Interaction of light and fast electrons with metallic nanoparticles

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The shape and size of nanoparticles can be tuned through chemical synthesis parameters, which results in a variety of morphologies. The electromagnetic response of highly anisotropic metallic nanoparticles on external stimuli (light and fast electrons) has been modelled using a full 3D boundary element method. A good agreement between numerical calculations and experimental spectra has been obtained.

INTRODUCTION

The last years have witnessed a tremendous increase in research activity on the behavior of electromagnetic fields at nanometer scales. In this context, the collective excitations that are sustained by valence electrons in a nanostructured metal, also known as plasmons, can play a leading role because they can be understood as a hybrid of electromagnetic energy and energy deposited on the metal electron gas. This leads to extreme localization of the electromagnetic field with resonances that happen to be in the visible and near-infrared for metals, such as gold and silver. The localization goes down to regions of a few nanometers, much smaller than the free-space light wavelength, in the range of hundreds of nanometers or a few microns. Accompanying this effect, the electric field undergoes a large enhancement in intensity that is being used for applications as diverse as bio-sensing and information-processing [1].

All of the above is favored by the availability of new techniques of fabrication, and most notably colloidal chemistry and nanolithography. Advances in the understanding of light interaction with nanostructured materials have been produced with strong collaboration between theory and experiment, and new methods of simulation of the electromagnetic field in this context are still needed to cope with the ever increasing complexity of new geometrical designs. The experimental study of the optical response of nanostructured materials relies largely on the ability to address the near field with good resolution in space and energy. Near-field scanning optical microscopy, electron-energy loss spectroscopy, and cathodoluminescence are the most promising techniques in this respect. In this work, the optical response of metallic nanoparticles to external sources (light or fast electrons) is computed numerically using the full 3D boundary element method (BEM-3D).

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RESULTS AND DISCUSSION

It was recently shown that the shape and size of gold nanoparticles can be tuned through chemical growth in N,N-dimethylformamide (DMF) that results in transition between nearly cylindrical nanorods and perfect octahedrons with a few intermediate morphologies between them, such as rods with close to square cross section and sharp tips at their ends [2]. It is crucial to monitor the evolution of optical response of these nanoparticles. Figure 1 shows a comparison between BEM calculation and experimental optical spectra for selected intermediate stages in the growth evolution. The TEM images of the particles are plotted in the bottom part of Fig. 1. The extinction spectrum of the initial nanorod dispersion displays a longitudinal surface plasmon (SP) mode and weak transverse. During the process, the longitudinal SP mode gradually blue-shifts, while the transverse red-shifts and gets significantly enhanced. Eventually, both bands merge into a single band. Obviously, observed spectral evolution arises from morphological changes of the particles that result in a steady decrease of the particle aspect ratio but also sharpening and formation apexes. A good agreement between numerical calculation (solid curves) and experiment obtained using a Cary 5000 UV-Vis-NIR spectrophotometer (dotted curves) is observed [3-4].

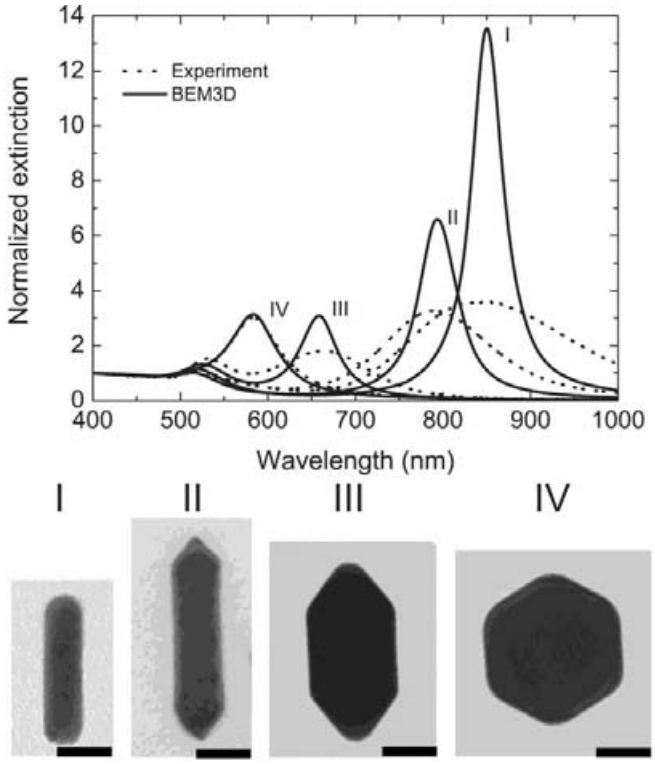

Figure 1. Comparison between measured (dotted curves) and BEM-3D calculations (solid curves) of the optical extinction spectra of gold particles immersed in DMF and obtained at intermediate steps during the growth process from circular nanorods to octahedral particles. The experimental optical spectra are scaled to match the calculated value at 400 nm. TEM images of the particles are shown in the bottom part of the figure. The scale bars equal 25 nm.

