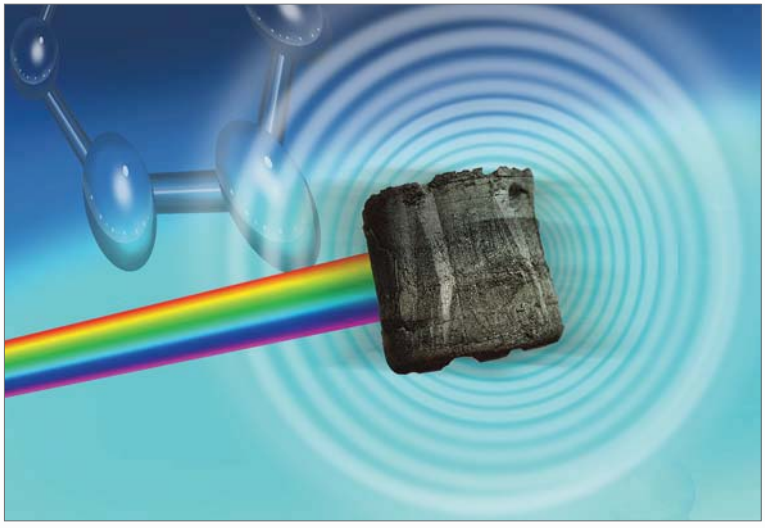
3D Graphene: From fundamental properties to applications



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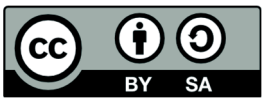

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Stefano Bellucci, Antonio Bianconi, Shuangming Chen, Francesco De Nicola, Paola De Padova, Luciana Di Gaspare, Neda Ghofraniha, Hengxing Ji, Andrea Liscio, Wen Liu, Stefano Lupi, Salvatore Macis, Augusto Marcelli, Andrea Notargiacomo, Andrea Perali, Liangti Qu, Milad Sani, Pengpeng Shang, Li Song, Xiaoming Sun, Silvia Tofani, Xiaojun Wu, Wei Xu, Zhipan Zhang, Yanwu Zhu.

*These authors presented the scientific reports collected in this book at the workshop held in Rome (Italy) on October 1-2, 2018.

Papers presented at the Italian and Chinese bilateral workshop "3D Graphene: From fundamental properties to applications"

Rome, Italy October 1-2, 2018

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Preface

Graphene is the first thermodynamically stable two-dimensional material discovered in nature. Its properties are extraordinary: from the very high electric mobility based on linear dispersion electrons (Dirac electrons), to the strong interaction with the electromagnetic field, to the high thermal conductivity, to the remarkable mechanical hardness.

In recent years research has focused on providing a third dimension to graphene. Recently three-dimensional (3D) graphene-like materials have been discovered with micro and nano-porous structures, or made by mesoscopic filaments that are distributed on macroscopic spatial scales. These topological structures allow preserving the extraordinary electrical and thermodynamic properties of 2D graphene extending them in 3D.

The porous or filamentous nature, and the high surface/volume ratio of these 3D architectures open interesting application scenarios and opportunities for fundamental physics researches: batteries and supercapacitors, flexible electronics, IR and THz photonics, plasmonics and finally, the manufacture of novel highly-efficient devices capable of transduce light into sound. This research triggered and will continue to stimulate also the physics of all carbon based materials and their technological applications.

Stefano Lupi and Augusto Marcelli

Preface

石墨烯是第一种自然界中发现的、热力学稳定的二维材料，各项性能优异：包括基于线性色散关系电子（狄拉克电子）而产生极高的载流子迁移率，与电磁场的强相互作用、热导率很高、卓越的机械硬度。

近年来，研究集中在为石墨烯提供第三个维度。最近发现了三维（3D）类石墨烯材料，或具有微米、纳米多孔结构， 或由分布在宏观空间尺度上的介观纤维构成。这些拓扑结构保留了二维石墨烯优异的电学和热力学性能，并将其扩展到三维体系中。

这种多孔或纤维的自然状态、以及这些三维构造中较的高比表面积，为基础物理研究创造了有趣的应用平台和机遇：电池和超级电容器、柔性电子器件、红外和太赫兹光子学、表面等离子体光子学、以及高效光声转换器件的制造。

Il grafene è il primo materiale 2D termodinamicamente stabile scoperto in natura. Le sue proprietà sono straordinarie: dall'elevatissima mobilità elettrica basata su elettroni a dispersione lineare (elettroni di Dirac), alla forte interazione con il campo elettromagnetico, all'alta conducibilità termica, alla notevole durezza meccanica.

Negli ultimi anni la ricerca si è concentrata sul fornire una terza dimensione al grafene. Recentemente sono stati scoperti materiali grafenici tridimensionali (3D) con strutture micro e nano-porose, oppure costituite da filamenti mesoscopici che si distribuiscono su scale spaziali macroscopiche. Queste strutture topologiche permettono di conservare le straordinarie proprietà elettriche e termodinamiche del grafene 2D estendendole nel mondo tridimensionale.

La natura porosa o filamentosa, e l'elevato rapporto superficie/volume di queste architetture 3D aprono interessanti scenari applicativi e di fisica fondamentale: dall'uso nelle batterie e nei supercondensatori, all'elettronica flessibile, alla fotonica IR e THz, alla plasmonica ed infine alla costruzione di dispositivi ad altissima efficienza capaci di trasformare luce in suono.

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Hybridizing nanocarbons with 2D layers

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Keywords: Carbon Nanomaterials, Layered Nanostructures, Hybridizing Interface, Synchrotron-based Study

Notably, the dimension of nano-materials has an immediate relevance on their physical and chemical properties, thus dominated the fields of specific applications. Thus, it is interesting topic to rationally hybridize 2D layers with various dimensional nanocarbons. In this talk, our recently studies will be presented, mainly focusing on the design and relazation of hybridized nanostructures with novel physical and chemical properties. Combining with theoretical calculations, the local electronic and micro structures of hybrids have been investigated by synchrotron radiation-based characterization techniques, including XAFS, XANES, ARPES and mass spectroscopy, which proved the existence of strong interaction among the hybrids and provided insight for better understanding the correlation between structure and performances.

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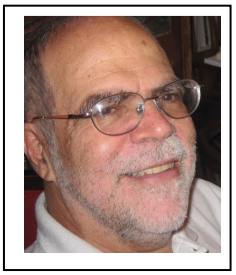
Unconventional topological superconductivity driven by Fano resonance at Lifshitz transitions in graphene superlattices



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Keywords: graphene superlattices topological superconductivity, topological matter, Fano resonances

Unconventional superconductivity in magic-angle graphene superlattices has been recently reported [1,2]. In twisted double-layer graphene at a small magic angle Moire bands are formed [3] and the multi-band flat-steep scenario [4] is realized where tuning the chemical potential the system shows topological Lifshitz transitions for the appearing of a new flat Fermi surface spot. Moreover recent papers have indicated of a possible superconducting transition above room temperature in natural graphite crystals at two-dimensional interfaces between the domains of highly oriented pyrolytic graphite [5,6]. These results open a new field of material design of graphene heterostructures at atomic limit to realize unconventional topological superconductors at room temperature, which has been recently observed in pressurized LaH_{10} [7].

