well as unprecedented computational power and theoretical advances have brought forth a new era of materials research in which experiments, simulation and modeling are performed side by side, e.g. [1]. Accordingly, this talk aims to present an overview of our recent studies of the mechanics of graphene, other 2D materials (e.g. fracture, deformation and friction) and related 3D composites (e.g. bio-inspired, hierarchical and self-healing), e.g. [2]. Finally, we will present recent results on silkene (spider silk with graphene spun by spiders) with unprecedented mechanical properties [3].

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Crystallization, reentrant melting, and resolubilization of virus nanoparticles

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Crystallization is a fundamental and ubiquitous process that is well understood in the case of atoms or small molecules, but its outcome is still hard to predict in the case of nanoparticles or macromolecular complexes. Controlling the organization of virus nanoparticles into a variety of 3D supramolecular architectures is often done by multivalent ions and is of great interest for biomedical applications such as drug or gene delivery and biosensing, as well as for bionanomaterials and catalysis. In this presentation, we show that slow dialysis, over several hours, of wild-type Simian Virus 40 (wt SV40) nanoparticle solution against salt solutions containing $MgCl_2$, with or without added NaCl, results in wt SV40 nanoparticles arranged in a body cubic center crystal structure with Im3m space group, as a thermodynamic product, in coexistence with soluble wt SV40 nanoparticles. The nanoparticle crystals formed above a critical $MgCl_2$ concentrations. Reentrant melting and resolubilization of the virus nanoparticles took place when the $MgCl_2$ concentrations passed a second threshold. Using synchrotron solution X-ray scattering we determined the structures and the mass fraction of the soluble and crystal phases as a function of $MgCl_2$ and NaCl concentrations. A thermodynamic model, which balances the chemical potentials of the Mg^{2+} ions in each of the possible states, explains our observations. The model reveals the mechanism of both the crystallization and the reentrant melting and resolubilization and shows that counterion entropy is the main driving force for both processes [1].

Figure

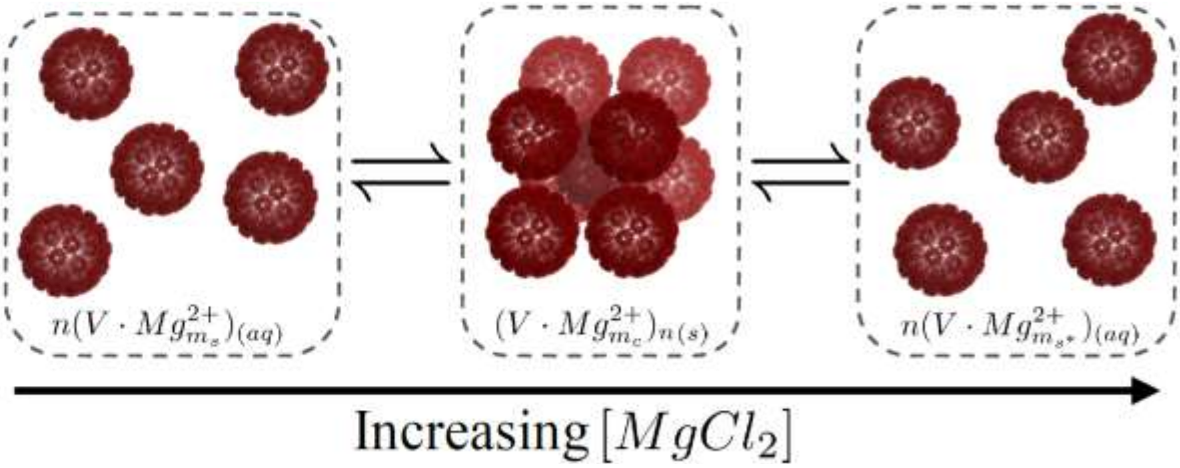

Figure 1. Effect of increasing $MgCl_2$ concentration on wtSV40 crystal formation and resolubilization

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Graphene Phase Modulators for Optical Communications

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Graphene in photonic integrated circuits is a material that can be operated both in electro-absorption and in the electro-refraction regime. These two regimes depend on the amount of carrier doping of the material. Interestingly in the electro-refractive regime the main effect is a change of index of refraction with minimum contribution of the absorption counterpart. This property indicates that graphene can be used as phase modulator also for complex modulation formats. In terms of electrical properties graphene shows an electrical mobility dependent on carrier density largely superior than Si, InP and InGaAs and this property may influence the transparency in high doping regime. The combination of efficient electro-refractive effect and possible low absorption due to the high carrier mobility makes graphene a good candidate for good figure of merit phase modulators of potential importance for optical communications.

In the electro-absorption regime graphene shows simultaneous occurrence of absorption and phase change. This property, negligible for short reach interconnects, plays a role in fiber transmission for the chirp contribution. Electro absorption and electro refraction regimes can be independently selected on the base of the bias applied to graphene. For comparison in plasma dispersion effect, commonly used in Si Photonics, the electrically induced change in the carrier concentration provides a simultaneous change in material absorption and refractive index proportional to the carrier density. Absorption and refraction effects in plasma dispersion based devices cannot be separated. The same holds for Franz–Keldysh effect and the quantum confined Stark effect (QCSE) that are alternative mechanisms used in Ge p-i-n or III-V quantum wells. In addition in these cases the effect is limited to the spectral band near the semiconductor band edge. As for plasma-dispersion-based devices, even in this case insertion loss due to carriers must be traded off with a large extinction ratio. The unique property of bias-induced separation of electro-absorption and electro-refractive modulation, along with the wavelength independence of graphene, makes this material suitable for any modulation scheme.

The cross section of the single layer graphene modulator is illustrated in the scheme of Fig.1. The Si photonic ridge waveguide can be realized in SOI, SiN or even silica platforms with no need of dopings as for Si photonics or InGaAsP modulators. Graphene layers are grown by chemical vapor deposition (CVD) on copper foil and then transferred on the waveguide. Phase modulation has been demonstrated with a Mach Zehnder modulator with graphene phase shifters on the two arms. With this modulator a modulation efficiency as small as $V\pi L$~0.28Vcm has been demonstrated, about 10 times better than charge depletion silicon modulators. This Mach Zehnder modulator has been successfully tested at 10Gb/s for a transmission on a 50km single-mode fiber link.[1] Graphene used as electro absorption modulator was realized on the same SOI waveguides. In this case graphene permitted the modulation of absorption to encode a 10Gb/s signal resulting in the modulation of the complex index of refration of graphene (absorption and refraction). The index variation added a positive chirp to the amplitude modulated signal that permitted an unprecedented transmission on a 100km long SMF optical link.[2]

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Integrated Neurophotonics: A new, all-optical paradigm for dense brain circuit interrogation at arbitrary depths

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Although our understanding of the properties of individual neurons and their role in brain computation has advanced significantly over the past several decades, we are still far from elucidating how complex assemblies of neurons – that is, brain circuits – interact to process information (Fig. 1). In 2011, six U.S. scientists from different disciplines banded together, outlined a vision [1,2], and managed to convince the Obama administration's White House office of Science and Technology Policy (OSTP) of the unprecedented opportunity that exists to launch a coordinated, large-scale international effort to map brain activity. This culminated in the U.S. BRAIN Initiative (Brain Research through Advancing Innovative Neurotechnologies), which was launched in 2013. Our perspective was predicated, in part, on the current level of maturity of diverse fields of nanotechnology and silicon-based very-large-scale integration (VLSI) that can now be coalesced to create unprecedented tools for massively parallel interrogation of brain activity. I will outline the immense complexity of such pursuits, the hopes we articulated, survey the existing technological landscape for assembling the requisite instrumentation, and then focus upon our collaborative efforts toward tools enabling multi-physical interrogation of brain activity. Especially promising is a new technological field we are calling integrated neurophotonics, which merges advances in photonic circuit VLSI with optogenetic molecular reporters and actuators.* We believe this new technology will engender a wide spectrum of unprecedented possibilities for both fundamental neuroscience and clinical neuromedicine

This work is being carried out in close collaboration with Professors Kenneth Shepard (Columbia University), Joyce Poon (University of Toronto), and Andreas Tolias (Baylor College of Medicine) – and members of our research groups.

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Figures

Figure 1. Portion of a mid-sagittal section of transgenic mouse brain imaged by confocal microscopy, with neurons color-coded for depth. credit: Dr. Laurent Moreaux (Caltech) and Dr. Stephan Junek (Max Planck Institute for Brain Research).

Nanodevices for the Study of NK Cell Function

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Immune cells recognize cancer and viral cells by binding their activating receptors to ligands presenting on the membrane of target cells. Although this recognition and following immune activation are extensively studied today, their exact mechanism is barely understood. Here, we engineered a biochip that act as an "artificial antigen presenting cell", and used it to study the role of the ligand arrangement in the activation Natural Killer cells – lymphocytes that belong to the innate immune system (Fig.1). The chip contained nanopatterned matrices with sub-10 nm metallic nanodots and functionalized with activating ligands. By studying the cell response to the matrix geometry, we discovered the minimal ligand distribution needed to stimulate cell adhesion and immunity.

Remarkably, in-vivo function of NK cells is regulated by the signaling balance of activating and inhibitory receptors. To study the spatila aspects of this signaling crosstalk, we engineered a novel multifunctional biochip that simultaneously regulates both receptors. The chip contains mixed nanodots of different metals, selectively functionalized with activating and inhibitory ligands. We fabricated the chip using novel nanoimprint lithography and sequential angle evaporation, combined with our recently developed orthogonal biofunctionalization[2].

Finally, we explored the nanoscale mechanical sensitivity of Natural Killer cells, by interfacing them with vertical ligand-functionalized nanowires. We indicated mechanical forces applied by the cells via enhanced cell contraction and the nanowire bending (Fig.2). Furthermore, we found that while ether nanowire topography or ligand presence was insufficient to stimulate cell immune response, their combination substantially boosted NK cell degranulation. In this sense, NK are analogous to a "Boolean AND gate" with two independent mechanical and chemical logic inputs. Our findings provide an important insight into the underlying mechanism of NK cell immune function, as well as demonstrate a novel toolbox for the study of the cell immune activation with an unprecedented spatial and mechanical resolution.

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Figures

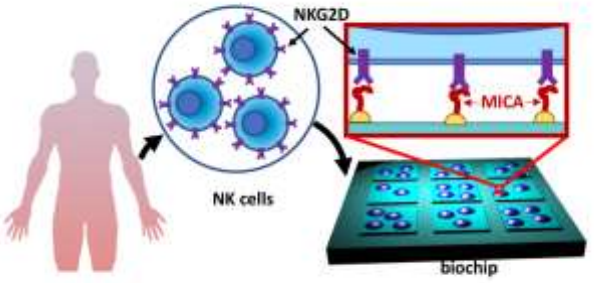

Figure 1. Scheme of the nanochip for NK cell study

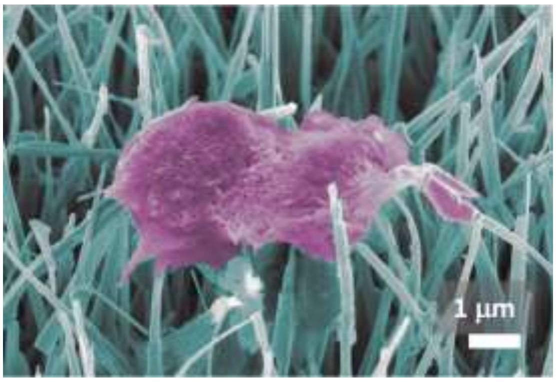

Figure 2. NK cells stimulated on nanowires - SEM

Nano-Patterned Polyelectrolyte Multilayers: A Non-Lithographic Approach

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Nano-patterned materials exhibit unique properties, such as increased surface area and morphology-dependent response. However, obtaining nanoscale patterns usually requires the involvement of electron beam lithography, which is limiting when device-scale patterns (typically spanning square centimeter areas) are sought.

The presentation will describe a modular approach for the construction of nano-patterned polyelectrolyte multilayers. This approach utilizes the surface patterns that are formed spontaneously in thin films of block copolymers as templates, which guide the assembly of polyelectrolytes using electrostatic layer-by-layer deposition. The presentation will discuss the fundamentals of selective polyelectrolyte adsorption on confined nano-domains and will delineate potential applications.

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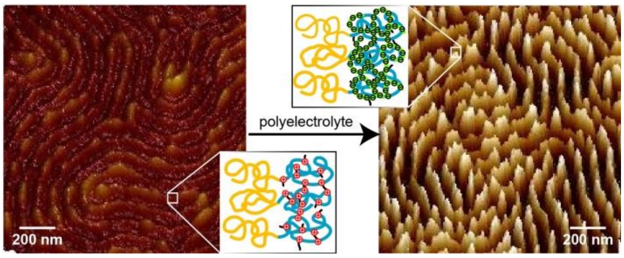

Figure. AFM height images showing a block copolymer pattern before and after selective deposition of a polyelectrolyte (height scales: left image: 5 nm; right image: 15 nm).

The Nonlinear Optics of Graphene: Welcome to the Wild West!

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The nonlinear optics of graphene has been the subject of a host of studies, both experimental and theoretical. For more usual materials, a first description of such processes that is sometimes reasonably accurate can be constructed at a perturbative level by introducing a third-order nonlinear susceptibility, often within an independent particle approximation where relaxation processes are only treated in a phenomenological way. Even when such an approach fails, it often provides a benchmark for more sophisticated calculations, and by comparison with experiment can help identify the physics that it itself cannot describe. We present such an elementary approach to the nonlinear optical properties of graphene, illustrate how a series of confusions in the literature have arisen in its introduction, and compare with experiment where possible.

Active Polymeric Fibers as Nanoreactors

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Abstract

In recent years there has been an ongoing endeavor to develop and construct nano- and microscale reactors, in which chemical reactions are performed in confined sub-microliter volumes. Such reactors have several important advantages over macroscale reactors including superb heat transfer and scale-independent synthesis. In addition, such reactors are a useful and flexible tool for examining the effect of sub-microliter confinement volumes on chemical reactions.

In this talk, I will discuss the potential of active microfibers as microreactors, and demonstrate the use of microfibers both as closed microreactors for obtaining freestanding metal-organic frameworks (MOFs) composite fabrics and as open microreactors for conducting catalytic processes in nanoliter environments.[1]

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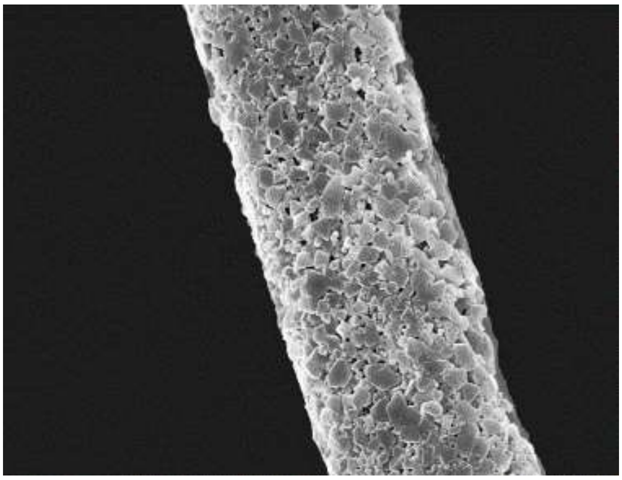

Figure 1. A polymer fiber acting as a reactor and a template for the synthesis of HKUST1 metal organic framework nanocrystals

Defect engineering and functionalization of 2D Transition Metal Dichalcogenides for Electrocatalysis and Molecular Sieving

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Among the family of 2D materials, transition metal dichalcogenides (TMDs) are intensively investigated for opto-electronic and electro-catalytic applications[1,2]. The properties of TMDs can be largely tuned by changing their elemental composition, their thickness and their atomic structure[1]. Besides phase engineering, the properties of 2D materials can be tuned by changing the defect concentration such as sulfur vacancies. In addition we have recently demonstrated that TMD nanosheets can be covalently functionalized which opens new avenues for controlling the surface chemistry and the opto-electronic properties of exfoliated TMDs[3]. Nanolaminate membranes made of two-dimensional materials (2D) such as graphene oxide (GO) are also promising candidates for molecular sieving via size-limited diffusion in the 2D capillaries[4]. Controlling the surface chemistry of the 2D nanosheets can provide additional tools for enhancing the sieving performance of the nanolaminate membranes (Figure 1). Through several examples, I will present our recent strategies for engineering exfoliated nanosheets of TMDs. My presentation will highlight how these strategies can be used for fine tuning the properties of the 2D TMDs and other 2D materials for electrocatalysis and molecular sieving.

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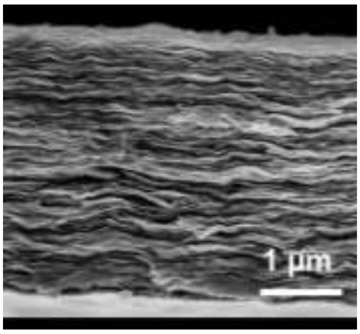

Figure 1. SEM images of a nanolaminate membrane made of exfoliated TMD nanosheets

TNT2018 Orals - Seniors Contributions

DFT study of the thermal transport properties of MoS_2: Application to thermoelectricity

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Transition metal dichalogenides (TMDC) have received an increased interest as a new family of two-dimensional (2D) material. Unlike graphene, TMDC exhibit a large band gap and have already been used promisingly as field effect transistor [1]. Moreover, 2D materials are expected to lead to higher thermoelectric figure of merit compared to bulk materials due to poor thermal conductivity [2].

We previously demonstrate that potassium doping seems a promising path to improve the Seebeck coefficient S and the electrical conductance σ [3]. However, the efficiency of thermoelectric modules depends both on the electronic and the thermal transport properties as the figure of merit ZT is defined as:

$$ZT = \frac{\sigma S^2 T}{\kappa}$$

During this talk, I will address the thermal transport properties of MoS_2 and its thermal conductance κ. The calculations have been performed using the SIESTA DFT package based on atomic orbitals. A comparison with a plane wave calculation is given on Fig.1.

I will mainly focus on the influence of sulfur vacancies [4] on κ and also the influence of adsorbed potassium. Using Green's function technic and the Landauer formalism, we will also present the influence of realistic disordering on κ.

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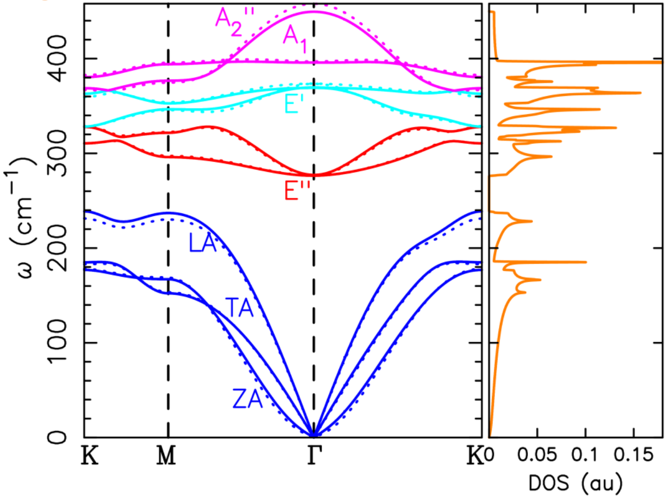

Figure 1. Phonon dispersion and density of states for MoS_2. The solid lines correspond to the SIESTA (atomic orbitals) calculation, the dotted lines to the VASP (plane waves) calculation.

Development of Carbon Nanotubes-based Porous 3D Scaffolds for Tissue Regeneration

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Carbon nanotubes (CNTs) are one of the most promising materials to interface with electrically active tissues, as neuronal and cardiac tissues. Their inherent electrical properties and their cylindrical shape are the key features to improve and boost the cellular growth and functionality. [1]

The combination of CNT with polymers has been extensively studied, and the materials produced showed a great potential in tissue regeneration. [2] Porous 3D structures based on PDMS doped with CNTs were previously tested as supports for neuronal growth. A three-dimensional cellular organization was demonstrated to be able to induce neuronal network outputs that strongly differ from the 2D constructs and maintain the unique capabilities of CNT to tune the genuine neuronal biological processes.[3] On the other side, the design of electrodes based on conductive polymers (CPs) in brain-machine interface technology offers the opportunity to reduce gliosis, improve adaptability and increased charge-transfer efficiency. However, very little is reported about the combination of CPs and CNTs, and only 2D films have been synthesized and tested *in vitro*.[4]

In the present work, we construct 3D porous composites of CPs and CNTs and incubated astrocitic and cardiac cells to study its biocompatibility. We have developed a new, easy and fast strategy, based on the Vapor Phase Polymerization (VPP) technique, where the monomer vapor is polymerized inside a template containing CNT and an oxidant agent (Figure 1a). The physical, chemical and electrical properties were evaluated, concluding that the resulting material is a very promising scaffold, with very low density, good porosity and high biocompatibility, thus paving the way for the development of new conductive 3D scaffolds by following a yet unexploited approach.

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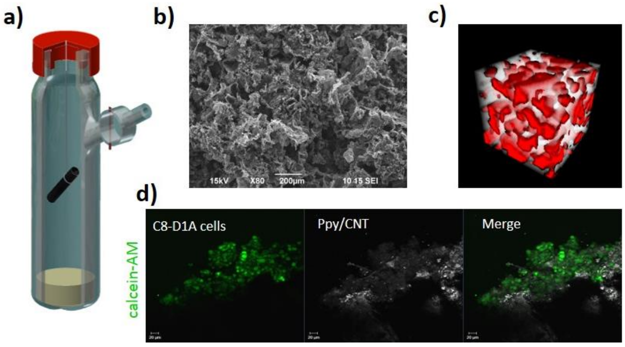

Figure 1. a) Representation of the derived- Vapour Phase Polymerization (VPP) methodology employed. b) SEM micrograph of the 3D scaffolds. c) 3D illustration of scaffold's pore distribution; pores are represented in red colour and matter in white. d) Calcein-AM stain of C8-D1A viable cells (green) after 2 days of culture.

An *In vivo* Study On Cobalt Ferrite Nanoparticles As Multi-Modal Cancer Therapy Combining Intrinsic Toxicity and Hyperthermia

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Magnetic nanoparticles under alternating magnetic field can convert the electromagnetic energy into thermal energy which, in turn can be exploited for hyperthermia (HT) therapy[1]. Besides Iron Oxide nanoparticles (IONPs) which are commonly used as heat hubs in magnetic hyperthermia, mixed ferrites of these IONPs with Manganese (Mn), Cobalt (Co) or Zinc (Zn) ions are also promising candidates for such magnetic HT treatment due to their improved magnetic properties. Cobalt ferrite nanocubes have shown very high specific adsorption rate (SAR) values (a measure of their heat performances) at clinically acceptable frequency and field conditions [2]. However, the use of Co-based nanoparticles for biomedical applications is still under debate. There are numerous evidences of intrinsic toxicity of $CoFe_2O_4$ NPs in cellular studies, with a toxicity profile being highly dependent on the cell types and concentration tested[3]. Due to the proven cytotoxicity, not much exploration has been made on cobalt-based nanoparticles in in-vivo conditions. We synthesized 17nm cobalt ferrite nanocubes by thermal decomposition method, which showed improved SAR values at lower field and frequency conditions compared to standard IONPs of similar size and shape[2]. Here, on a xenograft murine mice model, we demonstrate the synergic effects of cobalt ferrite nanocubes as magnetic hyperthermia inducing agents and intrinsic toxic agent with controlled Co ion release. The intra-tumoral injection gave us the control, by specifically inducing toxicity only at to tumor mass, avoiding uncontrolled toxicity to other vital organs. The animals treated with the combination of cobalt-ferrite injection and magnetic hyperthermia showed complete reduction in tumor volume as compared to untreated control and other groups studied (without HT, IONPs with and without HT). Furthermore, the same group showed the longest survival of up to 200 days post treatment. The survived animals showed no signs of distress throughout the study. Histopathological, TEM and elemental analysis were performed on tumor and organs such as kidney, liver and spleen to study in detail the fate of these nanoparticles in vivo. With the results obtained in our study, we demonstrated that the intrinsic toxicity of the Co ions in the cobalt ferrite nanocubes, when exploited in a controlled environment, can replace the usage of other chemotherapeutic drugs and act as a self-standing multi-modal therapy, all working under lower dosage and acceptable hyperthermia limits.

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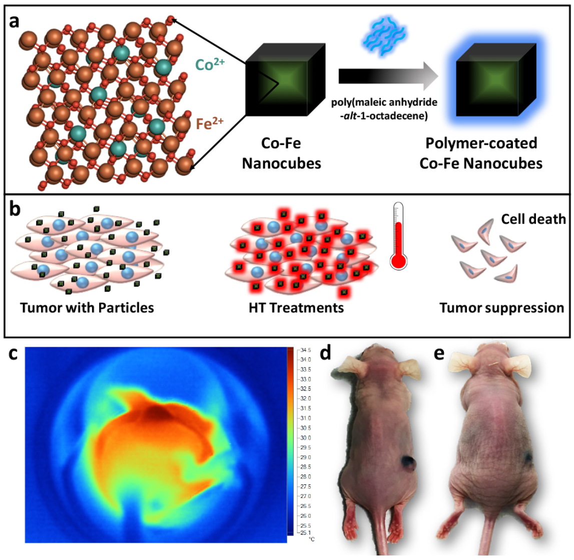

Figure 1. Schematic representation of preparation of cobalt ferrite NPs for biomedical application (a) and their function as HT inducing agents (b). IR image of animal injected with Cobalt ferrite and subjected to HT(c). Image of animal before and after treatment.

Expanding Perovskite Toolbox via Self-Assembly of $CsPbX_3$ and Cs_4PbX_6 Nanocrystals

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In this contribution we will discuss current trends in perovskites from the perspective of nanocrystals-based bottom-up fabrication together with our results in making micron-sized nanocrystal superlattices and their chemical transformations. Self-assembly is a cheap bottom-up technique to fabricate inorganic solids from colloidal nanocrystals.[1] There are two advantages of using nanocrystals: 1) the spatial composition of the solid can be modified in three-dimensions within 10-20 nm by starting from a mixture of different nanocrystals (such composition control is inaccessible or prohibitively expensive by more traditional methods like epitaxy); 2) the collective interactions between ordered nanocrystals may lead to enhanced or unique physical properties of the solid. Lead halide-based perovskites prepared in the form of colloidal nanocrystals have emerged in the past few years as one of the most promising materials for solution-processed light emitters and photovoltaics.[2] Fast advances in the synthesis made samples of monodisperse nanocrystals of 3D $CsPbX_3$ and 0D Cs_4PbX_6 readily available.[3, 4] In addition, chemically-triggered interconversions between these phases at the nanoscale (0D↔3D) provide novel means of modulating composition and properties of the resulting solid. [5]

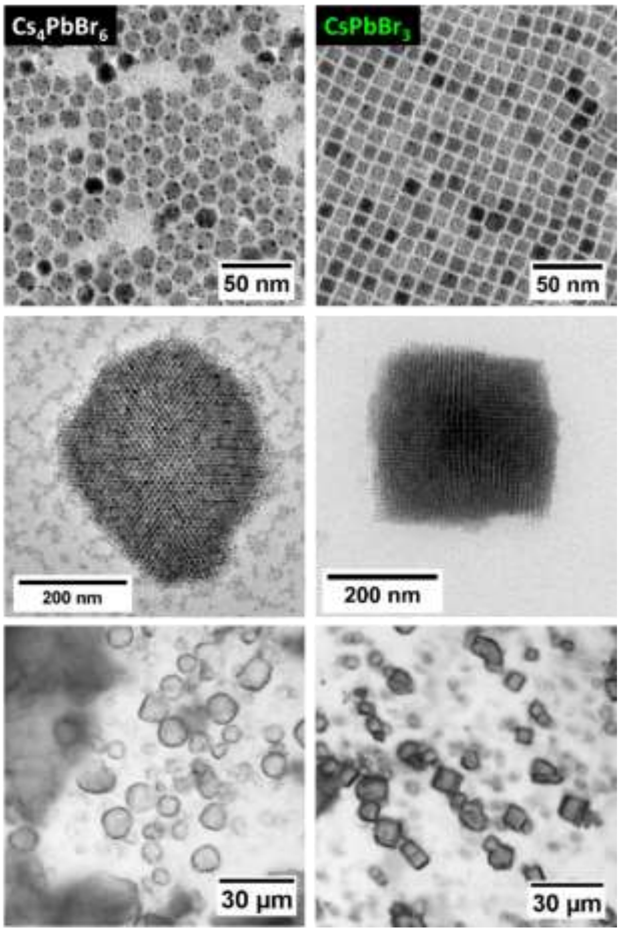

Figure 1. Various length scales of lead halide-based perovskite nanocrystals self-assembly. From monolayers to micron-sized crystals: left column – 0D phase Cs_4PbBr_6 nanocrystals, right column – 3D $CsPbBr_3$ nanocrystals.

