

Designing ligand-enhanced optical absorption of thiolated gold nanoclusters and plasmonic effects in gold nanostructures

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The absorption spectra of metal nanostructures are characterized by strong bands in the optical-UV region referred to as Surface Plasmon Resonances (SPR) [1]. This feature is very sensitive to the nanostructure environment: a first issue then arises because the environment (such as the shell of protecting ligands in thiolated clusters) can damp the absorption intensity in the visible region, thus e.g. requiring much larger particles observe the “birth” of SPR. This limits applications in molecule detection via Raman spectroscopy, enhanced plasmonic phenomena in metal nanogaps, biosensing, etc. Two different strategies are here investigated to overcome the issue of SPR damping and achieve intense SPR peaks in the whole near-IR/vis region.

The first strategy is based on fine tuning the chemical features of ligands in monolayer-protected clusters [2]. Focusing on thiolated Au nanoclusters with formulae Au₂₅(SR)₁₈, Au₂₃(SR)₁₆ and Au₃₀(SR)₁₈, whose atomistic structure has been determined for selected ligands, and predicting their spectra via time-dependent densityfunctional- theory (TDDFT) simulations, we show how large enhancements in absorption spectra in the whole optical region can be achieved by tuning the steric and electronic properties of the SR ligands. Charge decomposition via steric hindrance and delocalization via π -conjugation to achieve optimal band alignment are used as guiding principles to design candidate species whose integrated optical spectral intensity exceeds that of much larger clusters. This occurs via a resonance phenomenon in which many excitations, of composite Au/S/R character and involving the nanocluster as a whole, crowd in a narrow energy interval. A new tool is introduced to analyze the excited state wave function in terms of component fragments, allowing one to define effective model Hamiltonians for these systems. This strategy allows one to circumvent the issue of SPR damping by the environment (SPR “re-birth”), and represents a step forward toward the goal of an in silico design of nanoclusters with desired optical properties.

The second strategy is based on molecule/nanostructure resonance coupled with plasmon/plasmon interactions due to proximity effects [3]. Attention is focused on Au nanowires, which allow a computationally economical study of sizeable systems due to exploitation of translational symmetry. The coupling between the plasmonic modes of the metal nanoparticle and those involving Au-ligand bonds is explored as a prototypical example of metal/ligand interface, and the search for synergic interactions in the optical response will be discussed. The dependence of plasmonic peaks upon stoichiometry and chemical ordering will be analyzed, together with its dependence upon inter-particle distance to explore coupled plasmonics effects and ‘hot-spot’ enhancement of response fields in the presence of ligated species. The role of the coating ligand shell in terms of both structural and optical properties will be underlined.

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2. L. Sementa, G. Barcaro, A. Dass, M. Stener, A. Fortunelli, *Chem. Comm.* **51**, 7935–7938 (2015); (article in preparation).
3. A. Marini, G. Barcaro, F. R. Negreiros, A. Fortunelli, *ACS Photon.* **1**, 315–322 (2014).