# Annual Report - 2$^{nd}$ PhD Year

Nicolò Petrini (XXXVI cycle)

**Supervisor (UniGe)**: Francesco Buatier de Mongeot, buatier@fisica.unige.it

**Supervisor (IIT)**: Ilka Kriegel, ilka.kriegel@iit.it

During the second year of PhD, my research activity focused on establishing the building blocks necessary for the next 0D-2D heterostructure based on Indium Tin Oxide (ITO) nanocrystals (NCs) and $MoS_2$, which is the objective of Light-DYNAMO project (Grant 850875, I.K.). Therefore, my studies concerned the optimization and advancement of 2D-material gold-assisted exfoliation to obtain mm-sized monolayers that can be transferred on a desired substrate and electrically contacted. Besides, I reached control over NCs film thickness and coverage, and I began studying the photo-electrical response of the fabricated films. I also established a multi-layer optical model for MO NCs in solution which allows to access information on NCs electronic structure by studying the optical absorption spectrum. We used this model in our recent work[1] and a more detailed paper has been submitted for publication. Recently, we also build a 0D-2D hybrid heterostructure (HET) based on perovskite and $MoSe_2$ which shows evidence of energy transfer between NCs and the 2D material, representing a step forward the engineering of 0D-2D material coupling[2]. Hereby, I describe in more detail each research activity and outcome:

1. **Advancement on exfoliation of mm-sized 2D materials and transfer**. Gold-assisted exfoliation technique allows to obtain large-area monolayers of transition metal dichalcogenides (TMDCs), as $MoS_2$. We focused on increasing the yield and overall reproducibility of the process. We firstly changed the gold deposition technique, employing sputtered gold-foils, and we use ultra-flat crystal surfaces obtained by pre-cleaving the bulk crystals and employing the thin pieces that detached from them. We verified that the exposure to air of the crystal decreases the yield of monolayer area that can be obtained, thus it is better to use a freshly cleaved surface. We were able to obtain **large area (0.1-1 mm** later size), **reproducible** monolayers. Besides, we started studying a suitable procedure to deposit the gold-exfoliated monolayer on different substrates, in particular transparent-conductive oxide, as commercial ITO. The limitation is represented by the affinity of the target substrate with gold and the compatibility with the following wet-etching process. Surface functionalization experiments on different substrates are ongoing. We anyways were able to **transfer** smaller areas of the exfoliated flakes both with dry-transfer method and by employing wet-transfer technique, using PMMA as carrier layer. The possibility to deposit large area flakes on a patterned conductive substrate will be used for the final 0D-2D device. Eventually, the Raman and photoluminescence (PL) map characterization of exfoliated flakes highlights an enhancement in PL in folded monolayers of $MoS_2$ flakes, which we are currently investigating. The optical characterization of Janus monolayer (BiTeI) did not show the expected giant second harmonic generation effect.
2. **Establishment of semiclassical multi-layer optical model for MO NCs.** Following the results obtained in our recently published work[1], I investigated more thoroughly the models that are able to simulate the optical response of NCs, highlighting how it is possible to access inner electronic structure of NCs just by the observation of the absorption spectra of colloidal NCs solution. I specifically studied the application of a multi-Layer optical model on the study of different solutions of ITO NCs [1,3]. I identified the minimum number of parameters that are able to simulate the observed spectra and I validated the model by considering the spectra's feature evolution with NCs structural variation (core-shell structure) and with post-synthetic modification via photodoping. The appearance of double peak and the blue or redshift of the main peak can be associated with the inner electronic structure modification and the modulation of the depletion layer that forms at the NCs surface due to surface states and Fermi level pinning. This work is currently submitted at *Journal of Physical Chemistry C*.
3. **Fabrication and Characterization of NCs mono and multi-layer films**. We fabricated monolayer and multilayer films of ITO NCs by means of spin coating. Octane was found to be an optimal solvent, which leads to obtain the same film thickness and homogeneity in coverage with the same spin coating parameters. The morphological characterization of the film was done by means of SEM, while optical absorption spectra were compared to the colloidal solution ones. Plasmon resonance peak is broadened and redshifted compared to the colloidal spectrum. Curing the film at 300°C for one hour in air or in controlled glovebox atmosphere changes both the structure of the film, forming cracks and small aggregations, and the plasmonic response. Eventually, we characterized the films obtained by fabricating contacts by evaporation of Ti/Au and a shadow mask. We found that our films are

conductive and photo-responsive to UV light. The photoconductance showed long time scale response (seconds/minutes time constants) which will be better investigated in the next experiments.

