Strong plasmon-molecule interactions at the nanoscale: hot carrier generation and impact of microstructure

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Strong light-matter interaction is seeing use in various fields such as in energy harvesting, nonlinear optics and modification of material-related properties or chemical reactions. Plasmonic nanostructures, due to their large cross section for interaction with light, are very efficient optical antennas even when small in size and are of great interest for hot carriers generation. Light absorption in metal particles is efficient, however, the lifetime of hot carriers is short. By strongly coupling to a nearby molecule we can modify the properties of these hot carriers. To investigate hot carrier generation and evolution in a strongly coupled system, we consider a magnesium nanoparticle interacting with a small molecule: CPDT. We present a TDDFT study to access the physics of nanoscale nanoparticle-molecule assemblies, predict vacuum Rabi splitting and get insight into the hot carriers generation. The overlap of spectral resonances leads to the creation of Rabi splitting [1]. The relative CPDT orientation with respect to the nanoparticle affects the coupling strength that is explained by the creation of different hybridized states, Fig. 1a. The electric field enhancement shows that in LP/UP coupled system, the CPDT molecules focus the electric field, depending on the molecular orientation, Fig. 1bc, which leads to modifying the cavity and, consequently, its vacuum field, Fig. 1d. We predict the energetic and spatial distributions of generate hot-carrier in nanoparticle-molecule systems and reveal the impact of strong coupling on the hot carrier distribution [2, 3]. To gain more insight into the impact of strong coupling on the hot carriers distribution, we have investigated the generation of hot holes and hot electrons in function of gap distance. At small distances the hot electrons are transferred from the excited CPDT to nanoparticle leaving hot holes created after electrons excitation arising from the energetic states hybridization between CPDT and Mg nanoparticle. For gaps larger than 5 Å, the hot carriers remain in the subparts of the system in which they were generated, what is caused by relatively weak interaction between these subparts for larger gaps.

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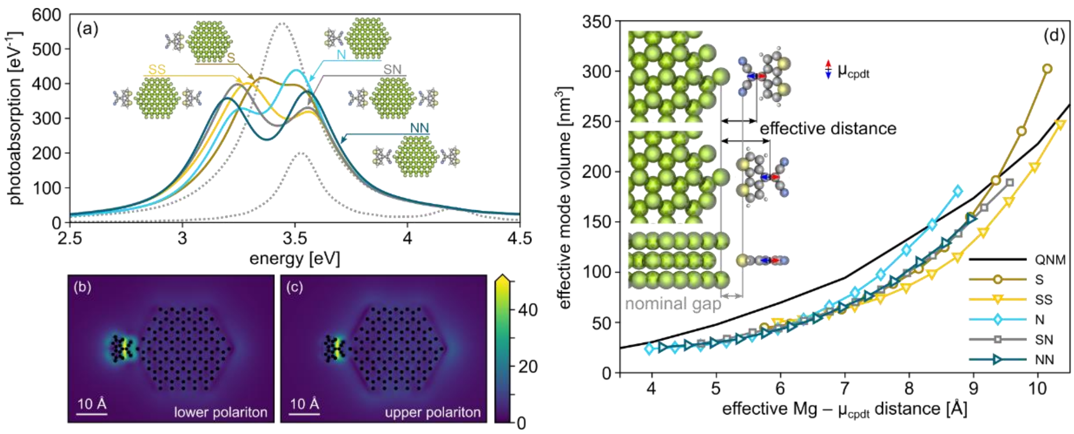

Fig. 1. Figure caption below the figure (10 points, Calibri, centered). The caption of the figure is optional. Text should not wrap around figures or tables.

[1] M. Kuisma, B. Rousseaux, K.M. Czajkowski, T.P. Rossi, T. Shegai, P. Erhart, T.J. Antosiewicz, ACS Photonics. **9**, 1065 (2022).
[2] T.P. Rossi, P. Erhart, M. Kuisma, ACS Nano. **14**, 9963 (2020)
[3] K. Kluczyk-Korch, T.J. Antosiewicz, Nanophotonics **12**, 1711 (2023)