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OPTICAL RESPONSE OF NOBLE METAL NANOPARTICLES

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ABSTRACT. The rich structure of surface plasmon modes localized in noble metal nanoparticles is explored by optical spectroscopy, spatially resolved electron energy-loss spectroscopy, and by electron beam-induced radiation emission. Spectral features and spatially-resolved maps of surface plasmon modes are calculated by using the boundary element method. Our results show the unmatched capability of electron beams for spectrally and spatially probing plasmon modes in metal nanoparticles.

1. Introduction

The current interest in the optical properties of metal nanoparticles is due to their ability to host localized surface plasmon (SP) modes, that are the collective resonant oscillations of the conduction electrons inside nanoparticles induced by external electromagnetic sources [1]. For the noble metal nanoparticles SP resonances occur in visible and near-infrared regions and produce strong effects in both the near- and far-field response of nanoparticles. Moreover, localized SPs can be tailored by controlling the size and morphology of metal nanoparticles. These unique properties enable a wide range of applications, such as switching, light guiding, light manipulation on the nanoscale, and bio-sensing. This has given rise to an active field of research aimed at finding new recipes for controlling the size and shape of metallic nanoparticles [2, 3] and developing advanced experimental techniques that give information on the spatial variation of the near fields associated to SPs with high energy and space resolutions [4].

The experimental study of the near field associated with particle plasmon modes by optical means is limited by the low resolution available in common techniques such as scanning near-field optical microscopy (around 50nm). In contrast, methods that are based on the interaction of fast electrons with nanostructures allow retrieving local information on plasmons with nanometer resolution. In particular, electron energy-loss spectroscopy (EELS), performed in a scanning transmission electron microscope (STEM), provides a powerful tool for studying plasmons in metal nanostructures [5]. The maxima in the energy loss spectra of transmitted electrons reflect the energies of the particle-plasmon excitations to which they couple. Part of these energy losses results in the emission of light (cathodoluminescence, CL), which has also been used to probe localized plasmons in metallic nanoparticles, performed in a scanning electron microscope (SEM) [6].

In this work, we present a study of the optical properties of noble metal nanoparticles prepared via lithography or colloidal chemistry. In particular, the rich structure of SP modes in nanoparticles of different morphologies (rods, decahedra, prisms, and split-ring resonators) is explored by optical spectroscopy [7, 8], spatially resolved EELS [9, 10], and by electron-beam-induced radiation emission [11].

2. Boundary element method

Spectral features and spatially resolved maps of SP modes collected for nanoparticles are calculated with theoretical STEM-EELS and optical excitation calculations obtained by using the boundary element method (BEM) [12]. This method is based upon rigorous solution of Maxwell's equations in which the scalar and vector potentials are expressed in terms of a set of surface integral equations involving interface charges and currents which satisfy the appropriate boundary conditions imposed by Maxwell's equations. The boundaries of the structure are approximated by a system of N interface elements (line segments in 2D or triangles in 3D). In each element the surface charges and currents are approximated as constants (eight unknowns parameters in each element). The structure under investigation is subdivided into a sufficiently large number of elements to guarantee convergence. The interaction between boundary elements is mediated by the Green function of Helmhotz equation within each homogeneous medium. This leads to a linear system of equations with respect to unknown charges and currents, which is solved by standard linear-algebra techniques in the presence of the external field.

3. Results

As an example, in this paper we present the numerical study of the optical response of an individual gold nanodecahedron that undergos external electromagnetic stimuli, either plane electromagnetic wave or fast electrons. The gold decahedron was synthesized according to the method explained in work [3]. The particle is characterized with the frequency-dependent dielectric function measured on gold films [13].