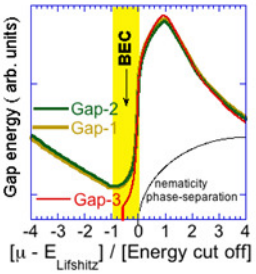

Figure 1: The BPV (Bianconi Perali Valletta) theory giving multi-gaps superconductivity at a Lifshitz transition, where BCS fails, by numerical solution of the Bogoliubov gap equation joint with density equation. The figure shows the superconducting dome where z is given by the chemical potential distance from the Lifshitz topological transition ELifshitz for the appearing of a new Fermi surface divided by the "energy cut off" of the pairing interaction. The BPV theory predicts a Feshbach resonance (Shape resonance) in the range of the Lifshitz parameter -1<z<0 (1<z<2).

The flat-steep band scenario was proposed as the mechanism driving superconductivity to high temperature [8] due to the formation of 2D incommensurate superstructures driven by misfit strain on cuprate perovskite heterostructures at atomic limit [9]. The Bianconi-Perali-Valletta (BPV) theory [10-15] of topological superconductivity was developed to describe the Bogoliubov superconducting phase at a Lifshitz transition where the BCS approximations are not valid. Figure 1 shows that the BPV theory predicts the emergence of Bose Einstein Condensation BEC at the Feshbach resonance with a minimum of Tc by numerical solution of the self-consistent anisotropic Bogoliubov gap equation joint with the chemical-potential density equation starting from the solution of the Schrödinger equation. The maximum of Tc in this unconventional superconducting state is driven by the exchange interaction at Fano Shape resonance between a quasi stationary BEC-BCS pairing state and delocalized pairing channels. A key feature of this scenario is the nanoscale phase separation at the Lifshitz transition [16,17] observed by scanning micro x-ray diffraction in many systems [18]. Finally the focus of the research is now on emergent topological non Euclidean hyperbolic geometry of the current pathways [19] to promote quantum coherence at high temperature this case of quantum complex matter.

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Enhanced Superconductivity and Superfluidity in Carbon Based Nanostructures: Theoretical Predictions and Experiments.

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Keywords: nanofilms, nanostripes, shape resonances, BCS-BEC crossover, multigap superconductivity, band edge, Lifshitz transitions.

Ultrathin superconductors of different materials are becoming a powerful platform to find mechanisms for enhancement of superconductivity, exploiting shape resonances in different superconducting properties. Since 2004, the observation of shape resonances in superconducting nanofilms of Pb and first evidences of shape resonances in the superconducting critical temperature in metallic nanowires of Sn and Al [1–2] clearly established the importance of the interplay between quantum size effects, leading to multiple bands, and superconductivity, when the lateral dimensions of the system are reduced to the order of the interparticle distance.
Moreover, superconductivity in iron-based, magnesium diborides, carbon-based and other high-Tc superconductors has a strong multi-band and multi-gap character [3,4,11]. Recent experiments support the possibility for a BCS-BEC crossover induced by the proximity of the chemical potential to the band edge of one of the bands, with evidences for Lifshitz transitions associated with changes in the Fermi surface topology [5, 6].
Here we present the simplest theoretical model which accounts for superconducting shape resonances and the BCS-BEC crossover in a multi-band/multi-gap superconductor, considering tunable interactions and nanostructured geometries. When the gap is of the order of the local chemical potential, superconductivity is in the crossover regime of the BCS-BEC crossover and the Fermi surface of the small band is completely smeared by the gap opening. In this situation, small and large Cooper pairs coexist in the total condensate, which is the optimal condition for high-Tc or even for room temperature superconductivity [7,8]. As a realizable example of enhancement of superconductivity in nanostructured materials, we consider here superconducting stripes organized in a parallel pattern (*Superstripes*), in which shape resonances and multigap physics at the band edge play a cooperative role in enhancing superconductivity in the crossover regime of pairing, while allowing for a sizable screening of the detrimental superconducting fluctuations [7,8,9]. A key prediction of this physics is the following: the isotope effect of the superconducting critical temperature in the vicinity of a Lifshitz transition, which has a unique dependence on

the energy distance (or density) between the chemical potential and the Lifshitz transition point [10].

The recent experimental indications of high-Tc superconductivity in potassium-doped para-terphenyl will be reviewed and discussed in this context [11], providing a possible theoretical framework for high-Tc superconductivity in quasi-1D quantum organic carbon-based materials.

Regarding excitonic superfluidity in graphene multilayers [12], here we propose a new graphene device to observe superfluidity and we predict enhanced electron-hole superfluidity in two coupled electron-hole armchair-edge terminated graphene nanoribbons separated by a thin insulating barrier [13].

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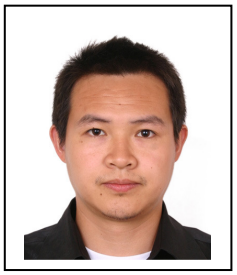
Nano Carbon based Materials design for Li-S batteries



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Keywords: carbon, shuttling effect, Li-S battery, energy storage

Based on the reaction of $16Li + S_8 \leftrightarrow 8Li_2S$, Li-S battery reaches a high theoretical energy density of 2600 Wh/kg, which is several times higher than that of traditional lithium ion batteries (LIBs). The low cost, high capacity as well as environment-benignity make Li-S battery as a strong candidate for next generation energy storage. [1] However, the development of Li-S battery is severely hindered by several problems, including the low conductivity of sulfur cathode, volume variation during charge/discharge and dissolution of lithium polysulfide (LiPS). These drawbacks cause low utilization of sulfur and poor cycling performance of batteries. To overcome these obstacles, researchers pay attention to regulating the construction of sulfur cathode, using mesoporous materials [2], core-shell types carbon [3] and graphene oxide [4] etc. The carbon based materials have significant benefit on the conductivity of the electrode and suppress the polysulfide dissolution to some extent. But the nonpolar carbon intrinsically has poor interaction with LiPS and lithium sulfide. Moreover, the lithium dendrite growth and electrode pulverization during cycling give rise to lower columbic efficiency and safety risks. Hence, the polysulfide trapping chemistry, sulfur electrode design and Li mental electrode protection are the key factors contributing to the cycling performance and stability of Li-S battery.
Herein, we propose polar materials including inorganic mental oxides [5], metal phosphides [6] and organic functional groups [7, 8], which further hybrid with nano carbons to construct bifunctional host for sulfur electrode. On one hand, the polar sites can strongly absorb LiPS, so that the dissolution of LiPS and shuttling effect can be reduced. On the other hand, polysulfide after absorption can quickly reacted with electrons and Li-ions, therefore improving the reaction kinetics and eliminating the bulky "dead sulfur" formation. Consequently, the Li-S batteries with the high performance sulfur electrodes can stably run for over 1000 cycles. The mechanism of sulfur trapping chemistry was also revealed by XPS characterization and theoretical calculation. [9]

