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On the extinction multipole plasmons in gold nanorods

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Abstract

On the basis of the T-matrix formalism and numerical simulations, we derive an explicit rule for partial multipole contributions to the plasmon resonances of gold nanorods at a fixed or random orientation. The parity of a given spectral resonance number n coincides with the parity of their multipole contributions l, where l is equal to or greater than n, and the total resonance magnitude is determined by the lowest multipole contribution. We also investigate the dependence of multipole plasmons on the size, shape, and orientation of nanorods with respect to the polarized incident light. It is shown that the multipole resonance wavelengths as a function of the aspect ratio divided by the resonance number collapse onto one linear scaling curve. This scaling is explained by using the plasmon standing wave concept introduced by Schider et al. [Plasmon dispersion relation of Au and Ag nanowires. Phys Rev B 2003;68:155427].

Keywords: Gold nanorods; T-matrix method; Multipole plasmon resonance; Light scattering and extinction

1. Introduction

Metal nanorods possess unique optical properties because of their tunable dipole plasmon resonances, as demonstrated in pioneering experiments [1,2]. Owing to the shape- and size-controlled scattering and absorption properties [3–9], the gold nanorods have found promising applications in diagnostic [10] and photothermal therapy [11] of cancer cells *in vitro*. New potentialities for biomedical application of metal nanorods are related to their enhanced plasmon resonance sensitivity to the dielectric environment [12–15] and orientation with respect to polarized incident light [16], including laser orientation alignment and trapping [17], strong light scattering oscillations induced by Brownian rotation [18,19], and unusual depolarization of scattered light [20,21]. Keeping in mind the recent advantages in synthesis [22,23] and functionalization [24] of gold nanorods, one can predict rapid progress in biomedical technologies using conjugates of gold nanorods with biomolecules. For a comprehensive discussion of chemistry, optics, and biomedical applications of metal nanorods, the readers are referred to recent reviews [15,16,25–28].

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By now, the dipole plasmon resonances of metal nanorods have been studied in detail, both theoretically and experimentally [3–9,14,15]. In contrast, there are limited data on the multipole resonances in metal nanorods. As far as we are aware, the first reports on quadrupole modes were published by Barber and coworkers [29] for the local field enhancement factor of silver spheroids and the extinction and light scattering spectra of gold 2D lithographic nanostructures. The quadrupole modes also have been studied for silver [30] and gold spheroids, right circular cylinders, s-cylinders (cylinders with semispherical ends), and rectangular prisms [4,31]. DDA calculations coupled with experimental measurements allowed identification of two distinct quadrupole resonances for silver [32] and gold [33] nanoprisms. The past few years have seen the publication of the first observations of multipole plasmon resonances in gold and silver nanowires deposited onto a dielectric substrate (see, e.g., Refs. [34,35] and references therein). Quite recently, Mirkin and Schatz's group reported on the first experimental observation and DDA simulation of multipole plasmon resonances in *colloidal* gold nanorods [36].

The assignment and interpretation of multipole resonances have been done on the basis of the standing-wave picture [37,38] and DDA calculations [36]. For a review of recent works based on DDA simulations, the readers are referred to Refs. [3,5–9,39]. However, the DDA algorithm does not include explicit multipole representation. Instead, it treats the optical properties of nanorods in terms of dipole interactions of a huge dipole array that mimics the electrodynamic properties of a real particle. Here we report on the first, to the best of our knowledge, T-matrix analysis of multipole excitations in gold nanorods. We derive an explicit rule for partial multipole contributions to the observed plasmon resonances of randomly oriented nanorods. In addition, we investigate the relationships between the multipole plasmons of nanorods and their size, shape, and orientation with respect to polarized incident light, on the *multipole basis* and in more detail than is provided in previous publications [4,36,39]. Finally, we show, for the first time, that the multipole resonance wavelengths as a function of the aspect ratio divided by the resonance number collapse onto one linear curve. This scaling property is explained by using the plasmon standing wave concept [37,38].

2. Models and methods

The shape of gold nanorods can be modeled by a right circular cylinder of length L and diameter d with flat (the hard template fabrication method [36]) or semispherical (the seed-mediated growth method [22], s-cylinder model [31]) ends. From a computational point of view, the prolate spheroid has certain advantages because of its regular shape, which retains the principal optical properties of metal nanorods (see, however, discussion of Fig. 3 in Section 3). Here we use the above three models, which can be specified by the nanorod minor size d (nm), the length L, or the aspect ratio $e = L/d$.

The dielectric functions of the surrounding medium $\varepsilon_m(\lambda)$ (water) and gold nanorods $\varepsilon(\lambda, R_{ev})$ were calculated according to Refs. [15,20], with the function $\varepsilon(\lambda, R_{ev})$ accounting for the electron surface-scattering effects through the equivolume radius R_{ev} and the size-limited particle damping constant $\gamma_p = \gamma_{bulk} + v_F/R_{ev}$, v_F is the Fermi velocity. By using R_{ev} for calculation of γ_p we follow, in a sense, the Coronado and Schtaz approach [40] in which the effective free path of conductive electrons is expressed in terms of the particle volume V and surface S, $L_{eff} \sim 4V/S$. Note that the need for inclusion of the size-limiting effects in nanoparticle optics through the $\varepsilon(\lambda, R_{ev})$ function is debatable at present, see, e.g., the discussion in Refs. [15,41]. Previous single-particle experiments with gold nanorods [42] and silica/gold nanoshells [43] were explained in terms of the bulk dielectric function $\varepsilon(\lambda)$, whereas recent resonance light scattering [44] and absorption [45,46] single-particle measurements confirmed the size-dependent surface-scattering contribution to the bulk damping constant. Although our calculations included thin nanorods, here we mainly discuss the multipole resonances excited in large particles, where the size limiting effects can be neglected.

The multipole contributions to the extinction, scattering, and absorption spectra can be expressed in terms of the corresponding cross sections, normalized to the geometrical cross-section πR_{ev}^2:

$$Q^{ext,sca,abs} = \sum_{l=1}^{N} q_l^{ext,sca,abs}. \quad (1)$$