Chemical Physics Letters 696 (2018) 36–41

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

A quantum mechanical study of the optical response evolution in nanorod dimers

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ARTICLE INFO

Article history:
Received 27 December 2017
In final form 14 February 2018
Available online 15 February 2018

Keywords:
TDDFT
Nanorod dimers
Gap plasmons
Charge transfer plasmons

ABSTRACT

Using the time dependent density functional theory calculations, we investigate how the optical response in Aluminium nanorod dimers evolve as a function of different tuning parameters such as gap distances (3–14 Å), structural configurations (compact, hollow and a combination of both) and relative spatial orientations (parallel and axial linkages). We found that the position and amplitude of the gap plasmons are continuously modified with decreasing gap distances in the case of nanorod dimer composed of compact structures, and below 6 Å, the electron tunnelling emerges in agreement with recent experiments. We have also investigated the gap plasmon modifications by placing a conducting molecule in the inter-particle gap region and found the molecule short circuits the junction and decreases the optical enhancement.

The collective excitations of the conduction band electrons of metallic nanoparticles (NPs) in response to light, known as localized surface plasmon resonances (LSPRs) [1,2], has been an active topic of research due to their unprecedented ability to concentrate light down to nanoscale volumes well below the diffraction limit, thus producing large electromagnetic enhancement regions known as "hot-spots" [3–14]. The usual LSPR tuning parameters are the size and shape of the NP, dielectric medium in which the NP is embedded and specific plasmonic material, allowing us to tune the optical response of a single NP. In the case of composite NPs of greater structural complexity, the plasmon modes of the constituent NPs hybridize to form coupled plasmon modes in a manner similar to how atomic orbitals interact and form molecular orbitals [15]. Since the seminal work of Nelayah [16] and Bosman [17], a variety of complex NP arrangements have been tested, including nanorods (NRs) [18,19], nanocubes [20–22], nanowires [23,24] and ordered NP arrays [25], thanks to the advancements in nano-fabrication techniques. Among the broad range of different structures explored, the most simple but versatile composite NP is the dimer. While dimers may not be the ideal candidates for electromagnetic field enhancements, they allow us to understand the key physical parameters of the electromagnetic field enhancements [15]. A special attention has also been focused on nanorods (NRs). They possess two plasmon resonances corresponding to the electron oscillation along the longitudinal and transverse axes. Thus, it is reasonable to believe that the NR dimers would show more complex plasmon coupling due to the shape induced absorption properties [26–28]. Complex plasmon coupling were reported in the case of NR dimers, for example, Ref. [29] shows that the axial and parallel linkages of Au NRs produce the longitudinal modes that red-shifts when the NRs arranged in an axial linkage, whereas the longitudinal mode blue-shifts and the transverse mode red-shifts when the NRs form parallel linkage. Another well established method for tuning the NR plasmons is to make hollow. It is reported that various hollow NPs can be obtained by simple galvanic replacement. It has also been shown that changing the concentricity of the inner cavity of hollow NPs changes the distribution of their near-field enhancement [30].

In this paper, we aim to elucidate the optical response of Al NR dimers using first-principles quantum mechanical TDDFT technique. In the past few years, Al nano-structures has drawn increasing attention due to its vivid plasmon response in the visible and ultra-violet region of the spectrum [31–33]. They form a self-terminating oxide layer that yield long-term stability [34]. Recent theoretical studies [35–41,43] show that for gap distances in the sub-nanometer length-scale the quantum effects emerge. One key hallmark of the quantum effect is electron tunneling, causing the emergence of charge transfer plasmon that greatly deteriorates the plasmonic response. Therefore, this problem needs to be solved using a fully quantum mechanical treatment since classical theories are incompetent due to the lack of nonlocal response in the dielectric function and inter-band transitions. But in reality, fully quantum mechanical calculations are limited only to small systems and for larger systems one should blend the quantum effects

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https://doi.org/10.1016/j.cplett.2018.02.045
0009-2614/

into the classical Maxwell's equation, one such model is the quantum corrected model [41]. In a recent work [42], the effect of band gap variation and surface reconstruction on the optical response of Cu_2O isolated NPs were investigated by combining Discrete Dipole Approximation (DDA) and quantum (TDDFT) mechanical techniques. The former method were employed for the size range from 100 nm to 240 nm and latter method in the case of ultra-small sized clusters ranging from 3 to 9 atoms.

All calculation in this work have been performed with the Turbomole software [44–46]. The optical response is computed using Casida's linear response formalism in the frequency domain [47]. We use the BP-86 generalized gradient approximation to the exchange and correlation energy 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. 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 1200 roots is adequate to cover the spectrum up to an energy of 4.5 eV. The smoothed spectra shown in the figures are convoluted with a Gaussian with a width of 0.2 eV. We found that the use of BP-86 functional together with the resolution of identity technique speeds up our TDDFT calculations significantly.

