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Aluminum nanorods subject to bending and twisting distortions: Optical response modulations using quantum mechanical simulations

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A B S T R A C T

Understanding how the optical response of a metal nanostructure modulates with respect to the various geometrical distortions are crucial for developing novel optical devices. In the present work, using first principles time-dependent density-functional-theory calculations, we explore the optical response modification of aluminum nanorods subjected to bending and twisting distortions. We vary the bending angle in the range of 5°–90° and twisting angle in the range of 1°–6°. We analyzed the optical excitations using the transition density plots. We found that bending and twisting distortions cause dramatic modifications in the optical absorption spectrum via gradual disappearance of longitudinal and transverse plasmon modes. In addition, the distortions resulted in significantly less absorption of the light in comparison to the undistorted aluminum nanorod.

1. Introduction

Metal nanoparticles find wide usage in areas as diverse as photocatalysis [1–3], plasmon enhanced light harvesting [4,5], and solar cells [6,7], to list a few. Thanks to the localized surface plasmon resonance (LSPR), the collective oscillation of conduction band electrons [8]. LSPR of a metal nanoparticle can be tuned to occur at specific wavelengths by proper structure modifications. Among a large number of differently shaped metal nanoparticles, nanorods exhibit unique optical response due to the bipolar character of the optical spectrum [9–13]. Apparently, the sphere-to-rod shape modification causes symmetry breaking along the elongation direction and causes longitudinal and transverse plasmon modes to appear in the optical spectrum. This optical anisotropy effect permits us to selectively excite different plasmon modes, promising for active chromatic displays [14]. In a different context, metal nanorods offer unique opportunities for studying the optical modulations with respect to various distortion mechanisms at the nanoscale [15,16]. Due to their large aspect ratios, nanorods are highly prone to distortions such as bending and twisting. Such distortions are pervasive in practice, as reported by several experiments [17–22]. In the present work, we aim to answer the important question "how do optical properties of a metal nanorod modulates with bending and/or twisting distortions".

Plasmonic nanostructures are commonly made from noble metals Au and Ag. However, their scarcity and high-cost limits their large-scale use. Aluminum has recently been emerged as a sustainable alternative candidate to Au and Ag [23–31]. It is one of the most abundant elements and much cheaper than Au or Ag. More importantly, Al nanostructures support LSPRs from deep UV to IR wavelengths [23]. Additionally, Al is compatible for integrated electronics applications, for example CMOS (complementary metal-oxide semiconductor processing) [32]. Combining the rich optical properties of metal nanorods with the geometrical distortions can be highly promising. Nevertheless, optical properties of distorted metal nanorods have not yet been reported hitherto. Based on the potentiality of Al nanostructures for plasmonics and optoelectronics applications, we investigate the optical response modulations of Al nanorods with respect to the bending and twisting distortions. The use of Aluminum for modeling is not only computationally convenient because of the 3 valence electron per atom needed in its description; it has also been successful in reproducing many of the common effects in plasmonics [33–35].

2. Computational aspects

Optical properties of metal nanostructures can be precisely calculated using classical Mie theory [36,37] or using its extensions such as the discrete-dipole approximation [38] and the finite-difference time-domain techniques [39]. However, it is found that as the system size reduces to a few nanometers, classical methods can no longer be expected to be valid and the quantum-mechanical nature of the system has to be taken into account [40,41]. This problem can be tackled using time-dependent density-functional-theory (TDDFT) based calculations. TDDFT technique has been employed widely for studying the optical properties of a variety of nanosystems [42–47]. All calculations performed in this study were carried out using the ORCA DFT/TDDFT software package (version 4.0) [48]. The pristine undistorted Al nanorod under investigation contains 128 atoms. It has a length of 3.50 nm and width of 0.90 nm (the atomic coordinates are provided in

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the Supplementary Information). This size is close to the smallest metallic nanorods produced in recent experiments [49].

The structural optimization of undistorted Al nanorod was performed using the PBE exchange-correlation functional [50] and the def2-TZVP basis set. The SCF convergence was maintained to 10^{-8}. A gradient convergence criterion of 10^{-6} and an energy convergence criterion of 10^{-6} were used in order to obtain a well-converged nanorod. We vary the bending angle in the range of 5°–90° in the steps of 15° and twisting angle in the range of 1°–6° in the small steps of 1°. We examine the dominant bands in the optical absorption spectrum using the transition density plots (the transition between the N^{th} excited state and ground state). The atomic coordinates of all the nanorods are provided in the Supplementary Information. The optical properties of the described nanorods are studied with TDDFT technique in frequency domain using *w*B97X long range corrected hybrid exchange correlation functional. Each Al atom contributes 3 electrons. Thus, the number of valence electrons in the nanorod is 384. We found 900 roots are needed to compute the spectrum up to an energy of 3.0 eV. All absorption spectra are broadened using a Gaussian smearing of width $\sigma = 0.15$ eV.

