Doping molecular semiconductors

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Recent development of organic semiconductors presents significant progress both in small-molecular crystals and semi-crystalline π-conjugated polymers, achieving high carrier mobility based on coherent electronic transport. Extremely thin crystal films of Cn-DNBDT small molecules are successfully grown to a-few molecular layers with the thickness of only 10 nm, so that very high carrier mobility more than 10 cm^2/Vs is achieved to the dimension of 30 cm x 30 cm. Current technologies for printed integrated circuits provides a manufacturable process for low-cost platforms for RFID tags, sensing circuitries, and large-area light-weight display sheets. Single crystal field-effect transistors of such materials display coherent band transport near room temperature as the result of Hall-effect measurement. In addition, mobility exceeding 1 cm^2/Vs are achieved for semi-crystalline π-conjugated polymers such as PBTTT, in which Hall-effect measurement indicate charge coherence over a-few-molecular distance. The presentation focuses recently developed methods of carrier doping without carrier mobility, which are essential for semiconductor functions but have been challenging due to difficulty in preserving crystalline order.

Employing a molecule composed of an elongated π-electron core and σ-electron units connected to both edges of the core, a quantum well is formed as the result of two-dimensional crystallization. We attach a electron-accepting layer on the surface of the ultrathin molecular crystals without modifying the crystal structure. Upon doping with an electric double-layer gate of an ionic liquid, the 2D crystal layer of the π-electron core is well protected from invasion of the anions, so that high carrier mobility exceeding 20 cm^2/Vs is preserved with 1/4 holes per molecule, resulting in the first observation of metallic phase in organic semiconductors [1]. At the high carrier concentration about 10^{14} cm^{-2}, which approximately fills 1/8 of the HOMO band, a pseudo-gap phase appears as the result of strong electron correlation.

In addition to the above surface doping, small dopant molecules and semi-crystalline polymers can locally form co-crystallized structures, so that the doping level to a fraction of density of repeating π-conjugated unit is achieved preserving high carrier mobility exceeding 1 cm^2/Vs. Furthermore, we recently developed a method to employ an ion-exchange reaction, so that stability of the highly doped conductive state is much improved as stable ions are replaced to redox active molecules which was necessary only in the doping reaction [2]. Very recently we also found that such ion-exchange process is useful even in aqueous solution. Proton-coupled electron transfer turned out to be extremely useful to precisely control the doping level, just like in living cells[3].

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Fermi level tuning in transition metal dichalcogenides

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Transition metal dichalcogenides (TMDCs) are layered materials with unique optoelectronic properties owing to their low dimension, making them potential candidates for the next-generation optoelectronic devices. In particular, MoS_2, $MoSe_2$, WS_2 and WSe_2 have attracted significant attention due to their ease of (large scale) synthesis, high carrier mobility, direct bandgap, and large exciton binding energy in their single-layer form. However, because of the low dimension of these materials, tuning their Fermi level may require different methods than those traditionally used, such as impurity doping, for conventional semiconductors. In this presentation, we use angle-resolved photoemission (ARPES) to explore the feasibility of Fermi level control of MoS_2 monolayers by tuning of the substrate work function and by molecular doping. We will present the energy level alignment at interfaces between MoS_2 and various substrates and show that Fermi level pinning occurs for substrate work functions below 4.5 eV while vacuum level alignment occurs above this value. In addition, we show that the charge injection barriers do not follow the expected Schottky-Mott rule due to the role of dielectric screening and subsequent bandgap renormalization. We will then examine the mechanisms of Fermi level tuning of TMDCs by adsorption of strong molecular acceptors and demonstrate the role of temperature in such process.

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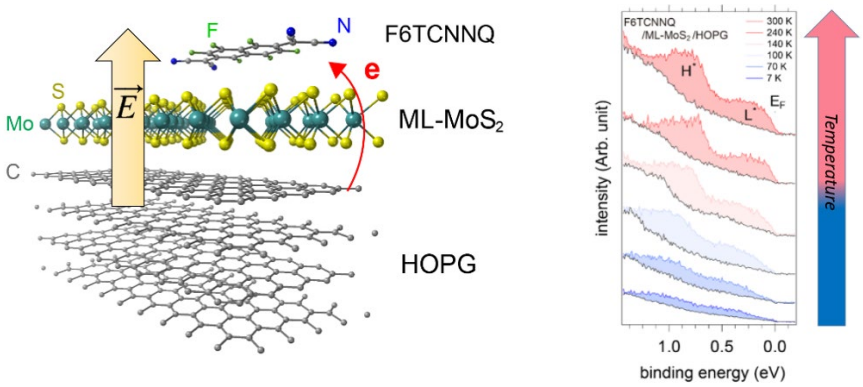

Figure: (left) schematic of the charge transfer mechanism at a molecular acceptor (F_6TCNNQ) / MoS_2 / HOPG heterojunction and (right) corresponding temperature-dependent photoemission spectra of the Fermi level region.

Transport properties of an organic topological insulator candidate α-$(BETS)_2I_3$

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A topological insulator is an exotic material in which the surface is metallic while the bulk is an insulator. Owing to the unique properties of the surface electrons, topological insulators are expected to serve as materials for next-generation electronics and spintronics. In particular, an organic topological insulator (OTI) is considered a dream material, as it is expected to possess characteristics that inorganic topological insulators lack, such as flexibility and lower environmental impact. Despite various theoretical proposals [1, 2], there have been no experimental observations to date.

α-$(BETS)_2I_3$ is a molecular charge-transfer complex that has recently been proposed as a promising candidate for an OTI. Although the first-principles calculations suggest it is a 2D topological insulator [3], experimental verification is still lacking. To understand the electronic state of this material in detail, we perform transport measurements, including electrical resistance and magnetic response. We observe a negative magnetoresistance proportional to B^2 at low temperatures, which can be attributed to the chiral magnetic effect, suggesting the presence of 3D Dirac electrons [4]. Furthermore, the temperature dependence of in-plane and out-of-plane resistance implies the emergence of surface metallic states below 20 K. These results suggest that the low-temperature electronic state of α-$(BETS)_2I_3$ is a 3D topological insulator candidate with a small inversion gap. In my talk, I will discuss the possible electronic state of this OTI candidate material and the origin of the unique transport phenomena.

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SYMMETRY AND NONLINEAR RESPONSES IN VAN DER WAALS 2D MATERIALS.

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A noticeable advantage of nanomaterials including 2D material is that their structural symmetry can be changed by forming nanostructures, i.e., isolating mono or few layers, or van der Waals (vdW) heterostructures, even though they are based on chemically identical materials. This is in marked contrast with bulk single crystals, where the structural symmetry is uniquely defined by their space group. In this presentation, we discuss the bulk photovoltaic effect (BPVE) and nonreciprocal transport in symmetry engineered van der Waals 2D semiconductors and conductors, respectively [1].