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Soret reverse saturable absorption of graphene oxide and its application in random lasers

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Keywords: Graphene oxide, nonlinear absorption, Soret effect

There is increasing interest in manipulating the intensity and shape of laser pulses in a number of advanced optical technologies using nonlinear optical materials. There are two main classes of materials with nonlinear absorption: (i) saturable absorbers, which give increased transmittance at high optical intensities and are useful for pulse compression, Q-switching and mode locking; and (ii) optical limiters, which give decreased transmittance at high energy and are useful for the protection of eyes and sensitive instruments from laser induced damage.
Carbon based materials have shown in past both saturable and reverse saturable absorption and among them in the last years the optical limiting behavior of graphene and graphene oxide (GO) caused by nonlinear scattering or fast nonlinear absorption effects at high excitation intensities have been consolidated [1].

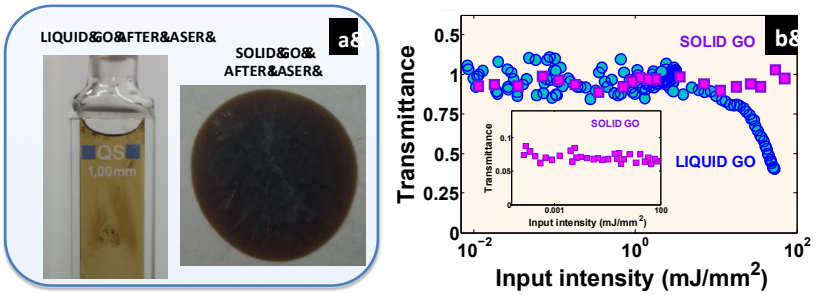

Figure 1: Pictures of GO dispersion after laser radiation compared to the solid GO thick film obtained by drop casting. The Soret effect is visible in liquid samples and completely absent in the solid one, as confirmed by the light transmittance curves reported in panel b.

Here we demonstrate the thermal diffusion of graphene oxide flakes in dispersion as a new nonlinear effect not yet explored. Specifically, under radiation the GO flakes absorb light and heat the solvent, the so obtained thermal gradient induce the migration of GO to the center of the input beam, where the temperature is higher, increasing in

this way the local absorption and breaking down the transmittance. We show a damping of 50% in the transmission and we follow its dynamics in time.
Moreover, this nonlinearity, known as Soret effect [2], is used to limit the emission from a disordered random laser reaching a decrease of about 90% of the emitted peak intensity without a substantial alteration of the cavity efficiency.

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CVD growth of graphene on Ge(100)

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Keywords: Graphene, Germanium, Catalysis, Chemical Vapor Deposition

Graphene integration in standard complementary metal oxide semiconductor (CMOS) technology requires large scale and scalable deposition technique for the synthesis of high quality graphene [1]. Catalyzed chemical vapor deposition (CVD) on metallic substrates has been largely predicted as one of the most promising techniques for this purpose. However, the integration in CMOS technology of CVD graphene catalytically deposited on metals is still hindered by metallic impurities and defects introduced by the growth process itself or in the transfer process on Si wafers. A significant advance toward a full compatibility of CVD graphene with CMOS-technology is represented by the recent achievement of metal contamination-free graphene grown directly on Ge or Ge/Si substrates, in particular on the technologically relevant (001) surface orientation [2-5]. However, "real-world" technological applications still need the improvement of the deposited graphene quality and the achievement of an accurate control over its properties. To this aim, we investigated the role of the process gas flows on the CVD graphene on Ge(001) and the early stage of the growth which is known deeply affect the graphene quality. The properties of the deposited material is assessed by using μ-Raman spectroscopy, x-ray photoemission spectroscopy, scanning electron and atomic force microscopies.
We find that by properly varying the gas precursor flows, we can tune the different growth regimes of graphene, ranging from nanoribbon formation, multi-layer graphene synthesis and finally to a layer by layer growth that allowed the deposition of a continuous single layer graphene with state of the art quality in a reproducible way.
We identified at the early stage of the growth the carbon precursor phase to graphene nucleation made of C atoms and/or CHx aggregates [6]. The C precursor phase evolves in graphene domains through a crystallization process that in turn results in the formation of a uniform single layer graphene. The nucleation of the small graphene domains is accomplished by the Ge surface proto-faceting that evolves in the characteristic Ge nano-faceting of SLG on Ge(001) with the exposure of the same {107}-{1010} facets at all the stage of the crystallization process.

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Towards an experimental validation at terahertz frequencies of Fabry-Perot Cavity leaky-wave antennas based on graphene

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Keywords: terahertz, leaky-wave antennas, graphene

A graphene sheet shows very interesting properties at terahertz frequencies, i.e. between 100 GHz and 10 THz, because its surface conductivity becomes mostly reactive. Hence, 2D graphene layers can profitably be used for the realization of fully-planar THz devices such as phase shifters, filters, or even antennas.
In the field of THz graphene antennas, the relaxation time of graphene is a crucial parameter for optimizing radiation performance in THz antennas based on either plasmonic [1] or nonplasmonic leaky waves [2]. In any case, no experimental results have been reported so far. Moreover, it is often numerically and theoretically assumed that graphene has the properties of a high-quality 2D material and the corresponding graphene THz antennas are fed by ideal dipole-like sources.
In this context, we aim at fully validating the radiation performance of the theoretical design in [3], which is based on a high-quality graphene sheet (namely, $\tau = 3$ ps). Differently from the structure analyzed in [3], here the Fabry-Perot cavity leaky-wave antenna (FPC-LWA) has cylindrical symmetry, which allows for obtaining omnidirectional conical beams over the azimuthal plane. This structure is fed by a realistic THz source, namely an open-ended waveguide feeding a quasi-resonant slot etched in the ground plane, and simulated on a commercial CAD solver (CST Microwave Studio). On the other hand, we aim at furnishing a more accurate estimation of the expected value of the relaxation time τ of graphene in the THz range. The transmittance of a chemical-vapor deposition (CVD) grown graphene sample transferred over a silicon substrate is therefore measured. The measurements are then compared with theoretical models assuming different values of τ to 'fit' the value that best matches the measurements. Results have shown that the relaxation time of a graphene sample is most likely in the range $0.025 < \tau < 0.25$ ps, thus confirming the discussion raised in [4], and the experimental results reported in [5]. These experimental results will lay the ground for the design of an ad hoc prototype, which will be more amenable for the future fabrication.