3. Results and discussion

Before discussing the optical response modifications of Al nanorod subjected to bending and twisting distortions, it is informative to examine the optical response of the undistorted Al nanorod. To this aim, we plot in Fig. 1 the optical absorption spectrum of undistorted pristine Al nanorod in the energy range of 0–3.0 eV. Notice that 5 bands [0.80 eV, 1.20 eV, 2.05 eV, 2.35 eV and 2.70 eV] emerge in the spectrum. By analyzing the transition density plots corresponding to the main bands, we gain further insight to the nature of excitation (longitudinal or transverse). From the visual inspection of the transition density plots, one confirms that the bands located at 2.35 eV and 2.70 eV exhibit electron charge-density oscillations resembling typical longitudinal and transverse plasmon resonance modes, respectively. It is worth mentioning that longitudinal and transverse plasmon resonance modes were reported by a number of research groups in the case of Au nanorods [51–53]. We found that both the longitudinal and transverse plasmon resonance mode is composed of many single particle excitations. The first peak at 2.35 eV is a linear combination of 30 different transitions [mainly composed of HOMO − 1 → LUMO + 2 (30%), HOMO − 2 → LUMO (30%) and HOMO − 5 → LUMO (5%)]

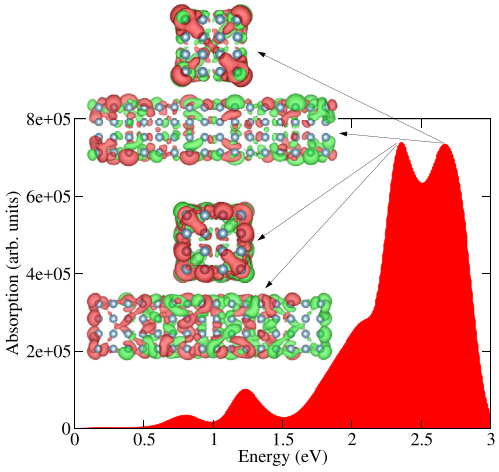

Fig. 1. TDDFT calculated optical absorption spectrum of undistorted Al nanorod. Transition density plots correspond to the main bands are also shown in Figure. Both end view and side view are provided for an easy visual inspection. Red and green color denote electron density accumulation (depletion) regions during the excitation, respectively. Both densities are plotted using the same iso-surface contour value. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

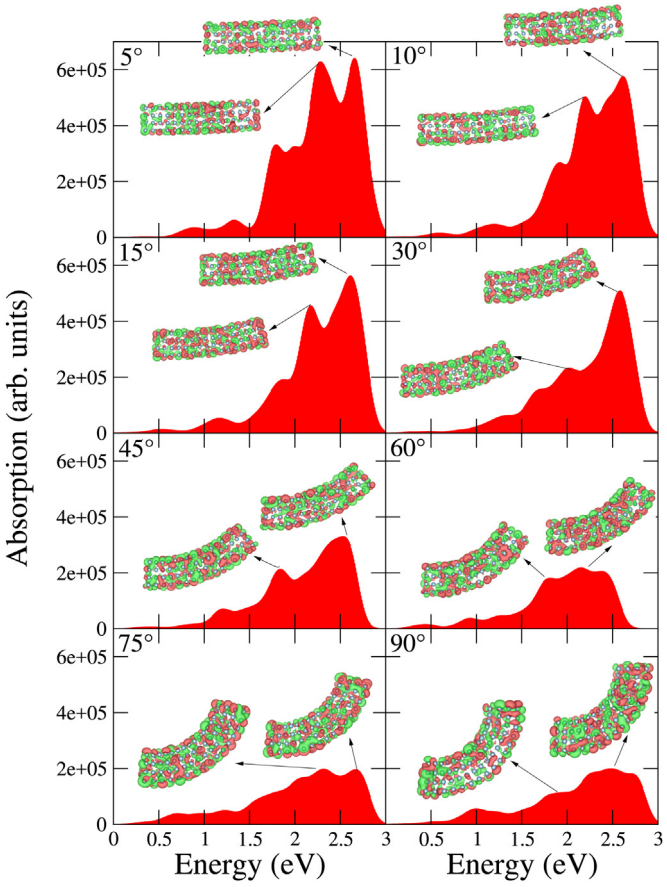

Fig. 2. TDDFT calculated optical absorption spectrum of Al nanorods subjected to bending distortions. The corresponding bending angle is also shown. Transition density plots correspond to the main bands are also shown in Figure.Both end view and side view are provided for an easy visual inspection. Red and green color denote electron density accumulation (depletion) regions during the excitation, respectively. Both densities are plotted using the same iso-surface contour value. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

confirming the collective nature of the optical excitation. Similarly, the second peak at 2.70 eV is also a linear combination of 25 different transitions [mainly composed of HOMO − 2 → LUMO + 4 (35%), HOMO − 4 → LUMO + 2 (30%) and HOMO − 6 → LUMO + 2 (10%)], once again confirming the collective nature of the optical excitation. It is of paramount importance to compare the present theoretical results with available theoretical and experimental data. Regrettably, a meaningful comparison is not possible since no study published yet reporting Al nanorods having similar size as in the present study. However, it is worth to mention that a previous theoretical study (using the discrete dipole approximation method) reported Al nanorods with length vary from 20 to 100 nm [54] and found that the longitudinal resonances of the Al nanorods can be tuned to the visible region, in tune with the present result. Note that producing small Al nanorods remains a synthetic challenge that, once resolved, will have large implications on the creation of Al nanorods for nanoplasmonic applications [11].

Having analyzed the optical response of the undistorted Al nanorod, we next analyze the optical response of Al nanorod subjected to bending distortions. To this aim, we plot in Fig. 2 the optical absorption spectra of Al nanorod subjected to bending distortions with the bending angle tuned in the range of 5°–90° in the steps of 5° and in some cases 15°. Let us now start our analysis starting from the smallest bending angle of 5°. One easily concludes that 5° bending causes dramatic modifications both in optical absorption spectrum and transition density plots in comparison to the undistorted case. For example, 5°