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Research paper

Strain induced plasmon tuning in planar square-shaped aluminum nanoparticles array

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ABSTRACT

Metal nanoparticle aggregate is an exciting platform for manipulating light-matter interactions at the nanoscale, thanks to the optically driven free electrons couple electrically across the inter-particle gap region. We use time dependent density functional theory calculations to investigate the optical response modulations in planar square-shaped aluminum nanoparticles array via morphology deformation (varying the inter-particle gap distance in the range of 2–20 Å) separately along one and two directions. We report the surprising observation that irrespective of the different morphology deformations, there exists a unique inter-particle gap distance of 12 Å for which, a maximum optical field enhancement can be achieved. We remark that plasmonic interaction between metal nanoparticles in an aggregate is controlled to a large extent by the size of the inter-particle gap distance. We believe that our quantum mechanical calculations will inspire and contribute to the design, control, and exploitation of aluminum based plasmonic devices.

1. Introduction

Recent advancements in nanostructure synthesis and characterization techniques made it possible to engineer tailor-made metal nanoparticles with blended optical properties supported by localized surface plasmon resonances (LSPR): the collective excitation of the conduction band electrons in response to light [1–3]. Applications of LSPR span over a large range of areas, including nanoscale light management [4], metamaterials [5], medicine [6], photovoltaics [7], solar energy [8], optoelectronics [9] and chemosensing [10]. Modifications of the shape, size or materials affect the LSPR [11,12]. Additional flexibility in LSPR tuning is possible via metal nanoparticle aggregates consisting of multiple nanoparticles in close proximity, as was explained by Prodan and co-workers [13] in their hybridization model. Metal nanoparticle aggregates enable strong plasmon-induced electromagnetic field enhancements, extremely confined in the inter-particle gap region known as "hot spot" required to observe single molecule surface enhanced raman scattering (SERS) [14].

There have been a tremendous surge in theoretical spectroscopy to complement the experimental spectra. Optical response in metal nanostructures can be accurately calculated using classical electromagnetic simulations based on Maxwell's equations [15,16]. However, as the size shrinks below 10 nm, quantum mechanical effects emerge and standard classical approaches to describe the optics of these systems fail [17,18]. Moreover, nanometer or sub-nanometer sized inter-particle gaps present in metal nanoparticle aggregates induces many unique effects, expanding the tool-set for modifying the optical response [19]. This necessitates the use of otherwise computationally expensive quantum mechanical techniques such as the time-dependent density-functional theory (TDDFT). In this letter, we report a TDDFT study investigating the effect of morphology deformation on the optical response of a planar square-shaped aluminum nanoparticles array (composed of 9 spherical nanoparticles having a total number of 387 atoms and 1161 free electrons). It is worth mentioning some of the important previous works on strain evolution of plasmon modes. For example, it has been shown recently how the mechanical strain along different directions in Al nanoparticles array useful for plasmon-enhanced molecular sensing application [20]. Qian and coworkers reported how the mechanical strain modulates the LSPR characteristics and enhance the light trapping of metal nanoparticle array of thin film solar cells [21]. Bao and co-workers reported tuning the LSPR properties of Au nanoparticles by controlling the plastic deformation [22]. In addition, it has been shown how the mechanical strain can be applied for the nanoparticles. For example, Huang and co-authors reported the stress-induced deformation process of a Ag nanocube with the edge length about 100 nm [23]. The morphology evolution of a 400 nm sized Au nanocrystal under various

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high-pressure conditions was also reported [24]. Finally, the deformation of nanocrystals has been investigated in 1D nanowires [25], 2D nano films [26], and nanopillars attached to a substrate [27].

It is noteworthy that aluminum nanostructures are the main focus of nanoplasmonics research nowadays owing to their wide spectrum tunability from the UV to the near-infrared region of the electromagnetic spectrum. Moreover, it is inexpensive, highly abundant, sustainable metal, and compatible with complementary metal-oxide semiconductor (CMOS) manufacturing techniques [28–32]. These factors make aluminum particularly attractive for large-area technological applications, including solar cells, photodetectors, and flat-panel displays. On top of that, the use of aluminum for modeling is not only computationally convenient and it has also been successful in reproducing many general phenomena of simple and noble metals in plasmonics.

2. Computational details

The primary focus of this work is to elucidate and understand the optical properties of the above-mentioned nanostructure. Representative snapshots of the morphology deformation process are shown in the top panel of Figs. 2 and 3 for stretching process along one direction and in the top panel of Figs. 4 and 5 for stretching process along two directions. Following the ground-state density functional theory (DFT) calculation (the SCF convergence was set to 10^{-8} and energy convergence criterion set to 10^{-6}) using *w*B97X [33] long-range corrected hybrid exchange correlation functional and def2-TZVP basis set [34] (further information regarding the DFT calculation parameters and/or the exchange correlation functional used is available in the ORCA manual), the optical spectra are obtained by solving time-dependent Kohn-'Sham equations using well-known Casida's method [35] as implemented in ORCA DFT/TDDFT software version 4.0 [36]. The optical spectra are computed by solving the following eigenvalue equation,

$$\Omega F_I = \omega_I^2 F_I \tag{1}$$

where Ω is a matrix consisting of products of occupied-virtual Kohn-Sham orbitals and the eigenvalues ω_I^2 correspond to squared excitation energies while the oscillator strengths are extracted from the eigenvectors F_I. The number of dipole-allowed transitions (roots) should be high enough to cover the desired range in the absorption spectrum. We found 1250 roots is adequate to cover the spectrum up to an energy of 5.5 eV. All absorption spectra are broadened by a Gaussian smearing of width $\sigma = 0.1$ eV. It is worth mentioning that each Al atom contributes one electron to the nanoparticle array. Unlike noble metals like Ag and Au, the core electrons do not need to be explicitly considered to evaluate the