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Superwetting Nanoarray Electrodes for Gas-involved Electrocatalysis

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The electrochemical catalytic reduction reaction (such as hydrogen and oxygen reduction) is the basic reaction of many energy conversion devices, and the high conductivity, high activity and high stability of the electrode material is the prerequisite to ensure the high efficient catalytic reaction. The non-precious metal nanostructures are expected to be the ideal electrode materials due to their stable crystal structure, excellent internal conductivity and feasibility of surface electronic state control, however, their practical applications are largely limited by the complicated synthesis process. From the angle of "topological chemical synthesis", "surface electronic structure tuning" and "interface superwetting regualtion", we develop a new method of topological chemistry synthesis of non-precious metal nano-catalysis materials according to the characteristics of electro-catalytic reduction system, and then establish an ordered multi-scale micro-nano composite electrode structure. The surface composition and electronic state controllability of non-precious metal-based catalysis materials, the optimal orientation of the crystal surface, the porous structure and the surface superwetting property are realized. The electrochemical performances of the nanoarray electrodes are studied, and the electrochemical reaction kinetics is analyzed on the macroscopic, mesoscopic and microscopic scales. The synchronous improvement of the activity, selectivity and stability of the electrocatalytic reduction reaction is realized through the nanoarray structure design and surface electronic regulation.

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Thermoelectric performance of spark plasma-textured n-type polycrystalline SnSe

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Thermoelectric materials, which directly convert heat into electricity based on the TE effects, have long been investigated to use in semiconductor refrigeration or waste heat recovery. [1] SnSe has attracted significant attention due to its high ZT in single crystals. [2] The polycrystalline SnSe materials were then prepared to improve the mechanical performance for large-scaled application. However, the polycrystalline SnSe processes considerably low ZT due to their poor electrical properties. We aimed to improve the electrical and thermal transport properties of the n-type polycrystalline SnSe by doping and texturing.

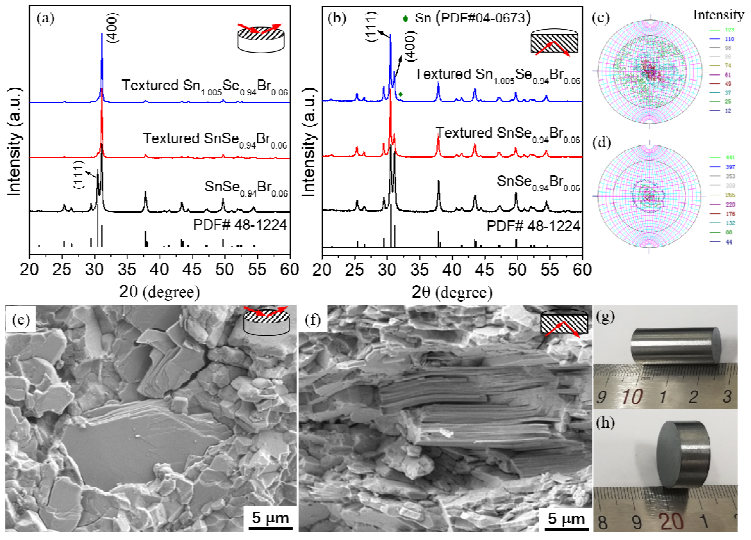

Figure 1: The XRD patterns (a, b), (111) and (400) pole figures (c, d) and fracture surface SEM patterns (e, f) of SPS-textured SnSe based bulks along the different pressure direction. Typical samples used in this study are shown in panels (g, h).

The effect of Br on the phase structure, electronic structure, microstructure and TE properties of SnSe was investigated. The spark plasma-textured structure boosts the electrical transport properties and the power factors as benefits of the layered microstructure. As a result, the ZT value is enhanced to be 1.5, owing to the distinct improvement of electrical performance and maintenance of low lattice thermal conductivity. The present investigation indicates that the TE performance of the n-type SnSe compound can be markedly improved by the texture modulation.

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Graphite Oxide-Derived Graphene Materials: from Fundamental Research to Industry

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Preparation of graphene materials from graphite oxide (GO) is one important approach to the large-scale production of graphene materials. The assembly or restructuring of graphene oxide (made by exfoliation of graphite oxide) leads to a broad range of GO-derived materials suitable to many potential applications. The functional groups in GO, which could be further customized if necessary, have brought more functions or flexibility in applications. This talk will review the preparation of graphene materials derived from GO, with specific focus on the progress in the industrial production. Some emerging applications of GO-derived graphene, e.g., as additive in various situation for improved performance and as precursor for new materials will also be summarized with highlight on the products in the market.

Terahertz and Infrared Plasmonic Absorption of 3-Dimensional Nano Porous Graphene

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Graphene Plasmonics hold promise of wide applications due to low-losses, tunability and extreme confinement at the nanoscale [1]. Three-dimensional Nanoporous Graphene (NPG) has recently been obtained with a new Chemical Vapor Deposition based fabrication process [2] (see Fig.1a) retaining the unique characteristics of mass-less Dirac fermions with high electron mobility. While NPG is the object of ongoing studies to demonstrated its application such as energy harvesting electrode [3], little is known about its optical properties. In this work we performed terahertz and infrared optical conductivity measurements. The optical conductivity (Fig.1b) exhibits, beside the typical interband absorption of graphene above the threshold of $2E_F$ (chemical potential of the system), a strong plasmonic absorption at terahertz (for low-doped samples) and mid-infrared (at high-doping) frequencies. We have shown that these plasmonic excitations strongly depend on the chemical doping and pore-size of the NPG 3D structure, following the behavior of 2D Dirac-Plasmons like in 2D graphene [4].

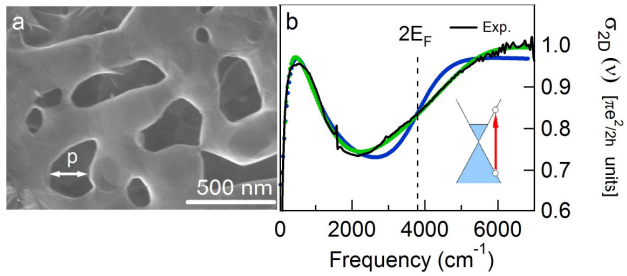

Figure 1: a) SEM image of Nanoporous Graphene with average pore size p=200 nm. b) A typical Infrared absorption spectrum for a doped sample shows two absorption features: interband transitions and a plasmonic peak, at high and low frequency, respectively.