BPVE means the photovoltaic effect or zero-bias photocurrent without p-n junctions. BPVE effect is a unique property of noncentrosymmetric materials, and it is the second order nonlinear phenomenon in terms of the electric field of light. Here we report emergence of BPVE in transition metal dichalcodgenide (TMD) nanotubes and vdW heterostructures, in contrast to the absence of BPVE in monolayer TMDs with trigonal symmetry [2-4].

Nonreciprocal transport is a kind of rectification behavior where the resistance for the leftward current is distinct from that for the rightward current. This phenomenon was discovered in the beginning of this century, and are recently understood from the microscopic viewpoint [5]. We extended this nonreciprocal transport to noncentrosymmetric superconductors [6-7], and nowadays superconducting diode effect [8] discovered by Ono's group is attracting significant attention. We will discuss about this symmetry controlled superconducting diode effect.

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Ultrathin Films of MoS_2, ReS_2, and BP and Their Heterojunctions in Back-Gated Field-Effect Transistors

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ABSTRACT

Two-dimensional (2D) materials, along with their van der Waals heterojunctions, hold immense promise for electronic and optoelectronic applications.
In this presentation, we delve into several critical aspects related to electrical transport and photoconduction within 2D materials, specifically focusing on black phosphorus (BP) and transition metal dichalcogenides like MoS_2 and ReS_2.
We investigate back-gate transistors with channels composed of either a single material or a heterojunction of two materials (e.g., BP/MoS_2). These studies are conducted under varying air pressures and temperatures, both in darkness and under illumination. The dominant n- or p-type conduction and the observed rectification of the devices can be understood through an energy band model that considers the van der Waals heterojunction together with the interfaces that the 2D materials form with the metal contacts.
Our findings reveal that temperature and air pressure significantly influence both electrical conductivity and photoconductivity. Photocurrent transient measurements highlight the dominance of slow photobolometric and even slower photogating effects in the photoresponse of 2D materials-based devices.
Temperature and light-induced desorption of adsorbates, such as O_2 and H_2O molecules, and photogating effect due to charge trapping contribute to the occurrence of positive and negative photoconductivity in the same device. These phenomena are gaining attention due to their potential for fabricating multifunctional devices, that can serve as memory elements or find applications in neuromorphic vision sensors.
In summary, this presentation sheds light on some intriguing properties of 2D materials and their potential for applications in the field of electronics and photonics.

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Biography:
Antonio DI BARTOLOMEO is a professor of Experimental Condensed Matter Physics at the University of Salerno, Italy, where he teaches Analog and Digital Electronics Laboratory and Nanoelectronics.

Antonio's current research focuses on nanostructured materials, including 2D materials, nanotubes and nanowires. He explores their optical and electrical properties. His investigations extend to van der Waals heterostructures, Schottky junctions, field-effect transistors, memories, solar cells, photodetectors and field emission devices.

Antonio earned his Ph.D. in Physics from the University of Salerno. His scientific career commenced at CERN (Switzerland), where he collaborated on experiments related to neutrino oscillations and heavy-ion collisions. He spent several years in the industry, working as a semiconductor device engineer for prominent companies, like ST Microelectronics, Infineon Technologies, and Intel Corporation.

Antonio is a senior member of the IEEE (Institute of Electrical and Electronics Engineers). He also holds the title of 2022-23 IEEE Nanotechnology Council Distinguished Lecturer.

He has been an invited speaker at over 150 international conferences. His scholarly output includes more than 200 publications in peer-reviewed journals.

Recent applications of X-ray fluorescence holography

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X-ray fluoresce holography (XFH)1) is a structural analysis method, which provides 3D atomic images of middle-range local structures around specific elements. Although XFH simply measures anisotropies of X-ray fluorescence intensities around samples or directional dependences of incident X-rays on X-ray fluorescence intensities, it can record both the amplitude and phase information of scattered waves from atoms, unlike ordinary X-ray diffraction. Therefore, by applying Fourier-transformation to measured holograms, 3D atomic images around target elements can be reconstructed without any prior models of structures. Another distinct advantage is the elucidation of middle range local structures up to several nanometers in radius. Owing to these features, we have used XFH to dopants and sometimes found interesting nanostructures, such as defect complexes. Recently, we applied XFH to ferroelectrics2), ferromagnetic semiconductor3) and III-V semiconductor4) and obtained remarkable achievements.

Most recent application is the investigation of local structures in K and Ca co-interrelated graphite.5) We measured Ca–Kβ and K–Kα holograms, and reconstructed the environments around Ca and K atoms. Since these atomic arrangements are different, it is found that $K_{0.7}Ca_{0.3}C_8$ did not take the solid-solution type random distribution of Ca and K atoms; instead, a nanoscale phase separation of CaC_6 and KC_8 was observed, which was also supported by the EXAFS results. Detailed analysis of hologram data indicated the scale of Ca sublayer, which dispersed within the sample, is ~10 Å, and the Ca nanolayer was offset from the center between the C sublayers. These features would be related to the superconductivity of this material.6)

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Exploring the properties of 2D materials at surfaces through synchrotron radiation.

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In recent years, the exploration of two-dimensional materials (2DMs) has sparked considerable interdisciplinary research within condensed matter physics and materials science. Surface-science techniques have been pivotal in uncovering many unique properties of 2DMs, despite the diverse experimental and theoretical approaches employed. Among these techniques, synchrotron-based X-ray photoelectron spectroscopy (XPS) has emerged as a crucial tool, offering detailed and precise characterization of 2DMs and elucidating their complex attributes.

The surface sensitivity and ability of XPS to disentangle differences in core levels related to the surrounding electronic environment make it essential for accurately understanding the factors controlling the chemical composition, structure, oxidation state, and reactivity of surfaces and interfaces. This extends naturally to the study of 2DMs. XPS has been instrumental in understanding the growth mechanisms of various 2DMs on surfaces and identifying the key parameters that influence these processes.

In my talk, I will highlight significant results we have achieved in the last years investigating the properties of several 2D materials, such as graphene, transition metal dichalcogenides (TMDCs), and borophene, using synchrotron-based high-resolution XPS as the principal technique. Our approach, combined with structural techniques such as low-energy electron diffraction, valence-band photoelectron spectroscopy, X-ray photoelectron diffraction, and scanning-tunneling microscopy, and complemented by density functional theory (DFT) calculations, has been instrumental in shedding light on a wide range of properties of this broad class of materials.