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CVD Growth of WS_2 and MoS_2 Centimenter Scale Films

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Abstract

Technological applications exploiting optoelectronic properties of Transition Metal Dichalcogenides, TMDs, (e.g., WS_2 and MoS_2) need synthesis methodologies able to deposit TMDs as a few layer continuous film with homogeneous thickness. Specifically, the thickness control is needed due to the strong thickness/band structure correlation in TMDs that provides an indirect-to-direct bandgap transition when going from bulk to monolayer form. Currently, WS_2 and MoS_2 films are typically deposited by two-step growth based on the physical deposition of the metal oxide (i. e, WO_3 and MoO_3) and the subsequent thermal treatment with sulfur. Although the two-step approach can lead to high quality TMDs crystals, the growth of continuous films results challenging.

We propose a one-step growth methodology for the deposition of WS_2 and MoS_2 that exploits volatile metal precursors for the deposition of few layer continuous films on the centimeter scale with a high substrate throughput. A full optical (Raman, Photoluminescence, ellipsometry), structural (FE-SEM), and electrical characterization (mobility, transport gap) of the deposited TMDs film is provided. The effect of post-growth chemical treatment on the physical properties of WS_2 and MoS_2 films is also presented.

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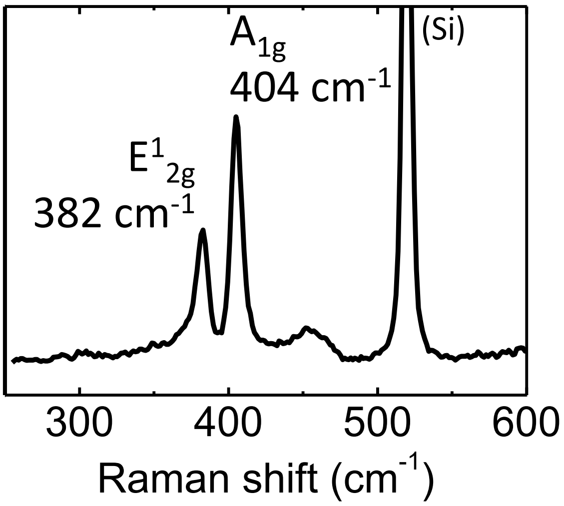

Figure 1. Raman spectrum of MoS_2 on Si/SiO_2 substrate

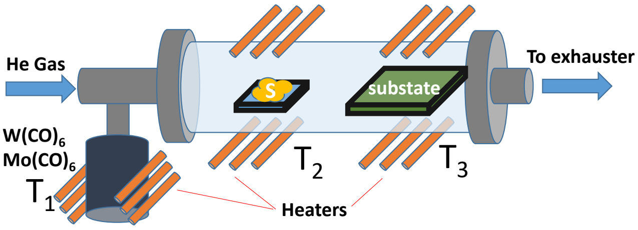

Figure 2. Schematic illustration of the CVD system used for the growth of WS_2 and MoS_2 films [1].

Interaction and coherence of a plasmon-exciton polariton condensate

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Hybrid particles of excitons in semiconductors and cavity photons, called polaritons, have shown fascinating phenomena including Berezinskii-Kosterliz Touless transitions [ref] and Bose-Einstein Condensation (BEC) recently observed at room temperature in organic-based microcavities [1]. In this context, a promising route for the exploitation of polariton physics at the nanoscale is offered by the Surface Lattice Resonances (SLRs) arising from the coherent radiative coupling of diffractive modes, propagating in the plane of an array of metallic nanoparticles, with the localized surface plasmons (LSP) of each individual naostructures [2]. The SLR systems showing a high electromagnetic (EM) field enhancement are characterized by a strong suppression of losses (higher quality factor) with respect to individual nanoparticle LSPs, at the expense of a less confined electromagnetic field (larger mode volume) [3].

By strongly coupling molecular excitons to a SLR in a 2D array of silver nanorods (NRs), we demonstrate the formation of an out-of-equilibrium plasmon-exciton-polariton (PEP) condensate with an extended spatial coherence over distances longer than the excitation spot. This is proved by time resolved experiments which evidence the picosecond dynamics of the condensate and a sizeable blueshift, thus measuring, for the first time, the effect of polariton interactions in plasmonic based cavities. These findings are very promising for studying properties of quantum fluids at room temperature with ultrafast dynamics, thus opening the way towards future plasmon-exciton-polariton based condensates and devices.

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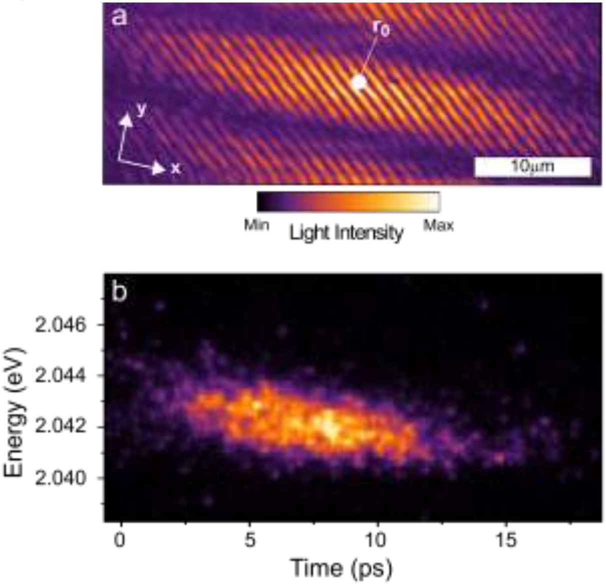

Figure 1. (a) Experimental interferogram of two-dimensional spatial coherence of the PEP condensate. (b) Time- and energy-resolved PL above PEP condensate threshold.

Fluorous Probes as Smart Imaging Tools

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Abstract

The search for novel sensitive, robust, and selective diagnostic tools for non-invasive *in vivo* imaging is a priority of current medical practice, in order to improve early diagnosis of diseases and implementation of targeted therapies. Our research in this field is focused on the development of new fluorinated contrast agents enabling ^{19}F-MRI, as a complementary tool to be coupled with other diagnostic imaging techniques, such as ^{1}H-MRI and ultrasound imaging (US), in order to overcome their present shortcomings, particularly in terms of sensitivity. ^{19}F-MRI has emerged as one of the most promising diagnostic tools providing hot spot imaging [1]. We recently reported aqueous emulsions of a unique fluorinated imaging agent (PERFECTA, Figure 1) bearing 36 equivalent ^{19}F atoms and therefore showing a single, intense resonance peak. Preliminary investigations have demonstrated excellent cellular compatibility and spectral properties (relaxation times and sensitivity) adequate for *in vivo* ^{19}F-MRI use [2]. Chemical modification of PERFECTA's branched scaffold allows its coupling to other functional moieties, giving multimodal nanoplatforms. Following this approach, a novel class of highly fluorinated gold clusters were obtained [3], and confined in protein-stabilized supraparticles working as water-soluble nanocontainers for fluorinated guest molecules [4].

Figures

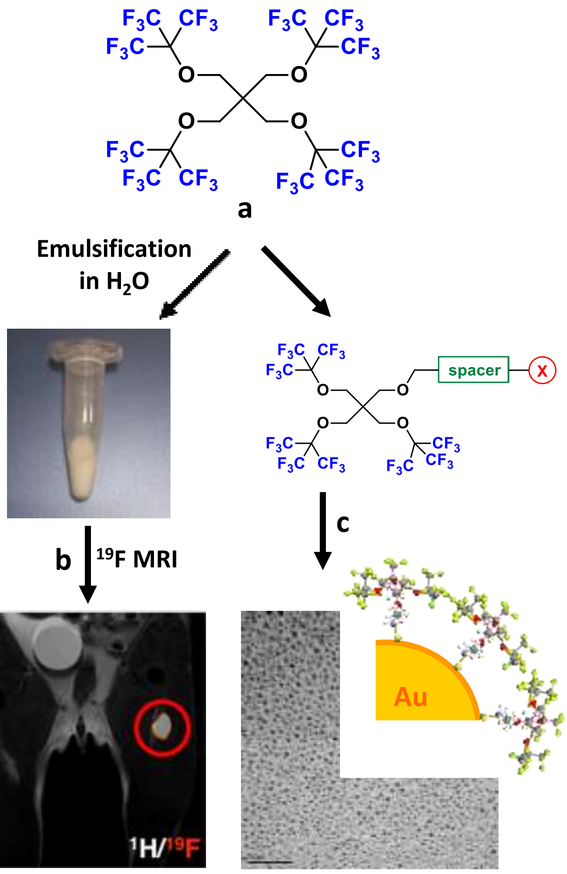

Figure 1. PERFECTA (**a**) yields stable aqueous emulsions that are suitable as contrast agents for *in vivo* ^{1}H/^{19}F-MRI (**b**). Chemical modification of its scaffold led to a highly fluorinated ligand that was efficiently used for the synthesis of fluorous gold clusters (**c**).

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Two-dimensional semiconducting Gold

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Within the two-dimensional (2D) material research of the past decade, we have seen a large variety of materials synthesized. The great majority of them derive from their layered homologue in three dimensions. This is the case for graphene [1], hexagonal boron nitride (h-BN) and (almost all) the transition metal dichalchogenides (TMDs), which are the main ingredients in the recent quest towards the realization of van der Waals heterostructures (vdWHs) with tailored electronic properties. Other 2D materials such as germanene (Ge), silicene (Si), bismuthene (Bi) and phosphorene (P) have been synthesized on various substrates, but those materials come from crystal structures, which are not layered in the bulk and are therefore intrinsically unstable. A category of materials which have proven to be arduous to synthesize on a large scale is represented by transition metals, where so far no large-area high quality crystal has been reported [2]. In this work we show that gold atoms, intercalated at the heterointerface between the Si-terminated SiC(0001) surface and its C-rich $\left(6\sqrt{3}\times 6\sqrt{3}\right)R30$ reconstruction [3], are arranged in a highly crystalline fashion and develop their own band dispersion, which is intrinsically two-dimensional. By means of angle-resolved photoemission spectroscopy (ARPES), we measured the electronic dispersion of 2D-Au, observing a maximum of the valence band slightly below the Fermi level [4]. Along the Au $\Gamma\mathrm{K}$ direction, the 2D-Au bands also exhibit a large spin-orbit splitting, which could turn out to be useful for spintronic applications. The graphene/gold interface was investigated in detail with several surface analysis techniques to assess its structure and chemistry. Scanning tunneling microscopy (STM) scans reveal an atomically clean and sharp interface, with gold developing a (13×13) moiré. We therefore present the first experimental observation and thorough characterization of a large-area 2D semiconducting gold layer. Being graphene-encapsulated, this also defines a novel type of van der Waals heterostructure.

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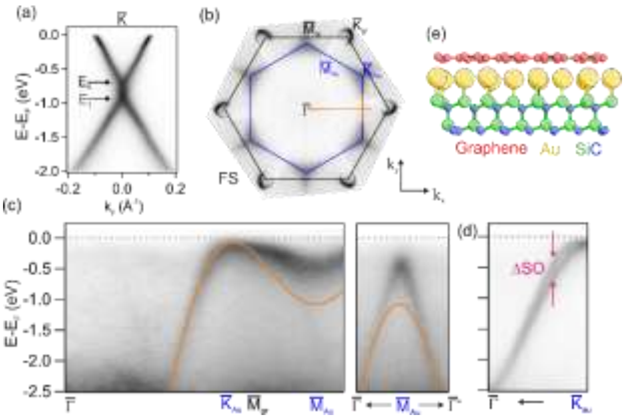

Figure 1. Electronic properties of 2D-gold graphene encapsulated.

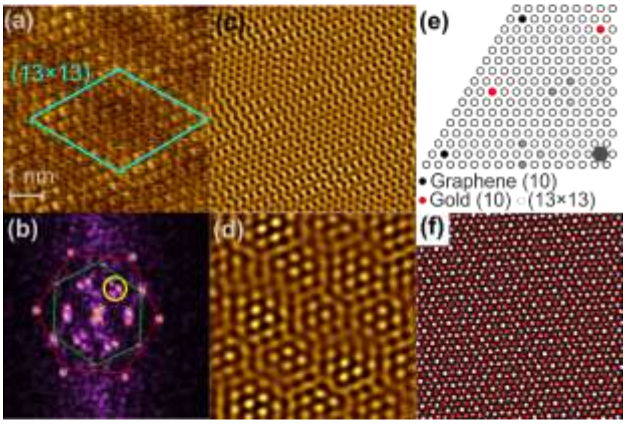

Figure 2. Local STM measurements of the moiré potential stemming from the Gr/Au/SiC(0001) interface.

Hamaker constant of freestanding graphene from STM and AFM measurements

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A direct measurement of the Hamaker constant of freestanding graphene is not straightforward. In force-distance curves on supported graphene the substrate will contribute significantly to probe-sample interactions. This makes it impossible to deduce a Hamaker constant being characteristic for the probe-graphene arrangement.

We have recently developed an approach, which utilizes STM measurements on freestanding graphene membranes in order to very sensitively measure tip-sample forces [1]. Additionally AFM force-distance curves allow to detect longer range interactions. The Hameker constants for the graphene probe arrangement turn out to be considerably smaller than those measured STM/AFM probes against highly oriented pyrolytic graphite (HOPG). This result could have been expected but the quantitative results provide a first impression how small a Hamaker constant resulting from a monolayer thick membrane really is.

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Figures

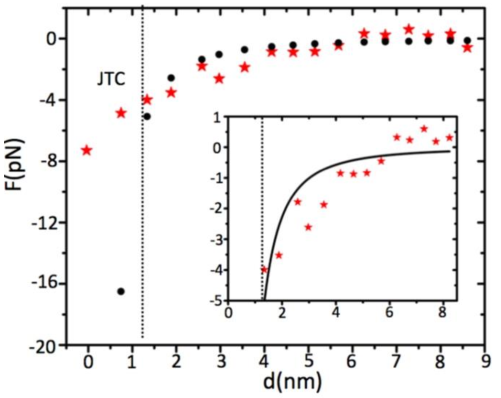

Figure 1. Force-distance curve on a freestanding graphene-membrane measured by AFM. The red points are averaged experimental results and the black points are obtained by fitting. The inset shows data prior to jump to contact (JTC) which is relevant for calculating Hamaker constants.

Novel MNPs-based isolation approach looking for 'the needle in the haystack'

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Magnetic nanoparticles (MNPs) have been widely exploited for the development of sensitive detection techniques. Due to their magnetic properties, this type of particles allows the isolation and concentration of the analyte, thus ensuring the detection of molecules even when present at low concentration. One of the problems related with the use of MNPs for the mentioned purpose is that once the magnetic field is applied both analyte-MNPs conjugates and free-MNPs are isolated. This can decrease the sensitivity of the detection method, since the presence of an excess of MNPs potentially interferes with the detection of the analyte. This limitation must be taken under consideration especially when the analyte is present at low concentration and if the quantification of the analyte is strictly related to the MNPs itself[1] (e.g. T2 relaxation time measurements). Several methods have been applied in order to overcome such limitation. In some cases, the MNPs are used only to isolate the analyte while the quantification occurs by a further recognition of the analyte-MNPs conjugates by a labelled-material[2],[3] (i.e. antibody, nanoparticles). Alternatively, the analyte-MNPs conjugates are physically entrapped while the free-MNPs are removed[4],[5]. Even though with these expedients some improvements have been achieved, each of them come along with other limitations such as the relatively high concentration of analyte required for fluorescence-based detection in the first case and false negative results given by the undesired MNP's aggregation in the second one.

We propose a novel method to improve the isolation of a selected analyte by using antibody-coated MNPs (Ab-MNPs). Once the analyte-Ab-MNPs conjugates is formed a second type of non-magnetic particle are employed, which interact only with the analyte-Ab-MNPs conjugates. The nanocomposite formed by the two types of particles is then selectively isolated allowing a precise quantification of the analyte even when present at low concentrations. The nanomaterials suitable for this detection techniques have been synthesised and characterised by dynamic light scattering (DLS), transmission electron microscopy (TEM) and the amount of biological material attached on their surface has been quantified by Bradford protein assay. Their behavior in the designed device has been extensively evaluated until the best conditions were selected (e.i. buffer, volume, concentrations, strength of the magnetic field). Thanks to the isolation-technique developed and the features of the selected nanomaterials the quantification of the analyte can be achieved using several analytical techniques (spectrophotometry, electrical measurements, Raman spectroscopy) which efficacy is currently under evaluation.

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Photoluminescence of porous silicon tunable by magnetic metal deposition

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In this framework luminescent porous silicon (PSi) is filled with a magnetic metal (e.g. Ni) to influence the photoluminescence (PL) by these deposits which happens in two ways. On the one hand the surface plasmon of the metal deposits is exploited to modify the luminescence [1] and on the other hand it is influenced by an external magnetic field. Due to the metal filling of the PSi the PL is blue-shifted and furthermore an increase of the intensity is observed. First the optical properties of the luminescent PSi are investigated, second Ni is deposited within the PSi samples and subsequently the nanocomposite specimens are characterized optically again and also magnetically. The optical properties are investigated with respect to the shift of the photoluminescence due to the metal filling. PL spectra of bare PSi show a maximum around 620 nm whereas in the case of Ni filled samples the peak is blue-shifted to around 580 nm and the luminescence intensity is increased.

Concerning the magnetic properties of the nanocomposite the embedded Ni structures can be superparamagnetic from the size of the pore diameters but due to the branched morphology the achieved deposits tend to be interconnected and thus do not offer necessarily a superparamagnetic behavior. Field dependent magnetization measurements performed with the magnetic field applied perpendicular and parallel to the sample surface show a high magnetic anisotropy. The coercivity of the samples strongly depends on the metal deposition time which determines the amount of metal and thus the degree of interconnections. It can be clearly seen that the samples offer a film-like behavior due to the interconnected Ni structures which is represented by the easy axis parallel to the surface (figure 1). The optical characterization of luminescent PSi with respect to its PL compared with Ni filled samples is discussed in detail as well as the corresponding magnetic properties of the nanocomposites. Furthermore the influence of an external magnetic field on the optical properties is elucidated. The presented systems are promising candidates for applications in optoelectronics and also for magneto optical integrated devices.

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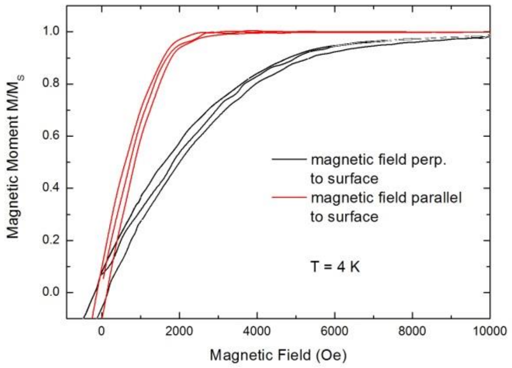

Figure 1. Magnetic measurements performed with an applied magnetic field parallel (red curve) and perpendicular (black curve) to the sample surface, respectively.

Gold nanoparticles decorated Reduced Graphene Oxide electrodes for detection of a cancer biomarker candidate

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The modification of graphene based materials with colloidal inorganic nanocrystals has recently attracted increasing attention.[1,2] A novel colloidal hybrid material, based on pyrene-carboxylic acid (PCA) functionalized Reduced Graphene Oxide (RGO) flakes, uniformly coated by a dense layer of organothiol-capped Au nanoparticles (NPs), is proposed. The Au NPs, 2-3 nm in size, have been synthesized with a reproducible control on size and shape by an *in situ* colloidal reduction method. The RGO flakes, which are achieved by exfoliation, in form of single- and few-layered sheets, allow to access the relevant structural properties of graphene, concomitantly permitting its solution processing, both for fundamental studies, and for achieving functional hybrid materials for advanced technological applications.[3]

The synthesis of the novel colloidal hybrid material has been optimized, so as to be suited for its application upon modification of Screen-Printed Carbon Electrodes (SPCEs) in the detection of the miRNA-221 sequence, a cancer biomarker candidate overexpressed in lung and breast cancer.

Electrochemical measurements performed on the modified electrodes show that the hybrid Au NP decorated RGO provides a twofold increase of the electroactive surface area, faster heterogeneous electron transfer kinetics at the electrode/electrolyte interface with a decrease of the resistance of the electron transfer with respect to the unmodified electrodes.

The hybrid modified SPCEs demonstrate an improved electrocatalytic activity towards red/ox reactions of 1-naphthol, a typical reagent involved in the Alkaline Phosphatase-amplified bioassay, showing a great potential as platform for the detection of the proposed cancer biomarker candidate.

The platforms have been found highly reliable and sensitive in the streptavidin-alkaline phosphatase catalized assay of the miRNA-221 sequence,[4] detected in spiked human blood serum samples with a LOD of 0.7 pM, and an average percentage standard deviation (RSD) of 13%, in a range of 1 – 5000 pM.

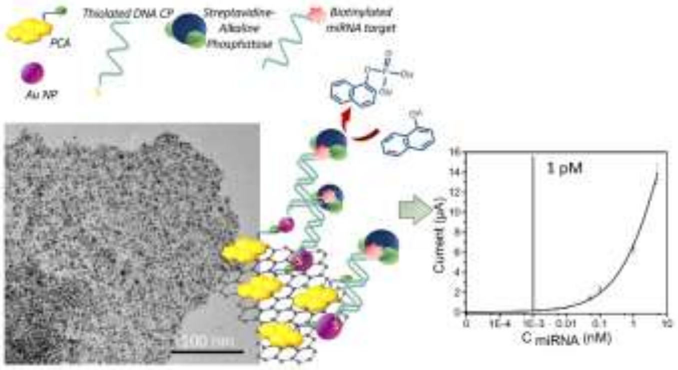

Figure 1. Electrochemical detection of miRNA-221 by a Streptavidin-Alkaline Phosphatase catalyzed assay. PCA-RGO/Au NP based SPCEs, modified by a thiolated DNA capture probe (CP) hybridized by the biotinylated mi-RNA 221target, upon exposure to 1-naphthyl phosphate, generate 1-naphthol, which is detected by DPV.

Acknowledgements. The authors acknowledge the National Project (PRIN 2012 prot. 20128ZZS2H).

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Nonlocal Optical Properties of Spherical Nanomatryoshkas

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We investigate nonlocal optical properties of spherical nanomatryoshka (NM) structures with sub-nanometer core-shell spacing [1] by using quantum hydrodynamic theory (QHT). We consider several plasmonic systems of Na metal with dimensions SF × (R_1, R_2, R_3) where SF is the scaling factor and R_i are the NM radii as shown in Fig. 1(a). We apply state-of-the-art QHT, which is a unique method to study near- and far-field optical properties of multiscale plasmonic systems [2, 3]. We study the effect of gap spacing and particle size on the optical properties of these core-shell structures. Absorption efficiency spectra for five Na core-shell structures, with SF taking an integer value from 5 to 1, computed within the QHT are shown in Fig. 1(b).

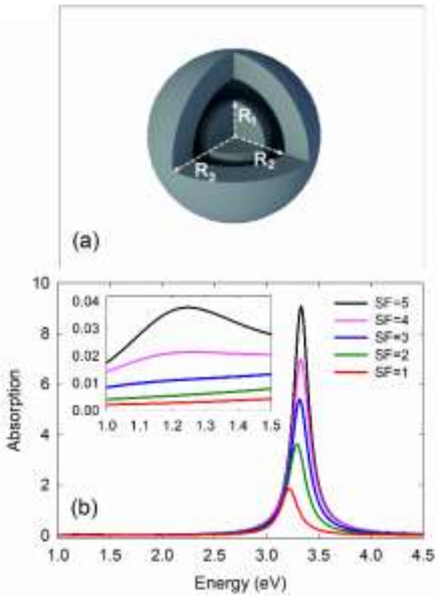

Figure 1. (a) Geometry of the problem (b) Absorption efficiency for Na NMs computed within QHT method. The scaling factor (SF) takes an integer value from 5 to 1.

We compute results using different theories and find that the results calculated within QHT method are in excellent agreement with the Density functional theory (DFT) computations [4], performed using an in-house developed code. To show the potential of QHT as compared to the other methods, we also include in our analysis the results calculated using local response approximation (LRA) and Thomas-Fermi hydrodynamic theory (TF-HT). Figure 2 presents a comparison for absorption spectra and induced polarization density, computed using different methods, for SF=4.

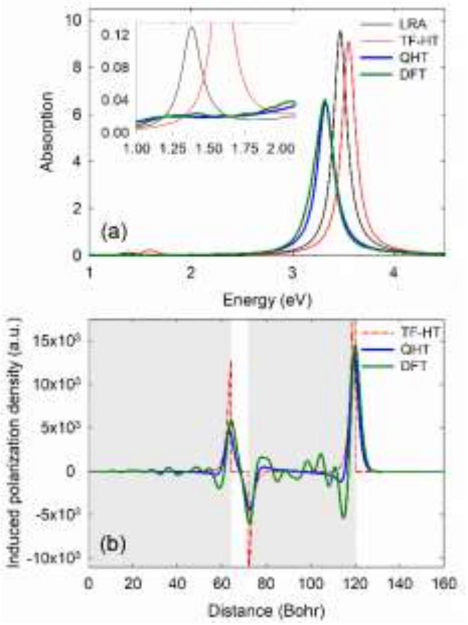

Figure 2. (a) Absorption spectra (b) induced polarization density for Na NM for SF=4 computed using different methods.

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Nanostructured Carrier Platforms for the Encapsulation of Drugs and Natural Bioactive Agents

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Abstract

Encapsulation of drugs, bio-active reagents, molecules and nanoparticles in nanoscale platforms is one of the most promising approaches in the development of nanomedicine that provides for efficient drug loading along with reducing systemic toxicity. Moreover, smart targeting of these nano-vehicular systems can greatly enhance the accumulation of the particular drug at its desired action site(s). Drugs encapsulated in nano- vehicular systems exhibit improved bioavailability, biodistribution and activity relative to non-encapsulated counterparts.In this work we report encapsulation of drug(s) and natural (refined) bioactive reagents for a number of different purposes. Tobacco Mosaic Virus(TMV) is a rod shaped plant virus that is 300 nm long and 18 nm in diameter with a 4 nm channel insde it. The plant virus had been encapsulated with Pt(II)-containing drugs followed by the effusion of it from the virus. Our group also encapsulated Virgin Coconut Oil (VCO) in Solid Lipid Nano-Particles (SLP). VCO loaded SLP showed improved skin penetration as well as better moisturization of the skin. Niosomes are the next generation of Nano-structured Lipid Carriers (NLC) that can be synthesized from non- ionic surfactants and cholesterol. Encapsulation of VCO along with emulsifying agents and nanoparticles showed great potential to inhibit growth of Multidrug Resistant (MDR) bacteria especially Staphylococcus aureus. The drug encapsulated niosomes gave extended release of the drug, which could result in decreased dose, lesser days of treatment and more patient compliance.