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The Atomic Intercalation and Synchrotron Radiation Characterization of Two-Dimensional Layered Nanomaterials

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Atomic intercalation of different agents into 2D layered materials can engineer the intrinsic structure on the atomic scale and thus tune the physical and chemical properties for specific applications. We first successfully introduce tin (Sn) atoms into the interlayer of α-MoO_3 nanobelts forming a new MoO_3−Sn intercalation with ultrastable structure.[1] Combining with theoretical calculations, our synchrotron radiation-based characterizations and electron microscope observations clearly reveal that the intercalated Sn atoms could bond with five O atoms, forming a hexahedron structure. Employed as anode for lithium-ion battery, the as-prepared MoO_3−Sn nanobelts display a much higher capacity of 520 m A hg^{-1} at 500 m A g^{-1} than α-MoO_3 nanobelts (291 $mAhg^{-1}$), with a Coulombic efficiency of 99.5%. Moreover, owing to the strong intercalation from Sn ions, the MoO_3−Sn nanobelts pose superior cyclability, durability, and reliability. Then, Co atoms were successfully intercalated into the interlayer of V2C MXene forming the V–O–Co bonding structure.[2] This Co-ion intercalated V2C MXene electrode achieved a superior energy-storage capability up to 1117.3 mA h g^{-1} at 0.1 A g^{-1}, along with a particularly stable and ultralong cycling performance over 15 000 cycles with almost no capacity loss. These results clearly suggest that 2D materials with an engineered interlayer distance will be a rational route for realizing them as superstable and high-performance Li^+ capacitor electrodes.

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Sound and Light in 3D Graphene Aerogels

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Light modulation plays a key role in modern data transfer technologies providing many advantages, such as low attenuation, large bandwidth, and electric noise reduction.
Recently, we have shown that in three-dimensional (3D) graphene aerogels the modulated intensity of light can be transduced in acoustic waves through a photo-thermo-acoustic mechanism [1]. Such a transduction is highly efficient due to the unique combination of mechanical, optical, and thermodynamic properties of graphene assembled in the aerogel structure.
So far graphene loudspeaker [2] has been implemented using thermoacoustic transduction of an electrical signal into heat and sound. These devices are based on a substrate-deposited single-layer graphene to achieve a good mechanical stability. Although, the major part of heat is dissipated in the substrate thus reducing the thermoacoustic conversion efficiency, those thermoacoustic devices are able to operate in a wide frequency range up to tens of kHz.
Here, we demonstrate a 3D graphene-based photo-thermal loudspeaker independent of light wavelength from the radio wave to ultraviolet range, allowing a full digital operation for frequencies from the acoustic to ultrasound range. The present results suggest a new pathway for light generation and control of sound and ultrasound signals, potentially enabling a variety of new technological applications from high-fidelity loudspeaker and radiation detectors for medical devices.

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Theoretical Design of 2D Hybrid Structures for Energy Storage and Conversion

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Keywords: first-principles calculations, 2D materials, hybrid structures, optoelectronic

Two-dimensional atomic-thick materials, such graphene and graphene-like inorganic materials, present novel physical properties and great potential in electronics, spintronics, optoelectronics, and energy. With large surface area, the interalayer vdW interaction always play important factor for their applications. Adopting the concept of superarchitecutre, we present theoretical designs of 2D hybrid structure with assembled properties by using covalent or non-covalent interaction, including graphene nanobud and 2D heterojunctions. The band alignments and optical adsorption behavior implies these hybrid structure can be used for optoelectronics with high quantum efficiencies. We believe these designs will stimulate the corresponding experimental investigations.

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On the appearance of an energy gap and he electrical conductance of graphene, depending on the ordering of impurities

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In recent times, a special attention has been paid to the possibility of a targeted modification of graphene with the help of purposely introduced impurities, formed defects, and atoms or chemical functional groups deposited on a surface. In this case, wide possibilities to change the physical properties of graphene are opened, due to the controlled introduction of impurities by the method of ion implantation.
The quasirelativistic spectrum of charge carriers determines the unique properties of graphene and, simultaneously, hampers the use of graphene in field-effect transistors due to the absence of a gap in its spectrum. It is known that the impurities can lead to the appearance of such a gap, whose width depends on the type of impurities and their concentration.
The recent investigations of the energy spectrum of graphene are based on the density functional theory. The numerical calculations made within the method have demonstrated the appearance of a gap in the energy spectrum of graphene caused by the presence of an impurity. However, in order to clarify the nature of this effect, it is necessary to supplement the mentioned numerical calculations by analytic studies of the influence of impurities on the energy spectrum and properties of graphene.
In the one-band model of strong coupling, the influence of substitutional impurity atoms on the energy spectrum and electrical conductance of graphene is studied [2]. It is established that the ordering of substitutional impurity atoms on nodes of the crystal lattice causes the appearance of a gap in the energy spectrum of graphene with width $\eta|\delta|$ centered at the point $y\delta$, where η is the parameter of ordering, δ is the difference of the scattering potentials of impurity atoms and carbon atoms, and y is the impurity concentration. If the Fermi level falls in the region of the mentioned gap, then the electrical conductance $\sigma_{\alpha\alpha}\to 0$ at the ordering of graphene, i.e., the metal–dielectric transition arises. If the Fermi level is located outside the gap, then the electrical conductance increases with the parameter of order η. At the concentration $y=1/2$, as the ordering of impurity atoms $\eta \to 1$, the electrical conductance of graphene $\sigma_{\alpha\alpha}\to\infty$, i.e., the transition of graphene in the state of ideal electrical conductance arises.

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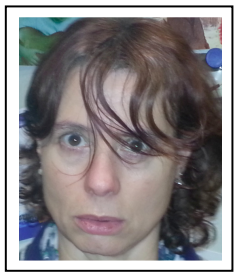
Multilayer Silicene: a New 2D Material



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Keywords: Silicene, multilayer silicene

2D multilayer silicene, the silicon analogue of multilayer graphene, usually grown on silver (111) surfaces, possesses a honeycomb $\sqrt{3}\times\sqrt{3}R30°$ reconstruction, after the initial prototype formation of the 3×3 reconstructed, silicene monolayer [1] Cone-like dispersion, by synchrotron radiation photoelectron spectroscopy, provided clear evidence of the presence of gapless Dirac fermions at the Brillouin zone centre due to band folding π and π^* states meet at ~0.25 eV below the Fermi level [2]. Recently, multilayer silicene has been synthesized for the first time upon Si deposition (in UHV) onto Si(111)$\sqrt{3}\times\sqrt{3}$-Ag substrates [3].
AES, LEED, STM/STS, in-situ Raman spectroscopy and energy dispersive in-plane x-ray diffraction were applied, yielding fingerprints of $\sqrt{3}\times\sqrt{3}$ multilayer silicene, whereas DFT calculations provided structural models of single, bilayer and 3-layer silicene on the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface. The single layer silicene retains its free-standing form, while the structural models, which are consistent with the experimental findings, exclude that the atomic structure is diamond-like Si [3].
Multilayer silicene, already synthesized on both single crystal Ag(111) [4] and on Si(111) after the interface formation of Si(111)-$\sqrt{3}\times\sqrt{3}$ Ag [3], displayed the ambipolar character in the realization of the first multilayer silicene-based field effect transistor [5].
Comparison between multilayer silicene grown on Ag(111) and Si(111)$\sqrt{3}\times\sqrt{3}$-Ag will be reported.

