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A simple Mie-type model for silica-coated gold nanocages

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ABSTRACT

Experimental extinction spectra of gold nanocages are much similar to those recorded for gold nanoshells on silica cores. This observation suggests that a simple spherically symmetrical Mie-type model can be applied to the prediction of extinction and scattering spectra for gold nanocage suspensions. Here, we show that such a model describes adequately not only extinction spectra of as-prepared gold nanocages but also experimental spectra and plasmonic resonance shifts for silica-coated gold nanocages. Furthermore, we demonstrate that the silica shell thicknesses, as determined from the plasmonic resonance shift, are in good agreement with the direct measurements based on transmission electron microscopy images.

1. Introduction

Gold nanocages (AuNCs) – hole-structured quasicubic gold nanoparticles with porous walls – have emerged as a novel class of plasmonic nanoparticles with tunable optical properties [1]. The tunability of the localized plasmon resonance (LPR) across the vis–NIR spectral bands, the porous particle structure, and the high colloidal stability make AuNCs an attractive platform for optical coherence tomography [2,3], photoacoustic imaging [4,5], photothermal cancer imaging and therapy [6–9], multicolor dot immunoassay [10], drug delivery [11], theranostics [1,12,13], and other biomedical applications [14].

The protocol of AuNC fabrication, as pioneered by Xia's group in 2002 [15], consists in titration of a boiled colloid of silver nanocubes by controllable addition of an $HAuCl_4$ solution. Owing to a galvanic replacement reaction between silver and gold atoms, the silver nanocubes are sequentially transformed into Ag/Au alloy nanoparticles, nanoboxes, and finally into Au nanocages [10]. The change in the Ag/Au ratio, together with the formation of holes and pores, results in a strong plasmonic shift from 430-470 nm for silver cubes to an 800–900 nm NIR band for AuNCs. It is this mechanism that ensures a precise and controllable tuning of the LPR for a desired optical range. In practice, as-prepared AuNC samples usually have a sharp extinction peak with a full width at half maximum (FWHM) of about 150 nm, comparable with the same parameter for gold nanorods [16], sub-50-nm gold nanoshells, and spherically symmetrical metal/dielectric/metal nanostructures [17].

Numerical simulation of optical properties for AuNC ensembles is not an easy task because of the random porous structure of the particles and because of their statistical distributions over size and orientations. Although the synthesis of AuNCs with controllable pore sizes and location has been reported [18], this approach did not find any wide applications. In general, despite the large amount of published work (2002–2012) on the synthesis, experimental characterization, and biomedical

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applications of AuNCs, the number of reports with theoretical simulations is still quite limited. One of the first simulation examples was presented by Chen et al. [19], who used the DDA method (DDSCAT codes) [20] to calculate the extinction, scattering, and absorption spectra of a hole Au nanobox with an edge length of 36.7 nm and a gold wall thickness of 3.3 nm. These spectra were calculated for light illumination perpendicular to the box wall. For simulation of the porous structure, all the corners were truncated to create eight triangular holes of 5 nm base dimension. The calculated extinction spectrum had its LPR position close to the measured one, but there were significant differences between calculated and measured FWHMs and between experimental and calculated maximum-to-baseline ratios. Similar results were obtained in Refs. [21–23] for simplified particle models such as nanoboxes and nanoboxes with truncated corners. In single-particle scattering experiments with 44- and 58-nm AuNCs [24], the surface electron scattering in thin metal shells and the radiative damping for larger particles were shown to be the basic mechanisms leading to spectral broadening. For nanoparticle colloids, an additional spectral broadening is caused by particle distributions over size, structure, and orientations. As DDA simulations for statistical ensembles are very time-consuming, all reported results were acquired for a fixed orientation of a particular nanocage model. Recently, we used an analytical variant of the coupled dipole method (CDM) [25] to calculate the extinction and scattering spectra for randomly oriented AuNCs. In this method, the AuNCs were modeled with an ensemble of small interacting spheres separated by a distance that was a bit smaller than the particle diameter. The single-particle polarizability was found from the first Mie coefficient. As a result, we were able to reproduce the spectral position of LPRs and to explain their shift to the NIR spectral band during the particle synthesis. However, the serious drawback of that method is the need for direct inversion of the dipole interacting matrix, thus limiting the total number of constitutive particles by a value of about 1000. Such a limitation reduces the overall accuracy of fast calculations that need no numerical averaging over orientations.