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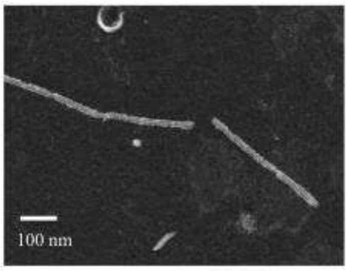

Figure 1. STEM image of TMV encapsulated with Pt(II)-containing drugs

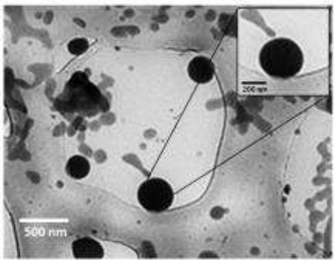

Figure 2. TEM image of SLP encapsulated with VCO. Inset shows a magnified SLP with a diameter of 220 nm

Figure 3. Niosomes encapsulated with VCO effectively eradicated MDR bacterial strains

Large magnetoresistance in oxygen deficient $SrTiO_3$

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Abstract

Ordinary magnetoresistance in metal has been intensively investigated so far [1]. Large magnetoresistance is uncommon phenomena, it has been observed in semimetallic system, such as bismuth [2].
Galvanomagnetic transport properties in oxygen deficient $SrTiO_3$ were investigated. To create oxygen vacancies, $SrTiO_3$ single crystals were annealed at high temperature in vacuum environment ($< 10^{-8}$ Torr). As annealing temperature increased resistivity was decreased, it means that higher annealing temperature cause much more oxygen vacancies in $SrTiO_3$ single crystals. Interestingly, non-linear Hall resistivity and magnetoresistance were observed under 100 K simultaneously as seen in Figure 1, which is frequently observed in two band-model [3]. As temperature decreased to 2 K, magnetoresistance increased up to about 3,000 %. Transport properties were well fitted by two band-model, electron-like carrier density and mobility were well matched with obtained by conventional Hall effect. The other type of carriers appeared about at 100 K and become influential as temperature decreased. Detailed parameters are shown in Figure 2. In order to find the origin of large magnetoresistance in oxygen deficient $SrTiO_3$, electrical and optical measurements have been conducted.

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Figures

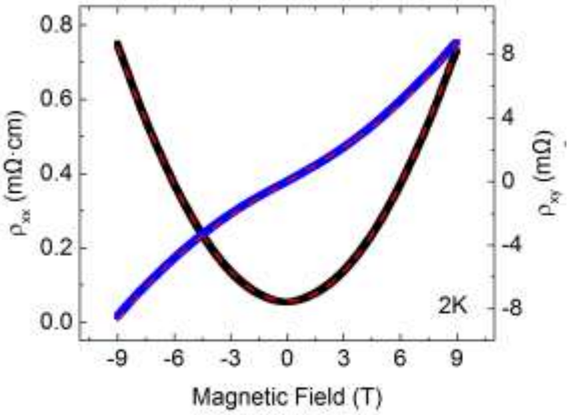

Figure 1. Resistivity (black line) and Hall resistivity (blue line) in oxygen deficient $SrTiO_3$ at 2K. Red dotted lines are fitted by two-band model.

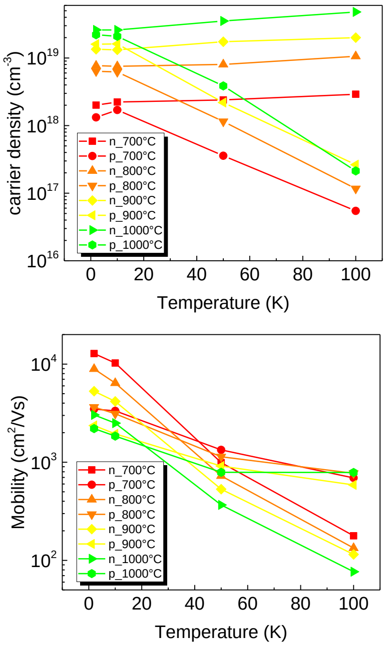

Figure 2. Extracted parameter of (a) carrier density and (b) mobility from two-band model.

Structural peculiarities of silicon after ball milling in the presence of different materials

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HRTEM studies of silicon after treatment in a planetary mill have been performed. It is shown that along with the initial phase of silicon (Si-I), the sample also contains some high-pressure phases: Si-III (Kasper phase) and Si-IV (lonsdaleite). Samples of powdered Si were prepared in a Planetary Micro Mill with addition of 0.5%-5% B_4C or nanodiamond. The duration of milling in the experiments was 5 min, 20 min and 2 h. The powder after the treatment was examined in a JEM-2010 TEM with EDS and EELS attachments. We studied the orientation relationship between the particles of different phases, finding that there are, in general, two mechanisms of formation of Si-IV: (1) through the stacking faults formation; (2) through the transformation first to the Kasper phase (Si-III), and then from the Si-III to Si-IV [1]. Estimations of temperature and pressure conditions in the planetary ball mill made previously are in accordance with the conditions of formation of the above-mentioned phases. In the next step we have processed a mixture of silicon and boron carbide powders. When pure B_4C was subjected to ball milling [2], no twins, polytypes or other crystal lattice defects were observed. In the samples where Si concentration prevailed (about 95%), we observed both twins and stacking faults in B_4C. For comparison we processed Si in the presence of diamond powder in the same proportions as before for a mixture of Si and B_4C. It is shown that as a result of processing of Si both in pure form, and in the presence of additives of boron carbide and diamond in the planetary mill in Si and B_4C, twins are formed with the same twinning planes (fig.1,2) as in the case of traditional deformation. It is shown that different variants of phase transformations are realized in silicon.

Figures

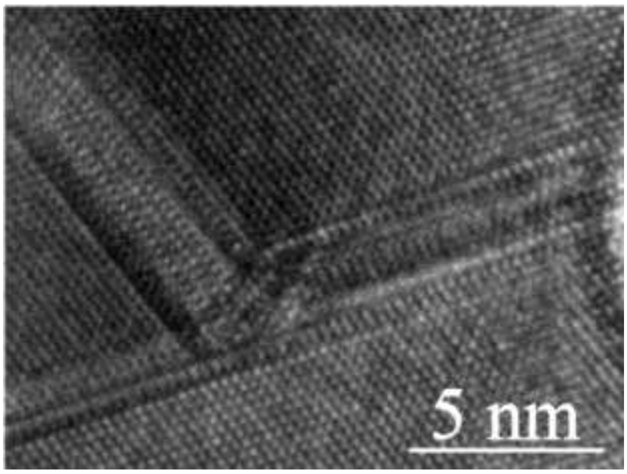

Figure 1. Two systems of {111} twins in silicon after ball milling. Twin boundaries compose a 70.53° angle.

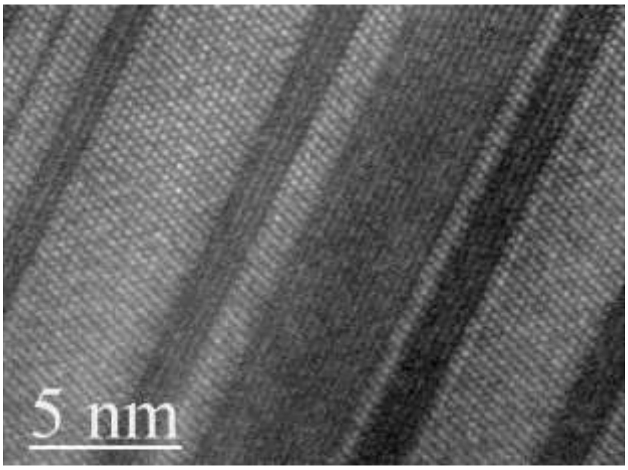

Figure 2. {10-11} twins in B_4C after ball milling.

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The Growth of Millimeter-Scaled Graphene Single Crystal through Nucleation Density Control in Height-Confined Reaction Slits

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I. INTRODUCTION

In conventional CVD process, the as-grown continuous graphene film over entire Cu foil could be regarded as the coalescence via many small graphene grains with lateral size less than 50-60 µm. The dense graphene boundaries on continuous graphene films would introduce severe carrier scattering which degrades carrier mobility of graphene films, therefore retarding graphene-related applications. In this work, the growth of high-quality large graphene grains through the nucleation density control in confined reaction slits will effectively reduce the perimeter of graphene grain boundaries of graphene films and enhance its physical properties.

II. RESULTS

The height-confined slit positioned in an enclosed graphite cavity is designed for graphene growth. The Cu sublimation is suppressed within the confined slit, therefore reducing the surface roughness of Cu substrate and graphene nucleation density. The less dendrite-edged graphene single crystals were successfully grown in graphite cavity and height-confined graphite slit as shown in Fig 1 (c) and (d). Besides the control of the growth environment, the oxidized Cu foils are utilized for the fast growth due to the low reaction rate within the confined slit. The surface oxygen not only passivate the Cu active sites to diminish the graphene nucleation density, but also lower the surface reaction barrier to accelerate the growth rate. Fig. 2 (d) shows the size of graphene grains is up to millimeter scaled before coalescence.

III. CONCLUSION

In cooperation of $FeCl_3$/HCl surface pretreatment and surface pre-oxidation, the millimeter-scaled high-quality large graphene single crystals can be achieved in confined reaction slits. Without height-confined reaction slits, the graphene nucleation also can be retained less than 600 nuclei/cm^2. The success of this work would pave a new way for graphene industrial production and their potential applications in the future.

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Figures

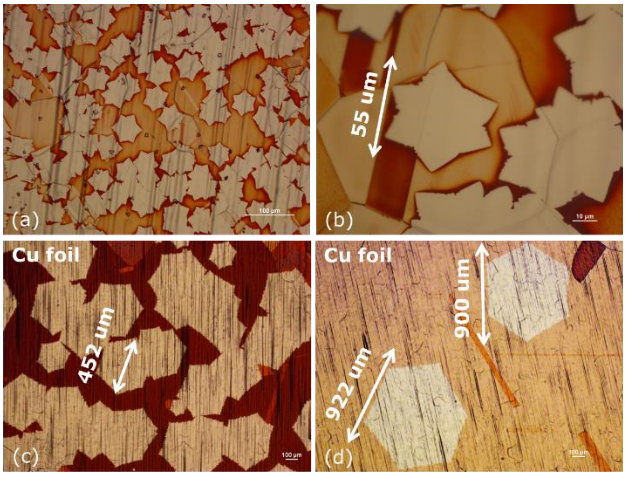

Figure 1. (a) Conventional CVD process. The size of graphene grains is normally less than 50-60 µm. (b) The close inspection of (a) shows graphene grains can grow across different Cu grains. (c) Cu surface pre-treatment in $FeCl_3$/HCl solution. About 600 nuclei/cm^2 has been successfully achieved. (d) the millimeter-scaled graphene single crystal grown on $FeCl_3$/HCl pretreated Cu foils can be further accomplished through a well-designed confined CVD reaction slit.

Advanced nano-electrical characterization of solar cells and 2-d materials with atomic force microcopy

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A Over the past 30 years, Atomic Force Microscopy has evolved from a microscope to measure just the surface topography to a wide variety of measurement modes that provides a way to characterize other atomic interactions or physical properties like magnetic field, electric field, nanoscale dissipation processes, thermal conductivity, electrical conductivity, resistance, surface potential, piezoresponse, Young modulus,… Electrical nanocharacterization with AFM has emerged as a powerful tool to map electrical properties at the nanoscale, like surface potential (work function) and conductivity. However, traditional setups in AFM make difficult to obtain accurate and repeteable results over several types of samples.

In this contribution we will show the capabilities new developed AFM modes: High Definition Kelvin Force Microscopy (HD-KFM), ResiScope, Soft-Resiscope and Scaning Microwave that overcome the intrinsic difficulties of electrical nanocharacterization with AFM. This techniques have been applied on a variety of 2-D materiales surfaces, like graphene or molibdene disulfide samples providing high stability, sensitivity and lateral resolution.

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Figures

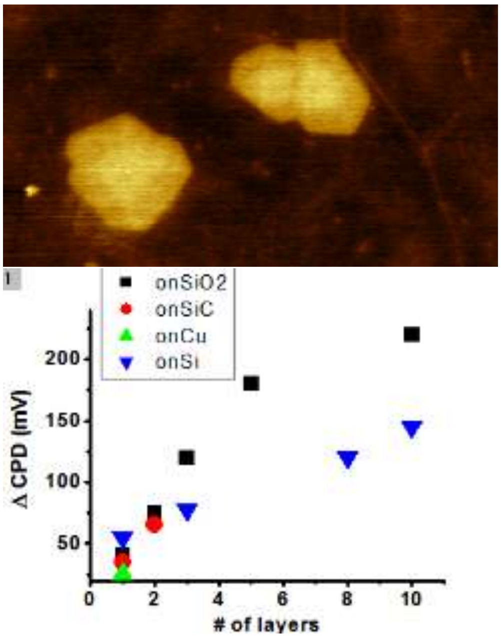

Figure 1. (Up) HD-KFM image of graphene on Si sample. Brown areas correspond to 1ML and yellow areas to 2ML/3 ML of graphene. (Down) SP values on of graphene on different substrates.

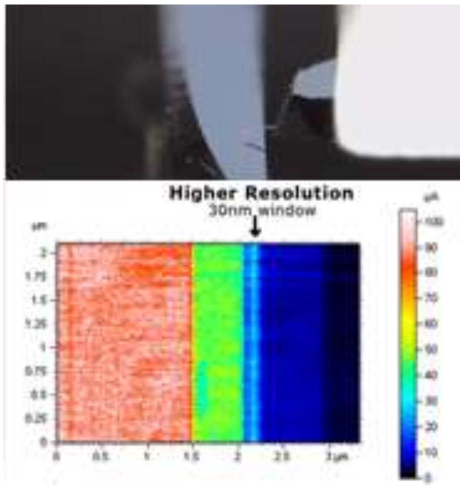

Figure 2. ResiScope measurement on a cleaved solar cell. (Up) lateral view of the conductive tip. (Down) Resistance image of the solar cell cross-section showing the cross-section of a cleaved solar cell showing the 30 nm back field layer.

Single-Enzyme Nanogels for High-Performance Nanobiocatalysis

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In order to potentiate biocatalytic processes, a simple, one-pot, enzyme encapsulation protocol was developed to produce single-enzyme nanogels (SENs).[1]
SENs exhibit overall improved resistance against thermal degradation and proteases, enhanced tolerability to organic solvents, as well as retention of catalytic activities of enzymes over broadened pH ranges.[1,2] Additionally, controlled surface immobilization of multiple SENs was successful by patterning *via* microcontact printing onto thiol-functionalized glass surfaces.[2]
A careful regulation of the overall reagent concentration during polymerization efficiently ensures full control over the generation of the crosslinked polyacrylamide layer at the surface of the enzyme molecules. Thicknesses in the range of 0.5–8 nm may be attained for SENs, ensuring regulation of catalytic activity vs. improved enzyme stabilization.
These features overall concur to the development of robust nanobiocatalysts, showing broadened ranges of enzyme applicability. Further, a library of hydrophilic polymers and enzymes were screened for the successful formation of SENs. The addition of 5 w/v% sucrose allowed for a surface-directed polymerization, without the need to pre-modify the protein surface.[1] Biocompatibility was ensured by the formation of SENs based on FDA-approved polymers that do not show any immunogenicity onto humans.[3] The formation of a thin crosslinked polymeric layer at the surface of biologically relevant enzymes is a solid approach for improved resistance to proteolytic degradation or immunogenicity, when compared to conventional surface grafting of linear polymers.[4]

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Figures

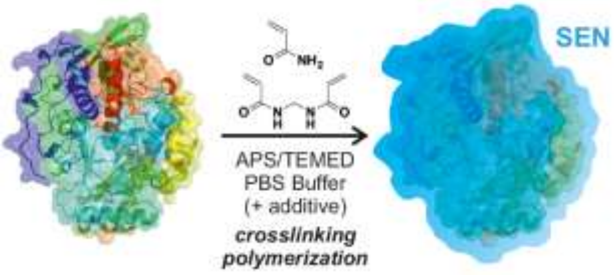

Figure 1. SEN formation via a one-step, free-radical crosslinking polymerization.

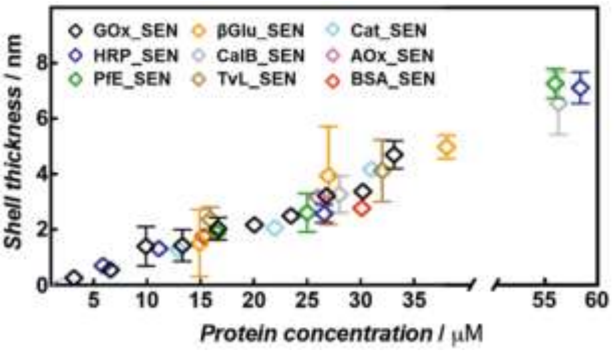

Figure 2. SEN formation as a protein-independent process.

Nanofibrous membranes with antifouling properties

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Decreasing supply of drinking and service water is a big worldwide problem that has an increasing tendency in these days and the need for new water supplies, or reuse of waste water, is crucial nowadays. In addition to the natural factors affecting the world water cycle system, people through their technological development, institutional and financial conditions are contributing to ever increasing demands to fresh water. This requires a new efficient low-cost form of sewage treatment with lower energy and chemicals consumption. This approach can guarantee that the environment will be less negatively affected and there should be sustainable development for all humanity.

Our research team tries to solve this problem through enhancing the current membrane filtration processes by modifying the fibrous polymeric substrate, which would allow the preparation and subsequent production of nanofibrous filter membranes with new properties. Basic fiber-forming matrix will be modified by incorporation ammonium quaternary salts into a polyurethane polymeric chain. The generalized polyurethane base unit is shown in Figure 1.

Selection of suitable primary monomers has an impact on the possibilities of preparation of a polyurethane matrix with properties compatible with an electrostatic forming device for preparation of nanofibrous membranes. This is a technological issue that has been solved within our research project. SEM images of nanofibrous structures are captured in Figure 2.

The main idea of our project is to prepare structures with increased resistance to the development of microbial biofilms through incorporation of suitable functional groups directly into the polymeric backbone of the basic copolymer and preparation of nanofibrous structures by electrospinning of the prepared matrix. The presentation will be divided to explanation of our approach to modification of polyurethane fibers by quaternary ammonium salts, to formation of nanofibrous membranes by electrospinning and finally to results from monitoring of dynamics of Escherichia coli (CCM 3954) and Pseudomonas aeruginosa (CCM 3955) biofilm development.

Figures:

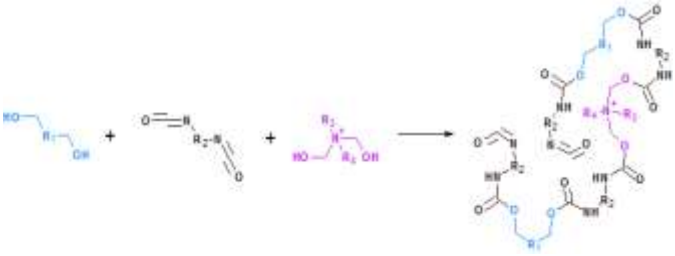

Figure 1. Generalized base unit of prepared polyurethane

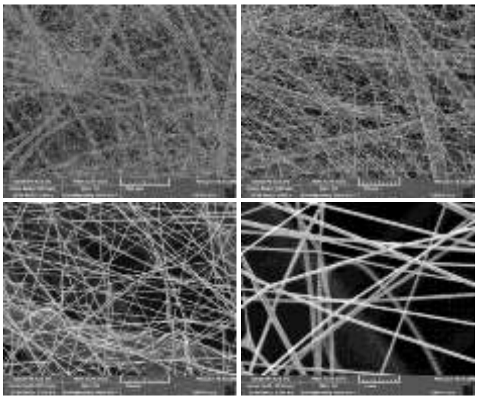

Figure 2. SEM images of prepared nanofibrous membranes

SHG enhancement by TiN metasurfaces

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Enhancing the nonlinear frequency conversion efficiency at the nanoscale plays an important role in advanced spectroscopy, material science and sensing. Prior work has shown that plasmonic structures can significantly enhance a nonlinear signal due to the localized surface plasmon resonance (LSPR) [1]. More recently, epsilon-near-zero (ENZ) materials have been shown to enhance optical nonlinearities if pumped at the ENZ wavelength in thin films [2]. Here, we explore a new mechanism to augment nonlinearities by combining the LSPR of nanostructures forming a metasurface and the ENZ enhancement of the nonlinear medium [3]. We probe the second harmonic generation (SHG) in nanofabricated titanium nitride (TiN) split-ring resonators at visible wavelengths, where TiN exhibits an ENZ resonance (Figure 1a). When the excitation polarization is parallel to the ring gap, both the electric mode (high energy), which arises from the electric dipole of the two vertical bars of the resonator, and the magnetic mode (low energy), which arises from the circulating current along the ring, are observed. By increasing resonator size, we can engineer both the electric and magnetic resonances, which are then red shifted. Here, the magnetic resonance of the meta-elements is designed to be resonant with the fundamental wavelength, achieving in this way a double resonance effect. Our experimental results show that the measured SHG signal is most strongly enhanced when the ENZ wavelength matches the SH wavelength, while simultaneously the magnetic resonance matches the excitation wavelength (Figure 1b).

With its refractive nature and CMOS compatibility, our results advocate considerable promise of TiN micro and nanostructures in integrated on-chip nonlinear optical devices.

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Figures

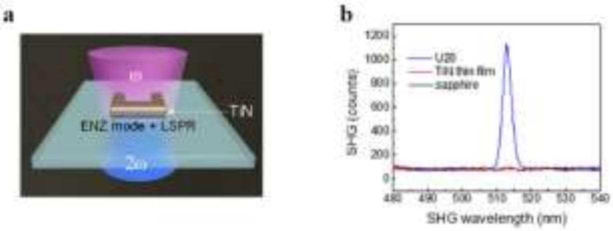

Figure 1. a) Schematic of the SHG in TiN nanoresonators which simultaneously sustain an ENZ resonance and LSPR. b) Comparison between the ENZ-enhanced SHG of TiN film and double resonance (ENZ + magnetic resonance) enhanced SHG in resonators. For TiN spit-ring resonators with a bar width of 20 nm, the SHG signal is much stronger than homogenous TiN thin film. The SHG of the substrate sapphire is displayed in black curve for reference.

Giant increase in mechanical Q-factor of SWCNT induced by external voltage

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Individual Single Wall Carbon Nanotubes (SWCNT) were grown *in-situ* by Field Emission (FE) assisted Chemical Vapor Deposition (CVD) at the apex of etched tungsten (W) tips using a procedure presented in previous work [1]. Mechanical flexural resonances were afterwards excited in Ultra High Vacuum (UHV) by bringing a nearby electrode at an oscillating potential V_{AC} at the mechanical eigenfrequency (f) while a constant negative voltage V_{DC} is applied on the W tip with SWCNT in order to extract electrons by FE, as presented on Fig.1. This FE current is then amplified by a Micro-Channel Plate (MCP) and sent to a phosphor screen where it forms a FE pattern. Mechanical motion of the nanostructure is detected either by the broadening of the FE pattern [2] or by lock-in downmixing in the amplified FE current of a low frequency component added in the AC signal by frequency modulation (FM) [3].

The FE voltage V_{DC}, on the order of 100V, induces an important axial stress on the SWCNT and therefore increases the eigenfrequencies, like on a guitar string [4] (Fig. 2). The novelty of this study made on four different SWCNT samples is that this high stress also induces a dramatic increase of the room temperature resonances' quality factor Q as presented on Fig. 2. Q factors superior to 25000 were obtained, exceeding by two orders of magnitude typical room temperature values in literature [5]. We attribute such high Q factors to the relative isolation of our sample, minimizing therefore external energy decay channels. Moreover, the relative increase in the Q factor with V_{DC} highly exceeds the eigenfrequency relative increase, therefore indicating an important reduction in dissipation.

Eigenfrequencies' and Q factors' tuning with V_{DC} can be described by a simple theoretical model based on viscoelastic behavior of the SWCNT (*i.e.* complex Youngs' modulus) and complex mechanical impedance at the clamping. The reason of the dramatic Q factor increase is that axial stress strongly decreases the rod's curvature, and therefore viscoelastic losses, and localizes this curvature at the clamped end increasing the impedance mismatch for acoustic waves radiated in the supporting tip.

We achieve here Q*f products exceeding 17THz, which opens new perspectives in extremely localized force sensing at room temperature.

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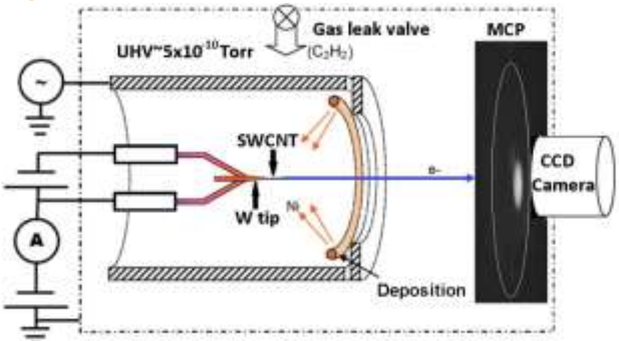

Figure 1. Experimental UHV setup.

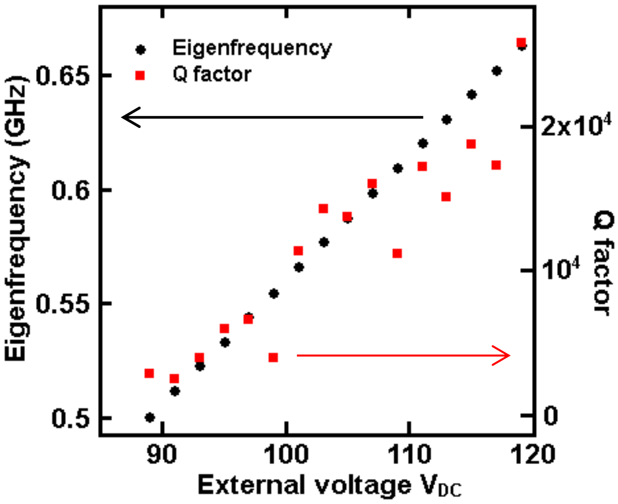

Figure 2. Evolution of the mechanical eigenfrequency and of the Q factor with the applied voltage.

GaAs-AlGaAs nanowire quantum well tubes: self-assembly and nano-scale spectroscopic imaging

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III-V compounds nanowires (NWs) have attracted considerable research interests in recent years, due to their potential applications to novel nano-scale photonic devices, such as nano-lasers, photo-detectors and solar cells. Radial modulation of NW composition to form core-(multi)shell hetero-structures impacts the design of such nano-devices by adding new degrees of freedom associated to quantum confinement [1,2]. Understanding of their nano-scale optical (radiative) properties and correlation with their self-assembly mechanisms are however, necessary to gain full control over their epitaxial growth.

In this work we report on the metalorganic vapor phase epitaxy (MOVPE) of free-standing GaAs-AlGaAs core-multishell NW quantum hetero-structures, their spectroscopic characterization by low temperature photoluminescence (PL) and cathodoluminescence (CL) measurements, and their correlation to the nanostructure dimensions. Dense arrays of vertically-aligned GaAs NWs were fabricated by Au-catalyzed self-assembly, and radially overgrown by two AlGaAs shells between which a few-nm thin GaAs shell was introduced to form a quantum well tube (QWT). Besides the free-exciton emission of the GaAs core, the PL spectra of present NWs show an additional broad peak at higher energy ascribed to recombination of electron and hole confined states within the GaAs QWT, whose emission blue-shifts with shrinking of the QWT thickness. CL imaging performed in a field-emission scanning electron microscope (FE-SEM) enabled to spatially resolve these emissions and to observe spatial inhomogeneity of the GaAs QWT emission along the NW trunk, further ascribed to thickness fluctuations of the QWT. Moreover, AlGaAs emission channels related to unintentional formation of Al-rich alloys within the nanostructure (as result of the Au-catalyst assisted growth mechanism [3]) is evidenced close by the Au-catalyst droplet. Present findings are discussed based on self-assembly mechanisms of NWs.

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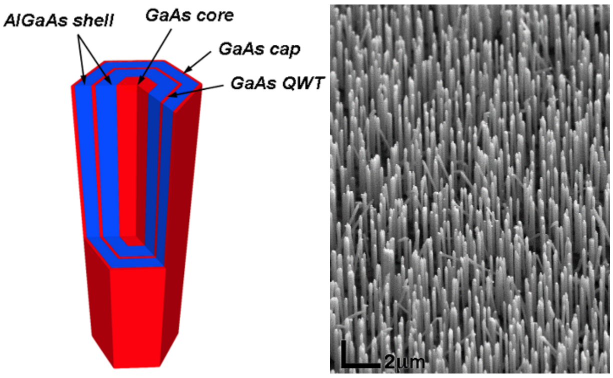

Figure 1. (a) 3-dimensional schematic of a GaAs-AlGaAs core-multishell NW quantum structure; (b) FE-SEM micrographs (45°-tilted view, 10,000× magnification) showing the morphology of as-grown GaAs-AlGaAs core-multishell NWs vertically standing on their original (111)B-GaAs substrate.

