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Research paper

Optical response tuning in nanorod-on-semicontinous film systems: A computational study

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ABSTRACT

Strongly confined and intense optical fields within the plasmonic metal nanocavities show outstanding potential for a wide range of functionalities in nanophotonics. Using time dependent density functional theory calculations, we investigate the optical response evolution as a function of the gap separation distances in nanorod-on-film systems comprised of a nanorod (NR) made of Al or Na on top of an Al film. Huge optical field modulations emerged in the chemically distinct Na NR – Al film system in comparison to the Al NR – Al film system, indicating the vital role of metals involved. We further study the optical response modifications by placing a conducting molecule in the gap region, finding strong spectral modulations via through-molecule electron tunneling.

1. Introduction

Plasmons [1–3], collective and coherent oscillation of conduction band electrons in metal nanostructures, have recently attracted significant research interest. They enable manipulation of light-matter interaction at the nanometer scale and have been exploited in various applications, for example, chemical and biological sensing [4–7], light harvesting [8,9], photodetection [10], hot-carrier generation [11], photo-thermal cancer therapy [12] and photocatalysis [13]. In the unending quest of discovering novel optical effects, a diverse set of designer nanostructures have been proposed and investigated to date, for example, nanorods (NRs) [14,15], nanocubes [16–18], nanowires [19,20] and ordered NP arrays [21]. The optical response of these composite nanostructures strongly depends on various factors such as the arrangement of individual nanostructures, interparticle gap distances and the underlying substrates and instigates various nanoscopic effects including Fano resonances [22,23] and charge transfer plasmons [24,25], and thus, expanding the toolkit for further optical response modifications.

One of the most interesting composite nanostructure is a particle-on-film system characterizing a spherical nanoparticle (NP) lying on top of a metal film [26–28]. The presence of an underlying metal film breaks the rotational symmetry of spherical NPs, leading to a strong coupling between localized plasmons of the NPs and continuum surface plasmon polaritons of the metal film. This leads to significant plasmon modifications, such as the large frequency shifts and huge optical field enhancements that very much depends on the gap separation distance between the two systems. In fact, previous investigations on particle-on-film systems were mainly focused on spherical NPs. However, little light has been shed on the system consists of a elongated NP (i.e., NR) on top of a metal film [29–31]. For example, Harrisson et al. [30] reported the role of near-field enhancement in laser ablation of a Si surface using Au nanorods. And Robitaille et al. [31] investigated plasmon-enhanced femtosecond laser ablation of Si using Au nanorods to produce sub-diffraction limit features. It is well-known that NRs show unique optical properties due to the bipolar character of their optical spectrum due to the elongated shape. For example, the light scattered from Au NRs exhibit strong optical anisotropy at spectral positions corresponding to the excitation of longitudinal (electron oscillation parallel to the NR length direction) and transverse plasmon modes (electron oscillation perpendicular to the NR length direction) [32–34].

Given the complexity of plasmon coupling in composite spherical NP and metal film system and the morphology of the nanogap can substantially modify the plasmon coupling, the composite NR-film system shall display more complexities in the plasmon coupling. In this paper, we present for the first time a systematic quantum mechanical study of an Al NR on top of a semi-continuous Al film, revealing intriguing optical response evolution as a function of the gap separation distance. Until recently, plasmonics field mainly exploited precious metals such as Ag and Au. However, the noble metals for plasmonics applications are ultimately limited due to their high cost and scarcity. In contrast, Al, the most abundant metal, found to have amazing plasmonics properties [35–40].

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In particular, the real part of the Al dielectric function is strongly negative and gives rise to a highly size-tunable localized plasmon that spans the UV and visible regions of the electromagnetic spectrum. By taking into account its low price together with its abundance, it is a promising candidate for large scale industrial production. Another appealing feature of Al nanostructures is their thin protective oxide layer that hinders further oxidation. It should be stressed that the choice of a semi-continuous film instead of a continuous film in this work is due to the fact that the former can sustain localized plasmons. In addition, we have also performed calculations using Na NRs.

In this work, we conducted a fully quantum mechanical study using the time dependent density functional theory (TDDFT). It is well-known that quantum mechanical effects such as electron tunneling [41–45] emerges in composite nanostructures having interparticle gaps in the nanometer scale, rendering it substantially different from classical predictions. However, there are major efforts to incorporate the quantum effects into the classical models, for example, quantum corrected model proposed in Ref. [46]. It is also reported that organic species inside the nanogap region enable electron tunneling over larger gap distances, and thus establish a novel platform for composite structures integrating molecular electronics with plasmonics [47]. We also have performed some representative calculations in this direction by placing a conducting molecule in the gap region. These systems are ideal test structures to examine the influence of electron tunneling and nonlocal screening in a fully quantum mechanical ab initio model.

