Annual Report – 3rd PhD Year

Nicolò Petrini (XXXVI cycle)

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During the third year of PhD, I finalized my research on improving Au-assisted exfoliation technique. I have achieved fundamental results that not only enable a remarkably high yield in a single exfoliation, but also empower the transfer of the flake onto any arbitrary substrate. Besides, my research activity focused particularly on the development of solutions to realize the heterostructure device formed by ITO nanocrystals and 2D MoS_2 flakes. I designed, realized, and tested successfully a micropatterning process based on UV-mask lithography which allows to obtain on the same chip more than 200 devices. The set of UV-masks can be utilized in a modular fashion to fabricate devices with diverse geometries and can also be employed to study NCs films, 2D materials and their combination. This concludes the phase of practical fabrication of the heterostructure devices, which is going to be investigated with a new optoelectronic setup, currently in process of realization. The developed patterning required the further study of different deposition techniques for the NCs, which have been deposited with dip-coating and self-assembly, the latter resulting the best option in terms of film homogeneity, reproducibility, and electrical response. Eventually, I explored a new technique used for the characterization of the obtained heterostructures employing Kelvin Probe Force Microscopy coupled with light illumination. The obtained results are encouraging and suggest this technique as an valuable characterization method to complement spectroscopy and electrical C-V measurement in the investigation of photocharging mechanism in our 0D/2D hybrid structure, paving the way for a broader use in the study of photodoping hybrid heterostructures. Hereby, I provide a more detailed description of each research activity and its respective outcome:

1. **Large area exfoliation and transfer over different substrate**. Metal-assisted exfoliation technique has emerged as a valuable method for obtaining large and high-quality exfoliation of 2D monolayers. However, the process yield can be dramatically decreased due to poor adhesion between the metal foil and the substrate. In this year of PhD, I solved this issue by the surface functionalization of the target substrate, employing (3-Aminopropyl)triethoxysilane (APTES). The introduction of APTES improves efficaciously the adhesion between the monolayers and hydrophilic substrates such as SiO_2, overcoming the limitations of the Au-exfoliation method. In collaboration with OptMatLab group at UniGe, we are preparing a thorough study on this specific use of APTES functionalization, characterizing the obtained flakes by means of ellipsometry, AFM, Raman and photoluminescence spectroscopy, demonstrating the effectiveness of the method and the superior outcomes in terms of yield and crystal quality. With this method, we were also able to obtain good quality of monolayer BiTeI and we recently published an article showing the theoretically predicted SHG. Moreover, we recently optimized a Me-assisted modified protocol for exfoliation that allows for the transfer of the exfoliated flake onto arbitrary flat substrate, demonstrating the possibility of achieving large area exfoliation on hard substrates (Si, SiO_2, ITO, Al_2O_3) as well as flexible substrates (PET, Kapton).
2. **Nanofabrication of hybrid heterostructure.** A major challenge in the realization of 0D/2D hybrid structure composed respectively by nanocrystals of ITO and monolayer of MoS_2 consisted in the fabrication of devices that allow for the photodoping of NCs while guaranteeing the electrical contact of MoS_2 and NCs in a separate way. To achieve this goal, I designed, fabricated and tested a modular set of masks for UV lithography, which allow for flexibility required by the random shape and dimension of the monolayer flakes, guaranteeing a large number of transistor-like devices with different channel length and width. This design is modular and can be employed not only for the fabrication of heterostructures, but also for the electrical characterization of the NCs films or 2D material separately. Since the patterning procedure involves resist coating, liftoff and etching, the compatibility of all these processes and the materials employed have been careful assessed and we found a good recipe for producing the devices that will be tested by means of a newcoming optoelectronic setup, with the possibility of C-V characterization to assess the capacitance of the device before, during and after illumination with suitable UV illumination.
3. **Characterization of NCs films**. In order to obtain a homogeneous film over the 2D material flake, we investigated dip coating and self-assembly techniques, since spin-coating lead to poor results due to the patterned resist. We recently published an article about the processing techniques for fabricating thin films of transparent conductive oxides. We employed the previously described modular design to fabricate and investigate numerous devices, in order to assess the reproducibility of our process. Electrical characterization indicates the expected large

