Master in Molecular Nanoscience and Nanotechnology

Master dissertation defense

September 12th, 2024. SS6 Seminar

13:00 María Amparo Lopo March
Assessment of the interaction to G4s, nucleotides and drugs of novel G4 supramolecular binders

13:30 Salvador Bertó García
Design and characterization of advanced 3D superconducting electrical circuits

14:00 Ricardo Aguado Collazo
Fabrication and characterisation of van der Waals heterostructures involving ferroic materials: towards multiferroic heterostructures and proximity magnetoelectric effect

14:30 Pause

15:00 Ana Puchades Ortiz
Optimisation of FAMAPI N-i-P perovskite solar cells in bifacial configuration

15:30 Turlough Brennan
Modulation of the Layer dependent Optical Properties in Magnetic 2D materials Investigated by Hyperspectral Transmission Microscopy

Master's Thesis in Molecular Nanoscience and Nanotechnology

Faculty of Chemistry
Institute of Molecular Science

ASSESSMENT OF THE INTERACTION TO G4S, NUCLEOTIDES AND DRUGS OF NOVEL G4 SUPRAMOLECULAR BINDERS

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Supervisors

Prof. Enrique García-España
Prof. Jorge González

Burjassot, 4th September 2024

ABSTRACT

Supramolecular structures such as capsules, cryptands or macrocycles are interesting systems for the selective recognition of small molecules and capable to transport cargoes through synthetic and natural barriers.[1] These systems could be applied in drug delivery, pollution remediation, catalysis and in many other areas. Of outmost importance, these supramolecular systems could target biomolecules such as nucleic acids or proteins and exert a synergetic effect of the encapsulated molecule and the capsule itself.

Among the novel biomolecular targets in drug discovery, epigenetic alterations, including histone modification, nucleosome remodeling and other non-coding mediated structures have attracted the attention in the last decades.[2] One of the most attractive non-coding structures in anticancer drug development are G-quadruplex (G4) DNA and RNA. G4s are non-canonical nucleic acid structures formed in guanine-rich sequences.[3] Strikingly, a large number of putative G-quadruplex forming sequences have been identified in the genomes of human, microorganisms and viruses, and the evidence suggest their pivotal role in key biological processes. In this line, telomeres are regions enriched with putative G4-forming DNA sequences and have been associated to ageing and cancer. Telomere sequences comprise hundreds of TTAGGG repeats which form a superstructure constituted by multiple G4s. Moreover, putative G4-forming sequences have been identified in multiple promoters of oncogenes such as *cMyc*, *c-Kit* or *k-ras*. In both regions, the formation of the G4 structure by synthetic molecules resulted in blocking telomere elongation and oncogene expression, highlighting their important application as therapeutic target in cancer.

Herein, we present our synthetic efforts to develop new organic capsules with multifunctional activity aimed to interact with G4s and deliver drugs. We have prepared a family of macrocyclic and cryptand ligands containing triphenylamine moieties.[4] We examine the interaction of a series of macrocycle and cryptand-like systems with G-quadruplex DNA located at proto-oncogenes and telomeres by a high-throughput fluorescence displacement assay (HT-FID). We then evaluated the interaction of these systems with anticancer drugs and other relevant biomolecules such as nucleotides by potentiometry to assess the capacity to transport them through cell membranes and deliver the cargo. Finally, to obtain further information on the capacity to cross cell membranes, we performed transport experiments in a U-tube, as this assay unambiguously reports on the presence of molecular carriers. Our theragnostic approach could be then applied to target the telomeric/oncogenic regions and other cancer-related pathways associated to the drug encapsulated.

Keywords: G-Quadruplex, drug delivery, supramolecular structures, G4 binders

VNIVERSITAT DE VALÈNCIA

EXCELENCIA MARÍA DE MAEZTU

MASTER IN MOLECULAR NANOSCIENCE AND NANOTECHNOLOGY

VNIVERSITAT DE VALÈNCIA

MASTER THESIS

"DESIGN AND CHARACTERIZATION OF ADVANCED 3D SUPERCONDUCTING ELECTRICAL CIRCUITS"

STUDENT:

SALVADOR BERTÓ GARCÍA

SUPERVISOR:

ROSA CÓRDOBA CASTILLO

SEPTEMBER, 2024

Abstract:

The integration of advanced nanofabrication techniques opens up new possibilities for the development of multifunctional devices at the nanometer scale. Three-dimensional nanofabrication using He^+ Focused Ion Beam Induced Deposition (He^+ FIBID) allows precise structuring at the nanoscale, allowing the creation of complex high-resolution nanostructures. Furthermore, irradiation with Gallium Focused Ion Beam (Ga^+ FIB) allows to modify the properties of materials at the nanoscale, making it easier to personalize these structures for specific applications. By integrating both techniques, it is possible to design superconducting electrical circuits with enhanced functionalities, potentially based on phenomena such as the superconducting diode effect.