2. Computational aspects

The optical absorption spectra are computed using Casida's linear response formalism in the frequency domain [48] using the Turbomole software package [49–51]. For the exchange-correlation potential, the generalized gradient approximation is used in the BP-86 parametrization and a triple-zeta plus polarization basis set. The multipole accelerated resolution of identity method is used for the Coulomb term and quadrature grids of m3 quality are employed. Note that this computational methodology had been employed successfully to study the optical response tuning in Al nanoparticle arrangements [52]. The general problem is cast in 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 1500 roots is sufficient to cover the spectrum up to an energy of 4.5 eV.

3. Results and discussion

The NR – semi-continuous film systems we are interested in are shown in Figs. 1 and 2 for Al NR – semi-continuous Al film and Na NR – semi-continuous Al film, respectively. We modeled a NR with diameter of 1.6-nm and length 2.8-nm (514), while the model semi-continuous film is 0.8-nm thick and 3.6-nm wide (904 atoms). Before analyzing the optical response of composite systems, let us start by briefly discussing the optical response of individual structures. Fig. 3 shows that individual Al NR and semi-continuous Al film exhibits distinct spectral features in the UV and visible region. In particular, Al NR exhibits pronounced peaks close to 2.3 and 3.6 eV, indicating the longitudinal and transverse electron oscillations, respectively, expected in the case of metal NRs. In contrast, semi-continuous Al film exhibits flattened peaks due to its planar shape. It is fascinating to analyze the electronic structure of the individual structures. To this aim we report in Fig. 4 the total density of states (TDOS). First of all, let us analyze the TDOS of the BDT molecule. One finds that the BDT molecule exhibits discrete electronic states, expected in the case of a molecule. Whereas, the rest of the structures exhibit continuum electronic states. Interestingly, the electronic structure of Al and Na NRs show marked differences in the effective bandwidth (Al and Na NRs show an effective bandwidth of 11 and 5 eV, respectively). These differences are of course consistent with the different nature

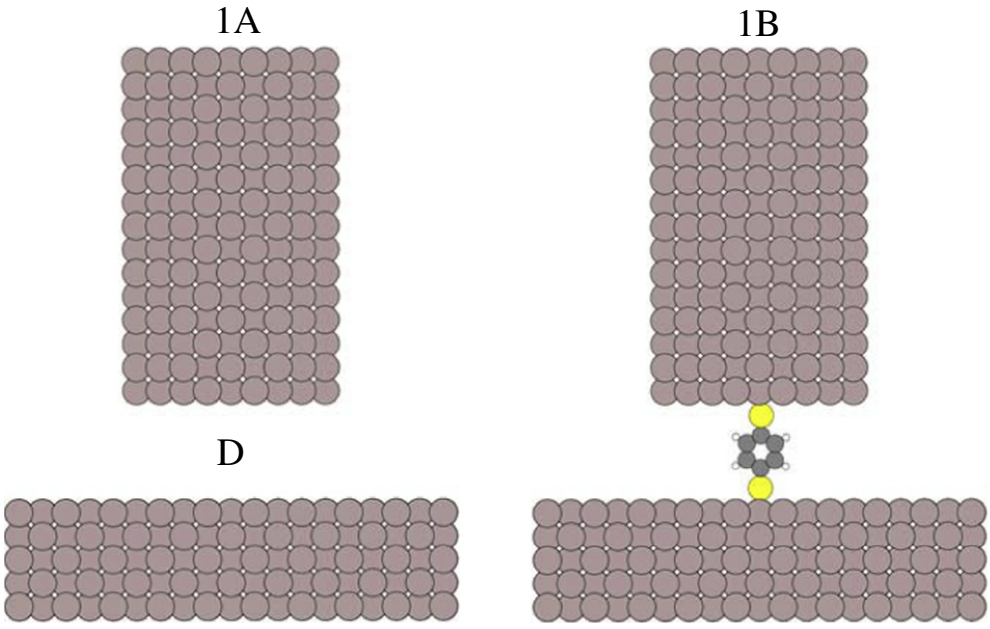

Fig. 1. Left: composite Al NR – semi-continuous Al film system (gap separation distance D (in units of Å)), Right: composite Al NR – semi-continuous Al film system with a conducting BDT molecule in the gap region.