Observation of the superstructure in van der Waals ferromagnet $Fe_{5-x}GeTe_2$ by X-ray fluorescence holography

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A series of Fe_nGeTe_2 ($3 \leq n \leq 5$) compounds have attracted much attention because these show ferromagnetic order with high Curie temperature (T_C); T_C = 230 K for Fe_3GeTe_2, T_C = 270 K for Fe_4GeTe_2, and T_C = 270 ~ 310 K for $Fe_{5-x}GeTe_2$. Scanning tunneling microscopy (STM) topography of the surface cleaved at van der Waals gap between Te layers of $Fe_{5-x}GeTe_2$ revealed $\sqrt{3} \times \sqrt{3}$ superstructure with ordered triangle trimer of Te atoms in the charge-ordered state at low temperature [1]. The ordered arrangement of the Fe atoms located below the Te layer was anticipated from the results.

In this study, we employed Ge *K*α and Te *K*α X-ray fluorescence holography (XFH) of $Fe_{5-x}GeTe_2$ to directly investigate the local structure in the charge-ordered state, *i.e.*, the $\sqrt{3} \times \sqrt{3}$ superstructure. The charge-ordered state has been confirmed by STM of either Te or Fe atoms, but the holography study should provide the detailed information of arrangements of Te, Fe and Ge in the crystal lattice. The XFH experiment was performed at BL47XU in SPring-8.

The reconstructed atomic images of Te were obtained from the Ge *K*α XFH at 298, 175, and 123 K. The atomic image demonstrates that the electron density gradually grows toward the center ($x = y = 0$) of z = 3.3 Å with a decrease in temperature (Figure 1(a)). Such behavior corresponds exactly to the evolution of short Te-Te distance in the *ab*-plane at 123 K, implying the evolution of the spatial area providing the Te triangle trimer ($\sqrt{3} \times \sqrt{3}$ superstructure). The Te−Te distances were established to be 3.4, 3.6, 4.0, and 4.6 Å from the four-way splitting of the line profile at 113 K (Figures 1(b) and (c)). The values are consistent with those obtained from the crystal structure and STM. Detailed results of Ge *K*α and Te *K*α XFH will be discussed in my presentation.

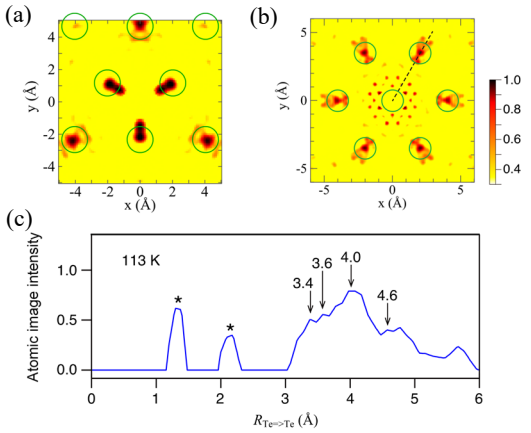

Figure 1. (a) Reconstructed atomic image of Te at z = 3.3 Å obtained by Ge *K*α XFH at 123 K. (The position at z = 0 Å correspond to the Ge layer.) (b) Reconstructed atomic image of Te at z = 0.0 Å obtained by Te *K*α XFH at 113 K. (The position at z = 0 Å correspond to the Te layer.) Green circles refer to the positions of atoms predicted from crystal structure. (c) Line profile of atomic images along the dashed line of (b) from the center toward the Te atom.

This work was supported by JSPS Grants-in-Aid for Transformative Research Areas (A) "Hyper-Ordered Structures Sciences".

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Tailoring the charge separation barrier at organic semiconductor interfaces

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Bound electron-hole pairs formed at an interface between different materials are referred to as charge transfer (CT) excitons [1]. Upon the absorption of a photon by an organic photovoltaic device, CT excitons are formed at the donor/acceptor interface as an intermediate step prior to charge separation. To increase the charge generation efficiency in such systems, an in-depth characterization of the CT dynamics is mandatory.
We use time-resolved two-photon photoemission (2PPE) to probe the CT excitons on the surface of thin films of perylene diimides (PDI): in particular, we compare PDI with a diisopropylphenyl-substituted (iPr) PDI. We show that the excited states in the latter are characterized by a lower binding energy, which translates to a smaller energy barrier for charge separation in a hypothetical device. This behavior is correlated to the different morphologies of the two molecular films which influence the dielectric constant, and thus the screening properties of the material. In fact, the influence of molecular orientation on the energy level alignment has already been reported [2]; we show here that PDI films grow flat on silver substrates, while the iPr functionalization makes the molecule non-flat, thus altering the self-assembly of the film. Based on our findings we suggest that molecular functionalization is a viable pathway for controlling also the binding energy of the CT excitons, which govern the charge separation processes at semiconductor heterojunctions.

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Very sharp switching operation of printed organic transistors

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Recent studies have shown that certain asymmetric rodlike organic molecules, characterized by extended π-electron skeletons linked with long alkyl chains, exhibit exceptionally high layered crystallinity [1]. These compounds can form single-crystalline organic semiconductor (OSC) ultrathin films with uniform molecular bilayer thickness over areas as large as wafer scale using simple solution coating processes [2–7], as presented in Fig. a. A variety of similar asymmetric rodlike molecules also demonstrate high layered crystallinity [8–14], leading to their classification as "molecular layer materials". Utilizing these materials, we successfully fabricated very clean semiconductor-insulator interfaces on highly lyophobic amorphous perfluoropolymer insulator layers through a unique extended meniscus guided coating technique, as shown in Fig. b. Field-effect transistors (FETs) with OSCs of Ph-BTNT-C$_n$, produced using this method, exhibit sharp on/off switching characteristics with an average subthreshold swing of 67 mV/dec, which is close to the theoretical limit, as presented in Fig. c [15–17]. In this presentation, I will discuss the origins of the high layered crystallinity, the unique solution process involving a layered liquid-crystalline phase at liquid-air interfaces [18], and the unique features of the sharp switching molecular layer FETs.

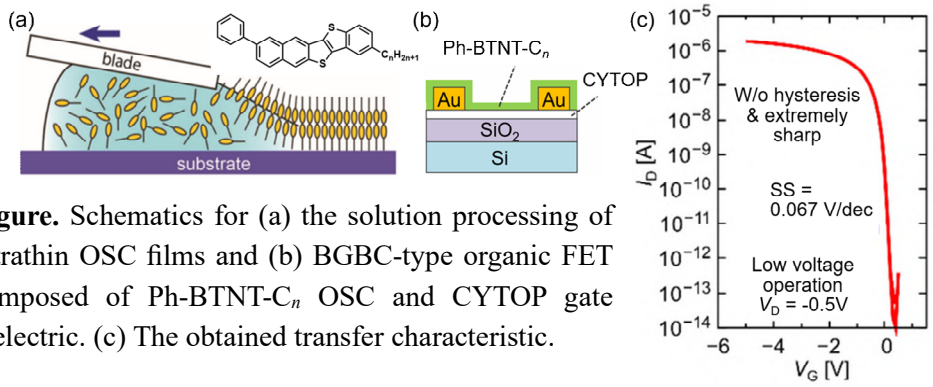

Figure. Schematics for (a) the solution processing of ultrathin OSC films and (b) BGBC-type organic FET composed of Ph-BTNT-C$_n$ OSC and CYTOP gate dielectric. (c) The obtained transfer characteristic.