This Master's Thesis focuses on the study and characterization of two superconducting three-dimensional nanohelices, the *modified nanohelix* and the *as-grown nanohelix*, manufactured using the He^+ FIBID technique. One of them has been specifically modified by focused Ga^+ ion beam irradiation to emulate the behavior of a superconducting diode effect, a phenomenon that allows the current flow in one direction but makes it worst in the opposite direction.

The work includes from the visualization in shape, geometry and the composition of superconducting 3D nanohelices. The superconducting properties and the effectiveness of the induced deformation that breaks the geometrical symmetry of the nanohelix are evaluated to observe the potential of this device as a superconducting diode. Both goals are performed using magneto-transport characterization.

In this study, it is shown how a non-reciprocal superconductivity is effectively achieved since the two defects induced by Ga^+ FIB irradiation applied to the *modified nanohelix* break with its geometric symmetry as they are on the side. In this way, we are able to show the efficiency of the rectifier as a function of the magnitude of the applied magnetic field, which for this type of device is at a low or zero value. The experimental results show a maximum rectification efficiency of 6.36 % for zero value of applied magnetic field and temperatures lower than 0.43 times of the T_c value ($t = \frac{T}{T_c} = \frac{3}{6.94} = 0.43$), confirming its ability to operate as a superconducting diode in these conditions. These effect decreases as the applied magnetic field increases erasing at values of magnetic field of ±1T.

This study provides new perspectives in the fabrication and application of superconducting nanostructures by using a helical geometry as a rectifier device and comparing it with a nanohelix without this added defect, the *as-grown nanohelix*. This superconducting diode effect reproduced in a 3D nanostructure makes it possible to take advantage of all the typical advantages of three-dimensional superconductivity such as vortex pinning or present greater critical temperatures.

FACULTY OF CHEMISTRY

MASTER'S THESIS

Master in Molecular Nanoscience and Nanotechnology

FABRICATION AND CHARACTERISATION OF VAN DER WAALS HETEROSTRUCTURES INVOLVING FERROIC MATERIALS: TOWARDS MULTIFERROIC HETEROSTRUCTURES AND PROXIMITY MAGNETOELECTRIC EFFECT

Author: Ricardo Aguado Collazo

Tutor: Dr. Efrén Navarro Moratalla and Dr. Marta Galbiati

Academic year: 2023-2024

Abstract

During the past decades a whole field covering the exceptional and unique physical properties of van der Waals (vdW) layered materials and their corresponding 2D materials has been developed. However, some of the interactions and cooperative phenomena that come to play within those van der Waals heterostructures still need more exploration. Multiferroicity is one of them. Including the possibility of having the presence of two hysteric orders in the same material to the 2D field unlocks novel potential applications and vdW multiferroic heterostructures, giving experimental support to fundamental mechanisms of the magnetoelectric coupling. For that purpose, in this work we have performed a proper characterization of the layered materials of interest has been done culminating in their integration in the magnetoelectric heterostructure and the electrical measurements. We focused on few-layer $CuInP_2S_6$, known to exhibit room-temperature ferroelectricity with out-of-plane polarization [1], and CrI_3, member of one of the first families (i.e., first group of compunds) of 2D magnets (insulating chromium trihalides CrX_3) which has been proved to be an Ising ferromagnet with out-of-plane spin orientation.[2]

An adapted set-up suitable for air sensitive materials that allows fabrication and transfer techniques in an inert atmosphere opened us the door for the realization of this work and to explore some of the known characteristics of vdW materials. By means of this newly developed cold pick-up and transfer, we were able to stack few-layer crystals one on top of another, building vertical van der Waals heterostructures. They were composed of a 2D ferromagnet (CrI_3) on top of a ferroelectric layer ($CuInP_2S_6$), enclosed in between two non-contacting graphite electrodes. The application of voltages on those electrodes allowed to tune the response of these materials properties and explore the arising proximity and coupling effects in between the ferroelecetric and ferromagnetic materials. These vdW heterostructures were built through top down approach, via mechanical exfoliation of crystals previously grown with CVT. AFM, PFM, I-V curves and PUND (sending several voltage pulses to analyze the current response) were carried out in order to characterize and further understand the behaviour of $CuInP_2S_6$ features. These experiments were always done either on an inert atmosphere (fabrication, AFM and PFM) or on vacuum conditions (electron transport measurements).

