Second year PhD report
Student: Elena Ghidorsi
Supervisor: Andrea Toma
Academic year: 2023-2024, XXXVIII cycle
Research activity
The second year of my PhD has been focused on the optical characterization of photonic nanocavities sustaining hybrid states formation under strong coupling regime. Within this context, I optimized the fabrication protocols previously explored (see first year annual PhD report), achieving heterostructures composed by low dimensional semiconductors and high reflective metals, here employed as mirrors in optical resonators. The aforementioned systems have been deeply studied through steady-state and ultrafast spectroscopies, with the aim of understanding their photophysical behavior and temporal dynamics [1]. The implementation and comprehensive investigation of polaritonic architectures for photocatalytic applications is indeed one of the main objectives of the ERC project in which I am involved.

Relying on Rabi splitting theory, the theoretical framework that more accurately explains the exciton-plasmon (or exciton-photon) coupling is the model considered in the Tavis-Cummings Hamiltonian [2]. This approach predicts that strong coupling is reached when the interaction between an ensemble of quantum emitters and a cavity mode is strong enough to overcome the single decay rates. More specifically, the comparison between the decay rates of the uncoupled oscillators (γ_{pl} , γ_{exc}) and the Rabi frequency (Ω_R) proves that strong coupling can be achieved if $\Omega_R > \dfrac{\gamma_{pl} + \gamma_{exc}}{2}$ [2]. Within this context, I performed absorbance spectroscopy to retrieve the energy splitting of nanocavities hybridized with prototypical quantum emitters and compare their absorption linewidths with that of the emitters excitonic response in free space and of the optimized bare planar cavities (*i.e.* Au-SiO_2-Au) resonating in the 550-600 nm visible range of the emitters.

For the steady-state optical characterization I used a home-built micro-spectrometer setup equipped with a pinhole to resolve the sample area (*i.e.* for spatial resolution) and a halogen lamp as white light source. Additionally, I implemented the steady-state absorbance measurements within the available pump-probe setup currently used to perform time-resolved spectroscopy. To do this, I exploited the white light supercontinuum (WLSc) generated in a bulk sapphire crystal from the fundamental 1030 nm radiation, setting the optical probe delay line at the time zero configuration.

For the analysis I wrote a Matlab script to fit the absorbance spectra with Lorentzian lineshapes that, in the case of J-aggregate embedded in planar nanocavities, revealed the presence of a Rabi splitting of 220 meV, which is larger than the FWHM of the bare cavity mode. To observe hybrid states (*i.e.* upper and lower polaritons) branches in terms of confined-photon energy dispersion, I fabricated samples with different thicknesses (from 80 to 120 nm for the SiO_2 film), thus detuning the cavity resonance frequency with respect to the material excitonic response. As predicted by Rabi splitting theory, anticrossing behaviour was observed, resulting in a parabolic dispersion curve [2].

Then, since pumping the coupled states in the ultrafast regime allows to understand their dynamics, I employed femtosecond transient absorption spectroscopy technique on the samples described above, in order to investigate the lifetime of hybrid polaritonic states and to understand charge carrier transfer processes that can occur in such photonic platforms [3]. Therefore, in collaboration with post-doc colleagues and other team members I implemented and improved the using of the pump-probe setup, carrying on measurements under different resonant conditions.

As presented in the poster session of the Quantum Optics and Nanophotonics Winter School of the University of Sheffield, UK (Jan 2024), the pump-probe spectral maps of the material-embedded systems (@525nm, 500μW, 50KHz) showed negative and positive transient absorption features here identified as ground-state photobleaching and photoinduced absorption, respectively. Considering the bleaching signals spectrally corresponding to the polariton states as a starting point, a possible interpretation of relaxation processes, dark state reservoir effects and correlated lifetimes of the spectral features was given. Fast decays at early stages and long-lived states were observed for the lower (2.04 eV) and the upper (2.24 eV) polariton bands, respectively, thus suggesting the existence of extended dark and vibrational states reservoir baths to which upper polaritons could relax instead of directly decay to the ground state [4,5]. Additionally, a possibly related progressive blue and red shifts of the lower and upper polariton bleachings were observed, respectively [6].

Furthermore, I focused on nanoparticle-on-mirror (NPoM) geometry systems integrated with semiconductors, through which interfacial charge transfer can be enhanced at the expense of hot electrons relaxation [7]. Thus, in collaboration with Prof. Manohar Chirumamilla of Aalborg University, DK, I'm carrying on pump-probe measurements on vertical nanocavities, obtained through physical vapor deposition (PVD) of gold nanocrystals as top plasmonic resonators on a TiO_2-Au platform, which showed photoexcited absorption dynamics in correspondence of the coupled states generated from cavity mode and nanocrystal localized surface plasmon resonances [1,7]. In this case, transient spectra were obtained pumping at a wavelength value between the two coupled states (550nm, 500μW, 50KHz).

Other activities and collaborations

IIT seminars, invited by supervisor Toma:

- N. Asger Mortensen, University of Southern Denmark, DK, Mesoscopic electrodynamics in surface-polariton systems (19 Dec 2023)
- Alexander Kildishev, Purdue University, USA, Multipole Expansion Centers: Uniqueness & Multiplicity (15 May 2024), Inverse-designed Spaces for Light (16 May 2024)
- Marco Peccianti, Loughborough University, UK, Applications of Photonic Complexity in Integrated optics and Teraherts at the Emergent Photonics Research Centre (9 Jul 2024)

Collaboration:

- Manohar Chirumamilla of Aalborg University, DK

Exams and attended courses:

- Nanophotonics and nanofabrication (exam given)
- Electronics and data acquisition
- Introduction to the foundations of quantum mechanics and applications
- Optical properties of materials
- Advanced electron microscopy, IIT

Winter School:

- Poster presented at the Quantum Optics and Nanophotonics Winter School (15-17 Jan 2024), University of Sheffield, UK

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