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Exploring the role of Indirect Excitons in the Spectroscopic Properties of 2D Materials: Insight from First Principle Many-Body Perturbation Theory

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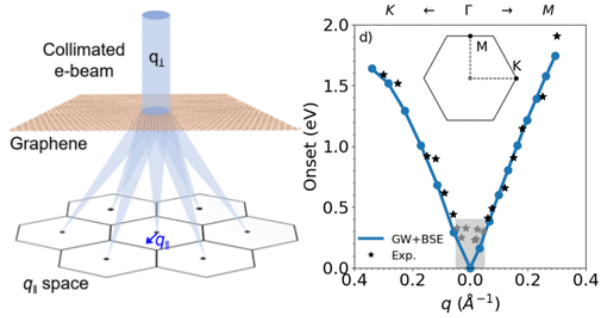
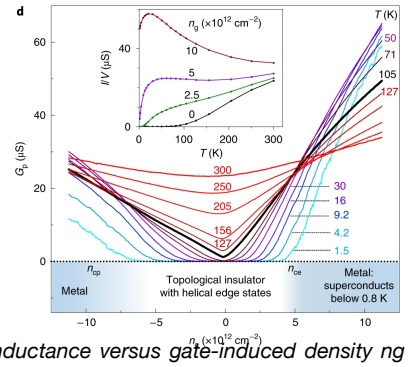
Many-Body Perturbation Theory (MBPT) is a powerful approach for predicting the spectroscopic properties of materials, including quasiparticle energies and optical spectra. The Bethe-Salpeter equation, in particular, has been instrumental in elucidating excitonic features within the optical absorption spectra of semiconductors. In this talk, we introduce a recent implementation in the Yambo code [1], specifically tailored for characterizing finite-momentum indirect excitons, excited states where electrons and holes occupy distinct regions of the Brillouin zone. Our research showcases recent outcomes, highlighting the essential role of electron-hole interactions in achieving Electron Energy Loss Spectroscopy (EELS) spectra that are in qualitative and quantitative agreement with high-resolution experiments conducted on free-standing graphene [2,3]. Furthermore, I will discuss the role of indirect excitons in the exciton instability in monolayer WTe2 below a critical temperature, providing insights into the realisation of the long-sought excitonic insulator (EI) phase [4,5,6,7]. This phase is a permanent Bose-Einstein condensate of excitons forming in the absence of optical excitation. The ab-initio solution of the Bethe-Salpeter equation reveals that the exciton binding energy exceeds 100 meV and the radius is as small as 4 nm, which explains the observed formation of excitons at high temperature sand doping levels [7]. A multi-valley mean-field calculation of the EI chemical potential as a function of doping shows quantitative agreement with the experimental results.



Calculated and experimental onset dispersion of EELS experiment in free standing graphene with high energy and momentum resolution.



WTe2: Conductance versus gate-induced density ng at a series of temperatures T on the same device. Inset: temperature dependence at positive values of doping.

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Charge transport in 2D materials thin films: role of surface chemistry, morphology and assembly

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Realistic devices made of 2-Dimensional Materials (2DMs) are often made by networks of randomly stacked nanosheets, where interfaces play a fundamental role in determining the charge transport mechanisms. Here we address the fundamental problem of how charges move across disordered multilayers of 2DMs through a comprehensive study of a prototypical system made of reduced graphene oxide (rGO), where we are able to tune the chemical, morphological and geometrical properties across several orders of magnitude, ranging from individual to billions of sheets [1]. By the analysis of the charge localization length ξ, we show how the various parameters modify the charge transport characteristics and we finally propose a microscopic model for the charge transport, taking into account the degree of overlap of sp2 aromatic domains belonging to different nanosheets, leading to quasi-one-dimensional charge transport paths with an extension of up to several microns. Our observations, reproducibly found for all geometries and defects of the nanosheets, suggest a generalized description of 2DMs thin films, further corroborated by applying a similar approach to another 2DM such as electrochemically exfoliated graphene nanoplatelets (EGO) [2].

In the final part of the presentation we show how defect engineering can be used to tune the surface electronic properties of 2DMs. Using MoS_2 thin films as a proof-of-principle case, we report the fabrication of sulfur atomic vacancies using electrochemical nanolithography (ECL). ECL combines high resolution down to the nanometric scale with the possibility to fabricate large area devices in a time-effective procedure. By analyzing the material characteristics after the creation of sulfur vacancies, we demonstrate changes in the optical and electronic properties, as well as the enhancement of the electrocatalytic activity for the hydrogen evolution reaction. Surface defect nanopatterning can be regarded as a new and promising way to tune and enhance 2DMs properties for nano-electronic and electrochemical applications.

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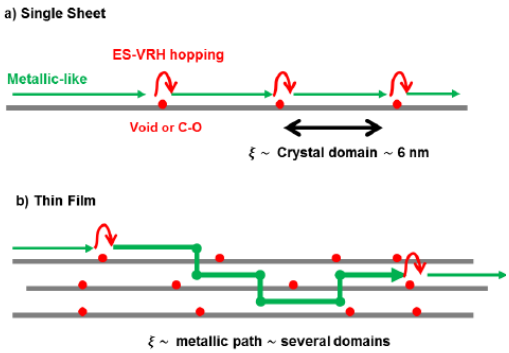

Figure 1: scheme of the charge transport mechanism in rGO single layers and thin films. While in single layers the transport is semi-metallic only within the aromatic domains and the presence of defects induces hopping, in the case of stacked sheets charges can move in three dimensions due to π–π stacking, allowing to circumvent the defects.

Scalable synthesis, integration and processing of graphene for high-performing electronic and photonic devices

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Graphene has emerged as an ideal platform for optoelectronics with high potential for applications in next-generation telecommunications, but its commercialisation has been limited so far due to challenges in scalable synthesis and processing of high-quality material. For similar reasons, fundamental studies have also mostly relied on exfoliated flakes despite continuous progress in CVD synthesis of graphene.