It is intriguing to see how the individual NR spectrum evolve into coupled modes as the gap distances between them reduced gradually. NR dimers we interested in are shown in Figs. 1 and 2 for parallel and axial linkages, respectively. The compact (hollow) NR monomer has 515 (328) atoms, respectively. Though the NRs employed in this work are thinner than a realistic experimental situation, it still allows us to perform a qualitative study of the optical spectra and give key information regarding the onset of quantum effects. In several recent experiments and theoretical studies it has been shown that when two metal NPs placed next to each other forming a NP dimer, the plasmons of the individual NPs interact, resulting in coupled plasmon modes with energies that can be strongly red-shifted/blue-shifted relative to the plasmons of the individual NPs. The interaction energy of a NP dimer can be written using a simple equation of the form, $V \propto P_1P_2/D^3$, where P_1 and P_2 are the magnitudes of the dipole moments [15]. To illustrate the nature of the plasmon coupling occurring in NR dimers, we find it useful to present results for gap distances that continuously reducing from large to small gap distances of 14–3 Å. We identified that the absorption spectra can be classified into three distinct regimes, (a) 14–10 Å, where the electron tunnelling is negligible or very small; (b) 10–5 Å, where the electron tunnelling emerges; (c) 3 Å where a direct overlap of the ground state electron densities.

To understand the optical response evolution in NR dimers, we start by analysing the optical response of systems 1A and 2A, i. e., compact NR dimers with parallel and axial linkages, respectively, see Figs. 1 and 2 and gap distances reduce from 14 to 4 Å in small steps of 1 Å. It should be mentioned that the axial linkage retains the fivefold symmetry whereas this symmetry is broken in the parallel linkage, and this has significant implications in the absorption spectra, as clearly established in Fig. 3. Note that the compact NR monomer exhibits multiple peaks in the spectrum, however, no dominant peaks. By contrast, as soon as the NR dimer forms via parallel linkage, there starts to emerge a strong gap plasmon in the visible region (between 2.5 and 3.0 eV) of the electromagnetic spectrum. The gap plasmon exists from 14 to 6 Å, although slight variations in its energetic position and amplitude can be observed. As the gap distances reduced further, the electronic wave functions from individual NRs start to overlap, and a conductive channel is formed, allowing electron flow across the gap. There are several things to note from this result. When potential between the two NRs gets narrower, the electron tunnelling completely modifies the behaviour of the optical response. Fig. 3 clearly shows that the dramatic transition of the gap plasmon to charge transfer plasmon appears for a gap distance of 5 Å. Most importantly, this crossover mechanism occurs before the two NRs touch physically. For small gap distance of 3 Å, the optical response is identical to that

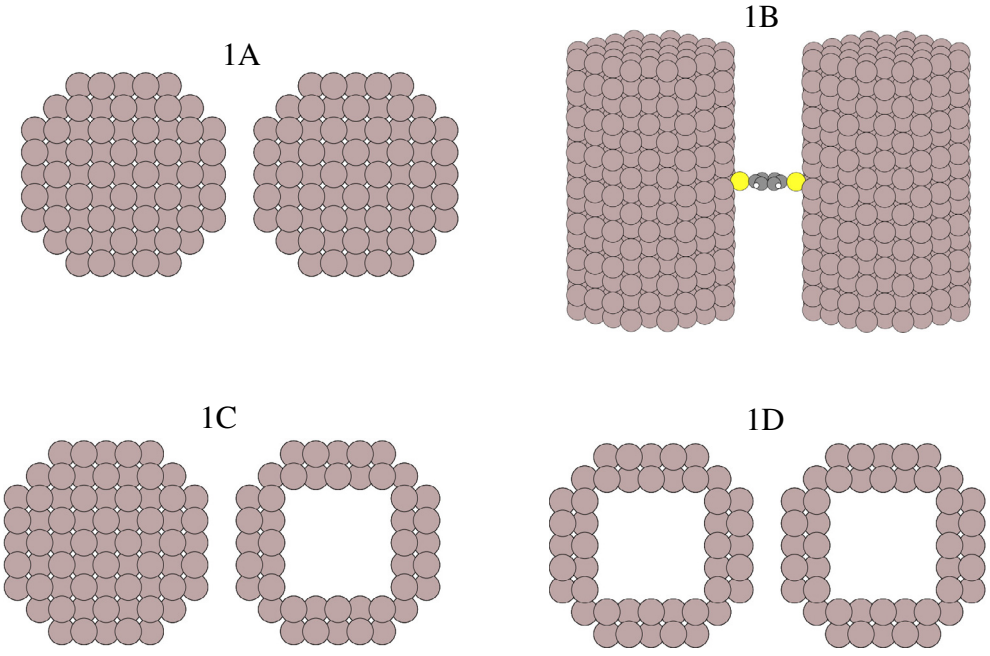

Fig. 1. The NR dimers arranged in parallel linkage fashion.