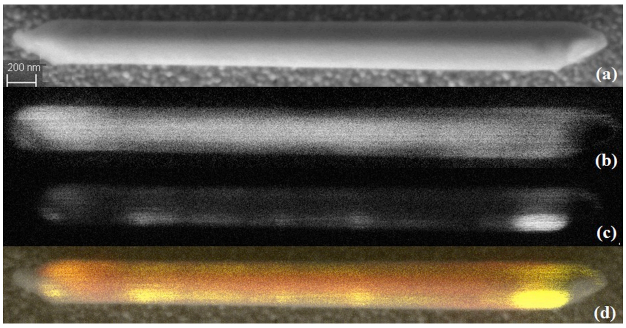

Figure 2. (a) FE-SEM micrograph of a single core-multishell NW. Monochromatic CL images of the NW emission recorded at (b) 1.507 eV (core emission) and (c) 1.540 eV (QWT emission). (d) color-coded (red: core; yellow: QWT) superposition of the two images in (b) and (c).

Arrays of exchange coupled magnetic nanostructures for permanent nanomagnets

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The purpose of this work is to fabricate nanostructured silicon with two different materials of embedded magnetic nanostructures to exploit the magnetic properties of both metals and gain control of the exchange coupling between the two metals especially with respect to their volume ratio. Furthermore a variation of the structure size and the proximity of the metal deposits modify the exchange coupling and thus the energy product.

Two different templates, porous silicon (PSi) and porous silicon nanotubes (SiNTs) are utilized to achieve such nanocomposites. The morphology (pore diameter, tube diameter) of the two systems is comparable. In the case of the utilization of PSi templates a mesoporous morphology with average pore diameters of 50 nm are used and these oriented and separated pores are filled with two different metals, namely as a first attempt Ni and Co. The two metals are deposited alternatingly by electrodeposition. A further approach is the chemical growth of Co nanoparticles within SiNTs [1] and the additional deposition of a Ni layer on the outer surface of the tubes which is shown in figure 1. Since the silicon wall of the tubes offers a porous structure the Co particles, which are localized near the pore surface on the wall of a given nanotube, can touch the Ni layer. An alternative structure involves the deposition of an additional Si layer (after the growth of Co particles inside the tubes) as a spacer before the Ni deposition.

In the presented work the dependence of the magnetic properties of a nanostructured silicon/bi-metal nanocomposite on the volume ratio of the metals, on the proximity of the nanostructures and also on the size of the metal deposits has been figured out. If the distance between the deposited bi-metal structures is small enough magnetic exchange coupling between them is present which could be observed. By tuning the bi-metal deposition an optimized energy product is achieved which gives rise to self-assembled nanocomposite systems containing permanent nanomagnets and arrays of them, respectively for on-chip applications.

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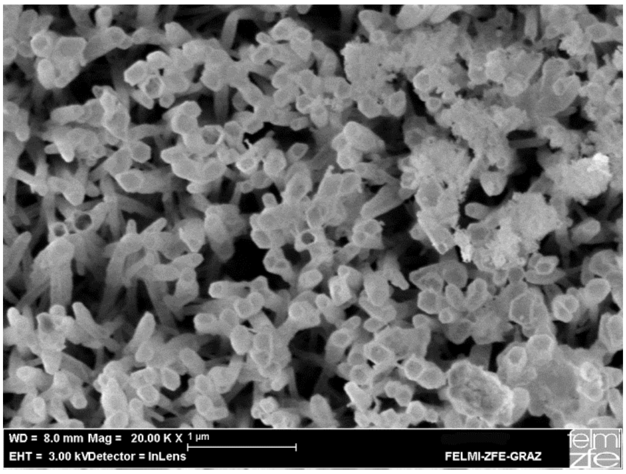

Figure 1. Silicon nanotubes with chemically grown Co particles inside and a Ni layer covering the outside of the tubes.

Implementation of 2PL 3D nanofeatured microscaffolds and optogenetics

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Abstract

Optogenetics is a relatively new technique combining optics and genetics to gain control (activating or deactivating) over specific molecular events in cells, tissues or organisms.

One great advantage of this technique is the possibility of using light-activated molecular tools to get control of whole-cell or whole-tissue dynamics as well as on sub-cellular compartments, in both cases with high spatio-temporal resolution in intact systems[1,2] .

The approach we are developing is based on the combination of 2PL structures and optogenetic tools to gain optical control over invasive properties of human tumor cell lines within three-dimensional environments. This will be achieved by developing an optical setup able to redirect a laser beam in three-dimensions to guide the cells within 3D environments with different stiffness. The possibility offered by the optical setup opens the road towards the study of tumor cell invasiveness of 3D environments in real time while modulating their mechanical properties.

The molecular tool we exploit to gain control over cell dynamics has been described by Wu and colleagues[3], who conceived a photoactivatable form of the cytoskeletal protein Rac1 (PA-Rac1) by fusing a light-oxygen-voltage (LOV) sensitive domain expressed in plants to Rac1 N-terminus. Since Rac1 is physiologically involved in cytoskeletal rearrangements, we stably express PA-Rac1 in human tumor cell lines for studying cell mechanics upon light activation (Figure 1).

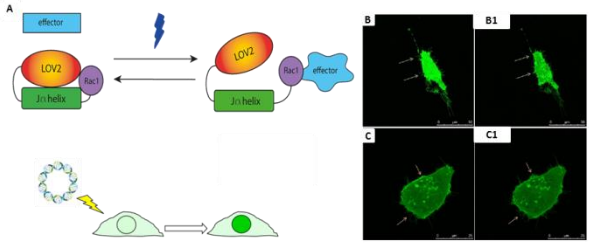

***Figure 1 PA Rac1 transfection.** Panel A show a schematic representation of Rac1 photoactivation upon 470 nm light illumination and the mechanism to make tumor cells expressing PA Rac1. Panels B-C1 show Rac1 expression in HeLa transfected cells.*

Since Rac1 takes part in many intracellular pathways (including transmigration at the nuclear envelope and nucleoplasm), we exploit our results on 3D micro cages and PA-Rac1 transfection to determine how and at which extent nuclear mechanical properties influence the invasive process. This is possible by controlling Rac1 activation with high spatio-temporal resolution.

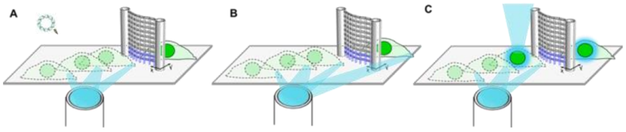

***Figure 2 Implementation of 2PL 3D microscaffolds and optogenetics**. Schematic representation of photoactivation of Rac1 in 3D microfabricated environments to study cell mechanical properties (invasiveness/stiffness)*

Overall, the combination of 3D 2PL and optogenetics will allow for simultaneous **photoactivation, live cell imaging and cell dynamic control in 3D microenvironments** thus finally discriminating between "external" and cellular contribution to the invasive or, more in general, cell mechanical cell behaviour.

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Effect of Benzo perylene monoimide on opto-electronic properties of Cd-doped ZnO nanostructures

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Abstract

CdZnO nanostructures have sparked worldwide interest because of increased surface to volume ratio which has great effect on material properties leading to its potential applications in nano-scale optoelectronics [1]. It is crucial to obtain highly ordered nanostructures to enhance performance of such devices. Hybrid inorganic/organic nanostructures comprising of layers of benzo perylene monoimide and Cd-doped ZnO called CZO nanohybrids were electrochemically synthesized on Ga-doped ZnO/Si [2]. Inorganic Cd-doped ZnO called CZO nanorods were also synthesized in order to study the effect of the peptide organic surfactant.

FESEM studies in Figure 1 reveals formation of inorganic CZO nanorods and ordered lamellar CZO nanohybrids without and with the use of benzo perylene monoimide, respectively.

Low temperature photoluminescence measurements were performed with the temperature variation from 80 K to 300 K. White emission was seen from both CZO nanorods and nanohybrids at low temperatures while orange emission around 600 nm associated due to peptide was evident in case of nanohybrids. The temperature dependent PL spectra follow characteristic band gap shrinkage according to Varshni relation Figure 2.

Temperature dependent photosensitivity measurements reveal the nanohybrids were highly photosensitive. The nanohybrids were 8x and 4x more photosensitive than nanorods at 80 K and 300 K, respectively. These nanohybrids have potential applications as photodetectors and light-emitters.

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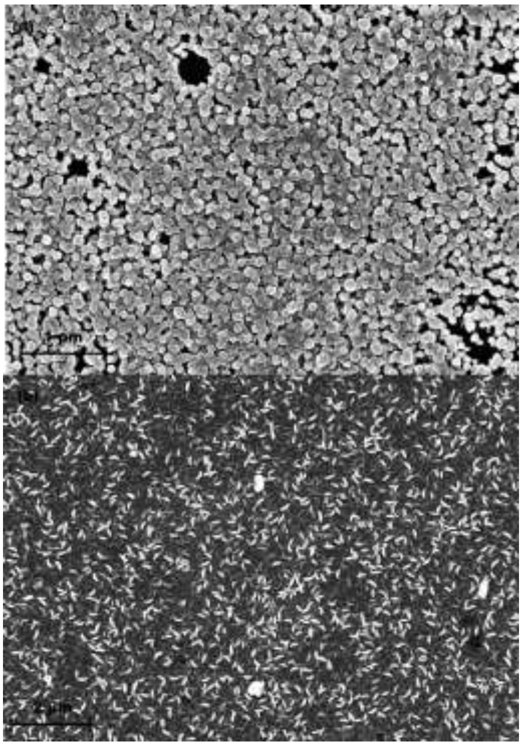

Figure 1. FESEM images of a) CZO nanorods and b) CZO nanohybrids.

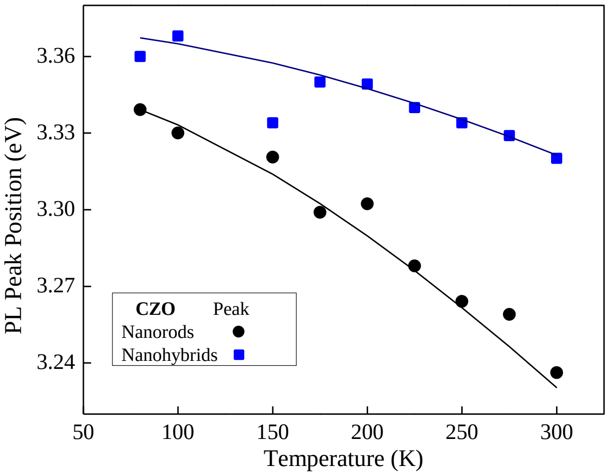

Figure 2. Varshni fitting for CZO nanorods and nanohybrids.

Fabrication via Contact Printing: Chemical and Physical Sensors from Cross-Linked Nanoparticles

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Layered nanocomposites based on graphene, carbon nanotubes, or noble metal nanoparticles are excellently suited for the fabrication of various types of healthcare sensors. For example, layered nanocomposites deposited onto polymeric substrates can be employed as epidermal pulse wave sensors or for monitoring of muscle activity [1,2]. Further, thin films of gold nanoparticles (GNPs) can be used as highly sensitive chemiresistors [3], rendering them interesting for the detection of volatile compounds transpired from skin or contained in exhaled breath. Thus, these sensors can be used for medical diagnosis [2].

However, the development of robust and cost-efficient fabrication schemes for such sensors remains extremely challenging. Here, we present a simple and versatile method for printing physical and chemical sensors based on layered nanocomposites.

In particular, we show how thin films of cross-linked GNPs can be transferred onto various substrates via contact printing to produce different types of sensors. In one approach, spin-coated GNP films are peeled off with a PDMS stamp and transferred via contact printing onto flexible or rigid substrates equipped with suitable electrodes. For example, we present the fabrication of very sensitive and robust strain gauges by stamping GNP films onto flexible polyimide substrates. When taped onto the skin, these sensors can be employed to monitor muscle movements. Further, such sensors can also be applied as flexible chemiresistors, which are interesting for the design of wearable gas sensors. In another example, we printed GNP-films onto 3D-structured substrates to produce freestanding GNP membranes. These microelectromechanical systems (MEMS) can be employed as resistive pressure sensors [4] (see Fig. 1a), or as electrostatically driven resonators [5], which can also be used as gas sensors [6].

Finally, using a modified approach, we prepared an all-printed, highly flexible pulse wave sensor. First, a PDMS sheet is furnished with silver paste electrodes via dispenser printing. The PDMS sheet is then used to peel off the spin-coated GNP film. After taping the thus fabricated all-printed strain sensor onto the skin above the radial artery, well-resolved pulse wave signals could be recorded, enabling a clear discrimination of diagnostically valuable waveform components (see Fig. 1b).

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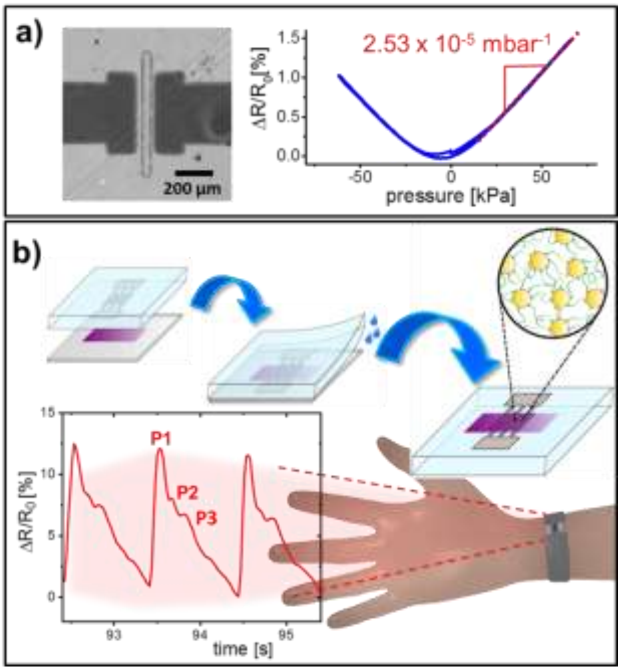

Figure 1. a) Micrograph of printed barometric pressure sensor based on a GNP membrane (left); transfer function (right). b) Scheme for the fabrication a GNP based pulse wave sensor with measured transients.

Printable Down-/Up-Conversion Fluorescence Inks for Anti-Conterfeiting Applications

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Abstract

Fluorescence materials including up-conversion and down-conversion fluorescence materials play a crucial role in encoding information for anti-counterfeiting because of their inherent optical properties and stability against degradation. However, the current optical anti-counterfeiting labels have a limited capacity for information storage or complexity to prevent counterfeiting. Here in, we developed a series of anti-counterfeiting labels based on various fluorescence inks of $CsPbX_3$ (X=Cl, Br, I) perovskite quantum dots (PQDs), red-green-and blue (RGB) emissions $NaYF_4$ up-conversion micro-particles (UCMPs) [1-2] and dual-mode luminescent $NaYF_4$:Er,Yb (Tm)/carbon dots [3] via straightforward and low-cost strategies, including spin-coating, stamping, screen printing, inkjet printing and roll-to-roll printing. Under ambient conditions, the printed patterns are invisible, while, all the patterns could display colorful, designable and high-resolution patterns under near-infrared (NIR) or ultraviolet (UV) light excitation. All tunable and versatile transparent anti-counterfeiting labels based on as-prepared fluorescence inks possess the merits of easy-manufacture and high concealing, underlying the practical application for high-capacity information encoding and protecting the switch of authentic goods.

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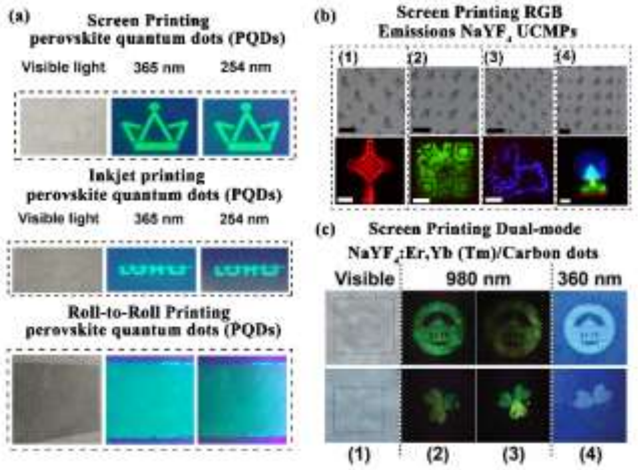

Figure 1. Versatile optical micrographs of the printed patterns based on different fluorescence inks through various printing strategies. (a) Screen printing, inkjet printing and roll-to-roll printing perovskite quantum dots (PQDs) inks. (b) Screen printing RGB emissions $NaYF_4$ UCMPs inks. (c) Screen printing dual-mode luminescent $NaYF_4$:Er,Yb (Tm)/carbon dots inks.

Figure 2. Printable up-/down-Conversion fluorescence inks including PQDs, UCMPs and dual-mode luminescent UCMPs/carbon dots inks for banknotes protection applications.

Partially reduced graphene/silicon interfaces via electrochemical reduction

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Abstract

The relatively recent progresses in the characterization of true graphene deposits have allowed a much better interpretation of results in the field, also allowing for a comparison between the outcomes of distinct synthetic strategies aimed at partially reduced forms of graphene oxide.[1,2] A notable goal in view of studies and applications of graphene is the obtainment of handy forms of this material, allowing for developments in real conditions. To achieve applications, a large-scale production of high quality graphene sheets in an efficient and effective way is required.[3]

Wafer-scale integration of reduced graphene oxide with H-terminated Si[111] surfaces has been recently accomplished by electrochemical reduction of a thin film of graphene oxide deposited onto Si by drop casting.[4,5] Distinct reduction methods have been assayed and carried out in solution. The resulting interface has been characterized in its surface composition, morphology and electrochemical behavior by X-ray photoelectron spectroscopy, Raman spectroscopy, atomic force microscopy and electrochemical measurements. The results evidence that few-layer graphene deposits on H-Si[111] were obtained after reduction, with a very limited surface oxidation of the Si substrate and a very low oxygen-to-carbon ratio. The described approach is fast, simple, economic, scalable and straightforward, as one reduction cycle is already effective in promoting the establishment of a graphene-Si interface. It avoids thermal treatments at high temperatures, use of aggressive chemicals and the presence of metal contaminants, and enables preservation of Si[111] surface from oxidation. This may favour applications in biomedicine, rapidly growing innumber and importance in the last few years.[6]

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TNT2018 Orals - Students Contributions

Protein stabilized nanoformulation of a superfluorinated 19F-MRI contrast agent

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19F-MRI has indeed emerged as one of the most promising diagnostic tools providing hot spot imaging along with 1H-MRI. Here, we report a unique fluorinated imaging agent PERFECTA [1] bearing 36 equivalent 19F atoms and therefore showing a single, intense resonance peak. Most of the superfluorinated contrast agents are highly hydrophobic, which makes their use it difficult to be used as they are in biological environment systems. In this work, an ampiphilic molecule protein, hydrophobin (HFBIIfb), which is a natural biosurfactant protein with filming properties, was used to disperse PERFECTA in aqueous solutions. We optimized a protocol to obtain colloidally stable formulations of PERFECTA. The obtained formulations were characterized by NMR, DLS, 19F-MRI and FTIR. The results showed that these nanoformulations were composed of monodispersed PERFECTA nanoparticles coated by a HFBIIfb shell and have good NMR relaxation times to be used as 19F-MRI tracking contrast agents [Figure 1]. Cytotoxicity and cellular uptake studies in HeLa and MG 63 cells also demonstrated nanoparticle biocompatibility. Thus, the obtained nanoparticles represent a versatile theranostic platform that could be further used to deliver therapeutic drugs and nucleic acids.

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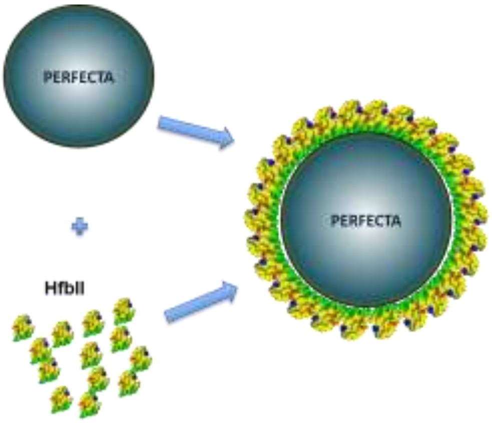

Figure 1. Nanoparticleformulation of the superfluorinated contrast agent PERFECTA coated with a HFBII shellfb.

Abbreviations: MRI-Magnetic Resonance imaging; H-MRI: Hydrogen MRI; F-MRI: Fluorine MRI; Hfb-Hydrophobin

Atomistic far-field currents in graphene – how to include DFT-precision regions in large-scale tight-binding

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Graphene has proven to host outstanding mesoscopic effects involving massless Dirac quasiparticles travelling ballistically over several µm [1]. Atomistic large-scale simulations of the current distribution far from the injection source (“far-field currents”) in graphene are accessed via the tight-binding (TB) model for π-orbitals, where specific parametrizations can be used to include a wide variety of effects such as p-n junctions, magnetic fields or absorptive apertures [2,3,4]. These simple empirical models, however, cannot capture the chemical details of the injection region and/or defects, which are of highest importance due to localized effects such as e.g. charging effects and deformations.

Here we present an atomistic multi-scale method to include regions treated with Density Functional Theory (DFT) into large-scale parametrized TB models within the context of non-equilibrium Green’s function (NEGF) transport calculations. We will show how the far-field currents look by injecting electrons from DFT-precision STM tips in atomic contact with graphene-based devices and highlight how the symmetry of the states at the point contact are reflected in the far-field. We will also provide an overview of the used computational methods, based on the TranSiesta, TBtrans and sisl toolboxes [5,6], whose combination allows for extreme scale NEGF transport calculations.

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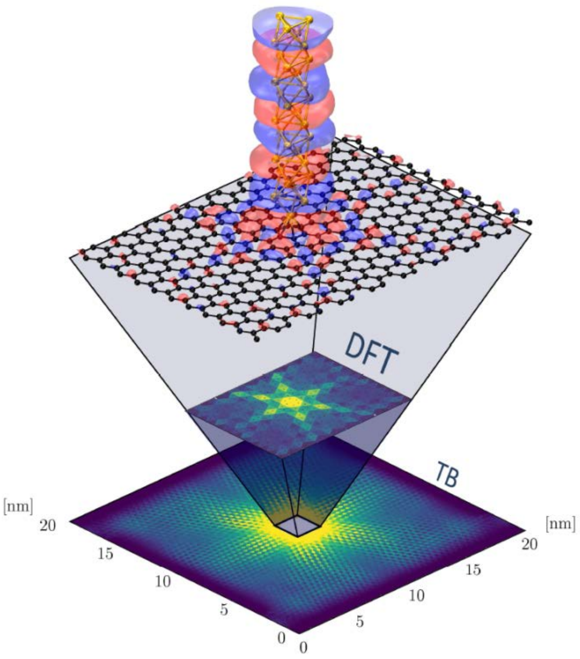

Figure 1. DFT-precision region with STM tip in atomic contact with graphene, embedded into a larger TB pristine graphene region. The six-fold symmetry of the transmission eigenchannel (top) is reflected in the near- and far-field currents observed in DFT (center) and in the larger TB (bottom).

Evidence for Strong Coupling Phenomena in Molecular Plasmonic Switches: a Density Functional Theory Study

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The recent field of quantum plasmonics offers the possibility to connect the apparently distant worlds of molecular electronics and photonics [1]. This represents nowadays a fascinating challenge for the scientific community, opening crucial topics such as the electro-optical control at the nanoscale of the properties of hybrid metal-molecule systems.
Here, we propose a *Time-Dependent Density Functional Tight-Binding* (TD-DFTB) study with the aim to understand, through a full quantum mechanical approach, the physics of interactions between an optically switchable molecule and a localized surface plasmon excitable in a cluster of a few silver atoms.
In more detail, figure 1 clearly shows how the plasmon excitation of the tetrahedral Ag_{20} cluster can be optically controlled by putting the nanoantenna in proximity of the same molecule (stilbene) in two different spatial conformation (-*trans* and -*cis*). By simply activating the molecular switch, it is possible to move from a small shift of the plasmonic peak registered in the case of -*cis* configuration (see grey curve compared to the orange one) to a couple of well distinguishable peaks resembling, in the -*trans* case, the Rabi-splitting usually appearing in presence of strong-coupling phenomena.
This results in the proof-of concept of a plasmonic switch behavior in which one can activate (-*trans* state) or quench (-*cis* state) the splitting by coupling or decoupling, on demand, the molecular and plasmonics counterparts.

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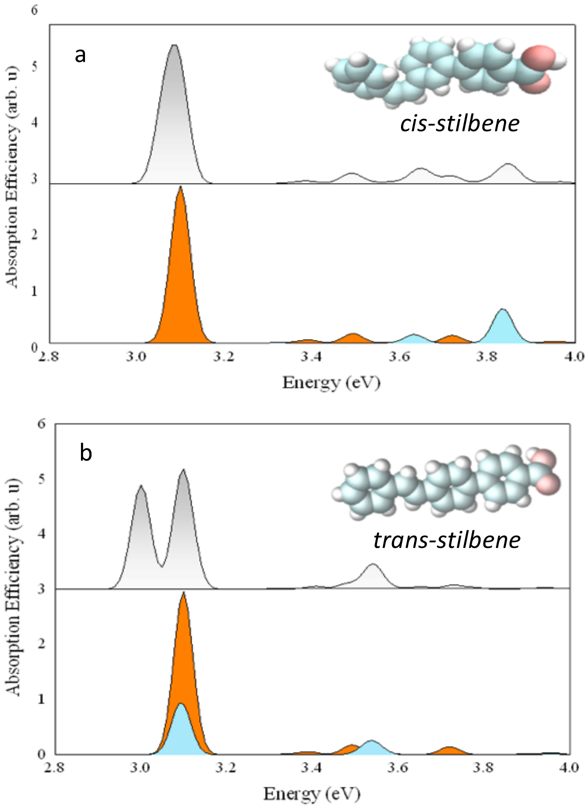

Figure 1.
Optical control of the plasmon excitations of silver nanostructures through the activation of the stilbene *cis-* (panel a) and *trans-* (panel b). The grey filled curves are the TD-DFTB absorption spectra of the whole systems while the orange and light blue filled curves are the TD-DFTB absorption spectra of the Ag_{20} and the molecules, respectively.

Scanning tunneling microscopy and spectroscopy on Au islands on top of graphene/Rh(111)

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Using scanning probe techniques we investigated how graphene (gr) electronically interacts with substrates in the presence of metallic islands on top of the gr layer. In the case of rhodium (Rh) as a substrate, the band structure is significantly altered with respect to freestanding graphene due to the hybridization of the Rh *d* orbital with the p_z orbital of gr [1].

Using scanning tunneling spectroscopy (STS) the electronic properties of Au Islands on top of gr were investigated. The islands were deposited by in-situ evaporation. Subsequently their relative orientation with respect to the gr lattice was analyzed by scanning tunneling microscopy (STM) in as shown in Figure 1. The STS measurements on and in the vicinity of the islands show locally varying electronic properties of the Au/gr/Rh(111) system. One related phenomenon is an increase in conductivity at the boundary of the islands, compared to the conductivities at the center and also to that of gr. Measurements show that this increase in conductivity is restricted to that area of the islands which directly adjoins to the gr. An Rother phenomenon consits in conductance steps at the center of the gold islands observed at room temperature.

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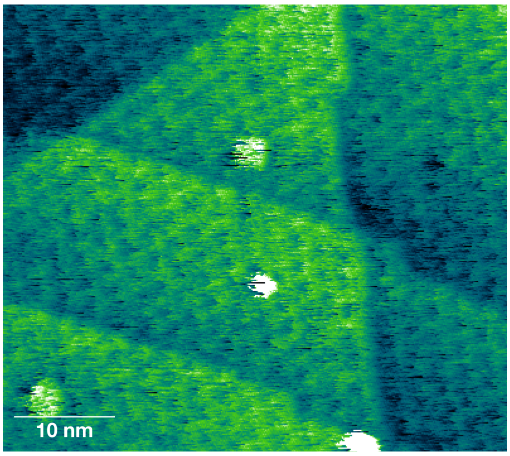

Figure 1. STM image of four Au islands on graphene/Rh(111). The graphene on Rh(111) forms a regular Moiré pattern that is clearly visible. Sample bias *U* = 0.1 V, tunneling setpoint I_T = 0.1 nA.