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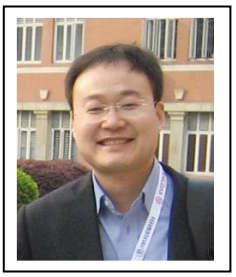
Graphene Platforms for Energy Conversion and Storage



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Nowadays, energy generation and storage are two important topics. Unfortunately, conventional energy generators are not capable of responding to environmental changes, while traditional energy storage devices lack special functionalities apart from supplying electricity. Benefitting from exceptional physicochemical properties, graphene-based materials help to address the aforementioned issues. In this presentation, we introduce our recent results in graphene-based smart energy generation and storage systems, including moisture-triggered actuators and electric generators, together with smart batteries and supercapacitors of deformability, wearable-ability, stimuli-response, etc.

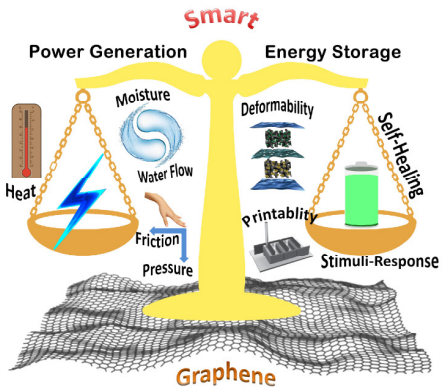

Figure 1: Graphene platforms for power generation and energy storage

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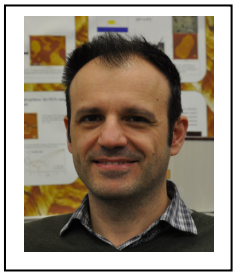
Understanding the exfoliation processes of Graphene and Related Materials: from a single piece to a large-scale production.



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Keywords: graphene based materials, large-scale production, fragmentation

The understanding the exfoliation processes of Graphene and Related Materials (GRMs) is a key-point for the upscaling production of such materials. Focusing on Liquid Phase Exfoliation approaches, we visualized and characterized the different processes known so far for exfoliation and intercalation of 2D layered materials. Aiming at the fundamental understanding of these processes and possibilities for optimizations in terms of composite production (such as GRM-host interactions) is mandatory to provide standardised approaches to manage such materials at industrial scale.
For this reason, we explored two routes:

- New scalable protocol of electrochemical exfoliation: new routes to produce GRMs compatible with large-scale industrial application.[1,2] Tunable properties of the produced materials. Step-by-step in-situ and ex-situ monitoring to minimize the defects without significant loss of processability or properties.
- Beyond solution monitoring.[3] Small molecules as surfactants to stabilize GRMs in low-boiling point solvents Direct understanding of solution properties. Development of experimental protocols and mathematical/statistical tool dedicated to the quantitative analysis of large scale GRMs.

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Graphene-based Systems for Catalysis

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Efficient photoelectrochemical catalyses are important prerequisites for a range of energy devices such as fuel cells, solar cells and certain secondary batteries. In recent years, we have used different methods including electrochemical scissoring, *in-situ* assembling and bal-milling to prepare graphene structures ranging from 0D graphene quantum dots, 2D graphitic carbon nitride nanoplatelets to 3D graphene networks. In particular, we have studied the performance of these structures in electrocatalysis and photocatalysis, with emphasis on oxygen reduction reaction, oxygen evolution reaction and hydrogen evolution reaction.

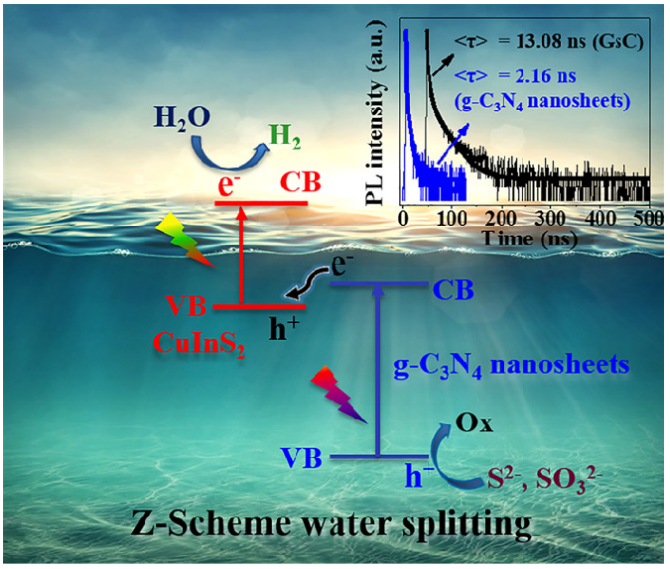

Figure 1: Graphene-based systems for photocatalysis—a case of Z-Scheme water splitting

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Anderson localization of surface plasmons in monolayer graphene

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Graphene is a two-dimensional material that has been highly regarded with its unique features to excite surface plasmonic waves. The graphene based plasmonic nanostructure allows the manipulation of electromagnetic energy strongly beyond the diffraction limit. Also the graphene surface plasmons (GSPs) display broad optical exciting wavelengths from the near-infrared to the terahertz (THz) regions.
On the other hand, researchers have a lot of interest in studying and observing the Anderson localization (AL) of surface propagating plasmon waves. The plasmonic waves in conventional plasmonic material such as metals have radiation leakage and inherent ohmic loss, so the inducing of AL of surface plasmon waves in these material has been a challenging task.
In this work, we present the Anderson localization (AL) of surface plasmons in monolayer graphene [1]. we proposed an active plasmonic device that consists of a monolayer graphene on silicon random grating to trap the surface plasmons in local cavities that are created by random multiple scattering. Several new localized GSP modes with higher intensity and quality factor are occurred with respect to corresponding modes in periodic substrate structure.
In this work the localized GSPs are directly generated and confined in the graphene layer by interacting normal incident light with random grating as a substrate of the graphene layer. These GSPs could not propagate along the graphene and this feature limited the practical applications of these highly localized GSPs. Recently, we introduce the AL of propagating GSPs which are excited before entering the graphene based random structure (see figure 1) [2]. The AL of propagating GSPs is created by randomly modulating the surface conductivity of graphene by using a silicon random grating structure.
Although tuning the resonance wavelengths belonging to AL GSPs is a difficult task due to its random nature, here we tune these wavelengths by adjusting the Fermi energy of the monolayer graphene. We believe that these tunable highly localized GSPs will open new window to development of optoelectronic devices. Also, it may facilitate the preparation of next-generation optical integrated systems based on graphene nanostructure such as graphene based solar cell (increasing the solar absorption bandwidth), spatial light modulators and plasmonic sensors.