We present our approaches for the synthesis and processing of high-quality single-layer graphene (SLG) with focus on wafer-scale integration [1] (Fig. 1a). Seeded growth [2] and deterministic transfer allows tailored integration of monocrystalline graphene for optoelectronic applications, matching the geometry of the target photonic circuits (Fig.1b) for the fabrication of high-performing graphene modulators [1] and detectors [3] (Fig. 1c, d). Ultraclean processing is used to prepare scalable arrays of graphene Hall bars on Si/SiO_2 substrates with record magnetic sensitivity >5000 V A^{-1} T^{-1}, thanks to the high carrier mobility >10 000 cm^2 V^{-1} s^{-1}[4].

By encapsulating our CVD graphene with flakes of hexagonal boron nitride (hBN), we can preserve its ultrahigh intrinsic quality, comparable to that of exfoliated graphene. The properties of such heterostructures are studied in the high mobility regime, particularly, in the field of twistronics. As-grown twisted bilayer graphene (TBG) crystals with a 30° twist angle show decoupled transport [5], while moiré effects are observed [6] in manually assembled small-angle (~2.5°) TBG, exploiting the crystallographic alignment of seeded graphene crystals (Fig. 1e). hBN/SLG/hBN heterostructures are integrated onto photonic wafers to fabricate opto-electronic mixers (Fig. 1f), enabling wireless data transmission at sub-THz frequencies [7].

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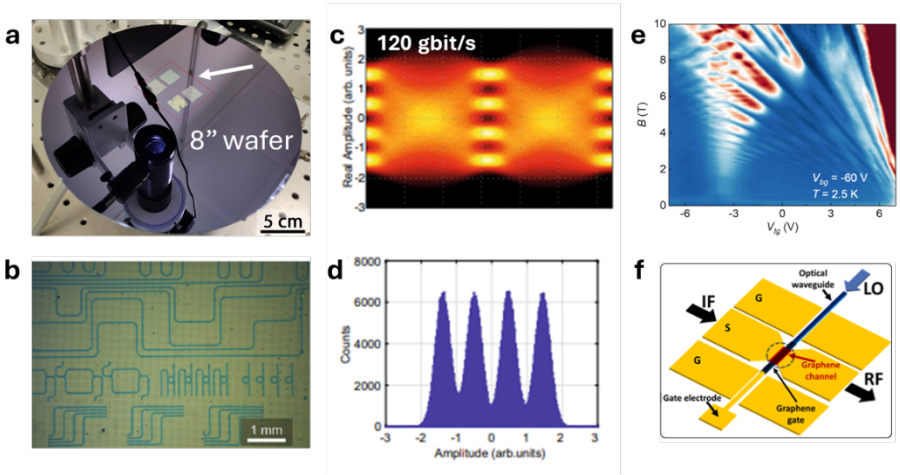

Figure 1. a) Dry stamping of graphene coupons on an 8” wafer. b) Graphene crystal array on photonic waveguides. (c) Eye diagram and (d) histogram of signal amplitude of graphene photodetector at 120 gb/s. e) Electrical transport moiré signatures in small-angle TBG CVD graphene. f) Optoelectronic mixer based on high-mobility graphene heterostructure.

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Emerging oxidized and defective phases in low- dimensional CrCl3

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Two-dimensional (2D) magnets like chromium trihalides CrX3 (X = I, Br, Cl) represent a frontier for spintronics applications and, in particular, $CrCl_3$ has attracted research interest for its relative stability in ambient conditions without rapid degradation, as opposed to CrI_3. Herein, mechanically exfoliated $CrCl_3$ flakes are characterized at the atomic scale and the electronic structures of pure, oxidized, and defective monolayer $CrCl_3$ phases are investigated employing density functional theory (DFT) calculations, scanning tunneling spectroscopy (STS), core levels X-ray photoemission spectroscopy (XPS), and valence band XPS and ultraviolet photoemission spectroscopy (UPS). As revealed by atomically resolved transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) analysis, the $CrCl_3$ flakes show spontaneous surface oxidation upon air exposure with extrinsic long-range ordered oxidized O-$CrCl_3$ structure and amorphous chromium oxide formation on edges flakes. XPS proves that $CrCl_3$ is thermally stable up to 200 °C having intrinsically Cl vacancy-defects whose concentration is tunable via thermal annealing up to 400 °C. DFT calculations, supported by experimental valence band analysis, indicate that pure monolayer (ML) $CrCl_3$ is an insulator with a band gap of 2.6 eV, while the electronic structure of oxidized and Cl defective phases of ML $CrCl_3$, extrinsically emerging in exfoliated $CrCl_3$ flakes, show in-gap spin-polarized states and relevant modifications of the electronic band structures [1-5].

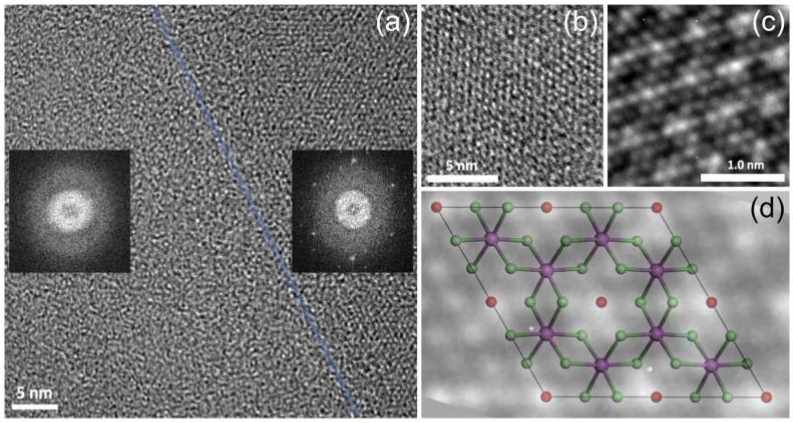

Fig. 2 High-resolution TEM image acquired at the boundary between a few-layer/bulk region on a $CrCl_3$ flake. The insets in panel (a) are fast Fourier transforms relative to the amorphous (left) and ordered (right) surface regions. A light blue semitransparent line has been artificially superimposed to the TEM data to mark the boundary between the two regions. High-resolution TEM images acquired at different magnification 590k × (b) and 1000k × (c), over the right ordered area of panel (a). (d) O-$CrCl_3$ model structure superimposed to a detail of the frame of panel (c). Cr, Cl, and O atoms are represented in violet, green, and red spheres, respectively.

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Unconventional superconductivity in topological kagome metals

The recently discovered kagome lattice superconductors AV_3Sb_5 (A = K, Rb, Cs) [1] possess a unique band structure with van Hove singularities and Dirac dispersions, in which unusual charge-density-wave (CDW) orders with time-reversal and rotational symmetry breaking have been reported. One of the most crucial unresolved issues is identifying the symmetry of the superconductivity that develops inside the CDW phase. Recent theory predicts a variety of unconventional superconducting symmetries, including a chiral order parameter with sign change. Experimentally, however, the phase information on the superconducting gap in AV_3Sb_5 is still lacking.