Polydopamine-functionalized superparamagnetic clusters as theranostic system

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Abstract

In recent years, the applications of nanotechnologies have made it possible to design smart nanosystems able to respond with physical-morphological modifications to the environmental characteristics typical of tumor tissues.[1] In this work, we propose and demonstrate the synthesis of bioinspired polydopamine-functionalized superparamagnetic clusters (MNC@PDO) to be applied as a magnetic field-guided theranostic system. This nanocomposite combines the capabilities of highly sensitive magnetic resonance imaging (MRI) and the delivery of cisplatin for cancer therapy. In this scenario, the first synthetic step is based on an oil-phase evaporation-induced self-assembly strategy, to fabricate the magnetic nanocrystal cluster (MNC). We demonstrated that the choice of the best size and volume of SPIONs, the adopted solvent and the surfactant concentration are very important parameters. With this approach, we can produce nanoclusters with a high density of magnetic cores, a size comprised between 90 and 100 nm, and a multilayer structure. Secondly, the surface of the MNCs was functionalized with polydopamine (PDO) for improving their stability;[2] moreover, different concentrations of dopamine were assayed to determine the best compromise between stability of the clusters and loading capacity. Finally, the cisplatin was grafted to the surface of stable MNC@PDO systems (MNC@PDO-cisplatin), studying its release efficiency from these nanoparticles. The MNC@PDO systems reveal to be promising models for the uptake and specific tissue delivery of chemotherapeutic drugs. Furthermore, the MNC@PDO nanosytem shows a pH-responsive behaviour of great significance in controlled drug delivery and targeting of specific sites. The antitumor potential of MNC@PDO-cisplatin was tested against HeLa (cisplatin-sensitive human cervical cancer cells) and MCF-7 (cisplatin-resistant human breast cancer cells). As expected, the drug carrier significantly improves the cellular uptake of platinum drugs. The cytotoxicity of the drug-loaded system is higher, or at least comparable, than cisplatin administration.

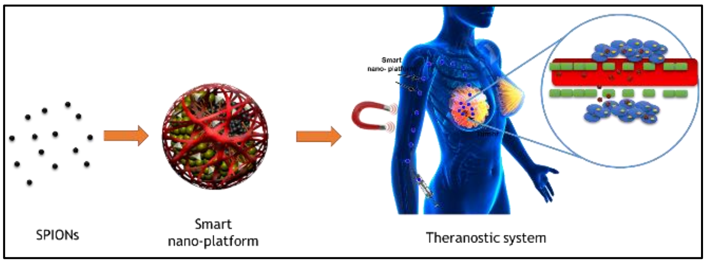

Fig. 1 Illustration of the synthesis procedures and magnetic field–directed theranostic applications of the theranostic MNC@PDO system.

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Ultrathin flexible AlN-based smart patch for vascular graft monitoring

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Prosthetic vascular grafts are widely used to bypass diseased vessels. However, prosthetic failure can occur without premonitory symptoms; thus continuously monitoring the system can provide useful information not only to extend graft life but even for optimization of patient therapy. In this respect, various techniques have been used but all of them affect the mechanical properties of artificial vessel because of their dimensions, extreme stiffness, and the need to be in contact with the blood stream[1,2]. To overcome these drawbacks, a smart microsystem based on flexible Aluminium Nitride (AlN) piezoelectric sensor integrated on the extraluminal surface of prosthesis has been proposed.

The sensor is developed by implementing the piezoelectric stack, composed by highly c-axes oriented AlN film (1µm) embedded between two molybdenum electrodes, on polyimide structural layer [3]. An insulating film of polyimide is then deposited to prevent short-circuits. Finally, a thin layer of PDMS is added to further increase the overall flexibility of the system, glued on the graft using an appropriate adhesive layer (Figure. 1).. The total thickness of ~20µm preserves the young modulus of the graft. Moreover the intrinsic biocompatibility and non-toxicity of the AlN, together with low fabrication cost make the system well suited to be implanted in human body. The system response has been preliminarily tested by varying the piezoelectric active area of sensors placed on a PDMS membrane and then on a graft, both applying a pressure between 5kPa and 50kPa [4] to match the blood pressure range of blood. The observed output voltage generated by each sensor showed a linear trend (Figure. 2) in the operating range. These preliminary experimental results demonstrated that the device is able to monitor prosthetic function under different conditions, opening new perspective for vascular graft surveillance and even for monitoring critical blood vessel.

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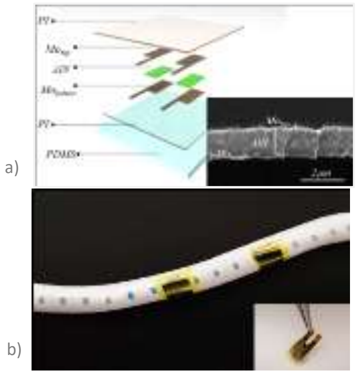

Figure 1. a) Device structure scheme. In the inset a SEM image cross-section of the AlN thin film. b) Piezoelectric flow sensors integrated on the extraluminal surface of a PTFE vascular graft. In the inset an image of the sensor (m-size).

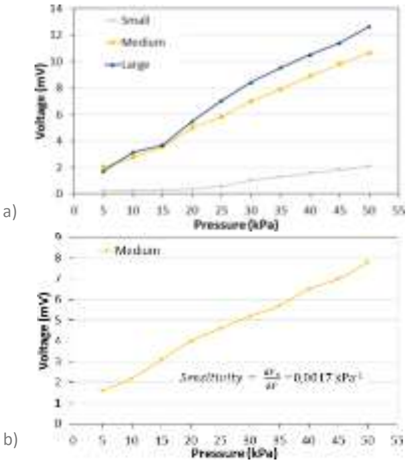

Figure 2. a) Output voltage of piezoelectric sensors with different active area at different pressure conditions on PDMS membrane. b) Output voltage of piezoelectric sensor at different pressure conditions on vascular graft.

Local chemical modification of MoS_2 layer using AFM lithography

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As the demand for nano scaled devices is increasing, Two dimensional (2D) materials have been theoretically and experimentally investigated in the last few decades. Among 2D materials, TMD(Transition Metal Dichalcogenide) materials which have layered structure shows extensively magnetic, electrical, and mechanical properties [1]. Especially, hydrogenation of MoS_2 by high temperature and MoS_2 irradiated by proton shows unexpected ferromagnetic behavior which would lead to new spintronics devices [2].

In this works, we fabricate locally hydrogenated or oxidized MoS_2 using AFM lithography and confirm specific magnetic properties. Through Raman measurement, we identify that the pure MoS_2 surface modify hydrogenated or oxidized one under different lithographic condition. Also, Magnetic Force Microscopy (MFM) measurement support that hydrogenated or oxidized MoS_2 using AFM lithography shows novel magnetic properties comparing with pristine MoS_2. This result may attribute to the H or O atoms deposited on MoS_2 defect by AFM lithography.

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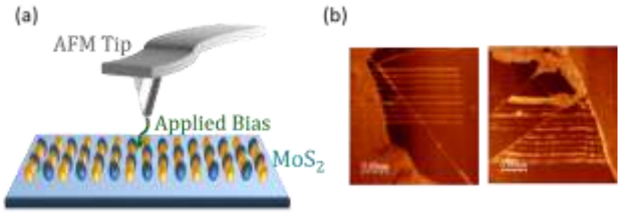

Figure 1. (a) Schematic image of AFM lithography method and (b) AFM image of hydrogenated or oxidized MoS_2 using AFM lithography

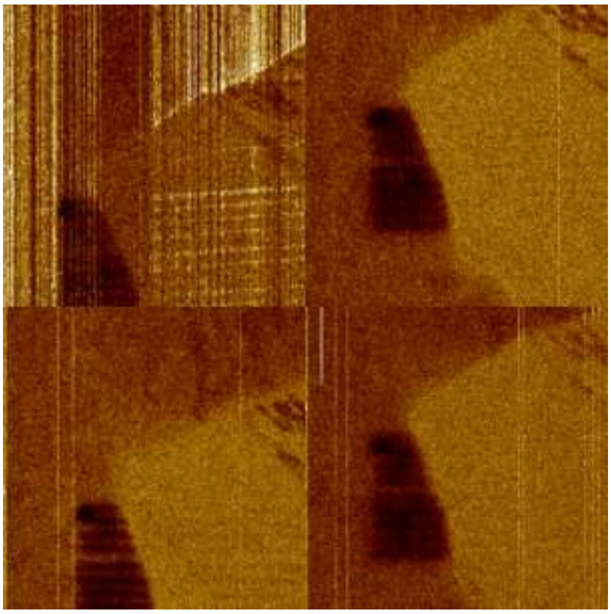

Figure 2. MFM image of hydrogenated MoS_2 applied 1T or -1T

Native oxide film reduction on stainless steel for direct growth of carbon nanotubes

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Native oxide film on stainless steel (SS) gives a high resistant to degradation by oxidation or by corrosion processes, which is attributed to the formation of the surface chromium oxide film. This chemical stability allows the use of SS in environments where is critical to avoid undesired reactions. A particular use is as a substrate for carbon nanotubes (CNTs) forests. Hence, it is possible to manufacture electrodes for batteries or supercapacitors that are in contact with liquid electrolytes, which are extremely corrosive environments for other conductive materials like cooper. Several works use the native oxide films as part of the diffusion barrier system to obtain CNTs. However, this film has two drawbacks: low electrical conductivity and shielding of the catalytic activity of metal (iron) nanoparticles. Here, we present our results about the chemical reduction of the native oxide film on SS 304 using hydrogen/argon plasma. Through this process, it is possible to keep the original surface properties such as electrical and thermal conductivity as well as catalytic activity. The samples were heated up to the annealing temperature (AT) in a hydrogen atmosphere. After reaching the AT, the argon gas was introduced. During three minutes the samples were exposed to a RF hydrogen/argon plasma. The growth process of CNTs was carried out directly, without the need of a diffusion barrier and using the alloy elements of SS (Fe, Ni) as catalysts. To evaluate the catalytic activity of the substrate, two processes were used: plasma enhanced chemical vapor deposition (PECVD) and water assisted chemical vapor deposition (WACVD). By this method, a uniform forest of CNTs were obtained on 9 cm^2 samples at 730°C. The optical emission spectroscopy (OES) spectra, obtained during the reduction time, shows the gradual decrease in intensity of the peaks generated by the interaction between the hydrogen and the oxygen atoms. In addition, scanning electron microscope (SEM) images show the morphology of the CNTs. With PECVD, the CNTs are short and present a uniform distribution and orientation. But, with WACVD the CNTs are longer, present a uniform distribution and random orientation. In both cases, the density of the CNTs is lower than that of the samples produced in our laboratory on silicon wafers. Finally, using Raman spectroscopy, the quality of CNTs was evaluated. With PECVD, there is a presence of amorphous carbon. The G-band and the D-band peaks are not well defined, and the G'-band peak does not appear. Whereas for the samples obtained by WACVD the G-band, D-band and G'-band peaks are sharper, which indicates that with WACVD the amorphous carbon was removed.

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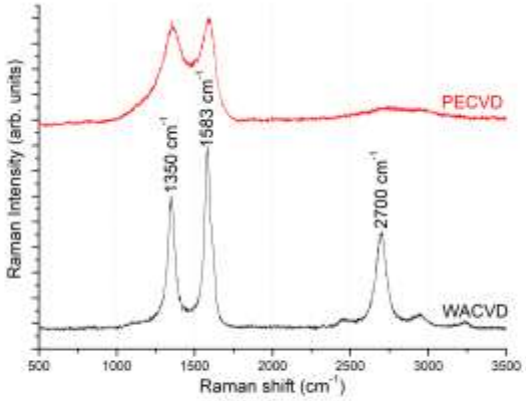

Figure 1. Raman spectra for directly growth of CNTs at 730 °C on stainless steel 304 by PECVD and WACVD.

Plasmonic Zero Mode Waveguide for enhanced confined fluorescence emission

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Single-molecule fluorescence[1] has been successfully applied to many fields in biomedicines, including DNA sequencing,[2,3] diagnostics, and molecular biology. One of the most used platforms for single molecule sequencing is based on zero-mode waveguides (ZMWs). A ZMW reduces the detection volume by 3 to 6 orders of magnitude, with respect to a standard confocal microscope, allowing for single-molecule detection. Nevertheless, in ZMW the emitted fluorescence is not enhanced. In contrast, optical nanoantennas fabricated on Ag or Au films are known to provide field and fluorescence enhancement (FE), thanks to plasmonic effects.

Inspired by the theoretical work by Zhao and co-workers[4], we have fabricated a bilayer, Au-Al plasmonic rectangular nanoslot (Fig. 1a,b) that provides the tiny detection volume of a ZMW, but with a 20 fold fluorescence enhancement[5]. These features allowed us to perfom single-molecule fluorescence detection.

Here we report on the performed simulations, on the encountered fabrication challenges, and on the gathered experimental fluorescence correlation spectra measurements.

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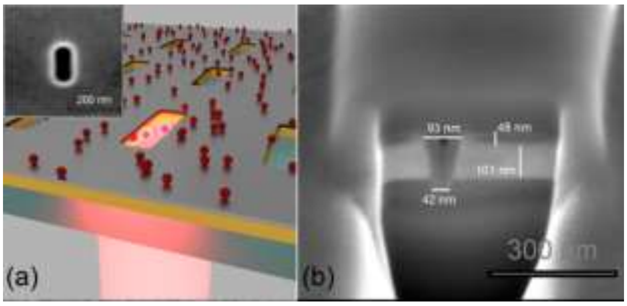

Figure 1. SEM images of the fabricated structures. (a) Schematic illustration of the Au-Al nanoslots; **Inset**: SEM micrograph of a fabricated nanoslot; (b) Au-Al nanoslot, cross section. A 101 nm gold layer and a 48 nm aluminum layer are visible. A platinum layer is visible on top, deposited to improve the cross section cut.

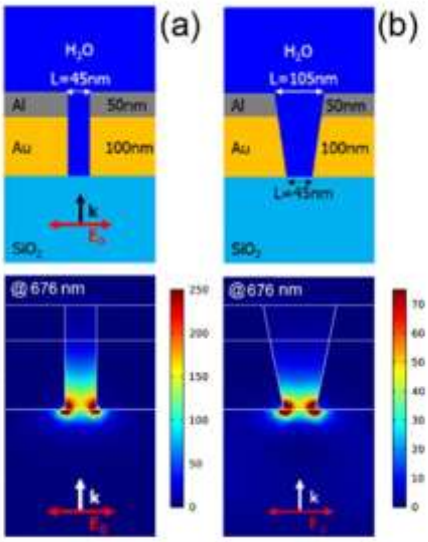

Figure 2. **Top**: ketch of a section of the ideal (a) and fabricated (b) rectangular Au-Al nanoslot. **Bottom**: near-field distributions of the ideal (a) and fabricated (b) Au-Al nanoslot at the experimental excitation wavelength (676 nm). The section planes of the rectangular antennas are parallel to the short axis.

3D-microfabrication by 2PP sacrificial stencil mask

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Two-photon polymerization (2PP) is a promising technique for fabricating 3D nano-structures without any further processing [1-3]. In case of nano-sensors or actuators, different materials are needed to combine and apply nano-structures on supports. This is normally done by challenging steps such as separate lithography and pattern transfer techniques. For instance, recently, a Subtractive Photoresist Platform for Micro- and Macroscopic 3D Printed Structures has been developed exploiting different chemical properties of photoresists and multiple exposure steps [5]. Here we report about the exploitation of 2PP for building a sacrificial nano-stencil mask together with the 3D support structure for nano-sensors or actuators in one single exposure and development process. This mask was used for generating shadows of different materials by vapor deposition through the stencil. We first spin coated a 20µm thick layer of SU8 for defining the anchoring zones for the permanent and temporal structures resp. After pre-exposure baking and short UV flashing, for conditioning the SU8 top surface, we deposited a droplet of IPL resist [4]. In one single 2PP lithography step, we first exposed the anchoring areas in the SU8 layer, and then the 3D structures on top of them, while the stencil mask was exposed in the volume on top of unexposed SU8 areas. For the current demonstrator experiments, the stencil mask was a plain slit, placed on top of a 50µm high, hollow tower and the 3D structure a plain square pedestal. After the development of the IPL in IPA (which does not develop SU8), Cr was evaporated (Fig. 1 and 2). Then, the stencil mask was lift-off by developing the unexposed SU8.

Figure 3 shows the metal-shadow deposited on the pedestal. The location of this deposit could be shifted by tilting the axis of the tower relative to the line-of-sight with the evaporation source. The red dashed line indicates the normal projection of the stencil. A shift of 3.1 µm (center to center) was measured due to the parallaxes between the position of the sample and the Cr source. The combination of sacrificial polymer structures with permanent ones opens new possibilities in 3D MEMS design.

This technique allows incorporating electronic sensors and switches e.g. piezoresistive or metal-insulator-metal thin film diode elements. Improving the mechanical stability of the stencil and decreasing the divergence of the evaporation beam will further increase the definition of the structures demonstrated in this paper.

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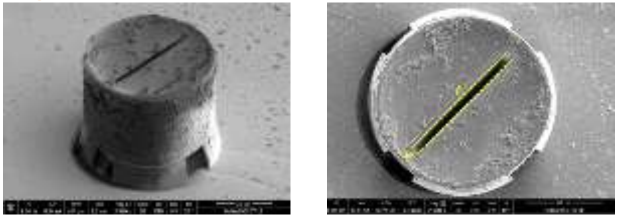

Figure 1. SEM image of the 3D structure with sacrificial stencil mask after the metallization with Cr. The length ℓ was 40µm and the width w 3µm. The yellow dashed line reproduces the outline of the stencil.

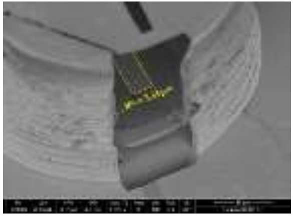

Figure 2. SEM image of a stencil mask opened by Focused Ion Beam milling. It is possible to see the metal structure (yellow dashed line) which has a width of w_s = 3.4µm.

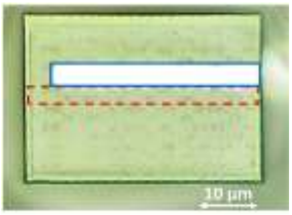

Figure 3. Optical image of the metal structure after lift-off of the stencil mask. The structure (continuous line) has a length of 35.4µm, a width of 3.7µm. It is shifted by 3.1µm relative to the normal projection of the stencil.

Wearable gravimetric sensor based on hydrogel for pH sweat levels monitoring at nL scale

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Abstract

Sweat pH is one of most important parameter commonly utilized, for example, to describe hydration status of athletes [1]. Currently wearable device present in literature are based on colorimetric and electrochemical sensors [1, 2]. In this work we present a flexible gravimetric device for sweat pH monitoring as new kind of wearable device. Here, we show the integration of pH responsive (CEA/PEGDA 10kDa) hydrogel photopatternated onto free standing AlN membranes [3]. The lithography process is sketched in figure 1: pre-polymer solution, consisting of CEA/PEG-DA 10kDa and Irgacure®819, was spun onto AlN membranes with silane pre-treated surface, and proximity photolithography was performed by mask aligner (SussMicrotecTM). The final device is show in figure 2. The hydrogel geometrical variations were studied through confocal microscopy acquisition. In particular Figure 3a and 3b show shrunk (at pH 3) and swelled hydrogel (at pH 8), respectively. Laser Doppler Vibrometry (LDV) was utilized to study the free standing AlN membrane as a gravimetric flexible sensor, in which the mass changes according to the hydrogel water absorption condition. The frequency sweep was obtained by directly driving the piezoelectric transducers. Experimental spectra (displacement vs frequency) are reported in figure 4 for dry (dotted line) and wetted (solid line) hydrogel. The frequency shift from 180 kHz to 160 kHz showed in figure 4 is due to hydrogel weight changes before and after water absorption of approximately 0.3 nL. Selective swelling at different pH conditions of sweat can therefore be measured directly as a frequency shift in this frequency range. We believe the combination of pH sensitive hydrogel and flexible piezoelectric membrane is a promising technology for the development of wearable, innovative and cheap devices for pH sweat monitoring.

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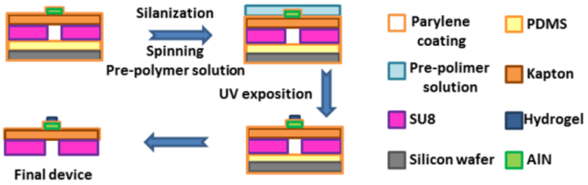

Figure 1. Hydrogel patterning flow process onto AlN membrane.

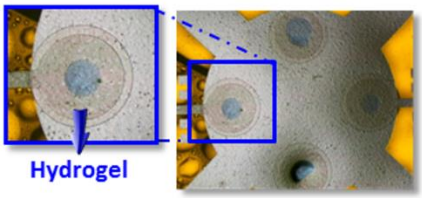

Figure 2. Top view optical image of the free standing membrane surmounted by cylindrical hydrogel.

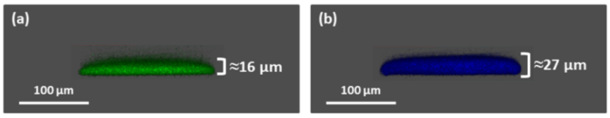

Figure 3. Side view confocal image of shrunk (a) and swelled (b) hydrogel when soaked with pH 3 and 8 solution, respectively

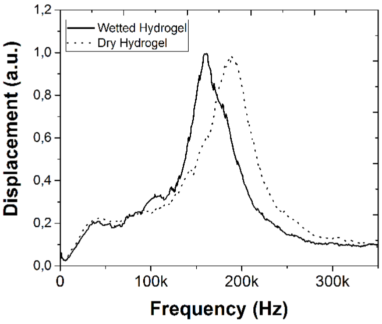

Figure 4. Resonance frequency shift of the free standing membrane due to hydrogel mass changes

Absorption band tuning and photocatalytic activity enhancement in hybrid plosmonic oxide Ag/ZnO nanostructures

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Zinc oxide is a wide band-gap semiconductor with intense applications in optics, electronics, catalysis, energy storage devices and environmental remediation [1]. However, with band gap of 3.2 eV ZnO is activated by UV irradiation. In this regard, different efforts have been made to modify the absorption band edge towards visible light [2]. Combining ZnO with plasmonic metals represents one of the most promising methods to decrease the band gap and increase visible light absorption [3].

In this work, we have coupled silver nanoparticles to ZnO nanocrystals to synthesize Ag/ZnO hybrid nanostructures (HNS) with two different approaches [4, 5]. In both methods, wurtzite ZnO nanocrystals were synthesized by arc discharge of zinc rods in water. Ag/ZnO-chem sample was prepared using trisodium citrate to reduce the Ag^{3+} ions in 0.1 mol L^{-1} AgNO$_3$ aqueous solution to Ag and deposit it on the surface of the ZnO nanostructures. In Ag/ZnO-PD sample instead, UV irradiation was used to reduce Ag^{3+} ions to Ag nanoparticles on the surface of the ZnO nanostructures. The fabricated Ag/ZnO HNS have different optical and photocatalytic properties. Figure 1. a) reports the UV-vis absorption spectra of both samples with respect to the bare ZnO nanoparticles. The absorption spectrum of the Ag/ZnO-chem HNS is extended further to the visible spectral range due to the plasmonic resonance of the deposited Ag nanoparticles. In the Ag/ZnO-PD sample the spectrum did not change remarkably in comparison with the pristine ZnO sample, most probably due to the small size of the deposited Ag clusters. Photocatalytic methylene blue degradation mediated by the Ag/ZnO HNS was investigated using a Xenon 100 W solar simulator. Figure 1. b) shows the photocatalytic activity of the Ag/ZnO-PD sample, which degraded the dye after 10 minutes of solar irradiation followed by 1 hour stirring in dark. Notably, the Ag/ZnO-chem sample completely degraded the dye after 30 minutes in dark, i.e. without the involvement of radiation. Neither ZnO nor Ag nanoparticles could degrade the same dye in the absence of light. Currently, we are investigating this highly efficient photocatalytic activity of Ag/ZnO-chem HNS and the role of the Ag-ZnO Schottky barrier formed in hybrid plasmonic oxide nanostructure.

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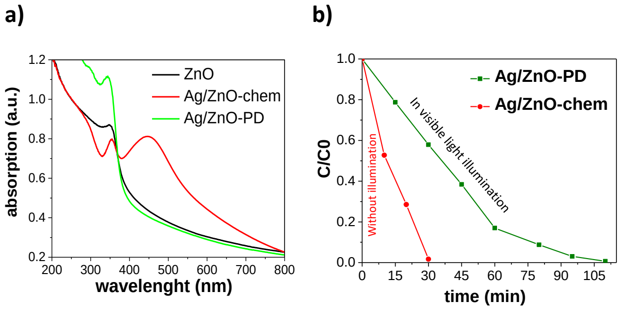

Figure 1. a) UV-vis absorption spectra and b) Relative dye concentration during photocatalytic activity of ZnO and Ag/ZnO.

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Study of the Mechanical Behaviour of Thin Film Solid Electrolytes Using Atomic Force Microscopy

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As the application of Li-ion batteries (LIBs) to power consumer electronics and electric vehicles increases, the safety, size, energy density and power density of the batteries become major concerns. Unlike conventional liquid electrolytes in LIBs, solid electrolytes (SE) are non-flammable and stable [1]. Miniaturized all-solid-state LIBs embedded in a 3D architecture have shown improvements in energy and power density by increasing the surface capacity [2]. However, the formation of microcracks and eventually mechanical breakdown due to the internal and extremal forces at the interface of SE/electrodes leads to reduced ionic conductivity and battery capacity. Furthermore, microcracks at a high current density can provide a pathway for Li dendrite growth and cause shortcuts within the cell [3].Therefore, understanding mechanical behaviour of SEs are necessary for improving battery performance [4]. To date detailed knowledge of the mechanisms behind the mechanical breakdown is limited. In this research, we studied the mechanical behaviour of two promising amorphous thin film SEs, Lithium Tantalate (LTO) and lithium phosphate (LPO) (Li conductivity of 2x10^{-8}mS.cm^{-1} and LPO is 3.3x10^{-8} mS.cm^{-1} at 26 °C, respectively) [5, 6].

LTO and LPO thin films were prepared using atomic layer deposition (ALD) (at 225 °C and 250 °C, respectively) which can fabricate uniform, crack and pinhole free ultra-thin films for 3D structures [5-7]. Thin film SE were deposited over a holey silicon nitride TEM grids (hole diameter of 2.5 μm) with a single layer of CVD graphene on top used to support the deposited LTO and LPO. The mechanical behavior of ALD prepared SEs films studied using an Atomic Force Microscopy (AFM) based indentation technique (Figure 1. a). A range of thicknesses of amorphous thin film SEs (e.g 5 nm, 15 nm, and 25 nm) were studied in order to investigate the influence of the thickness on the mechanical properties of the SE films. Studies of the elastic behavior reveal that by increasing the thickness of the film the mechanical effect of graphene supporting layer vanishes and intrinsic behaviour of the films dominates the mechanical responses to mechanical loadings [8]. However, LTO shows higher stiffness as compared to LPO films at all thicknesses. Moreover, fracture behavior of SE films was studied by indenting the films until failure (Figure 1 b and c). Both LTO and LPO SEs show brittle failure. LTO films were found to fail at higher forces (3.031 ±0.05 μN) as compared to LPO film (1.97 ±0.07 μN) with a similar thickness. These results suggest that the crack formation is delayed in LTO compare to LPO film and LTO has greater potential to suppress the crack formation at the SE/electrolyte interface that can improve the overall performance of the battery.