The understanding of these attributes can bring us closer to the accomplishment of the project objectives, more focused on the fundamental physics and science beneath them than on their potential applications, always present though.

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Master in Molecular Nanoscience and Nanotechnology

Optimisation of FAMAPI N-i-P perovskite solar cells in bifacial configuration

Ana Puchades Ortiz

Directed by: Henk J. Bolink

September 2024

Abstract

Due to the depletion of fossil fuels and the environmental issues they have caused, there has been an urgent need to find renewable energy sources that can replace them. Photovoltaics, and more specifically solar energy, emerge as one of the most promising options. Among these, perovskite solar cells stand out, as they combine hybrid organic-inorganic materials and have demonstrated outstanding optoelectronic properties, such as high light absorption, charge diffusion coefficient, transparency, and compatibility with tandem devices, among others.

This work focuses on the study of perovskite solar cells in a bifacial configuration using the N-i-P structure. This type of cell have transparent electrodes on both sides of the stack which allows sunlight to enter from both the front and the back (via reflection on the ground) leading to higher efficiencies. Additionally, as the cells are semitransparent they can be used in building integrated photovoltaics or as front cells in combination with a Silicon back cell. Herein, the process of optimizing a bifacial N-i-P cell is presented, utilizing a low bandgap perovskite as the absorber. Through optimization of the device stack, via different hole transport and electron transport layers, their thicknesses and the transparent top electrodes, very efficient solar cells are achieved. Bifacial (semitransparent cells) with power conversion effiencies of 16-17% were achieved when illuminated from the substrate and top contact, respectively. When the top contact is replaced with a non-transparent metal the efficiency reached 18 %. These are very good efficiencies and demonstrates that the bifacial cells hold great promise.

Modulation of the Layer dependent Optical Properties in Magnetic 2D materials Investigated by Hyperspectral Transmission Microscopy

Submitted by Turlough Brennan

Supervised by Dr Marta Galbiati and Dr Efrén Navarro-Moratalla

Submitted in fulfilment of the requirements for the degree of

Masters in Molecular Nanoscience and Nanotechnology

Institut de Ciència Molecular

Facultat de Química

Universitat de València

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Abstract

Magnetism in two-dimensional materials was the final building block needed to achieve the full range and capabilities of the electric and magnetic properties of layered materials. At this regard, the discovery in 2017 of magnetism down the monolayer in CrI_3 [3] was a significant milestone, creating great interest and excitement at the possibility of studying magnetism at the 2D layer limit and the development of new applications as ultimately thin magneto-optic devices, spintronics devices, quantum-computing and advanced sensor technology [25-27]. Approaching the single atomic layer thickness, magnetism exhibits exotic behavior, for example a magnetic transition from ferromagnetic to layered antiferromagnetic is observed in CrI_3 when decreasing towards the monolayer limit. The full understanding of the fundamental magnetic properties of these materials will be hence essential to integrate them in modern device and even create new device perspectives.

To unravel the origin of the magnetic conundrum, a deeper understanding of the electronic properties is needed. Studying the light-matter interaction via the complex dielectric function is an effective approach to extract this information from layered materials. At this aim, researchers have turned to studying the complex optical dielectric function of magnetic CrI_3 using hyperspectral transmission microscopy [2]. This revealed a modulation of the optical properties as the layer count increased from the monolayer to the bulk material in this material, with a crossover point thickness somewhere around 50 layers, similar to where observed the magnetic transition, hence hinting at a similar origin for the optical and magnetic modulation.

To gain a deeper insight into this modulation effect, we investigate other 2D magnetic materials, using hyperspectral transmission microscopy as a simple and non-destructive method with high throughput, to obtain information on the optical properties as a function of the layer count. To this aim, we chose two-dimensional materials displaying similar qualities to that of CrI_3; VI_3 as it displays a similar structural transition with temperature as CrI_3 bulk material, and $CrBr_3$ as it also displays layer dependent magnetic behavior at the 2D layer limit. From our results we observe a modulation in peak position with layer count similarly to CrI_3, but we also unveil an intrinsic contribution of Fabry-Perot interference even at the thin layer limit. To gain more insight about this intrinsic contribution, MoS_2 thin layers were