Here we report the impurity effects in CsV_3Sb_5 using electron irradiation as a phase-sensitive probe of superconductivity [2]. Our magnetic penetration depth measurements reveal that with increasing impurities, a highly anisotropic fully-gapped state changes gradually to an isotropic full-gap state without passing through a nodal state. Furthermore, transport measurements under high pressure show that the double superconducting dome in the pressure-temperature phase diagram survives against sufficient impurities. These results support that CsV_3Sb_5 is a non-chiral, anisotropic *s*-wave superconductor with no sign change both at ambient and high pressure, which provides a clue to understanding the relationship between CDW and superconductivity in kagome superconductors.

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Origin and magnetotransport properties of the multifunctional 2DES at the $LaAlO_3/EuTiO_3/SrTiO_3(001)$ interface

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Two-dimensional electron systems (2DES) developing in $SrTiO_3$-based heterostructures possess a wide range of properties which are largely tunable thanks to the system band structure and carrier density [1]. A joint experimental and theoretical approach is becoming essential to gain detailed understanding of these novel heterostructures showing exceptional properties, and as a guide for future design of materials for advanced applications.
Recently, it was demonstrated that by introducing a thin layer of a magnetic oxide between $LaAlO_3$ and $SrTiO_3$, as in $LaAlO_3$ /$EuTiO_3$/ $SrTiO_3$ (LAO/ETO/STO), a superconducting spin polarized 2DES can be engineered [2]. We use a combination of transport and spectroscopy measurements and DFT calculations to resolve the nature of this 2DES and to understand the mechanisms leading to spin-polarization of its carriers [3]. In particular, we highlight the role of the carriers belonging to the Ti $3d_{xz,yz}$ states in establishing a ferromagnetic coupling, thanks to hybridization with specific Eu states.
We show also how the properties of the 2DES can be modulated by using electric field effect gating in combination with visible light irradiation [4]. The latter enhances the stabilization of ferromagnetic correlations in the 2DES. Indeed, above the carrier density threshold corresponding to the Lifshitz transition, we do see evidence of the appearance of carriers with highest mobility, i.e. $3d_{xz,yz}$. The mobility vs. carrier density analysis suggests a larger enhancement of the mobility by light irradiation compared to back-gating and, at the same time, an increase of the anomalous Hall resistance. This effect could be related to light induced excitation of spin-polarized carriers at the interface, which distribute over the 2DES thickness well inside the STO.

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Electronic structure in topological kagome metals

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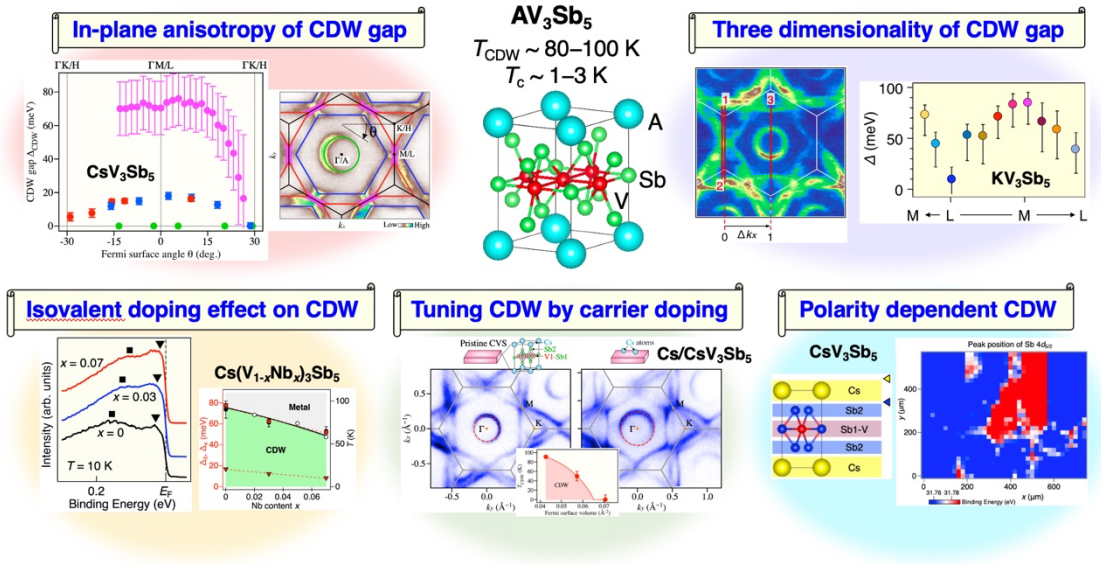
The kagome lattice, consisting of a two-dimensional network of corner-sharing triangles, serves as an excellent platform for exploring novel quantum phenomena originating from geometrical frustration in real space and nontrivial band topology in reciprocal space. Recently, significant attention has been directed to non-magnetic kagome metal AV$_3$Sb$_5$, in which various electronic phenomena have been unveiled. These phenomena include charge-density wave (CDW), superconductivity, nematic ordering, time-reversal symmetry breaking, pair density wave, and the giant anomalous Hall effect. To elucidate the electronic states responsible for these exotic phases, we have conducted high-resolution angle-resolved photoemission spectroscopy (ARPES) of AV$_3$Sb$_5$. In this presentation, we present our recent achievements, with a particular emphasis on the CDW-induced electronic reconstructions [1-6].



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Quantum properties of atomic layer films studied by *in situ* ARPES and transport measurements

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Recently, thin films with thicknesses of a few atomic layers (atomic layer and two-dimensional materials) have been fabricated in high quality and in large areas, and the realization of novel physical properties of such materials that differ from those of three-dimensional bulk materials and the elucidation of their mechanisms have attracted attention from both fundamental and applied perspectives. In this talk, I would like to introduce our recent fundamental studies on such atomic layer materials utilizing in situ ARPES and transport measurements, correlating the electronic structure with their macroscopic properties.

The first topic is the discovery of a new method to introduce magnetism into topological insulators. By using these systems such as $MnBi_2Se_4$ or $Mn_4Bi_2Te_7$, the relation between electronic states and magnetization properties measured with XMCD and in situ Hall measurements are clarified [1].

The second topic concerns the superconducting transition temperature Tc determined by gap opening and transport measurements in atomic layer high-temperature superconductors with a higher Tc than the bulk. In general, the Tc of superconductors usually decreases by making them thinner and thinner, but contrary to this conventional wisdom, a single-layer thin film was reported to have a higher Tc in monolayer FeSe/STO. Combined with in situ STM/STS measurements, we uncover the role of the substrate surface on this system as well as on the cousin compound FeTe/STO [2].