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Figures

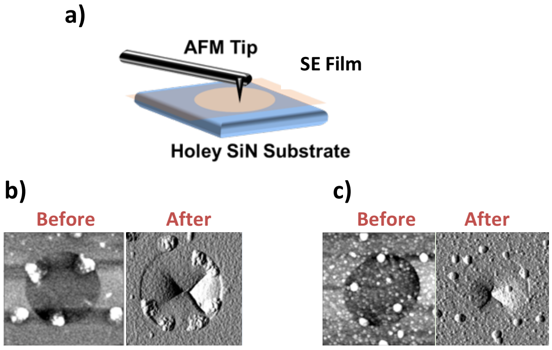

Figure 1. a) Schematic of AFM indentation experiment conducted on SE films, b and c) AFM image of 25 nm thick LTO and LPO films before and after AFM indentation to failure experiment, respectively.

Production of carbon-based materials, from graphite eletrodes (waste), for applications in Mechanical Engineering

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Abstract

The study, based on a circular economy concept, aims to develop a feasible, reliable and secure method that can be carried out on an industrial scale, by transforming graphite electrodes (waste from EDM processes) into new carbon-based materials - graphite functionalized or not with oxygen, reduced, or even graphene - in order to reuse them in another form in final products.

Various exfoliation techniques were studied: electrodes friction, ball milling, cryogenic milling and detonation. The materials were characterized using different techniques, such as, Raman spectroscopy, Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM).

The obtained raw materials can be used as reinforcement additives/reinforcements of polymeric materials, improving their physical and mechanical properties.

Figures

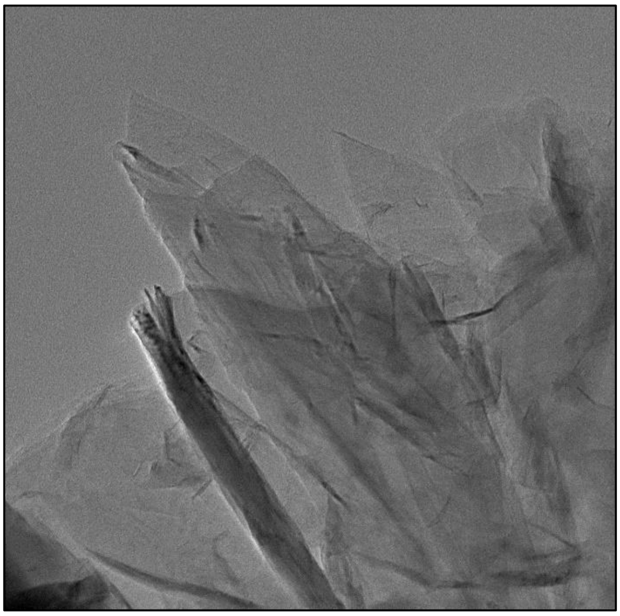

Figure 1. Multilayer graphene production using ball milling technique (TEM analysis).

The study of making a hexagonal single-crystal graphene island used CVD method on copper foil

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Since its discovery, graphene has attracted a huge attention from researchers for its excellent optical and electrical properties. There is no doubt that the industrialization of graphene will lead to a revolution in optics and electronics. However, obtaining uniform, single crystalline and large area graphene is among required properties for graphene to host integrated devices. Among all methods of obtaining graphene, chemical vapor deposition (CVD) is the most promising method for synthesis of graphene with such properties.

In general, when graphene is synthesized using cvd, a copper foil is usually used. As is well known, the copper foil is poly crystal, so when graphene is continuously synthesized on it, the grain boundaries occur. However, grain boundaries are supposed to debase the electrical and mechanical properties. Thus, efforts have been made to synthesize single-crystal graphene without grain boundaries to address these problems. [1-3] However, these experiments are difficult to implement under normal experimental conditions because special material or methods are used. In this experiment, we tried to overcome these shortcomings by making it easier than the previous experiment, and used CVD method to create a hexagonal single-crystal graphene island, ranging from tens to hundreds of micrometers. We utilize optical microscopy, Raman spectroscopy and SEM images to study the chemical bonding and surface topography status of our synthesized graphene.

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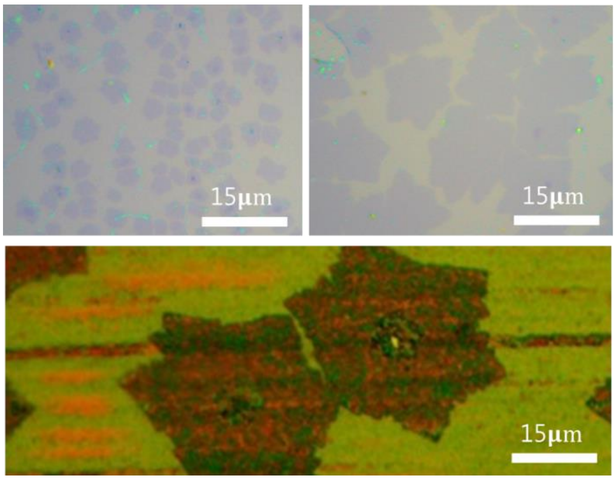

Figure 1. Optical image of a graphene island transferred on SiO_2 substrate and graphene array on oxidised Cu foil. All scale bars are 15μm.

Catalytic activity and stability-enhanced polyelectrolyte brush-grafted catalysts

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Three types of surface treatments, namely, polyethyleneimine (PEI) coating, short PEI (S-PEI) grafting, and long PEI (L-PEI) grafting, were performed on polydopamine (Pdop)-based catalysts to enhance their catalytic activity and stability. Brush-grafted catalysts were prepared by the stepwise synthesis of Au and short (or long) PEI brushes on Pdop particles (PdopP/Au/S- or L-PEI grafting). PEI-coated Pdop-based catalysts (PdopP/Au/PEI coating) were also prepared as non-brush-grafted catalysts. Among the surface-treated PdopP/Au catalysts, the brush-grafted catalysts (S-PEI and L-PEI grafting) exhibited excellent and stable catalytic performance because the brush grafting enabled the protection of the catalysts against harsh conditions, effective transfer of reactants to the catalysts, and confinement of reactants around the catalysts. The brush-grafted catalysts could also more effectively decompose larger dyes than the non-brush-grafted catalysts. The process-to-effectiveness of PEI coating is the best because the release of Pdop from PdopP/Au was moderately inhibited by the presence of only one layer of PEI coating on the PdopP/Au. Thus, this approach could be an alternative method to enhance the stability of PdopP/Au catalysts.

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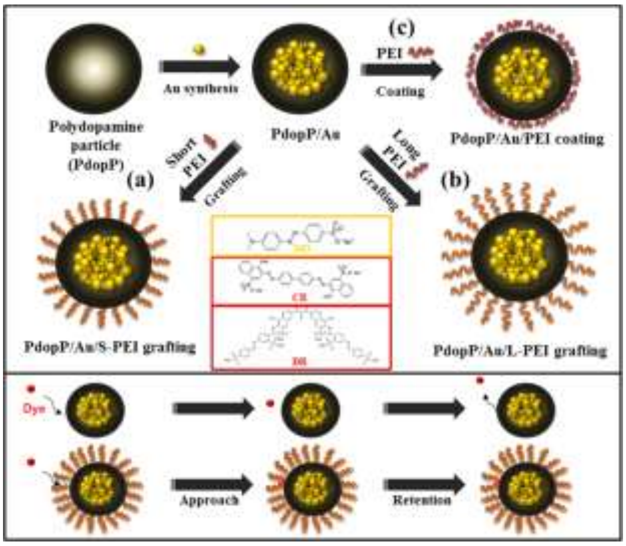

Figure 1. (Upper panel) Schematic illustration of the synthesis of three types of surface-treated PdopP/Au catalysts, including catalysts (a, b) with and (c) without brushes. Brush-grafted catalysts: (a) PdopP/Au/S-PEI grafting and (b) PdopP/Au/L-PEI grafting. Non-brush-grafted catalysts: (c) PdopP/Au/PEI coating. (Lower panel) Schematic illustration showing characteristics of brush-grafted catalysts. The PEI was selected as a PE brush because the PEI can be easily grafted onto the surface of PdopP by the grafting-to method using a Michael-addition reaction. Among the PEIs, branched PEI was used to maximize the content of amine groups of the brush chain.

One-pot synthesis of silica-based nanostructures

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Due to inspiration from naturally occurring biomineralization, biopolymers and proteins have attracted interest in the materials science community as scaffolds for templated synthesis of inorganic materials [1]. Biomolecule-controlled nucleation and growth of inorganic hydrated silica (SiO_2) regulates, in the marine environment, the nanopatterned cell wall architecture of the unicellular microalgae diatoms [2]. The ability to *in vitro* precisely template inorganic nanomaterials provides an opportunity for the development of green nanomaterials.

In this work, opposite approaches for the synthesis of organic/inorganic silica-based nanostructures are proposed: (1) A top-down approach aiming at extract and isolate SiO_2 nanoblocks (NBks) from *Thalassiosira weissflogii* diatom cell walls (Fig 1). Thereafter, the quasi-spherical shaped NBks, immersed into a fluidic vortex, rearrange themselves in intriguing geometrical intermediates, from spherical to toroidal, forming super assembled units (major axis, 150-300 nm). (2) A biomimetic bottom-up approach has been developed to synthesize SiO_2NPs miming the natural processes of silica formation in diatoms living organisms (Fig 2). The organic-based scaffold is an aqueous solution of spermidine, a polyamine presenting chemical common features of diatoms silica-nucleating long chain polyamines. The chance to *in vitro* control the 3D self-assembly aptitudes and the underlying patterns results in several unique SiO_2NPs. By slightly varying reaction parameter settings, SiO_2NP design varies from a spherical to a *pacman-like* shape, exhibiting a dense or hollow structure and presenting diverse average diameter dimensions in the range between 250 nm to 600 nm. NP surface chemistry and chemical stability permit a selectively functionalization for various applications from targeting to imaging [3]. Moreover, in the present proof of principle studies, SiO_2NPs are proposed as a platform for oligonucleotide delivery as well as gold NPs-decorated assemblies for nanomedicine application or integration within optical micro devices.

Looking ahead, the capability to regulate the formation and the arrangement of the inorganic structures using organic matter principles, is a very attractive and sustainable route for the development of structurally-complex and chemically- and/or bio-active tunable materials.

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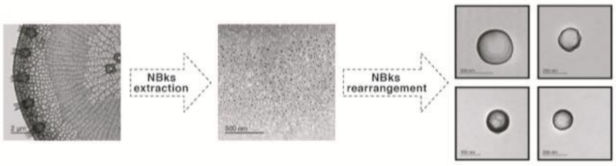

Figure 1.
Top-down approach. SiO_2NBks isolation from the cell walls of the diatom *Thalassiosira weissflogii* and rearrangement in super assembled units.
The authors thank prof Farinola and collaborators who provided diatom samples.

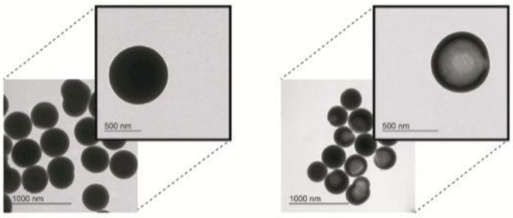

Figure 2.
Biomimetic approach. Different SiO_2NPs obtained by varying the one-pot synthesis starting parameters.

An atomically thin and high-k multi-functional oxide for electronic and opto-epectronic devices.

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The incorporation of high-*K* transition metal oxides improves the performance of the semiconductor devices which remains challenging due to the difficulties of the deposition methods.

In this work we show that the incorporation of the HfO_x by laser oxidation (with dielectric constant *k* ~15) into a wide range of van der Waals heterostructure (vdWh) devices such as flexible field effect transistors based on graphene, MoS_2 and WSe_2, resistive switching random access memories (ReRAM) and Light emitting and detecting quantum wells based ultra-thin HfO_x tunnel barriers leads to interesting electronic and optoelectronic properties.

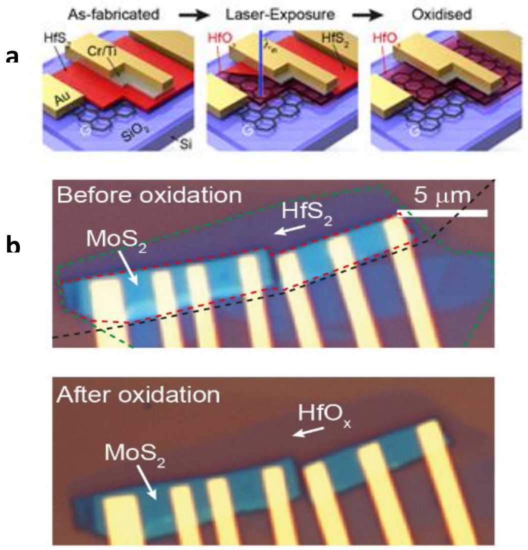

Figure 1. **Heterostructure processing route**. **(a)** The heterostructure is fabricated via dry transfer peeling from PDMS membrane (left), the area containing HfS_2 is exposed to laser light (centre) and the HfS_2 is converted into HfO_x (right).**(b)**Optical image of a Graphene/HfS_2/MoS_2 heterostructure before (top) and after (bottom) oxidation. Black outlines the region of the graphene back gate, green -outlines the HfO_2 and red the MoS_2.

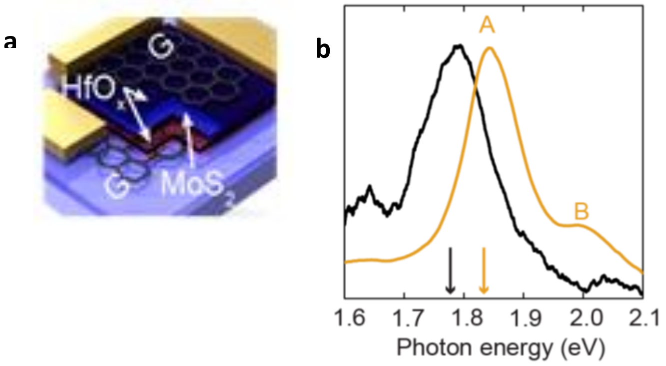

Figure 2. ***Thin HfO_x barriers for optoelectronic applications*** **(a)** Illustration of the device architecture. **(b)** El (black) and PL (brown) at *V_{sd} = 2.5 V and V_{sd} = 0V respectively.*

Stimuli responsive PGA Nanoparticles as safe agents for non viral gene delivery

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Abstract

Nanoparticle (NP)-based therapeutic systems developed in recent years have shown efficient delivery of drugs and/or nucleic acids with low toxicity and sustained cargo release.

Recently, more attention has been paid to stimuli sensitive delivery systems that are promising strategies for active agent release. Many techniques have been developed to produce systems that could be used for effective encapsulation of active agents, as drugs or genes. External and internal stimuli, such as temperature, [1] pH, [2] light, [3] and protease, [4] could be utilized to control the active agent release in delivery systems. Among all these strategies, release systems based on pH variation have obtained more attention, because the pH difference between different intracellular compartments could be used for targeting systems design.

For gene delivery application, NPs can accommodate large DNA plasmids, RNA or proteins and may be produced at low cost on a large scale. NP-based systems overcome safety problems and limitations of viral vectors. FDA-approved polymers are particularly attractive for *in vivo* drug/gene delivery applications. Recently, we have developed a polymeric system for drug and gene based on pH-responsive, core/shell NPs using the FDA approved PCL polymer. [5-8]

Another, attractive polymer for gene delivery applications is polyglycolic acid (PGA), which has been approved by the FDA. PGA degradation is quicker *in vivo* and *in vitro*, and the degradation product, glycolic acid, is non-toxic and it can enter in the tricarboxylic acid cycle.

For gene delivery, we have developed pH-responsive core-shell polymeric NPs showing that they mediate efficient cDNA delivery. Our PGA NPs (Figure 1) with size about 300 nm, obtained by the emulsion-diffusion-evaporation method, are composed of a core with DNA molecules and a PGA shell. Using PGA NPs loaded with GFP cDNA in different cell lines, we observed relative numbers and mean fluorescence intensity of transfected GFP-positive cells comparable to those achieved with standard reagents used to promote transfection.

PGA NPs, thanks their properties, as biocompatibility, biodegradability and a good transfection efficacy, can be used as efficient tool of transfection overcome viral vector problems.

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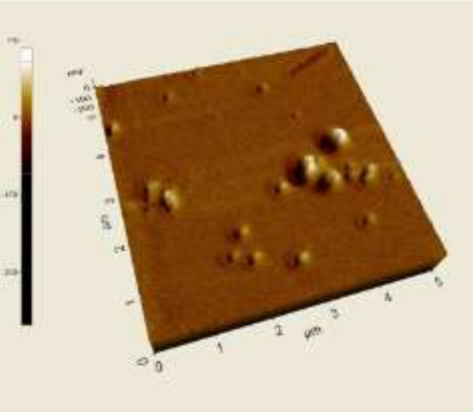

Figure 1. AFM image of PGA NPs.

Acknowledgement

This study are supported by Tecnomed (FIRS project of nanotechnology, photonics and precision medicine) and partially by Italian Association for Cancer Research (AIRC) through the grant MFAG n. 16803

Membrane Resonators Consisting of Cross-Linked Gold Nanoparticles: Influence of Geometry on Vapor Sensing Characteristics

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With progressive downsizing of mechanical devices, nanomaterials gain significant importance, especially regarding sensing elements[1]. Nanometer-thin composite membranes may constitute a promising active component for future microelectromechanical sensing elements.

Thin films of interconnected gold nanoparticles (GNPs) feature intrinsic environment-dependent properties, making them applicable as sensing element, for example as chemiresistors[2]. By transferring spin-coated GNP thin films onto three-dimensionally structured silicon substrates, a novel type of microelectromechanical resonator has been fabricated, as reported recently[3]. Examining the vibrations of dithiol cross-linked GNP membranes at reduced pressures (~20 mbar) enables the detection of volatile organic compounds (VOCs) due to a sizable, reversible frequency shift of the membrane's fundamental resonance mode. This effect is caused by a decrease of the membrane's pre-stress as well as a total mass increase by molecule sorption[3].

Due to strong damping at higher or ambient pressure, however, the detection of resonance modes becomes increasingly challenging. Here, we address this problem by modifying the resonator geometry. The vibrational behavior of the resonators can be manipulated by a number of customizations. Adding micrometer-wide channels to otherwise confined cavities enable a much easier gas flow into and out of the resonator's cavity (Figure 1). Appropriate modifications render measurements of resonance frequencies and, thus, the usage of such resonators as highly responsive microelectromechanical chemical sensors at ambient pressure feasible. This was shown for toluene vapor with concentrations as low as 0.5 ppm for which Frequency shifts as low as 1 kHz could clearly be resolved (Figure 2).

Additional experiments revealed a dependency of the fundamental frequency-shift transient upon exposure to VOCs on the accessibility of the resonators' cavity volume. Doubly-clamped membranes over elongated trenches featured quasi-instantaneous responses, while confined resonators exhibited much slower transients. Square resonators featuring diagonally arranged air channels displayed an intermediate behavior. Consequently, multiple sensors displaying distinct response characteristics are manufacturable from the same raw materials and can be used in combination for highly selective analyte detection.

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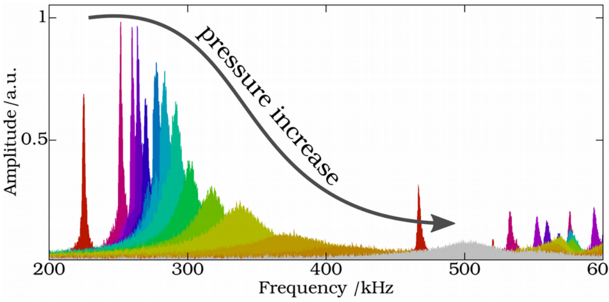

Figure 1. Damping of the device depicted below, measured in the range between 1.5 mbar to 1007 mbar.

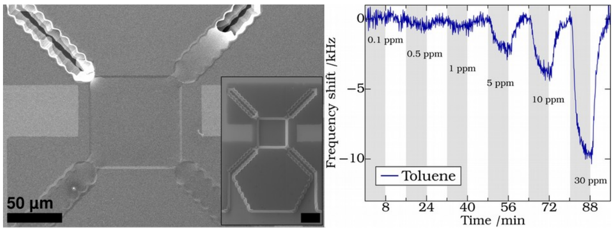

Figure 2. SEM image of microelectromechanical resonator (left); Substrate before membrane transfer (inset); Frequency-response transient for small comcentrations of toluene vapor at 1007 mbar (right).

Ultrafast lead-acid battery with nanostructured Pb and PbO_2 electrodes

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Lead-acid batteries (LABs) are still extensively used in the field of energy storage, owing to a well-known and reliable technology. LABs can deliver high power and store energy for a very long time. In addition, they are reliable and easy to produce. The raw materials for their manufacture are practically unlimited, and about 95% of the materials can be recovered and reused. However, the lower specific energy storage (about 30-40 Wh kg^{-1}), in comparison with other storage systems, limits their use in the most emerging and challenging applications, like electrical mobility, due to the high atomic weight of lead [1]. One of the principal limitations in the use of LABs in electric vehicles (EV) is related to the inadequacy of the negative plates in accepting high charge/discharge currents. Besides, LABs operate in EVs at high rate partial state-of-charge, which leads to rapid sulphation of the negative plates.

Many approaches were proposed in order to overcome these problems and make LABs suitable for emerging applications. A possible approach is based on electrodes with nanostructured active materials, which are progressively emerging as an alternative to the conventional plates because their high aspect ratio and consequent high superficial area allow to fabricate LABs with high specific energy and power density.

We have developed template electrodeposition as an easy and direct technique for fabrication of nanostructured electrodes, with very large active area, consisting of PbO_2 and Pb [2-3]. Both active materials (Pb and PbO_2) were electrodeposited using a nonporous template to obtain the regular arrays of nanowires shown in Figure 1, well attached to a compact film of the same material, acting as a current collector and mechanical support of the nanostructures.

Nanostructured PbO_2 and Pb electrodes were assembled and tested using aqueous 5 M H_2SO_4 solution in a zero gap configuration, and was discharged up to 90% of the gravimetric capacity to a cut-off voltage of 1.2 V.

In comparison to commercial LABs, which usually deliver about 30 mAh/g for only 15-20 cycles at 1C rate, our batteries are able to charge and discharge at very high rate without fading up to 1500 cycles with a cycling efficiency of about 90%. Besides, nanostructured electrodes show better performances without time-consuming curing and formation process. These performances are attributable to their large surface area (about 70 times higher than the geometrical one), leading to a new LAB with high specific energy and power density. Another interesting finding is the ability of our batteries to be cycled up to 30C [4].

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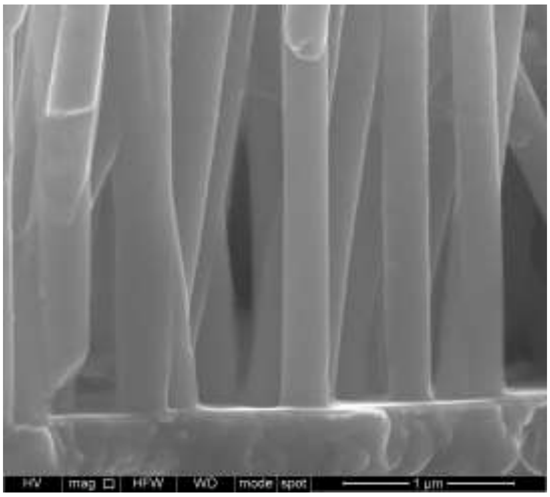

Figure 1. Cross-Sectional view of PbO_2 nanowires

Electronic properties of chrome-doped Zinc sulphide nanosheet

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Abstract

Zinc sulphide (ZnS) is a semiconductor with a wide band gap of about 3.77 eV. Based on the recent achievements regarding the electronic applications of this material, in the present work, we are going to investigate the electronic properties of the pure and Cr-doped ZnS nanosheet within the framework of density-functional theory (DFT) implemented in Quantum Espresso package using the General Gradient Approximation (GGA) with a Pedrew-Burke-Ernzerhof (PBE) describing the correlation potential. Results verify that doping the Cr atoms reduces the band gap down to 1.5 eV, yielding half-metallic properties for the ZnS nanosheet.

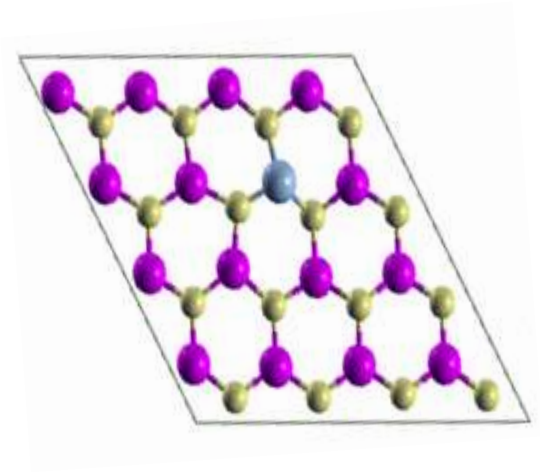

Figure 1. Cr-ZnS nanosheet

A Novel Fabrication of 3.6nm High Graphene Nanochannels for Ultrafast Ion Transport

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Fluidic nanochannels have presented the possibility as an outstanding molecular sieve due to the fast and selective transport of water, gas, and ions[1]. Theoretical studies predicted that the hydrophobic nanochannel could transport water and gas much faster, but the experimental studies in nanochannel are rarely explored. Here, we fabricate graphene-based 2D nanochannels with rectangular shapes, for the first time, of 3.6, 10, and 50 nm heights and a 2 µm width, and report their ion transport properties.

We fabricated the 3.6 nm high, rectangular graphene nanochannels in which the water solution flows along the graphitic surface for the first time to study the ion transports in these nanochannels. The fabrication options of nanochannel inscription and the novel technique of graphene conformal coating altogether enabled us to create graphitic nanoconfinements with no limitation to particular nanomaterials, such as carbon nanotube, thereby leading to diversified investigation of the unique nanofluidic phenomena in the graphitic environment.

Under the electric field to transport the ions, the 3.6 nm graphene nanochannel conducts ions 115 times faster than the nanochannel without graphene in a deionized (DI) water solution, also yielding similar results using other electrolytes. The prepared 3.6 nm high graphene nanochannels take a clean and smooth surface and show ionic conductance ≈115 times larger than that in the SiO2/Si nanochannels (with larger nanochannels with 10–50 nm heights showing significantly less enhancements). Detailed mechanistic understanding remains to be further investigated. These graphene-based artificial nanochannels promise to offer new opportunities for applications such as fast desalination, ion field effect transistors, and energy harvesting and storage in its nanofluidic confinement.

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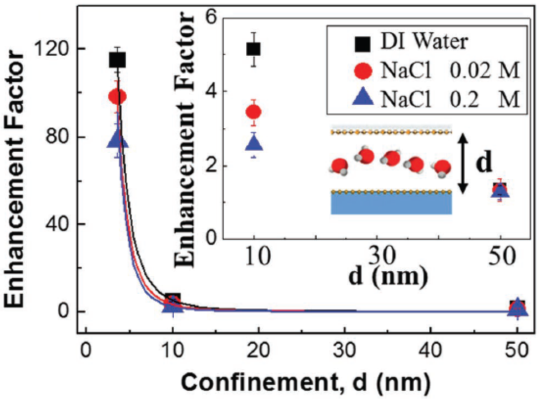

Figure 1. Flow enhancement factors of graphene-based nanochannels compared with SiO2/Si nanochannels. Inset figure shows the enlargement of the enhancement factors of 10 and 50 nm channels.

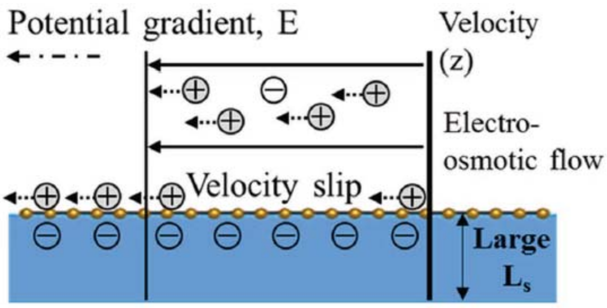

Figure 2. Concept illustrations of the enhanced electroosmotic flow in graphene-based 3.6 nm channels having a high hydrophobicity, large slip length, and nanoconfined properties.