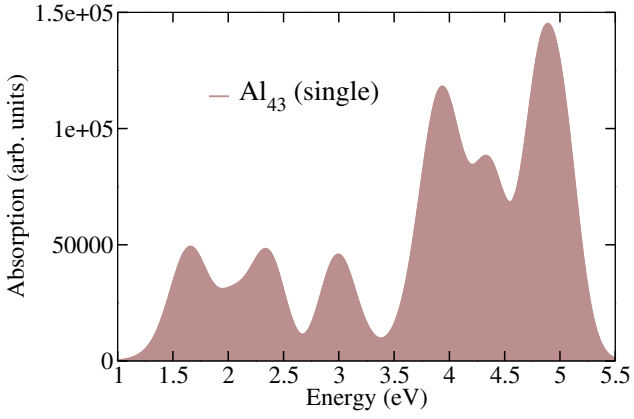

Fig. 1. TDDFT calculated optical spectrum of single Aluminum nanoparticle.

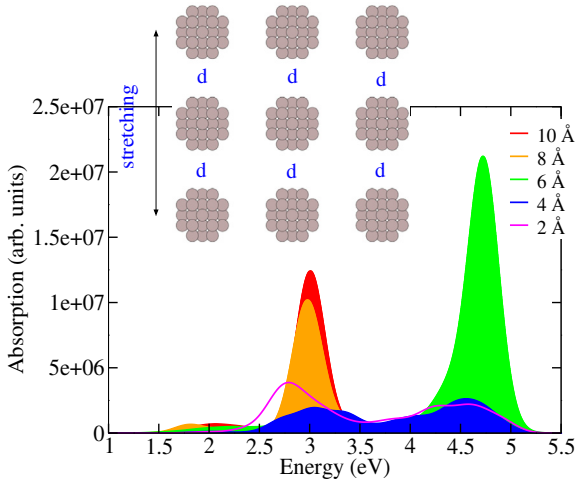

Fig. 2. TDDFT calculated optical spectra for the morphology deformation along one direction in which the inter-particle gap distance progressively increased from 2 to 10 Å.

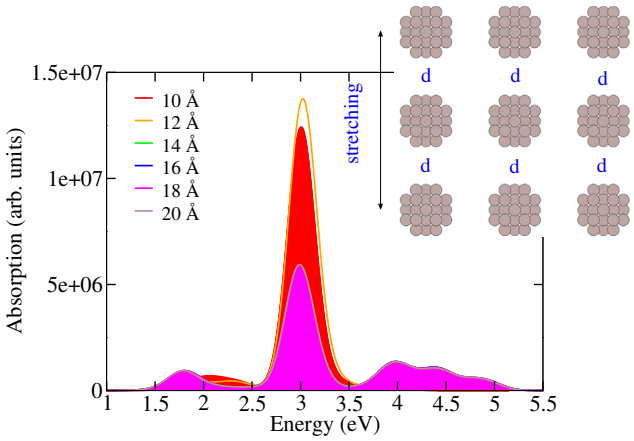

Fig. 3. TDDFT calculated optical spectra for the morphology deformation along one direction in which the inter-particle gap distance progressively increased from 10 to 20 Å.

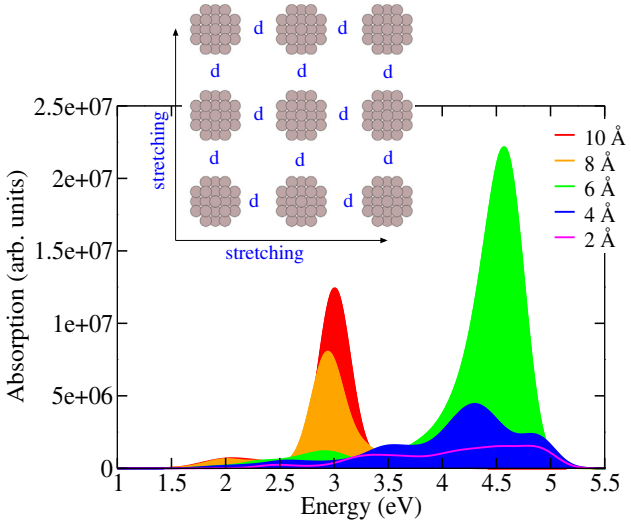

Fig. 4. TDDFT calculated optical spectra for the morphology deformation along two directions in which the inter-particle gap distance progressively increased from 2 to 10 Å.