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Artificial Multiferroic oxide 2D-electron gas

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Advances in growth technology of oxide materials allow single atomic layer control of heterostructures. In particular delta doping, a key materials' engineering tool in today's semiconductor technology, is now also available for oxides. Here I will present the engineering of ferromagnetic, ferroelectric, and coupled ferromagnetic/ferroelectric two-dimensional electron gases (2DEGs) by combining band-insulating oxides characterized by different functionalities [1-3]. A fully electric-field-tunable spin-polarized and superconducting quasi-2D electron system (q2DES) can be artificially created by inserting a few unit cells of delta doping $EuTiO_3$ antiferromagnet at the interface between $LaAlO_3$ and $SrTiO_3$ oxides. Spin polarization emerges at the Lifshitz transition and is due to the exchange interaction between the magnetic moments of Eu-4f and of Ti-3d electrons. A ferroelectric 2DEG is realized by simply growing LaAlO3 on the Ca-doped (1%-2%) $SrTiO_3$ single crystal. Finally, a ferromagnetic and ferroelectric 2DEG is finally engineered introducing few unit cells of EuTiO3 between LaAlO3 and Ca-doped STO.
I will provide evidences of ferromagnetism, ferroelectricity and coupled ferromagnetism/ferroelectricity from magneto-transport and Hall effect measurements, polarization vs back gate electric field, and in particular by polarization dependent x-ray absorption spectroscopy. In particular, by performing x-ray linear dichroism measurements across the FE-transition temperature and as function of the remanent polarization, I will show that Polarization direction affect the orbital splitting of the t2g states in a non-volatile manner. Moreover, I will show that also the magnetic moment of the Eu-ions, measured by x-ray magnetic circular dichroism, is modified by the FE polarization direction, providing a direct proof of magneto-electric coupling in the LAO/ETO//Ca-STO. The results are compared to DFT+U calculations on the heterostructure.

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Chiral Spintronics and Time-Reversal Symmetry

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Chirality has been considered as just a problem of molecular shape when it is discovered. In order to express chirality in quantum mechanical levels, however, one needs to find an appropriate way to describe chirality by wave functions. Recently, we have proposed to use electrical toroidal monopole G_0 as a quantum mechanical definition of chirality which has a monopole structure in reciprocal space [1]. This definition is consistent with a classical definition of chirality proposed by Barron who also considered time-reversal symmetry [2]. One of the interesting things in our new definition is that this monopole in *k*-space can be converted to a magnetic monopole (M_0) in real space once it is integrated in the time domain [3]. This monopole structure may explain some observations related to chirality-induced spin selectivity (CISS) effect [4], such as enantio-separation by magnet surface and magnetoresistance larger than spin polarization of ferromagnetic electrode. We have experimentally proved such a conversion from G_0 to M_0 using chiral molecular superconductor [5]. Using this phenomenon, we have also successfully enantio-separated helical supramolecular nanowire made of achiral molecules by magnet [6]. The role of such an emergent chirality in conjunction with novel spintronics will be discussed.

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2D MoS_2 doping and stability in high temperature controlled atmosphere

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The emerging family of 2D materials comprises the transition metal dichalcogenides that are particularly interesting due to their versatile properties for electronic applications. Among them the MoS_2 is a semiconducting material that in the monolayer 2D state is characterized by a direct bandgap of 1.8-1.9 eV and an exciton recombination photoluminescence at about 1.8 eV. As already known, the 2D materials properties are generally affected by the interaction with their neighborhood and in this context both the effects of interacting molecules and the physical substrate on which the material is finally deposited are of particular concern. In details, the doping, the strain and the electronic features can be modified or tuned properly by the interacting neighboring species and are of current interest in the research of these materials.

In this work 2H-MoS_2 monolayer (1L) and few layers have been grown by chemical vapor deposition (CVD) or by gold assisted exfoliation (GAE) on different conducting (Au), semiconducting (GaN) and dielectric substrates (SiO_2, Al_2O_3). The physical features of MoS_2 have been studied mainly by MicroRaman spectroscopy, Microphotoluminescence, and Atomic Force Microscopy (AFM). To evaluate the stability and doping potentialities the samples have been subjected to post-growth thermal treaments in controlled atmosphere of inert (Ar) or active (O_2) gas up to 300°C.

It will be reported how the substrate affects the doping and strain features of the 1L-MoS_2 and the exciton recombination evidencing the influence of the specific interaction on the charge carrier dynamics and material structural features. Moreover, it will be shown that the thermal processing of the 1L-MoS_2 is responsible in affecting the doping of the material and the exciton recombination with evident effects on the Fermi level positioning and in the bandgap tuning as well as in the charge carrier coupling in exciton and trion.

Tunable quantum interferometers in magic-angle twisted bilayer graphene

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Magic-Angle Twisted Bilayer Graphene (MATBG) hosts a variety of quantum states, such as superconductivity and correlated insulating phases, which are tunable via gating. The mechanism of these correlated phenomena is still a mystery and has been the subject of active theoretical and experimental research.

We realize a gate-defined quantum interferometer (Fig. 1a) in magic-angle twisted bilayer graphene (MATBG) and observe coherence effects such as the Little–Parks and the Aharonov–Bohm effect [1]. In the device architecture, we exploit the variety of tunable correlated states in MATBG and confine a superconducting or normally conducting ring by a correlated or band insulator (Fig. 1b).

For a superconducting ring, we observe the Little–Parks effect as oscillations in the resistance and critical current of the ring in magnetic field. Additionally, we also show a novel probe of the Little–Parks effect by directly measuring the oscillation of the superconducting phase diagram as a function of carrier density and magnetic field. From the h/2e-periodicity of the oscillations, we confirm an effective charge of 2e for the superconducting carriers.

In the normally conducting regimes, we report h/e-periodic Aharanov-Bohm oscillations and demonstrate that the phase coherence length of moiré electrons exceeds several microns at 50 mK. Intriguingly, we identify a regime where h/e-periodic oscillations coexist with superconductor-like transport.

We have shown previously that gate-defined devices are excellent platforms for studying and controlling superconductivity in MATBG [2, 3, 4]. In this work we demonstrate that tunable quantum interferometers enable the study of coherent phenomena of correlated quantum states.