Figure 2a shows the calculated optical extinction spectra of an individual Au nanorod (length/diameter, 176/22 nm) [5]. The interaction between the rod and incident light with electric field polarized along (solid curve) and perpendicular (dotted curve) to the rod long axis produces strong light excitation assisted by three respective SP modes (A, C, and D). The mode A is a longitudinal mode excited by parallel polarization and involving an induced dipole dominating along the rod axis, whereas mode D couples to the transversal polarization with an induced dipole perpendicular to that axis. They are dipole-driven SPs. Mode C is a higher-order longitudinal mode. Interestingly, a second-order longitudinal mode B cannot be excited by external light either with electric field polarized along or perpendicular to the rod long axis due to its symmetry; i.e., it has two nodes along the rod, rather than one, as the first-order longitudinal mode. In contrast, the plane wave moving toward the direction of polar angles (30, 40) with polarization given by angles (20, 30) (dashed curve) can excite this mode.

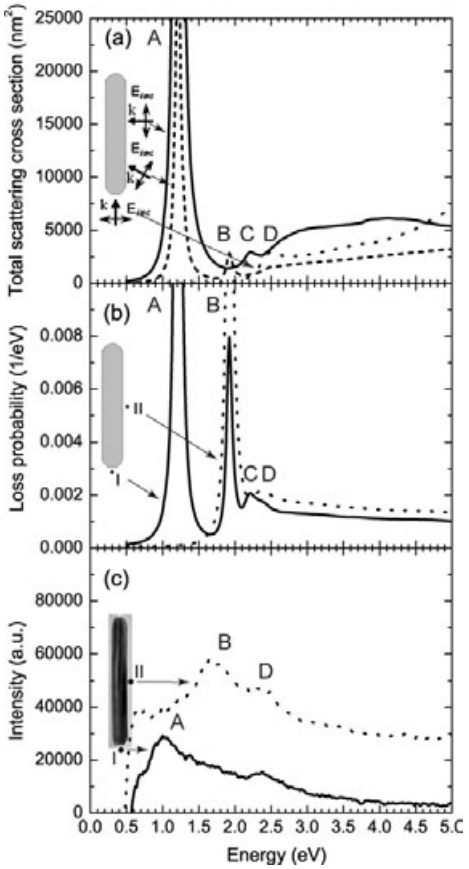

Figure 2. (a) Total scattering cross section as a function of energy for Au nanorod (length/diameter, 176/22 nm). The incident-light electric field is parallel (solid curve) and perpendicular (dotted curve, multiplied by 3 to improve readability) to the rod axis. The dashed curve corresponds to a plane wave moving towards the direction of polar angles (30, 40) with polarization given by angles (20, 30). (b) Calculated electron energy loss probability for locations I (solid curve) and II (dotted curve) of the electron beam relative to the rod under grazing incidence with respect to its surface. The loss probability is given per incoming electron and per electronvolt for a given lost energy. (c) Experimental counterpart of (b).

Figures 2b and 2c show numerical (BEM3D) and experimental (obtained using a scanning transmission electron microscope, FEI Tecnai F20, operated at 200 keV and equipped with a Wien-filter electron monochromator) electron energy loss spectra for an incident electron beam at locations I and II relative to the nanorod, in grazing incidence with respect to the nanoparticle surface. Probing the nanorod with electron beam also leads to the same SP excitations induced by optical illumination. The measured spectral positions of the SP modes (Fig. 2c) are in agreement with those obtained from numerical calculations (Fig. 2a,b). Obviously, the electron beam can excite bright SP modes as optical illumination does.

CONCLUSIONS

We have developed a 3D boundary element method to describe the electromagnetic response of metal nanoparticles with arbitrary morphologies. The method is computationally efficient and presents several advantages with respect to other currently used methods. We have calculated optical and electron energy loss spectra for different metallic nanoparticles and illustrated examples in which theory gives predictive results.

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