4. **Fabrication of 0D-2D hybrid structure of $CsPbBr_3$ and $MoSe_2$.**[2] This device has the same architecture that will be exploited to build a phototransistor-like device, which will be used to characterize electrically and optically the interaction between the 2D material and the 0D NCs film. Within this work, I build a photoconductor heterostructure (HET) with the channel made by $MoSe_2$ monolayer, exfoliated with gold-assisted technique, and placed the Ti/Au electrical contacts by means of mask photolithography. Then, we covered the surface by spin-coating $CsPbBr_3$ nanoparticles, obtaining an even monolayer film. We characterized the device by SEM and μ-PL spectroscopy, finding that the PL of NCs on the HET was quenched by the presence of the $MoSe_2$ beneath, while the PL of $MoSe_2$ showed an enhancement. The increase in $MoSe_2$ emission in the HET accounts only for a fraction of the calculated energy transfer. The excess energy generates extra carriers that lead to an enhanced photocurrent.

Besides these projects, I continued improving the optical setup that we use for Micro-Raman and Micro-photoluminescence by implementing nm-piezo stage and using open-source ScopeFoundry Python libraries to control all the setup hardware with a user-friendly GUI. This allows faster and more stable conditions for our measurements.

## Courses attended

| Course | Teachers | PhD Course | Exam Status |
|---|---|---|---|
| Optical Microscopy at the Nanoscale | Alberto Diaspro | UniGe | Passed |
| Atomic force microscopy, theory and practice | M. Salerno (IIT) | IIT | Passed |
| Nanomaterials and nano heterostructures: colloidal synthesis and chemical transformations | L. de Trizio (IIT) | IIT | Exam in preparation |
| Biosensing | O. Cavalleri, E. Angeli | UniGe | Exam in preparation |

## Conferences:

- **NanoGe Spring Meeting 2022** (NSM22), Oral Presentation of "Multi-Layer Optical Model for Core-Shell Metal Oxide Nanocrystals" March 7th - 11th, 2022 : Online
- **Gordon Research Conference,** Colloidal Semiconductor Nanocystals, Poster Contribution "Control of Electronic Band Profiles by Depletion Layer Engineering in Core-Shell Metal Oxide Nanocrystals", July 3 - 8, 2022: in presence

## Publications:

- Ghini, M.; Curreli, N.; Lodi, M. B.; Petrini, N.; Wang, M.; Prato, M.; Fanti, A.; Manna, L.; Kriegel, I. Control of Electronic Band Profiles through Depletion Layer Engineering in Core–Shell Nanocrystals. *Nat. Commun.* **2022**, *13* (1), 537. https://doi.org/10.1038/s41467-022-28140-y.
- Asaithambi, A.; Kazemi Tofighi, N.; Curreli, N.; De Franco, M.; Patra, A.; Petrini, N.; Baranov, D.; Manna, L.; Stasio, F. Di; Kriegel, I. Generation of Free Carriers in MoSe 2 Monolayers Via Energy Transfer from CsPbBr 3 Nanocrystals. *Adv. Opt. Mater.* **2022**, *10* (14), 2200638. https://doi.org/10.1002/adom.202200638.

## Manuscript submitted for review:

- "Optical modeling of plasmonic nanoparticles with electronically depleted layers", N. Petrini, M. Ghini, N. Curreli, I. Kriegel, submitted to J. Phys. Chem. C

## References


1. Ghini, M. *et al.* Control of electronic band profiles through depletion layer engineering in core–shell nanocrystals. *Nat. Commun.* **13**, 537 (2022).
2. Asaithambi, A. *et al.* Generation of Free Carriers in MoSe 2 Monolayers Via Energy Transfer from CsPbBr 3 Nanocrystals. *Adv. Opt. Mater.* **10**, 2200638 (2022).
3. Gibbs, S. L. *et al.* Dual-Mode Infrared Absorption by Segregating Dopants within Plasmonic Semiconductor Nanocrystals. *Nano Lett.* **20**, 7498–7505 (2020).