In this work, we show that the experimental extinction spectra of water suspensions of 45- and 60-nm AuNCs covered by a variable silica shell from 10 to 120 nm can be described by a simple three-layered Mie model. The basic model parameters are as follows: (1) the inner core diameter, which is equal to the edge of the silver cubes used as templates; (2) the gold shell thickness; and (3) the silica shell thickness. The first and third parameters are determined from transmission electron microscopy (TEM) images. The spectral LPR location is very sensitive to the gold shell thickness, which is used as a fitting parameter consistent with independent TEM measurements. For nanoparticle ensembles, the calculated spectra should be averaged over the inner and outer diameter distributions. This simple model describes quite adequately not only the extinction spectra of as-prepared gold nanocages but also the evolution of spectra during the coating of AuNCs with a variable silica shell from 10 to 120 nm. Finally, the plasmonic shifts as a function of the silica shell thickness can serve as a calibration for a simple and fast estimation of the ensemble-averaged shell thickness around plasmonic nanocages.

2. Models and methods

Consider a multilayered geometrical model for a silica-coated gold nanocage (Fig. 1) consisting of a water core with a radius r_0 and a refractive index n_0, a gold nanoshell with a radius of r_1 (so the shell thickness is $s_g=r_1-r_0$) and a refractive index n_g, and a silica layer with a radius r_2 (so the shell thickness is $s_s=r_2-r_1$) and a refractive index n_s. In our simulations, the inner diameter, the gold shell thickness, and the silica shell thickness were varied within the ranges 30–80 nm, 2–6 nm, and 5–120 nm, respectively. The surrounding medium under experimental measurements and numerical simulations was water.

The normalized extinction cross section $Q_{ext}=C_{ext}/\pi r_2^2$ was calculated by known formulae [26], in which the usual Mie coefficients were replaced by their multilayered counterparts [27] as previously described for colloidal gold [28] and gold nanoshell [29] bioconjugates. The dielectric function of bulk gold was corrected for surface electron

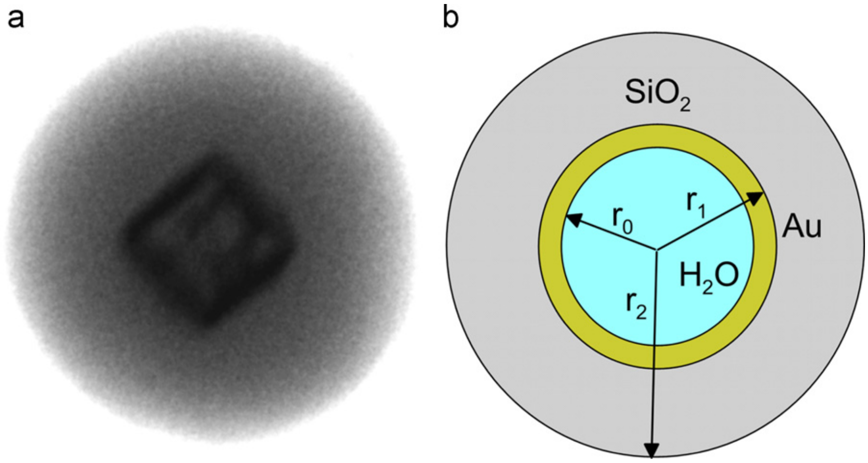

Fig. 1. TEM image of a silica-coated AuNC (a) and its geometrical model (b).