Ultrasharp light-scattering resonances of structured nanospheres: effects of size-dependent dielectric functions

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Abstract. Recently, Chen et al. [*J. Biomed. Opt.* Vol. 10, 024005 (2005)] reported on the concept of multicolor molecular imaging, which uses resonant light-scattering spectroscopy of multilayer nanospheres. They claimed that the resonance scattering peaks of three-layer nanoshells can be designed so that the ultrasharp widths are as narrow as 10 nm. Here we show that such ultrasharp labels cannot be fabricated in reality because the effects of size-dependent dielectric functions result in the five- to tenfold broadening of resonant scattering peaks. Furthermore, contrary to the data of Chen et al., we did not find any significant advantages of three-layer structures, as compared with the usual silica/metal nanoshells. © *2006 Society of Photo-Optical Instrumentation Engineers.* [DOI: 10.1117/1.2337526]

1 Introduction

The unique optical properties of plasmon-resonant particles together with the high specificity of biomolecular recognition opens new possibilities for applications to extrasensitive detection of different analytes,[1] biomedical diagnostics and therapy,[2] targeted drug delivery,[3,4] laser killing of cancer cells,[5–7] and optical imaging.[8–10] However, for optical imaging at the cell and tissue levels, the most popular labels are quantum dots (QD)[11–14] rather than noble metal nanoparticles. The basic advantage of semiconductor nanocrystals, in comparison with plasmon-resonant (PR) noble metal particles, is in the remarkably narrow fluorescent peaks of QDs vs light-scattering plasmon resonances. The fluorescent spectra of QDs can be tuned to a desired spectral band by varying the QD size and composition, and functionalization of QDs with recognizing biomolecules allows one to produce multicolor biospecific labels for target molecules and cells.

The essential drawbacks of QD labels are the need to use UV exciting light, the quenching of fluorescence caused by the adsorption of biopolymers on the QD surface, and the biological toxicity of most QDs. Furthermore, there are difficulties in the functionalization of QDs while transferring the particles from primarily the organic synthesis phase to a water-saline environment, which needs to be done with all biospecific molecular probes. Most of these difficulties may be overcome by using PR particles, but the optical properties of these particles should be tuned in a proper manner to ensure the desired resonance quality and position. In particular, the solid gold and silver spheres are poor candidates for multicolor labeling, as their size-dependent spectral tuning covers rather narrow spectral intervals[15,16] and the spectral width of the PR scattering resonance of gold spheres is about 50–100 nm.

Among the numerous particle structures made available through the existing synthetic technologies,[17] the gold nanoshells are of significant interest for applications to biosensorics,[18] immunoassays,[19] laser phototherapy of cancer,[20–22] and optical imaging.[7] The silica/gold nanoshells can easily be tuned to a desired spectral band[23] from VIS to NIR. However, a typical full width at half-maximum (FWHM) of silica/gold nanoshell spectra is about 150–200 nm, which enables one to use only three or four distinct biomarkers in the whole VIS-NIR range.

Recently, Chen et al.[24] reported on a theoretical investigation of three-layer nanoparticles with a metal core, an intermediate silica layer, and a surface metal shell. Such structures, in the authors' opinion, may be used as multicolor labels for spectral tissue imaging. The principal result obtained by Chen et al.[24] is that the three-layer metal-dielectric-metal (MDM) nanoparticles possess ultrasharp light-scattering resonances, which can be tuned from VIS to NIR spectral bands by varying the structural MDM parameters. By contrast with silica/gold nanoshells, the spectral widths of MDM resonances were found[24] to be weakly dependent on particle polydispersity—a property that could be important for applications of MDM multicolor labels in light-scattering spectroscopic imaging, optical coherent tomography, and other fields.

However, the theoretical computations of scattering spectra in Ref. 24 were carried out without taking into account the size-dependent correction of dielectric functions of thin metal shells. It is well known[15] that various mechanisms contribute to the bulk dielectric function of metals on a nanometer