resistance for the monolayer films, which decreases by an order of magnitude when the ligands are removed by the effect of thermal annealing. The use of different geometry allows us to calculate in a more precise way the resistivity of the films and to assess the crucial contact resistance. Eventually, we tested the film devices as photo-conductors in a controlled vacuum environment under illumination with UV light, demonstrating the increase of current over minute timescale which we attribute to surface modification due to the absence of gas and humidity. In the new optoelectronic setup, we aim at shed light onto this phenomenon by controlled gas flush (O_2, N_2, CO_2) in a controlled atmosphere chamber.

4. **Photo assisted-KPFM study of 0D-2D hybrid structure of ITO and MoS_2**. Through the patterning procedure previously described, we fabricated hybrid structures combining large area exfoliated MoS_2 flakes and ITO NCs. The devices were analyzed with photo-assisted Kelvin Probe Force Microscopy (pa-KPFM), an atomic force microscopy (AFM) technique which combines the illumination of a suitable light source with the study of contact potential difference (CPD) by means of AFM-KPFM. Light induced modifications of CPD have been verified over the analyzed samples, both with 532nm, 400nm and 365nm light source, indicating that there is a charging effect which can be attributed to photodoping. We are currently investigating the different changes happening over MoS_2 and NCs and on the heterostructure in order to better understand the mechanism of photodoping and get insight on the possible charge transfer between the two materials. This part of the work was performed at the Molecular Foundry (CA, USA) in collaboration with Imaging and Manipulation of Nanostructures facility.

Courses

Course	Teachers	PhD Course	Exam Status
Nanomaterials and nano heterostructures: colloidal synthesis and chemical transformations	L. de Trizio (IIT)	IIT	Passed
Biosensing	O. Cavalleri, E. Angeli	UniGe	Passed

Conferences:

- **Spectral sHaping For biomedical and energy applications 2022** (SHIFT 22), Poster Contribution "Multi-Layer Optical Model for Metal Oxide Nanocrystals" October 10^{th} - 14^{th}, 2022 : in presence
- **European Material research Society Fall Meeting 2022** (EMRS 22), Poster Contribution "Depletion layer role in Multi-Layer Optical Modeling of Metal Oxide Nanocrystals", September 19^{th} - 22^{th}, 2022: in presence

Publications:

- Petrini, N., Ghini, M., Curreli, N., Kriegel, I. Optical Modeling of Plasmonic Nanoparticles with Electronically Depleted Layers. *The Journal of Physical Chemistry C.*, **2022**, 127. 10.1021/acs.jpcc.2c05582.
- Curreli, N., Lodi, M., Ghini, M., Petrini, N., Buono, A., Migliaccio, M., Fanti, A., Kriegel, I., Mazzarella, G. Numerical Study of the Optical Response of ITO-In2O3 Core-Shell Nanocrystals for Multispectral Electromagnetic Shielding. IEEE Journal on Multiscale and Multiphysics Computational Techniques. **2023** 11. 10.1109/JMMCT.2023.3235750.
- Rebecchi, L., Petrini, N., Maqueira Albo, I., Curreli, N., Rubino, A. Transparent conducting metal oxides nanoparticles for solution-Processed thin films optoelectronics. *Optical Materials: X.*, **2023**, 19. 100247. 10.1016/j.omx.2023.100247.
- Petrini, N., Asaithambi, A., Rebecchi, L., Curreli, N. Bismuth telluride iodide monolayer flakes with nonlinear optical response obtained via gold-assisted mechanical exfoliation. *Optical Materials: X.*, **2023**, 19. 100255. 10.1016/j.omx.2023.100255.

Manuscript in preparation:

- "Optimizing Gold-Assisted Exfoliation of Layered Materials with (3-Aminopropyl)triethoxysilane (APTES): A Promising Approach for Large-Area Monolayers"

Research period abroad

- Visiting period at the Molecular Foundry, Lawrence Berkeley National Laboratories, CA, USA under presented project #8306 "Light-driven capacitive charging of doped metal oxide nanocrystals measured with Kelvin Probe microscopy"