First Year PhD Report (XXXIX Cycle)

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During the first year of my PhD, I joined the Italian Institute of Technology as part of the project ERC-2020-COG REPLY dealing with plasmonic-based hybrid materials for photocatalytic applications. The goal of the project is to achieve strong light-matter interaction (SC) between plasmonic nanoantennas (NAs) and low-dimensional semiconductors (e.g. quantum dots - QDs), then study the photophysical properties of the newly formed hybrid states and optimize the overall architecture via collective effects, such as surface lattice resonances (SLRs).

To improve light-matter interaction metallic nanostructures sustaining localized surface plasmon resonances (LSPRs) are commonly used. Moreover, the diffractive coupling achievable in periodic arrays of nanoparticles, can lead to SLR effects, thus improving the overall quality factor of plasmonic modes [1]. In line with this, for the present research activity silver was used as a plasmonic material due to its intrinsic characteristics, including low losses (such as the resistive ones) and high electrical conductivity, which facilitate strong electromagnetic field trapping and enhancement via plasmonic resonance [2]. Furthermore, the low-dimensional semiconductor chosen was cadmium selenide (CdSe) QDs, which efficiently absorb and emit visible light due to their high quantum efficiency and tunable optical characteristics [3].

In the initial phase of the PhD, the primary focus was on the understanding and using of two main fabrication techniques. The first based on electron beam lithography (EBL), and the second, after a detailed study of the EBL-made structure with optimization, on focused ion beam (FIB) approach [4]. These techniques have indeed remarkable precision and control over size and shape of nanostructures, i.e. the morphological parameters essential to control/enhance their optical properties.

The fabrication procedure started with sample preparation, where the substrates (silica, silicon, and CaF_2) have been cleaned using acetone, isopropyl alcohol, and water in ultrasonic bath, followed by plasma cleaning. Then, electron-resist PMMA layer was deposited using spin coating technique, followed by the deposition of a thin aluminum layer using a thermal evaporator (PVD75, Kurt J. Lesker Company) to avoid charging effects caused by the substrate insulating character. On the prepared samples, the first fabrication step was performed using EBL system (Raith150-Two, Raith GmbH). Honeycomb, hexagonal, and square patterns were generated in the EBL software and transferred onto PMMA layer in the e-beam lithography step, covering areas as large as 100 μm × 100 μm (sometimes expanding them to 200 μm × 200 μm). After the patterning step, the conductive aluminum layer was removed, followed by the development of PMMA. Then, plasmonic materials such as aluminum, silver, and gold were deposited using conjugated e-beam/thermal evaporator (KE500ET, Kenosistec S.r.l.). Finally, the nanostructures were obtained by performing the PMMA lift off process in acetone.

In the second fabrication method, we focused on the realization of nanostructures by using FIB. This approach was specifically used to generate more compact honeycomb structures with great accuracy, working with dimensions of 50 μm × 50 μm and employing silver and gold as plasmonic materials. The dual-beam system, comprising of a SEM column for imaging and a FIB column for milling, allows for highly precise modifications of the structures in real time.

Once fabricated, the sample were used to reach the SC regime between SLRs and exciton resonances in CdSe QDs [5]. In this regard, CdSe QDs have been placed in close contact with resonating nanostructures by drop casting and/or spin coating techniques. To precisely control the QDs positioning over the NAs, several spin coating recipes were tested to study the influence of QD film compactness and thickness on SC regime.

Morphological investigations as well as preliminary optical characterization confirmed the successful fabrication of NA-based devices, exhibiting SLRs resonating at various wavelengths in the visible spectral region. In particular, the precise tuning of the optical response was achieved, by adjusting periodicity, height, and diameter of NAs arrays. We obtained a general trend where increasing the periodicity and diameter of the structure led to a red shift in the resonance, enabling fine tuning of the device to work in the visible region. This was possible not only thanks to the acquired fabrication know-how, but also to the fruitful collaboration with other team members as well as the significant discussions with the project supervisor, whose previous work constitutes a solid background for the research here presented.

The aforementioned results with Ag NAs lay the groundwork for our next goal, which is to improve and optimize strong coupling with QDs. Therefore, the main objective for the next months will be focused on the accurate characterization of the fabricated structures. This will require in-depth optical investigations, including absorption, transmission, and reflection studies, to better understand and improve the light-matter interactions.

Attended Courses

- Atomic Force Microscopy (Prof. Marco Salerno, Feb-April 2024, DIFI, 3 CFU)
- Microscopic and spectroscopic techniques for the analysis of surfaces and interfaces (Prof. Renato Buzio and Prof. Letizia Savio, March-June 2024, DIFI, 3 CFU)
- Quantum Optics (Prof. Dario Ferraro, March-May 2024, DIFI, 3 CFU)
- Biosensing (Prof. Dario Ferraro, Mar-June 2024, DIFI, 3 CFU)
- Introduction to the Foundations of Quantum Mechanics and Applications (Prof. Paolo Solinas and Prof. Pierantonio Zanghí, May-July 2024, DIFI, 3 CFU)

Summer School

LIMNI Summer School on Exploring Novel Materials and Advanced Fabrication Techniques for Micro-and Nanosystems (Location: Leuven, Belgium, September 16-20, 2024, with online sessions from September 9-13, 2024)

Reference

1. Hertzog, M., et al., *Strong light–matter interactions: a new direction within chemistry.* Chemical Society Reviews, 2019. **48**(3): p. 937-961.
2. Zhu, X., et al., *Beyond noble metals: high Q-factor aluminum nanoplasmonics.* ACS Photonics, 2020. **7**(2): p. 416-424.
3. Wang, H., et al., *Dynamics of strong coupling between CdSe quantum dots and surface plasmon polaritons in subwavelength hole array.* The journal of physical chemistry letters, 2016. **7**(22): p. 4648-4654.
4. Horák, M., et al., *Comparative study of plasmonic antennas fabricated by electron beam and focused ion beam lithography.* Scientific reports, 2018. **8**(1): p. 9640.
5. Sidler, D., et al., *Polaritonic chemistry: Collective strong coupling implies strong local modification of chemical properties.* The journal of physical chemistry letters, 2020. **12**(1): p. 508-516.