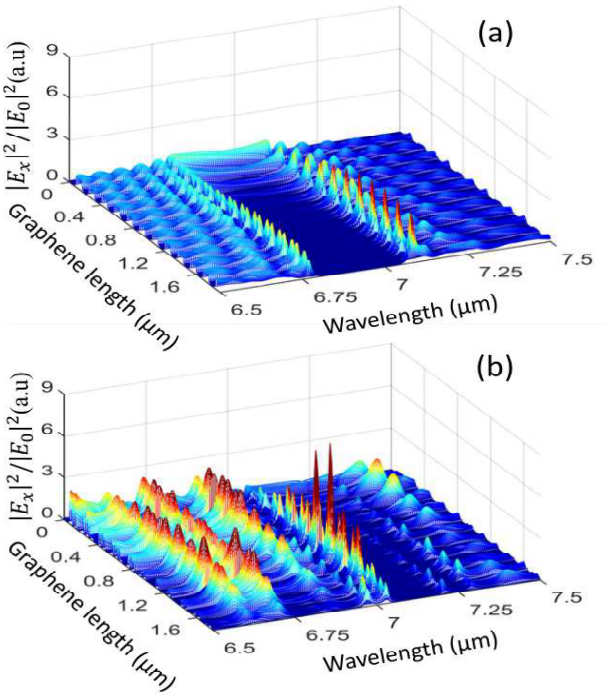

Figure 1: The normalized field intensity distribution on the graphene layer as a function of frequency and the position on the graphene for (a) periodic grating and (b) random grating. (Here $|E_0|^2$ is the maximum value of $|E_x|^2$ for periodic grating).

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Carbon based current collectors for lithium metal anodes

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The Li-based batteries are a hot research topic because they are the most popular energy storage system for high-energy-density devices. As an important component of the battery, current collectors in both cathode and anode are used to support the active materials, deliver electrons between active materials and the external circuit, and expand internal thermal heat generate in the electrode film. In order to achieve this function, the current collectors have to be (1) free-standing or self-supporting with macro-scale size, (2) mechanically robust, (3) electronically and thermally conductive, (4) electrochemically inert, (5) light in weight, and (6) low cost.
Carbon as the most versatile element manifests itself in a wide variety of allotropic forms that exhibits a diverse range of properties, is one of the most important materials in energy storage applications. sp^2-hybridized carbon materials exhibit excellent electric/thermal conductivity, structural stability, and chemical inertness due to the highly delocalized π electrons. In addition, carbon allotropes have a lower mass density (~2.3 g cm^{-3} for graphite) than metal used for current collectors. Combination of these carbon materials used in complementary ways makes it the promising building constituents for current collectors.

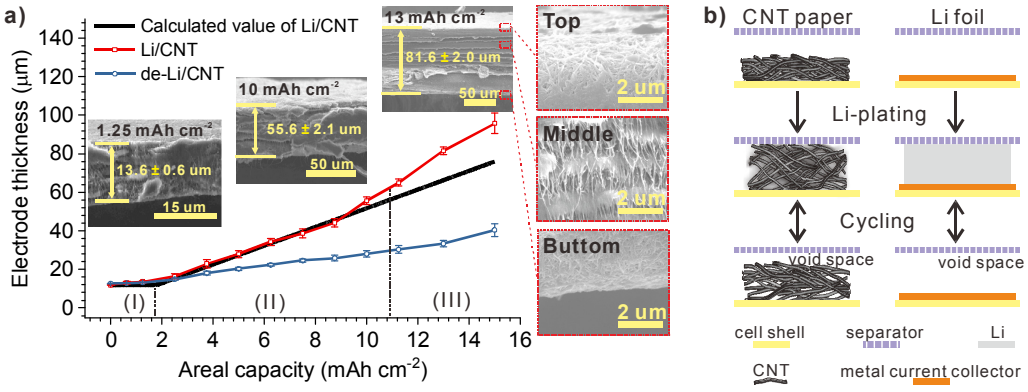

Figure 1: a) Thicknesses of Li/CNT and de-Li/CNT at different Li loadings. Insets show SEM images obtained from cross sections of Li/CNT with Li loadings of 1.25, 10, and 13 mA h cm^{-2}. b) Schematic of volume expansion Li/CNT and Li-metal foil as electrode during Li-stripping/plating.

We introduce our recent progress in constructing of 3D scaffolds made of sp^2-hybridized carbon constituents as current collectors for lithium based batteries.[1 – 5] The requirements and the challenges of the 3D carbon based current collector's design are discussed, which provide inspiration for further exploitation of the current collectors for Li-ion batteries and sheds light on batteries based on other electrochemistry.

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Poster presentations

Few-layered graphene platelets for microwaves and (bio)sensors applications

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Among their remarkable properties, graphene and graphene-related materials constitute an effective vehicle for the realization of new electronic devices operating at different frequencies. We overview the Synthesis and Electrical Characterization of few-layered Graphene along with some recently developed applications, such as:
- Theoretical and Experimental Characterization of a Graphene-Based Broadband Microwave Attenuator, Phase shifters, patch Antennas
- Bottom-up Realization and Temperature-Dependent Electrical Characterization of a Green, Low-Cost Graphene-Based Device
- Development of Sensors and Biosensors using Carbon Nanotubes and Few Layered Graphene.

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SPM lithography on graphene on Ge(100)

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Graphene is an extraordinary material with exceptional physical properties that make it an ideal candidate for a range of applications in electronics and optoelectronics [1, 2]. The CVD deposited graphene natively grown on a CMOS semiconductor such as germanium [3, 4] is an appealing emerging system suitable for the development of graphene-based CMOS-compatible devices. Scanning probe microscopy (SPM) lithography is a simple and rapid prototyping technique allowing for surface modification using a variety of approaches including field-assisted local oxidation and mechanical scratching [5], which were already applied on graphene transferred on host substrates [5, 6]. Here we report on the first SPM lithography experiments on graphene-on-Ge.

Samples with different graphene coverage, from sub-monolayer to few layers, were grown on Ge (001) substrates by means a commercial CVD system, using H_2 and CH_4 as precursor gases and Ar as a carrier gas. The control over the growth parameters allowed to obtain mono-layer graphene films with complete sample coverage, as confirmed by Raman and x-ray photoelectron spectroscopy. The sample morphology measured with atomic force microscopy (AFM) evidences a characteristic ordered faceting along [100] Ge substrate directions of the monolayer graphene.