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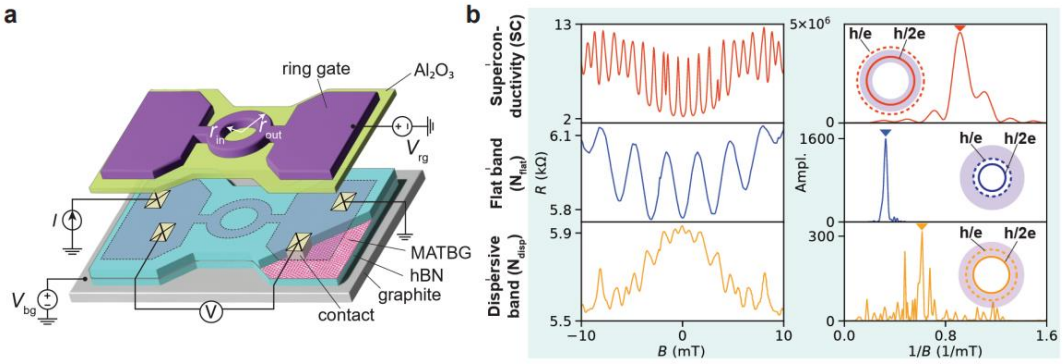

Fig. 1. (a) Device schematics. (b) Overview of quantum-interference effects in the superconducting and normal conducting regimes of the ring defined in a correlated insulator. Figure taken from reference [1].

Variable carrier mobility of graphene gated with an ionic liquid

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The field-effect transistor (FET) in double-gate structure, which has an ionic-liquid top gate and a solid bottom gate as shown in Fig. 1, enables us to control the carrier density and the electric field independently. The effect of the electric field on electronic properties is prominent in two-dimensional materials whose thickness is smaller than the penetration depth. Band structures of few-layer graphene (FLG) can be modified by applying a perpendicular electric field $\boldsymbol{E}$ to change the potential energy at each layer[1,2]. We found that the minimum conductivity and the field-effect mobility were significantly enhanced under $\boldsymbol{E}$, although the band structure of monolayer graphene (MLG) should not be modified by $\boldsymbol{E}$. To clarify the origin, the double-gate MLG FETs were prepared in Hall bar geometry to evaluate the carrier density and the mobility independently.

The conductivity σ and Hall coefficient R_{H} were measured by sweeping V_{tg} in two different setups for V_{bg}. In the setup 1, V_{bg} was also swept to hold $V_{\mathrm{bg}} = V_{\mathrm{tg}}$ to minimize the effect of V_{bg}. On the other hand, V_{bg} was fixed to 1.0 V in the setup 2 to add upward $\boldsymbol{E}$. The mobility measured in the setup 2 was about twice larger than that in the setup 1, consistent with the previous results. Analysis of the $R_{\mathrm{H}}(V_{\mathrm{tg}})$ curve in the setup 2 showed that the anions were trapped on the graphene to accumulate holes. In this case, it is energetically favorable that the anions are located on the positively charged impurities in the SiO_2 dielectric. Accordingly, the cancellation of the charges of the anions and impurities is the plausible reason why the application of a small amount of V_{bg} (= 1.0 V) increased the mobility. The result indicates a possible induction of novel functionality of graphene by controlling the electrostatic interaction of the charges at the top and bottom sides.

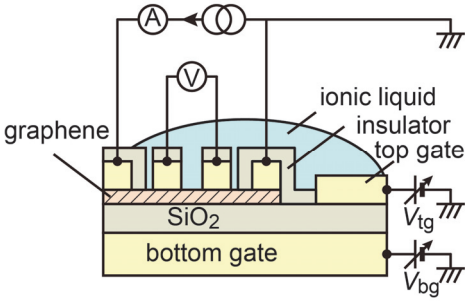

Figure 1. Schematic side view of a double-gate MLG FET.

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Many-body band renormalization in highly doped graphene

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The extreme simplicity of its electronic structure has affirmed graphene as an ideal testbed for the demonstration of many-body renormalization effects on band structure. In this talk I will propose: 1) an undisputable experimental demonstration of the electron-phonon origin of the kink at 170 meV; 2) a demystification of the band flattening at the van-Hove singularity proximity [2].

Regarding the first case [1], I will show an energy shift towards the Fermi level of the "kink" associated to the electron-phonon coupling once the graphene is made of only ^{13}C isotope rather than ^{12}C. Such an energy shift is in excellent agreement with the expected softening of the phonon energy distribution due to the isotope substitution. Apart from providing an indisputable experimental proof of the electron-phonon coupling origin of this "kink", I will discuss the experimental accuracy achievable with a proper robust analysis framework applied to the experimental data.

For the second case [2], I will present an alternative interpretation for the highly doped graphene band flattening once the Fermi level approaches the van-Hove singularity. By simulating the graphene spectral function from the density functional theory calculated bands, it is possible to demonstrate that the photoemission signal around the M point originates from the spectral function tail of the unoccupied band above the Fermi level. Such interpretation put forward the absence of any additional strong correlation effects at the van-Hove singularity proximity, reconciling the mean field description of the graphene band structure even in the highly doped scenario.

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Probing Kinetic Inductance and Pairing Symmetries in Magic Angle Twisted Bilayer Graphene

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The mechanism and pairing symmetry of superconductivity have always been at the forefront of the study of unconventional superconductors. The physics underlying the superconducting phases in magic-angle twisted bilayer graphene (MATBG) may provide revelatory insight beyond the moiré systems and extend into other strongly-correlated systems such as high-T_C superconductors.

Here, we combine DC transport and circuit quantum electrodynamics (cQED) techniques to characterize the kinetic inductance and, consequently the superfluid density, within MATBG samples. The hybrid superconducting circuit grants access to collective behaviors of the superfluid ensemble across the entire MATBG region.

We will present the temperature, DC bias current, and microwave power dependence of the superfluid density in MATBG samples and discuss their implication on the gap structure in MATBG. We stress that the hybrid superconducting circuits demonstrated can be utilized to study other atomically thin 2D superconductors in both DC and AC regimes.

Exotic superconducting state and high-field phase diagram of tetragonal $FeSe_{1-x}S_x$

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The isovalently substituted $FeSe_{1-x}S_x$ superconductors have attracted significant interest due to various exotic properties associated with the intertwining of nematicity, magnetism, and unconventional superconductivity [1]. Of particular interest is the abrupt change in the superconducting gap function that occurs at the nematic critical point at $x_c \sim 0.17$ [2-6], above which the formation of an ultra-nodal pairing state with a putative Bogolubov Fermi surface has been proposed [5-10]. Although the emergence of the Bogoluvov Fermi surface appears to reasonably explain the huge residual density of states observed in the tetragonal $FeSe_{1-x}S_x$, the nature of the exotic pairing state remains largely elusive, including the links between the ultra-nodal state and the colossal fluctuation-like behavior reported in the previous experiments [11]. Here, using the high-quality single crystals of $FeSe_{1-x}S_x$ and the precise measurements of thermodynamic and charge transport properties, we discuss the gap formation of the ultra-nodal pairing state, which deviates from the mean-field-like behavior. The results provide fresh insights into our understanding of the ultra-nodal pairing state.

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