Probing the nano-scale Schottky barrier of metal/semiconductor interfaces of Au (or Mo)/Bi_2Se_3 by Kelvin probe atomic force microscopy

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The effectivity of the thermoelectric materials could be increased by the presence of the metallic nano-inclusion used for electron energy filtering. This type of the nano-composite (metallic 1D/2D nano-particles on the surface of the highly organized layered crystal) could be hardly evaluated by the macroscopic techniques for their “averaging” of the effect for nano-particles of different sizes.

Kelvin probe force microscopy, one of the electric modes of the atomic force microscopy, enables measuring of electrical surface potential of each separated nano-particle and thus we can predict the behavior of the nano-composite in the bulk form with respect to the size and the chemical composition of the inclusions.

To verify this theory, we prepared the set of the Au nano-particles (Au-NP) on the cleaved surface of the layered semiconducting Bi_2Se_3 by the magnetron sputtering. The Au-NP height was 5 – 70 nm. The surface potential of the Au-NP decreased by -40 mV in comparison with the clean Bi_2Se_3 and the magnitude of the decrease correlated with the height of the Au-NP (Fig. 1).

We observed different behavior of Au and Mo metallic films. While Au diffused to the matrix forming mechanic mixture, Mo diffused forming nano-inclusion of the $MoSe_2$ due to the strong Mo-Se chemical bond. The metallic film was exposed by the e-beam lithography for local patterning. The exposed area (6x10 μm^2) topologically expanded over original surface for dozens of nm as the result of the diffusive reaction of Se with metallic nano-particle (Fig. 2). After exposition, the surface potential of the Au layer decreased for -62 mV in comparison with the initial Au surface. However, Mo layer after the similar exposition exhibits increase of the surface potential for 110 mV due to the formation of the $MoSe_2$ nano-inclusion.

Figures

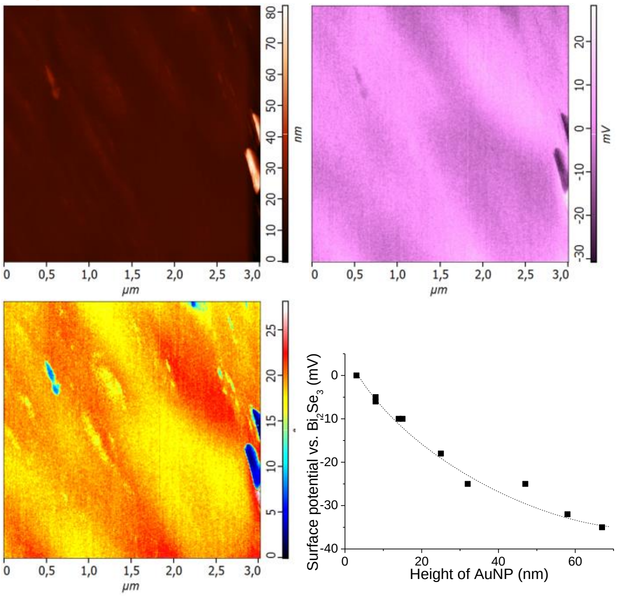

Figure 1. Nano-particles of Au on the Bi_2Se_3 surface detected on the map of the topology, surface potential (KPFM), mechanical behavior (phase-shift) and the correlation of the surface potential over Au-NP height

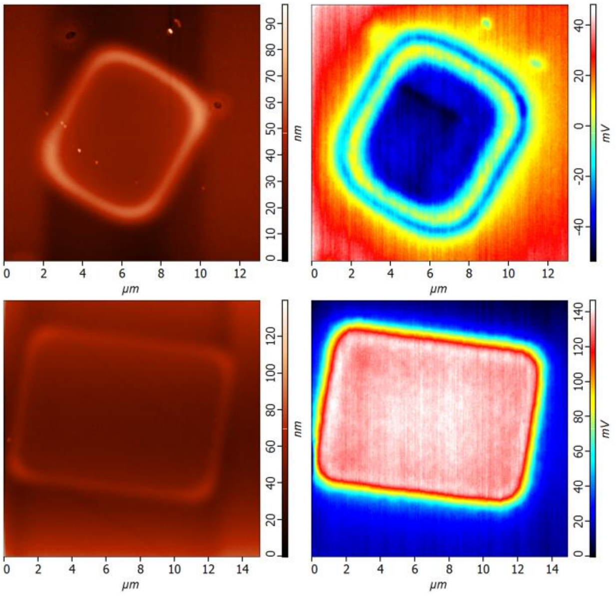

Figure 2. Topology (left) and surface potential map (right) maps of the Au(30 nm layer)/Bi_2Se_3 (upper row) and Mo (10 nm)/Bi_2Se_3 after local e-beam lithography

NPs-Graphene hybrids dispersion by electrochemical methods

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Nanohybrid materials containing graphene sheets have emerged as new model of materials with vast potentials in electronics, optoelectronics, energy technology, membrane design, sensing and biomedical applications. Last years, we have designed hybrid platforms with graphene and Nps in order to improve the surface analysis methods such as SERS (surface-enhanced Raman scattering) and TERS (tip-enhancement Raman spectroscopy).[1]

In this communication, we show simple electrochemical strategies[2,3] carried out for obtaining hybrid Nps-Graphene structures (Pd-GO and AuPd-GO) dispersed in solution. The free-standing hybrid structures in aqueous solution were obtained by galvanostatic electroreduction of GO dispersion in the presence of metallic precursors and stabilizing agents, under controlled agitation of the electrolyte (Fig. 1)[2].

The morphology and structure of hybrid materials were determined by optical, Atomic force and electronic microscopies (SEM and TEM), while the chemical information was recorded through EDS, XPS and Raman spectroscopies (Fig. 2).

Applications are shown by using the hybrid nanostructures as modifiers of the nickel surface for increasing the catalytic activity of the electrode for the evolution of hydrogen (HER). Electrocatalytic activity was comparatively performed by incorporation of Nitrogen-doped GO and MoS_2 particles in the nickel matrix[3].

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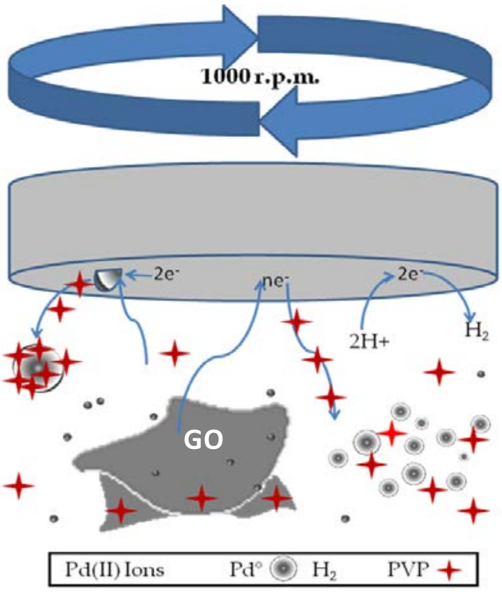

Figure 1. Representative scheme of the electrochemical process for the formation of stabilized PdNPs-GO hybrids.

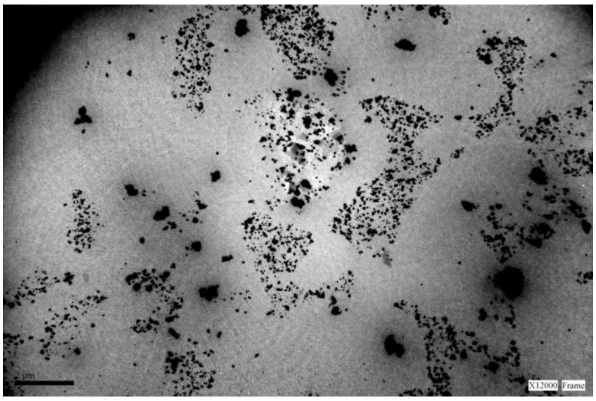

Figure 2. Transmision electron micrography of a AuPdNps-GO hybrid sample.

Measurement protocol for electrical characteristics of powder-type graphene materials

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Abstract

Graphene has attracted a great deal of attention as a next generation electronic material due to its extremely high mobility and ballistic transport of electrons. The unique properties of graphene are considered to be efficient candidates for use in electronic products such as transparent conducting films, electronic inks, supercapacitor, etc. Characterization of the electrical properties of graphene itself is essential to both manufacturers and users in order to develop innovative electronic devices or to improve existing electronic ones using it. Commercialized graphene products can be categorized by their manufacturing methods as follows: (i) graphene films grown by chemical vapor deposition (CVD), (ii) graphene sheets suspended in liquids, and (iii) graphene flakes in powder from. Many electrical properties of a powder-type graphene product are sensitively affected by its geometric and electronic parameters. Therefore, it is necessary to select the best representative parameter among its electrical properties which may exhibit the quality of graphene. There are many measurands to determine an electronic property of graphene flakes, e.g. sheet resistance, conductivity, resistivity, volume resistivity, and so on. Among them volume resistivity (or volume conductivity) was selected for the representative measurand which reveals the electrical property of powder-type graphene through a series of experiments. This work provides a standardized method for evaluating volume resistivity of commercial powder-type graphene flakes to enable users to select a product suitable for their applications.

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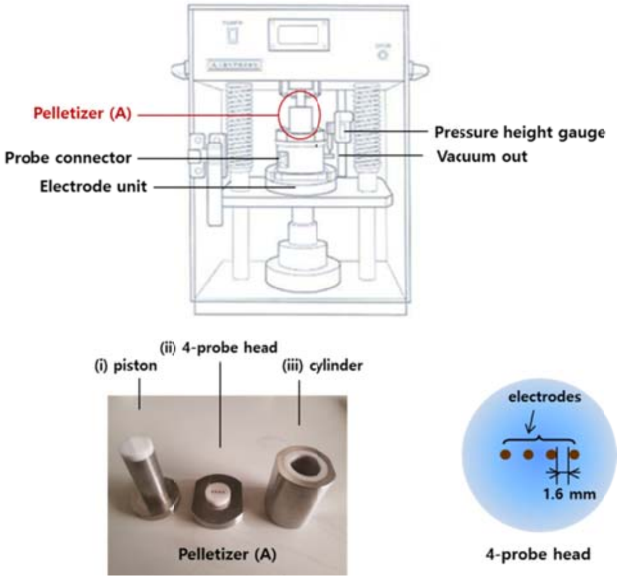

Figure 1. Schematic diagram of the measurement system and the photo of a pelletizer and 4-probe head.

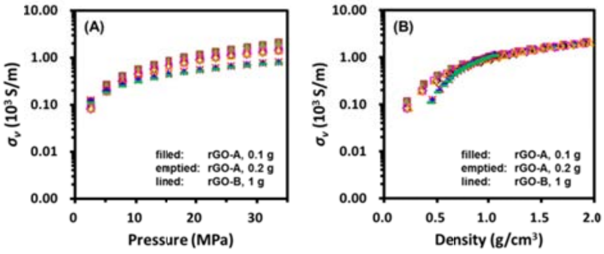

Figure 2. Plots of volume conductivity vs (A) the applied pressure, and (B) a density of reduced graphene oxide (rGO) pellets made of 0.1 g (filled), 0.2 g (emptied) of rGO-A, and 1 g (lined) of rGO-B.

The study of 2D van der Waals material based synaptic device

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The development of reliable memristor devices capable of storing multiple states of information has opened up new applications as neuromorphic computing.[1,2] Recently, Reported ion migration based synaptic memristor devices using two-dimensional (2D) layered transition metal dichalcogenides (TMDs) materials such as MoS_2 and WS_2. Native oxidized layer of sub nanometer thickness exhibits excellent synaptic plasticity and learning capacity close to the ~100mV level of neuron spike by electrically induced oxygen vacancy conductive bridge.[3] However, these devices has dimension limit as reducibility total thickness due to Native oxidized $MoOx/MoS_2$ and WOx/WS_2 heterostructure. Meanwhile, two-dimensional (2D) van der Waals (vdW) materials have recently attracted considerable attention due to their excellent electrical and mechanical properties. TmPSx (where Tm = a transition metal), which is a new class of 2D vdW materials, is expected to show various physical phenomena depending on the Tm used. In this paper, the unprecedented synaptic behavior of a vertical $Ag/CrPS_4/Au$ capacitor structure, where $CrPS_4$ is a single-crystalline 2D vdW layer, is reported. Multi-stable resistive states were obtained using an external voltage of less than 0.3 V. Both short-term plasticity and long-term potentiation were observed by controlling the interval of the external voltage pulse. Simple mechanical exfoliation was used to develop a synaptic device based on a very thin $CrPS_4$ layer with a thickness of ~17 nm. Therefore, it was demonstrated that vertical $Ag/CrPS_4/Au$ capacitors could be promising inorganic synaptic devices compatible with next-generation, flexible neuromorphic technologies.

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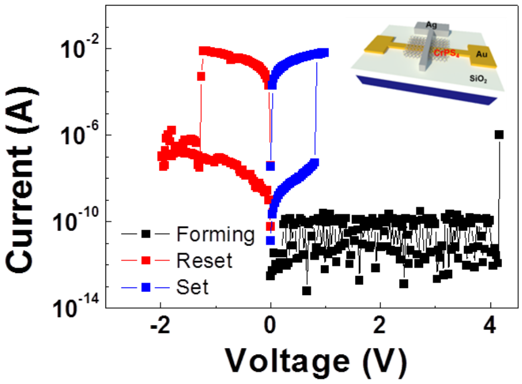

Figure 1. The current-voltage (*I-V*) curves show the bias-polarity-dependent bipolar resistive switching (RS) behaviors of the $Ag/CrPS_4/Au$ device.

Molecularly imprinted polymer as molecularly structured receptor for chemosensors based on SPR and SWS on plastic optical fiber for industrial application

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The development of new sensory methods, based on synthetic biomimetic receptors i.e. Molecularly Imprinted Polymers (MIP), suitable for the specific detection of different analytes in a real or native matrix, like biological or environmental samples and matrices of industrial interest, with an enhancement in the limit of detection and selectivity, is highly required [1]. The molecularly imprinted structure of the synthetic receptors (MIP) is crucial for obtaining good affinity and selectivity of the interaction sites. Specific cavities must be designed for the detection of the analyte molecule in the desired complex matrix. For this reason, identification of appropriate functional monomers was performed to optimize the MIP characteristics and obtain a proper receptor. To this aim, a computational method (Gaussian 09), has been employed in the present work to develop a MIP for dibenzyl disulphide (DBDS), an antioxidant of industrial interest. Non-covalent interactions (such as electrostatic or hydrogen bond) are considered to meet the prerequisites of an easy and rapid re-utilization of the sensor. The functional monomers interacts with the analytes molecule, which act as template, and create a pre-assembly. Then, by adding a cross-linking agent and an initiator, polymerization takes place around the pre-assembled molecule cluster mold and the 3D structure of the site is fixed. At the end of polymerization process, the template is removed by washing, so that sites with complementary shape are exposed.[2] An important point in the preparation of these nanostructured solid receptors is their physical form which must be constructed considering the sensing transduction method. In the present research MIPs were used as receptors in two kinds of optical platforms both relying on plastic optical fibers (POFs). One was based on surface plasmon resonance (SPR) [2] and the other on segmented waveguide (SWS) [3] platforms. In the first case the sensing is based on surface plasmon resonance (SPR) phenomena taking place at the interface MIP-thin gold layer. A shift in resonance wavelength is produced by the variation of the refractive index of the polymer when the analyte rebinds [2]. The segmented waveguide platform, SWS, is based on two plastic optical fibers coupled through a trench, filled with the MIP [3]. The relative output, i.e. the ratio of the light intensity from the two fibers (I1 /I2) decreases when the DBDS concentration increases. The instrumentation required is similar to that of SPR method but could be even simpler and cheaper. In both kinds of platforms MIP was polymerized directly on the platform. LOD of SWS platform of 6,25x 10^{-7} M is compared with that of SPR of 1,47x 10^{-8} M for DBDS in power transformer oil. The SWS platform has higher LOD than SPR platform, but it is more reproducible due to the simplicity of its fabrication.

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A molecularly structured receptor (MIP) for a chemosensor for furfural with electrochemical transduction

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The application of a molecularly imprinted polymer (MIP) [1] as a receptor for electrochemical sensing is demonstrated in the case of the determination of 2-furaldehyde (furfural, 2-FAL) in aqueous matrices. Furfural is a molecule largely diffused, since it naturally derives from the acid-catalyzed degradation of xylose in lignocellulosic biomass. Moreover, it is produced in food by sugar dehydration and by the Maillard reaction, and can determines the organoleptic properties of food. It is also of interest in the production of biofuels, and can provide a large quantity of useful derivatives, representing a sustainable, abundant and cheap source of different chemicals. For these reasons, the determination of furfural in different matrices is of high interest. Various methods have been proposed for the determination of furfural, much of them based on chromatographic techniques. They are generally quite demanding in terms of time and complexity of chemical operations and instrumentation.

Sensors appear to be the best solution for analytical determinations in a short time, and possibly in situ, since such devices are able to reduce handling operations and dimensions of the analytical apparatus.
Electrochemical transduction based on voltammetry can be considered as an ideal approach for the determination of electroactive substances [2], however it is not very selective.
The use of a molecularly structured medium in the electrochemical cell should improve this aspect, ensuring a better selectivity as previously shown in the case of a different substance [3]. MIPs are obtained by polymerization of a liquid mixture containing aggregates of the analyte of interest (furfural in the case here considered) with a polymerizable molecule. In the case here considered, the polymeric mixture consisted of the analyte (furfural), a functional monomer (MAA), and a crosslinker (EGDMA) at molecular ratio 1:4:40, and of a radical initiator (AIBN), sometimes with a porogen solvent. For the sake of miniaturization, the electrochemical cell consists in a commercial screen-printed cell (SPC) composed of a graphite ink-working electrode, a graphite ink auxiliary electrode and an Ag ink quasi-reference electrode on a polyester support. A MIP layer is formed directly over the whole cell by dropping a small amount of the prepolymeric mixture over it, and by polymerizing at high temperature (72°C) in the air. Furfural was extracted from the obtained polymeric layer by repeated washing with ethanol. For the sake of comparison, a corresponding NIP (Not Imprinted Polymer) was synthetized as well. The obtained MIP layer was microporous, with connected pores, so ensuring a good electrical conductivity of the medium in contact with the electrodes.
The affinity and the selectivity of the molecularly structured imprinted sites in the polymeric layer was determined by electrochemical measurements (cyclic voltammetry and square wave voltammetry) carried out in the MIP modified cell described, and compared with the same characteristics determined by batch adsorption procedure. Affinity constants as high as 10^6-10^7 M^{-1} could be obtained, with good selectivity even for compounds of similar structure, as other furanic derivatives.

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Captive-air-bubble aerophobicity measurements of antibiofouling coatings for underwater MEMS devices

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Micro and nanoscale electronic devices that are aimed at being employed in harsh environments, such as underwater, must be protected with electrically insulating coatings. Moreover, for applications involving flexible devices it is important that the external coating has some specific characteristics: it should be conformal, lightweight, not fragile and insulating. Furthermore, one of the main issues related to submerged objects is the accumulation of micro- and macro-organisms on the solid surfaces, i.e. *biofouling,* which could negatively affect the mechanical performance of the devices, especially in the field of MEMS micro-fabricated systems. In order to contrast the deposition of microbial organisms on micro-devices which have to work underwater, one commonly adopted technique is to control the physical and chemical character of the surface by modifying the morphology and the wettability.

In our work, we investigate the surface behavior of different selected polymeric coatings: parylene-C, poly-methyl methacrylate (PMMA), poly-dimethyl siloxane (PDMS), a mixture of diluted PDMS and molten poly-vinylidene fluoride (PVDF), a mixture of PDMS and PVDF powder, and parylene-C decorated with PVDF nanoparticles through sonication.

We analyze the wettability by measuring the contact angle and comparing the classical sessile-drop method (in air) with the captive-air-bubble method (for substrates submerged in seawater), in order to evaluate the underwater aerophobicity of the surfaces. Additionally, AFM measurements provide further information in terms of surface morphology.

We find that the application of PDMS diluted in Hexane solvent provides the highest air-bubble contact angle, but the nanoparticles-decorated parylene coatings show the best combination of a rougher surface (to reduce *biofouling*) and a higher aerophobicity (higher surface concentrations of PVDF nanoparticles provide higher underwater aerophobicity).

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Figures

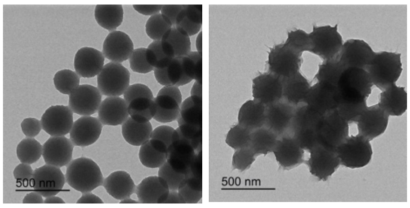

Figure 1. TEM images of PVDF nanoparticles in MEK at concentrations of 1mg/mL (left), 5mg/mL (right).

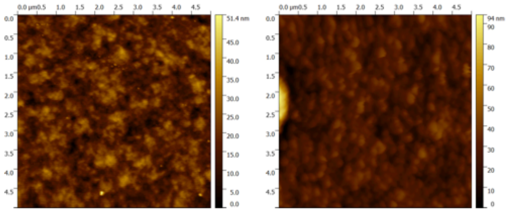

Figure 2. AFM images of parylene C decorated with PVDF nanoparticles from MEK solution at 1mg/mL (left) and 5mg/mL (right).

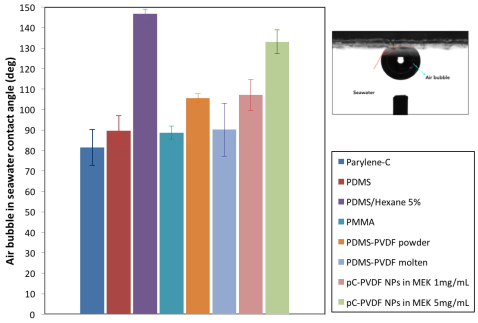

Figure 3. Captive air bubble method for measuring wettability underwater: comparison between different selected polymeric coatings.

Synthesis and characterization of graphene nanowalls / carbon nanotubes hybrid nanostructures

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In this work we propose a new method to obtain hybrid structures of carbon nanotubes (CNTs) and graphene nanowalls (GNWs). Both are carbon-based nanostructures that present high specific surface, high electric conductivity, chemical inertness and thermal and mechanical stability. These properties made them good candidates for several applications, such electrodes in supercapacitors [1, 2]. CNTs are obtained directly on stainless steel surface by plasma enhanced chemical vapor deposition (PECVD), without use of diffusion barrier and using the internal alloys elements of the substrate as a catalyst. With this approach is possible to obtain low resistance contact between the CNTs and the substrate [3]. GNWs obtained by inductively coupled plasma chemical vapor deposition (ICP-CVD) present catalyst free growth, so virtually they can be grown on every substrate that withstands the synthesis temperature. As a result, hybrid structures of GNWs-CNTs can be synthetized. The aim of the present work is to obtain different types of carbon hybrid nanostructures by combining GNWs and CNTs and to determine their properties. Characterization shows that various samples of independently CNTs, GNWs, and combination of CNTs-GNWs morphologies have been obtained.

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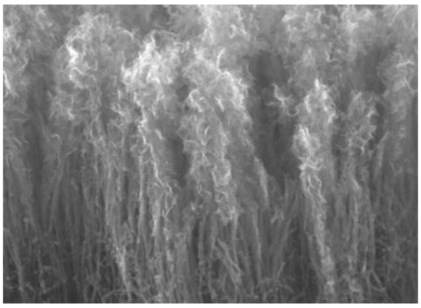

Figure 1. SEM image of GNWs grown on top of CNTs.

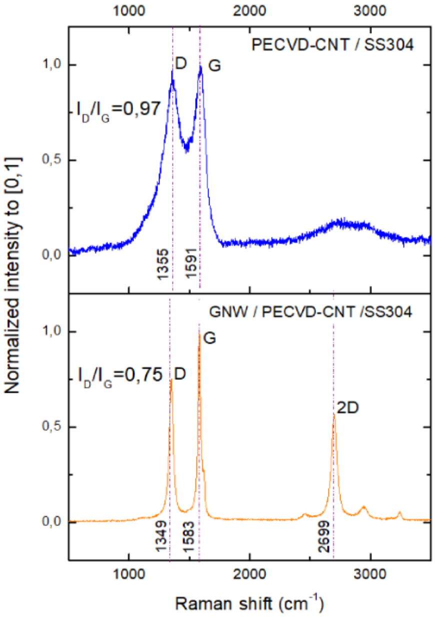

Figure 2. Raman spectra comparison of CNTs (Blue) and GNWs/CNTs (Orange). In GNW/CNTs spectra the characteristic peaks and ratios of GNWs can be appreciated.

Advanced nano-electrical characterization of solar cells and 2-d materials with atomic force microcopy

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A Over the past 30 years, Atomic Force Microscopy has evolved from a microscope to measure just the surface topography to a wide variety of measurement modes that provides a way to characterize other atomic interactions or physical properties like magnetic field, electric field, nanoscale dissipation processes, thermal conductivity, electrical conductivity, resistance, surface potential, piezoresponse, Young modulus,… Electrical nanocharacterization with AFM has emerged as a powerful tool to map electrical properties at the nanoscale, like surface potential (work function) and conductivity. However, traditional setups in AFM make difficult to obtain accurate and repeteable results over several types of samples.

In this contribution we will show the capabilities new developed AFM modes: High Definition Kelvin Force Microscopy (HD-KFM), ResiScope, Soft-Resiscope and Scaning Microwave that overcome the intrinsic difficulties of electrical nanocharacterization with AFM. This techniques have been applied on a variety of 2-D materiales surfaces, like graphene or molibdene disulfide samples providing high stability, sensitivity and lateral resolution.

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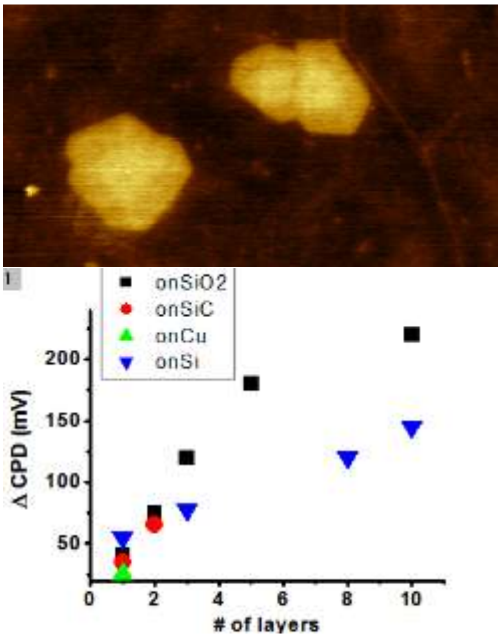

Figure 1. (Up) HD-KFM image of graphene on Si sample. Brown areas correspond to 1ML and yellow areas to 2ML/3 ML of graphene. (Down) SP values on of graphene on different substrates.

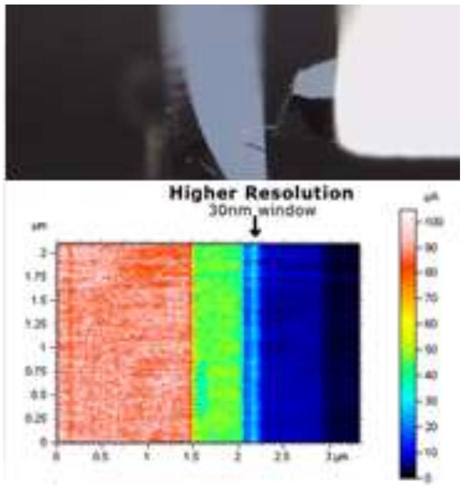

Figure 2. ResiScope measurement on a cleaved solar cell. (Up) lateral view of the conductive tip. (Down) Resistance image of the solar cell cross-section showing the cross-section of a cleaved solar cell showing the 30 nm back field layer.