On the monolayer graphene samples, the AFM was used in the contact mode employing silicon cantilevers with bulk Pt tips in order to perform lithography in the local oxidation configuration, i.e. negative tip-to-sample voltages applied while translating the tip across the substrates. Lines were patterned applying voltages in the (-8 ÷ -5)V range at a translation rate of 2 μm/s. For the lowest voltage no signature of surface modification was found while at larger negative tip-sample voltage protruding lines were found. The section profile analysis revealed a line-width of the protruding lines increasing from ~50nm to ~250nm as the voltage amplitude is increased from -6V to -8V. The protruding thickness increases from ~2nm to ~4nm in the same voltage range. These findings are compatible with the formation of graphene oxide and/or the oxidation of the Ge substrate underneath. Sets of line patterned as a function of the translation rate and number of repeated passes were also studied.

As an alternative lithographic approach, mechanical removal (scratching) of graphene from extended areas was made by imaging the sample at high enough contact forces.

Rectangular regions were defined, showing apparent localization of debris at the pattern borders. The debris, originated from scratching, are mainly accumulated at the shorter sides of the rectangular scan area, i.e. aside the fast scan direction during area imaging at high force applied. The complete removal of graphene was confirmed by conductive-AFM measurements: a uniform conduction pattern typical of CVD graphene grown on Ge was found to be still present outside the patterned area, while a negligible current intensity was detected inside the scratched area.

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The High Energy Resolution Spectroscopy beamline at HEPS-a suite of tools for probing elementary excitations and hyperfine field

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Keywords: Synchrotron Radiation, NRS, IXS, Huairou, HEPS, HXHERS

Properties of natural or artificial materials have been continuously discovered and manipulated by deciphering the intriguing relationship with structure and dynamics. The properties are related to the atoms, lattice and the charged/spin that are in-homogeneously distributed in certain order. Many researches are devoted to capture the structural or dynamical features that play crucial role in affecting the transport behavior or electronic structure in variety of functional systems, such as superconductors, topological insulators or even more complex biological systems.

Figure 1: Bird view of HEPS in feasibility study phase

The high energy resolution spectroscopies based on X-ray scattering provide a suite of tools to enable scientists capturing fundamental elementary excitations as well as hyperfine fields that govern the origins of exotic properties. For instance, the Resonant Inelastic X-ray scattering (RIXS) techniques allows for measuring the dispersions of elementary excitations with different origins. Whereas the nuclear resonant scattering (NRS) aims at measuring collective excitations, i.e. the isotope-specific phonon density of states. And it is the unique tools available at synchrotron facilities to probe the

hyperfine interactions of nuclei. Furthermore, the X-ray Raman scattering (XRS) enables collecting soft X-ray absorption spectroscopy using hard X-ray around 10 keV, with higher penetration depth suitable for demanding sample environment, e.g. high pressure, in situ. All the above techniques belong to the high energy resolution spectroscopies.

In the following years, the HEPS will be built in Huairou district, a.k.a., natural "oxygen bar" situated in northern Beijing, 50 km from the city center. The HEPS, running 6 GeV electrons with accumulated current~200mA, is a low-emittance, synchrotron radiation facility based on Multi-bend Achromat (MBA) lattice design [1-3]. The Hard X-ray High Enegy Resolution Spectroscopy (HXHERS) beamline, one of the 14 beamlines in Phase I at the High Energy Photon Source (HEPS). The HXHERS beamline (Figure.1) will provide three high energy resolution spectroscopies, i.e., RIXS, NRS and XRS. In this contribution, we present the preliminary design of the beamline and the end-stations for these techniques.

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High electric field breakdown test on MoO_3-carbon nanotubes coated on copper

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Keywords: carbon nanotubes, molybdenum trioxide, coating, THz, FEL, breakdown

Coatings are used in several technological and industrial applications. Metallic coatings, in particular, are used in aerospace and space applications to increase the lifetime of critical components or to enhance the resistance to friction, abrasion, corrosion, etc. The understanding of the properties of metallic surfaces and coatings characterized by a low secondary electron emission yield (SEY) is another important field of interest. In order to study the breakdown phenomenon and the change of the copper properties by the induced damage, we developed a procedure to growth a thin MoO_3 layer on a nanotube forest deposited on a smooth copper substrate. We exposed this structure at a high electric field generated by THz radiation emitted by the Free Electron Laser (FEL) operative at the Institute of Scientific and Industrial Research (ISIR) of the Osaka University.

Cu has many technological applications, e.g., in radio-frequency (RF) devices, which are mainly limited by the highest applicable electric field. New RF cavities with an acceptable length and a sustainable cost, are needed for high-energy physics accelerators, such as the future multi-TeV e^+-e^- collider that will only be possible thanks to extensive and challenging research and development [1]. Moreover, shorter accelerators can become suitable for many more applications and to a larger number of industrial users [2].

With the present materials and manufacture technology, breakdown phenomena occur for accelerating gradients > 100 MV/m. With the application of a high electrical field on a metallic surface we need to limit breakdowns and control the field-electron emission, another important parameter of accelerator structures. The breakdown phenomenon, which takes place in vacuum, depends on the material properties and conditions existing at and/or adjacent to the surface of the device. In spite of the studies performed and the technological efforts in manufacturing technology, since many competitive surface processes are involved, the scenario in which a breakdown may occur is far from understood [3]. It is, therefore, essential to characterize the surface (and bulk) properties of all materials used for these challenging applications.

Here we present the deposition process of carbon nanotube forest followed by a deposition of a MoO_3 thin film (see figure 1) 50 nm thick at RT. The MoO_3-carbon nanotubes couple, besides protecting the copper surface, is also highly conductive as showed by Esconjauregui *et al.* [4], a property fundamental to control the Q factor of a RF cavity. Also the MoO_3 film has a high work function (WF), while is conductive, further reducing the breakdown probability and dark current emission from the surface [5].

Figure 1: (Left) A 50 nm MoO_3 film coated on a low roughness Cu substrate with the typical purple color; (Right) a low roughness Cu substrate covered in the center region by a carbon nanotubes film 50 nm thick. Actually, later half of this substrate (the bottom one) is covered by a 50 nm MoO_3 film, as the purple color demonstrates.

High electric field THz irradiations were performed using coherent THz radiation focused on the samples surface where it generated multiple local breakdowns [6,7]. In our experiment radiation with a frequency of 3 THz has been concentrated in a 100 μm radius area, generating a local power density of 0.15 TW/cm^2 and a maximum electric field, on the center of the illuminated area, of ~5.8 GV/m.
After the irradiations the damaged zone was investigated with optical microscope for a morphological analysis, SEM and Raman spectroscopy, for structural and chemical characterizations. After 5000 macro pulses, each of which induces an electric discharge on the surface of the coated sample, the MoO_3 and C-nanotubes film appears damaged and in the central zone the coating is no longer visible while no visible damaging appears on the copper substrate.

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