Hot-carrier generation in strongly coupled nanoparticle-molecule systems

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Strong coupling between a metal nanoparticle and a molecule stems from the hybridization of electronic energy levels of both systems and leads to the appearance of new resonant frequencies, modifying various properties. Here we manipulate generation of hot carries by tuning the interaction in the coupled system. The hot carriers are generated at the excitation frequencies of the new coupling resonances, while additionally their energy distribution can be tuned by modifying the nanoparticle-molecule configuration, which yields new decay pathways from the new hybridized states. This indicates the possibility of increasing the hot carriers energy generation by adjusting the molecular structure.

The strong coupling regime of light-matter interaction is seeing research in various fields such as in energy harvesting, nonlinear optics and the ability of modifying the material-related properties or chemical reactions. Plasmonic nanostructures, due to their large cross section for interaction with light, can act as very efficient optical antennas even when small in size and can be of great interest for hot carriers generation. While light absorption in metal particles is efficient, they are characterized by short lifetime of hot carriers. However, by coupling to a nearby molecule, the hot carriers can be utilized to perform useful work, what is studied here in a strongly coupled plasmon-molecule system. To investigate hot carrier generation and evolution in a strongly coupled system, we consider a magnesium nanoparticle interacting with small molecules of CPDT. In this work, we perform a computational quantum study based on time-dependent density-functional theory approach 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 (see 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 (See Fig. 1b), which leads to modifying the cavity and, consequently, its vacuum field. 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]. 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 (See Fig. 1c). Upon small distances (2-5 Å), 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. Beyond 5 Å, the hot carriers generated still trapped in the subparts of the studied systems, which is explained by the weak interaction between these subparts over higher gaps.

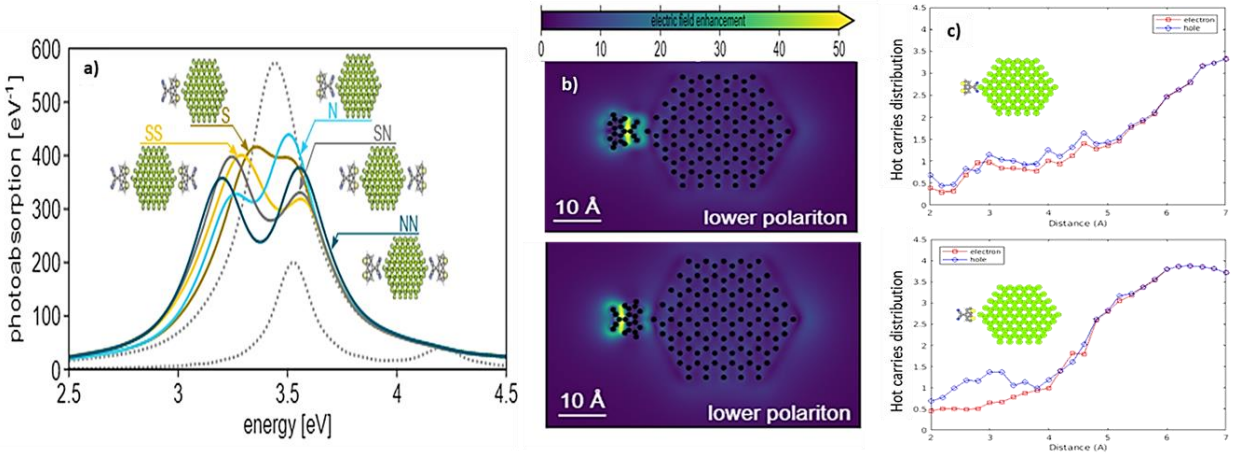

Fig. 1 (a) Photoabsorption spectra of the Mg170 nanoparticle, the CPDT molecule and the coupled Mg170–CPDT system with a 3 Å gap with different molecule orientation with respect to the particle. (b) Induced fields of the lower and upper polaritons of interacting systems with the dicyano group of CPDT facingMg170. (c) Hot carriers distribution within CPDT molecule in function of gap.

According to these results, we substantiate the impact of molecular structure on the strong coupling in nanoparticle-molecule systems. These results suggest the possibility of manipulation the generated hot carriers spatial distribution via strong interaction with molecules. The plasmonic systems with strong coupling of electronic and photonics states make them promising candidates for nanoelectronic and optoelectronic applications.

References

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