Figure 1a shows the extinction cross section spectrum as a function of energy for the gold decahedron with a side length equal to 58 nm calculated by using the BEM. A transmission electron microscope (TEM) image of a representative decahedral particle and electric field's polarization direction are shown in the insets. The interaction with the plane wave results in the excitation of a dominant azimuthal surface plasmon mode at the spectral position around 2.3 eV. This is a dipole-driven mode involving an induced dipole dominating along the pentagonal base of the decahedron. The calculated electric near-field distribution map associated with this mode is shown in Fig. 1c. The maximum field enhancement is at the corners of the pentagonal base of the particle.

Figure 1b shows the calculated electron energy-loss probability spectrum of the same particle for an incident electron beam in grazing incidence with respect to the particle surface, as shown in the inset. The loss probability is given per incoming electron and per eV for a given lost energy. The interaction with the electron beam results in the excitation of the same azimuthal surface plasmon mode at the same spectral position as in Fig. 1a. The calculated EELS excitation-intensity map of this mode is shown in Fig. 1d. As expected, the maximum of the energy loss is observed at the corners of the particle's pentagonal base.

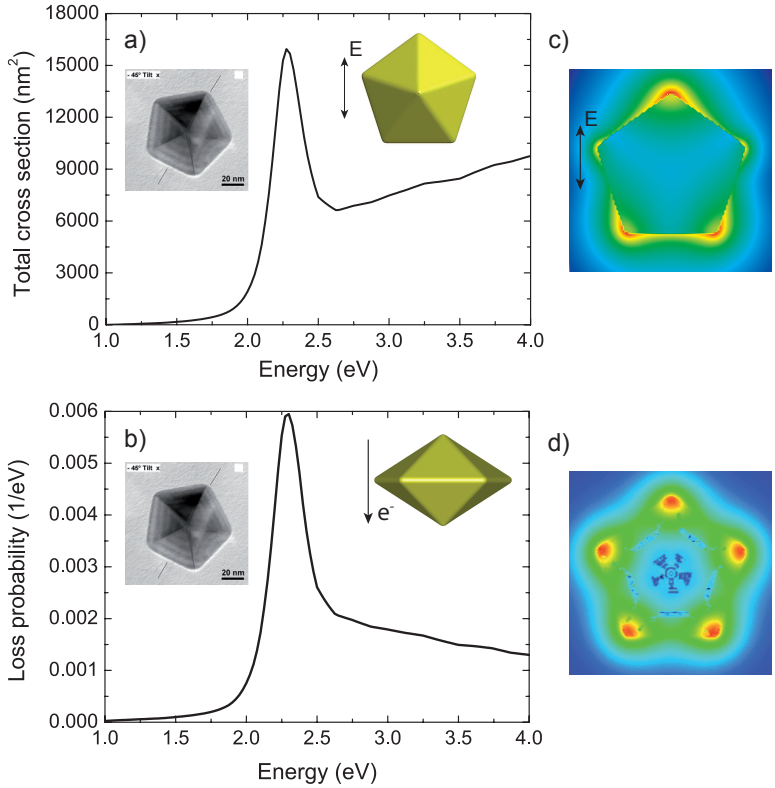

Figure 1. (a) Extinction cross section as a function of energy for the gold decahedron with a side length equal to 58 nm calculated by using the BEM. A TEM image of a representative decahedral particle and plane wave's polarization direction are shown in the inset. (b) Calculated electron energy-loss spectrum of the same particle. The loss probability is given per incoming electron and per eV for a given lost energy. The trajectory of the electron beam is shown in the inset. Calculated electric near-field (c) and EELS excitation-intensity (d) maps of the 2.3 eV plasmon mode.

4. Conclusions

We have developed the 3D boundary element method to describe the electromagnetic response of noble metal nanoparticles with arbitrary morphologies. This method is computationally efficient and presents several advantages with respect to other currently used methods. The structure of SP modes localized in metal nanoparticles is unveiled by optical spectroscopy and electron energy-loss spectroscopy. We have calculated spectral features and spatially-resolved maps of SP modes and illustrated example in which theory gives predictive results. Our results show the unmatched capability of electron beams for spectrally and spatially probing SP modes.

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