Nanofabrication of extra-cellular recording electrodes for neuroscience on tapered optical fibers

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Neuroscientific research is benefitting from technological advances that provide scientists with tools to interface with neural circuits. In this regards, the advent of optogenetics techniques[1] has prompted the development of implantable probes to stimulate and inhibit neural activity, including opto-electrodes based on µLEDs[2,3] or Tapered Optical Fibers (TFs) devices exploiting mode-division de-multiplexing strategies. TFs are a versatile solution to dynamically illuminate wide regions (fig.1a), spatially confined regions (fig.1b) or multiple optical windows opened on metal coated fibers (fig.1c)[4–7]. However, as traditional fabrication techniques are designed for planar substrates, the integration of extracellular recording electrodes on the highly curved surface of TFs is an open challenge. To circumvent this limit, we developed a nanofabrication technique that combines Focused Ion Beam (FIB) milling and Ion Beam Induced Deposition (IBID). The nanometric precision of this method allowed us to fabricate two independent electrodes and two independently addressable optical windows on the highly curved surface of a TF (fig.2). To do this, we coated the TF with multiple metal layers that were mutually insulated by alternating each metal surface with a parylene-c deposition (fig.3a). We then opened two optical windows by selectively removing metal at specific taper diameters with FIB milling (fig.3b). Then, we grew Pt electrodes by IBID in metal recesses positioned next to the optical windows (fig.3c). We validated these devices with electrophysiological by recording neural activity from single neurons in the mouse cortex *in vivo* (fig.4).

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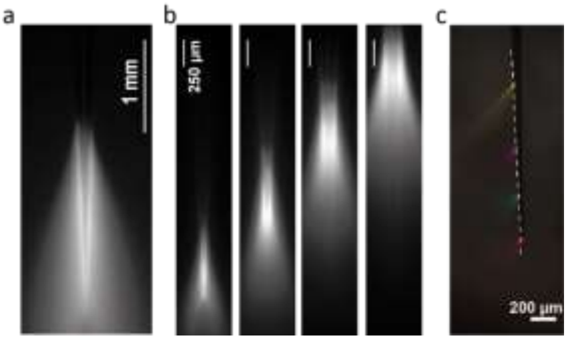

Figure 1. Light delivery geometries from TFs.

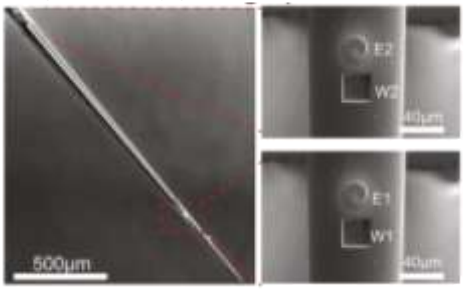

Figure 2. Scanning Electron Microscope micrographs of a two-windows two-electrodes device.

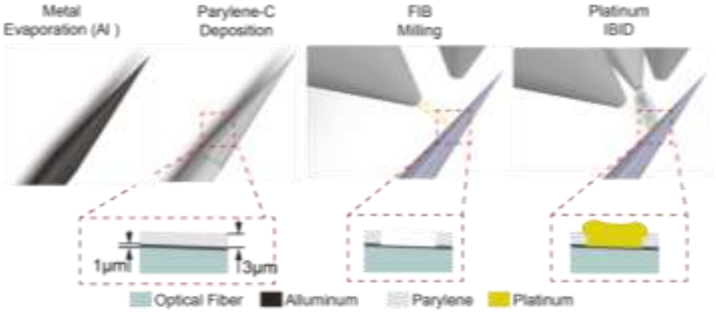

Figure 3. Nanofabrication of extracellular electrodes next to optical windows on TFs highly curved surfaces.

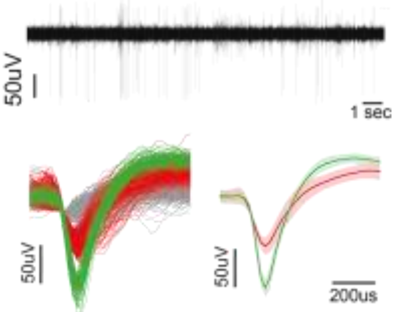

Figure 2. Example of raw traces (*top*) and distinct single units (*bottom*) recorded in mice cortical neurons.

The MBE Laboratory for van der Waals epitaxy of 2D layered heterostructures at IMM-CNR Lecce

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Van der Waals epitaxial (vdWE) heterostructures of crystallographically-oriented 2D materials offer a unique playground to tailor the physical properties of individual 2D materials by assembling them into novel 2D structures [1]. A series of emerging applications in electronics (FET, simple logic circuits, flexible transistors) and atomically thin opto-electronic devices (LEDs, laser diodes, PV cells, molecular sensors) have been demonstrated in the literature. However, most of these studies relies on device fabrication by mechanical stacking of single 2D monolayers onto a given substrate or another 2D material [2], so to obtain the desired 2D heterostructure. While this approach allows to obtain 'proof-of-concept' devices, it does not grant large-area industrial-scale production.

The grow of defects-free and azimuthally oriented 2D materials with control at the atomic-layer level is still a very challenging task. In recent years, the molecular beam epitaxy (MBE) growth of 2D materials has begun to be explored [3] as a viable alternative to chemical vapor deposition (CVD) for the sequential vdWE growth of 2D heterostructures on both metal and insulating substrates. Advantages of MBE technology over CVD methods are: (i) the occurrence of a self-limiting growth mechanism of 2D materials; (ii) the possibility to perform in-situ surface-science characterization, due to UHV conditions, and (iii) much easier control of monolayer growth over large diameter size.

In this contribution, we describe the MBE facility for the vdWE of 2D materials recently installed at CNR-IMM in Lecce within the framework of the PHASHYN Project funded by Regione Puglia. The MBE reactor consists of a RIBER Compact 21 CLS system [Figure 1] specifically designed to ensure deposition of 2D materials over a 2" dia. wafer, and process temperatures up to 1500°C. At present the reactor is equipped with a C sublimation source (heated up to 2300°C), utilizing a pyrolytic graphite filament, for graphene growth, but it has several UHV spare-ports; thus, its configuration can be upgraded with up to 7 sources to perform vdWE of hBN and transition metal dichalcogenides. The reactor is equipped with a RHEED system operating with a 12-keV electron beam for in-situ monitoring. The facility, the first one of its kind in Italy, is hosted inside the Semiconductor Physics and Technology Laboratory of University of Salento.

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Figures

Figure 1. Photograph of the MBE facility installed at IMM-CNR in Lecce.

Targeting mononuclear phagocytes for eradicating intracellular parasites

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Abstract

Mononuclear phagocytes such as monocytes, tissue-specific macrophages and dendritic cells are primary actors in both innate and adaptive immunity, as well as tissue homoeostasis.[1] They have key roles in a range of physiological and pathological processes, so any strategy targeting these cells will have wide-ranging impact. These phagocytes can be parasitized by intracellular bacteria, turning them from housekeepers to hiding places and favouring chronic and/or disseminated infection.[2] One of the most infamous is the bacteria that cause tuberculosis, which is the most pandemic and one of the deadliest diseases with one-third of the world's population infected, and 1.8 million deaths worldwide in 2015. Here we demonstrate the effective targeting and intracellular delivery of antibiotics to both circulating monocytes and resident macrophages, using pH sensitive nanoscopic polymersomes made of poly(2-(methacryloyloxy)ethyl phosphorylcholine)-co-poly(2-(di-isopropylamino)ethyl methacrylate) (PMPC-PDPA).[3] Polymersome selectivity to mononuclear phagocytes is demonstrated and ascribed to the polymerised phosphorylcholine motifs affinity toward scavenger receptors. Finally, we demonstrate the successful exploitation of this targeting for the effective eradication of intracellular bacteria that cause tuberculosis, *Mycobacterium tuberculosis*, as well as other intracellular parasites including the *Mycobacterium bovis*, *Mycobacterium marinum*, and the most common bacteria associated with antibiotic resistance, the *Staphylococcus aureus*.

Results

In this work, we have demonstrated that PMPC-PDPA polymersomes are an ideal candidate for targeting mononuclear phagocytes either after i.v. or topical administration, showing tremendous potential in using this approach for those diseases where these cells are critical actors. As a proof-of-concept, we showed that PMPC-PDPA polymersomes can be loaded with a large variety of antibiotics, including proteins (lysostaphin), small peptides (vancomycin), glycols (gentamicin), poorly water-soluble organics such as quinones (rifampicin) and functionalised pyridines (Isoniazid), thus covering a large repertoire of possible chemistries. We have shown that polymersomes can deliver antibiotics to treat intracellular pathogen-related infections, and to potentially decrease the dose and duration of treatment required for bacterial eradication. Both *in vitro* (in human cells) and *in vivo* experiments demonstrated that these nanoscopic synthetic vesicles were specifically internalised by macrophages, without inducing toxicity, through a combination of dynamin-independent endocytosis and phagocytosis. We have demonstrated that drug-encapsulated polymersomes were able to reduce *S. aureus*, Bacille de Calmette-Guerin (BCG - *M. bovis*), *M. tuberculosis*, and *M. marinum* bacterial burden, again using *in vitro* and *in vivo* approaches. Antimicrobial-loaded polymersomes were more effective compared with the same concentration of free drug, and in some cases were able to eradicate the intracellular microorganisms completely. We thus believe this technology can be exploited to reduce the effective dose required for therapy, with a consequent potential reduction in antimicrobial resistance. In addition, encapsulation of antimicrobials could help completely eradicate infection from the host more rapidly, by direct delivery of drug to the immune system to enhance the host-pathogen response.

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CONTROLLING CELLULAR TRAFFICKING BY NANOPARTICLE AVIDITY: FROM ENDOCYTOSIS TO TRANSCYTOSIS

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Therapeutic intervention in the central nervous system (CNS) is limited by the presence of the blood brain barrier (BBB) that controls the movement of molecules across the BBB. However, transcytosis mechanism can be hijacked to transport therapeutics to the CNS. Polymersomes, synthetic nanoscopic vesicles, represent a promising drug delivery system. They can accommodate a variety of drugs at high concentration and their outer surface can be decorated Angiopep2 peptide (AP2), which enables transcytosis. However, the mechanism regulating ranscytosis of nanoparticles into the brain is poorly characterised. We hypothesised that the intracellular trafficking of polymersomes decorated with AP2 is dependent on the density of ligands on the nanoparticle surface. To test this hypothesis we produced poly[oligo(ethylene glycol) methyl ether methacrylate]-block poly((diisopropylamino)ethyl methacrylate) (POEGMA-PDPA) pH sensitive polymersomes conjugated with different densities of AP2, and assessed transcytosis using a previously established BEC 3D transwell model3. We show that polymersomes decorated with AP2 bind LRP1 and are internalised by BEC. The rate of transwell crossing varies according to the densities of AP2 conjugated on the surface. Investigating the transcytosis mechanism, we found that a high AP2 density (60 AP2/polymersome) promotes the compartmentalisation of polymersomes in endocytic organelles positive for Rab5, 7 and 11. Contrarily, a medium AP2 density (25 AP2/polymersome) favours transcytosis through tubular structures. Real time live cell imaging studies and molecular dynamic modelling revealed that depending on the avidity of system, cells undergo endocytic vesiculation or tabulation followed by transcytosis. Polymersomes transcytosis is inhibited by small molecule inhibitors to the SNARE complex or dynamin, and also through depletion of cholesterol at the basolateral membrane, indicating an interdependency between endocytosis and exocytosis.

These results underline how ligand density contributes to the intracellular trafficking of nanoparticles. This work provides new insight into the mechanism of transcytosis through the BBB that be exploited for the design of nanotherapeutic vesicles targeting the CNS.

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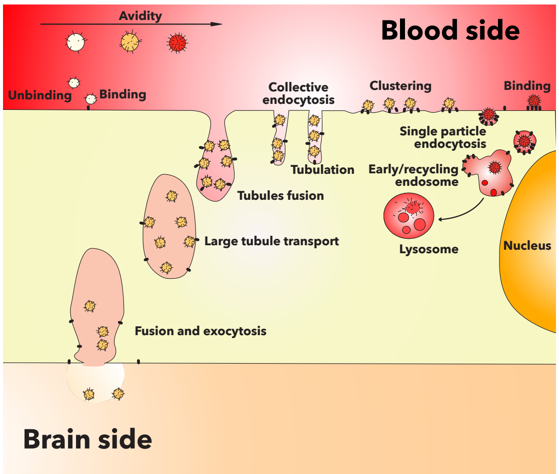

Figure 1. Schematic of the proposed mechanism of transcytosis mediated by nanoparticle avidity.

The Properties of 2D Materials on Functional Oxides

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As intriguing characteristics of two-dimensional (2D) materials including MoS_2, $ReSe_2$ and other transition metal dichalcogenides (TMDs) have been studied, the combination of 2D materials with various functional materials is attracting attention. Especially, high-κ dielectric or ferroelectric materials have been considered as promising candidates to study synergetic effects when integrated with 2D materials. Specifically, $SrTiO_3$ (STO) thin film can be used to aid at improving the performance of graphene device. We are interested in the properties of few-layer $ReSe_2$ and MoS_2 nanosheets or field effect transistor (FET) device on the functional oxides such as STO thin film or $BiFeO_3$ (BFO) nanodot array which attract much attention because of their potential applications to nanoscale devices required for the next-generation semiconductor industry. We made BFO nanodot arrays with 70nm in diameter on $SrRuO_3$ (SRO) /$SrTiO_3$ (STO) using porous anodic aluminum oxide (AAO) template and STO/Nb:STO thin film by pulsed laser deposition (PLD). And then we performed atomic force microscope (AFM), high resolution x-ray diffraction (HR-XRD) measurements for nanodot array and thin film. We also performed AFM and Raman spectroscopy for $ReSe_2$ and MoS_2 nanosheet to investigate their properties. We fabricated FET devices of TMDs using e-beam lithography and evaporator system and measured the electrical property of them. We are going to make the junction devices between TMDs and oxides by transfer method and investigate effects of oxides to their electrical and optical properties. For this, we will compare the experimental data with the simulation results.

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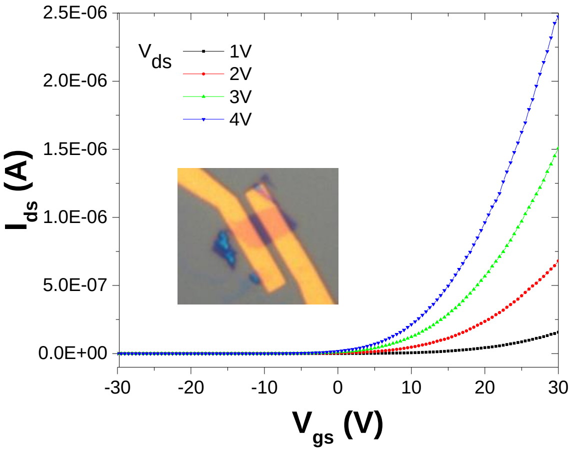

Figure 1. Transfer characteristics of few-layer $ReSe_2$ FET and optical image of device.

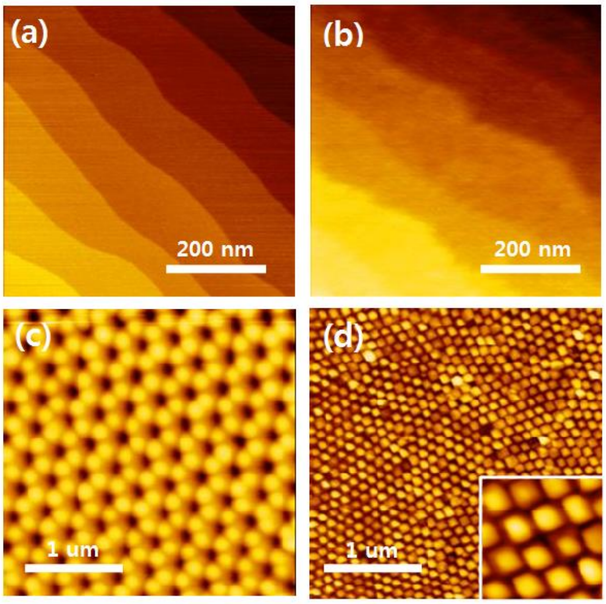

Figure 2. AFM topography images of oxides. (a) Nb:STO substrate which has terraces with smooth step edges. (b) STO thin film. (c) AAO template. (d) BFO nanodot array.

Graphene-based absobers exploiting guided mode resonances in nano-imprinted dielectric pillars

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The attractive optical properties of diffraction gratings have stimulated significant interest making them widely used in several applications ranging from sensing, spectroscopy and light absorption [1-2]. In this work, we propose the design of a two-dimensional (2D) array of polymethyl-methacrylate (PMMA) pillars deposited on different sputtered dielectric slabs (e.g. Ta_2O_5 and AlN) supported by a silicon dioxide (SiO_2) substrate (Fig. 1) or metallic films. The graphene monolayer is sandwiched between the PMMA pillars and the dielectric slabs representing the only material with absorption in the lossless system. The periodic structures are designed to phase-match the incident plane wave and couple discrete guided modes, also called guided mode resonances (GMRs) [3-4]. GMRs interact with the graphene monolayer enhancing the overall absorption.

The optical response is investigated by means of numerical simulations carried out by means of DiffractMOD (RSoft) that implements the Rigorous Coupled-Wave Analysis (RCWA) method. Fig. 2(a) and (b) show the absorption maps when the impinging source is tilted in the range 0°-90° for p- and s- polarizations in the case of PMMA pillars supported by a SiO_2 film. The maps clearly show a great variety of guided mode resonances that span from visible to near-infrared wavelengths.

Preliminary experimental results are reported where the PMMA pillars are realized by using nano-imprint lithography (NIL) by means of a silicon stamp.

In conclusion, the proposed configuration, based on guided mode resonances with sharp spectral features, will be exploited in a plethora of applications ranging from (bio)-sensors, biomedical applications, color control and filtering, nonlinear devices to optical absorbers.

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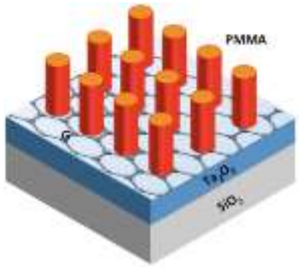

Figure 1. Sketch of the proposed device where the graphene monolayer is sandwiched between the PMMA pillars and the Ta_2O_5 slab supported by a glass substrate.

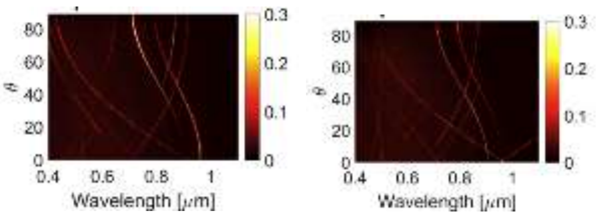

Figure 2. Numerical absorption maps for the (left) p-polarized and (right) s-polarized impinging field, respectively. The period and thickness of theTa_2O_5 slab are equal to 600 nm and 150 nm, respectively.

Investigation of Kinetic Functionals applied to metal nanoparticles

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In this contribution I present a study of Laplacian-level kinetic energy functionals [1] applied to metallic nanosystems [2]. The nanoparticles are modeled using jellium spheres of different sizes, background densities, and number of electrons. The ability of different functionals to reproduce the correct kinetic energy density and potential of various nanoparticles is investigated and analyzed in terms of semilocal descriptors. I find that the Laplacian contribution is fundamental for the description of the energy (and potential) of nanoparticles.

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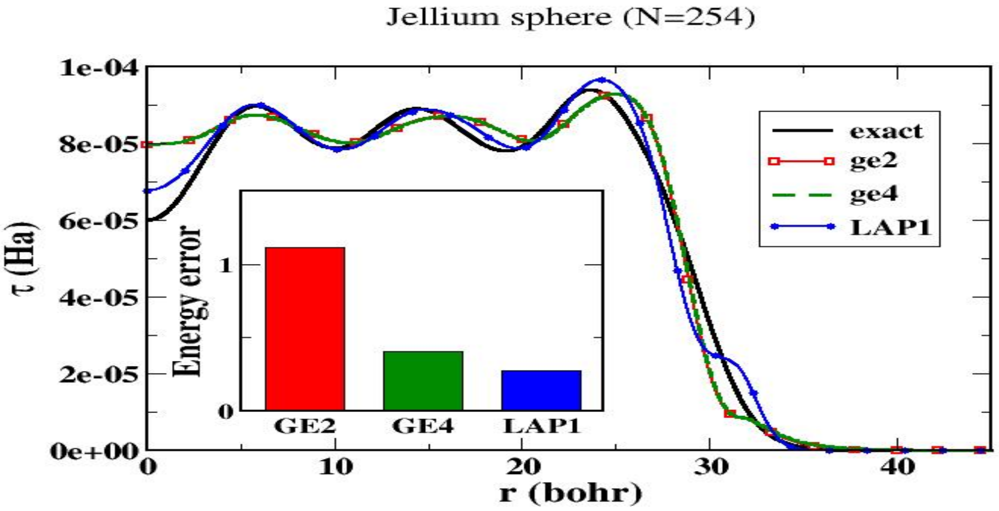

Functionalization of CVD-graphene controlled by QCN for the development of biosensing platforms

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Recently, carbon-based nanomaterials have provided an interesting approach for bioanalysis platform. Among them, graphene has attracted great attention in bioanalysis applications due to its remarkable electronic structure and high surface to volume ratio which contribute to the high sensitivity of graphene-based sensor devices [1].

The non-covalent functionalization of graphene with pyrene-based linker molecules brings great benefits, allowing to maintain unaltered the original graphene electronic properties and its low aspecific interactions with biological materials [2].

Although the interaction between aromatic systems and graphite surface has been investigated [3], the interaction mechanism and adsorption behavior of pyrenate amphiphilic molecules on graphene, has been reported in a very few papers.

In this work, we describe a non-covalent functionalization of graphene with a stealth-peptide bearing a terminal pyrene group (Peptide-Py), in view of the development of nanodevices such as tunable biosensor/bioanalyte concentrator. The terminal cysteine residual of the peptide would allow a further attachment of the capture antibody to the functionalized graphene.

Herein, the functionalization of graphene and thus the adsorption process and self-assembly morphology of the system onto nanoscale have been demonstrated both experimentally and by computational methods carrying out simulations to investigate the adsorption of a single molecule of peptide-pyrene on the graphene layer.

Graphene was grown on copper substrates via chemical vapor deposition (CVD) technique [4] and then transferred on Au coated quartz crystals for quartz crystal nanobalance (QCN). CVD graphene was self-assembled with the stealth peptide in flow and the functionalization was monitored by measuring the frequency variation using a QCN. To confirm the functionalization, the samples were characterized with several techniques.

Furthermore, we investigated the possibility to restore the pristine graphene layer applying a ramp of temperature, to allow the re-utilization of the sensor.

Acknowledgments

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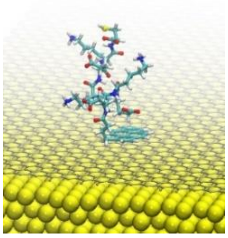

Figure 1. Scheme of the interaction between a single Peptide-Py molecule and graphene on Au/quartz crystal.

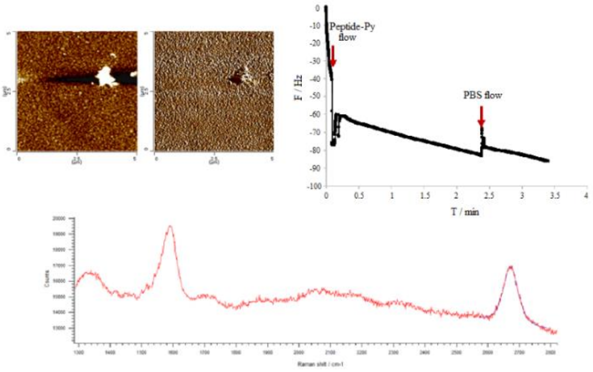

Figure 2. Functionalization of CVD graphene monitored by QCN and characterizations of the functionalized graphene layer.

Charge Trap Memory Devices of Balanced Ambipolar 2H-MoTe$_2$ Field Effect Transistors

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Transition metal dichalcogenides (TMDs) have been studied as alternatives of graphene since they are believed to overcome limits stemming from graphene's low ON/OFF ratio. TMDs solved this problem by having bandgap of about 1 eV ~ 2 eV.[1] Among them, 2H-molybdenum ditelluride (2H-MoTe$_2$) has bandgap of about 1.0 eV and high mobility of 200cm^{2}V^{-1}s^{-1} at room temperature was theoretically predicted.[2] The ON/OFF ratio was observed to be 5X10^2 and 2X10^3 for n-channel and p-channel 2H-MoTe$_2$ field effect transistors (FETs), respectively.[2] Most importantly, up to 10 layers, 2H-MoTe$_2$ field effect transistors showed ambipolar characteristics which were applicable for reconfigurable logic circuits.[3]

In this work, we fabricated and characterized few layer 2H-MoTe$_2$ field effect transistors annealed at different temperatures in the range of 200~300 °C. The annealed 2H-MoTe$_2$ field effect transistors showed balanced ambipolar behaviors while as-fabricated ones exhibited asymmetric n-type dominant ambipolar behaviors. These behaviors could be explained by adsorption of oxygen atoms on the Te vacancy sites and desorption of excess Te, which could reduce n-doping effect. Charge trap memory devices based on the ambipolar 2H-MoTe$_2$ field effect transistors were also fabricated by depositing top gate dielectric layers with charge trap sites through atomic layer deposition method.

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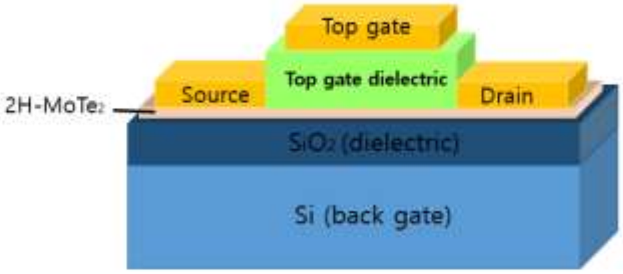

Figure 1. Schematic diagram of few-layer 2H-MoTe$_2$ charge trap memory.

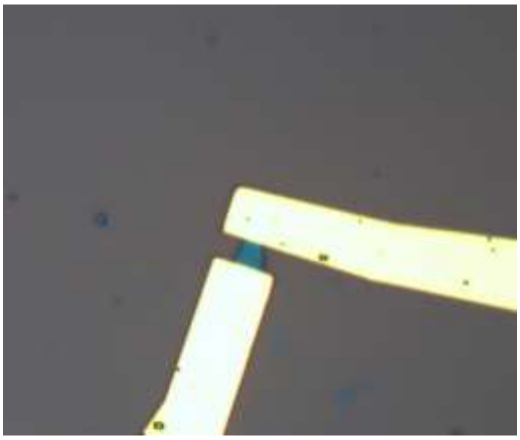

Figure 2. Optical image of few-layer 2H-MoTe$_2$ FETs

Synaptic Plasticity Selectively Activated by Polarization-Dependent Energy-Efficient Ion Migration in an Ultrathin Ferroelectric Tunnel Junction

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Abstract (Calibri 11)

Selectively activated inorganic synaptic devices, showing a high on/off ratio, ultrasmall dimensions, low power consumption, and short programming time, are required to emulate the functions of high-capacity and energy-efficient reconfigurable human neural systems combining information storage and processing.
Here, we demonstrate that such a synaptic device is realized using a Ag/$PbZr_{0.52}Ti_{0.48}O_3$ (PZT)/$La_{0.8}Sr_{0.2}MnO_3$ (LSMO) ferroelectric tunnel junction (FTJ) with ultrathin PZT (thickness of ~4 nm). Ag ion migration through the very thin FTJ enables a large on/off ratio (107) and low energy consumption (potentiation energy consumption = ~22 aJ and depression energy consumption = ~2.5 pJ). In addition, the simple alignment of the downward polarization in PZT selectively activates the synaptic plasticity of the FTJ and the transition from short-term plasticity to long-term potentiation.

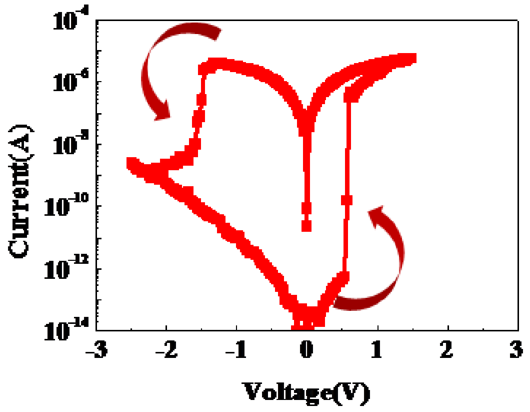

Figure 1. Resistive switching behavior.

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