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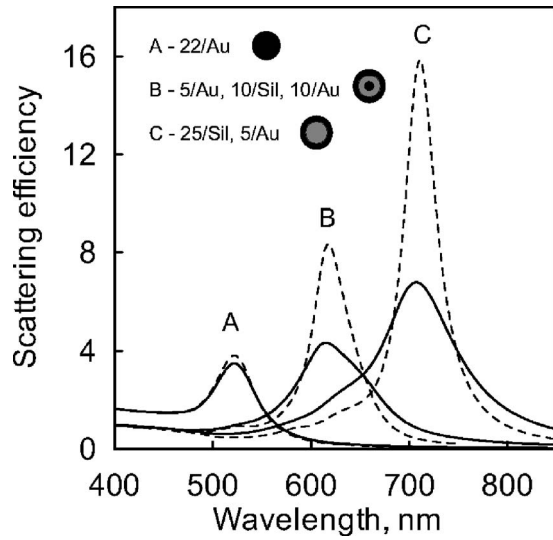
Fig. 1 Comparison of the resonant light-scattering peaks for solid, two-layer, and three-layer nanospheres. The solid curves correspond to calculations with a size-corrected Au dielectric function, and the dashed curves were calculated with bulk optical constants. The sphere structure is designated in the legend as (core radius)/(core material); (thickness of shell)/(material of shell). All dimensions are in nanometers. Here and in what follows Au, Ag, and Sil stand for gold, silver, and silica, respectively.
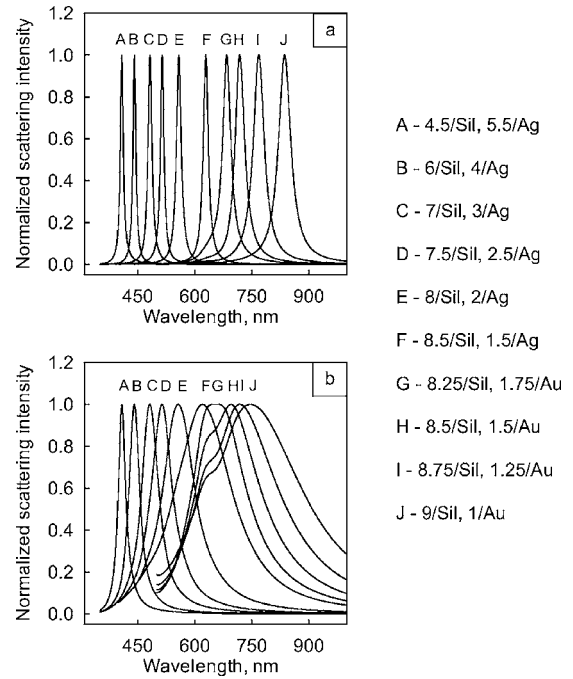

Fig. 2 Resonant light-scattering peaks of two-layer nanospheres with silica cores calculated without (a) and with (b) a size correction of the dielectric function. The overall radius of nanostructures with a variable relative dimension of the core versus the shell is fixed (10 nm). The dielectric/metal structure is designated in the legend as (core radius)/(core material), (thickness of the shell)/(material of the shell). All dimensions are in nanometers.

scale,[25] with the size-limiting correction[26,27] being the major factor in the case of two-layer metal nanoshells.[25,28,29]

Here we show that the size-corrected dielectric function is a crucial factor that limits the actual widths of the scattering plasmon resonances for three-layer MDM structures. Furthermore, contrary to Chen et al.'s data, we did not find any significant advantages of three-layer MDM structures in comparison with the usual silica/metal nanoshells, because the size-corrected absolute FWHM of both types of particles turned out to be similar. Thus, although several attempts at the improving MDM nanoparticle synthesis have been reported,[30–32] their optical advantages seem disputable at least.

2 Methods

We consider MDM nanoparticles (external diameter $d=2a$) embedded in a dielectric medium with the refractive index $n_m = \sqrt{\varepsilon_m}$ (in this case, water). The normalized scattering cross section, $Q_{sca} = C_{sca}/\pi a^2$, was calculated by the well-known formulae,[15] in which the usual Mie coefficients of a homogeneous sphere, a_n and b_n, were replaced by the corresponding coefficients of a multilayer sphere, $a_n^{(l)}$ and $b_n^{(l)}$ ($l \geq 1$ is the number of layers). To calculate the coefficients $a_n^{(l)}$ and $b_n^{(l)}$, we used the effective recursive algorithm of Wu and Wang,[33] which had previously been implemented for the case of gold/polymer conjugates.[34,35] For thin gold or silver nanoshells, the dielectric function of bulk metal should be corrected for the size-limiting effects, which restrict the mean free path of conductive electrons (for a review, see, e.g., Refs. 26 and 27). A thorough comparison of the experimental and calculated colloidal gold spectra[16,36] showed that only the imaginary part of the bulk metal permittivity should be corrected:

where L_{eff} is the effective mean free path of electrons, λ_p is the wavelength of plasma oscillations, and v_F and c are the Fermi velocity of electrons and the light velocity in vacuum, respectively. The dimensionless parameter A_L is determined by details of the electron scattering process[25,27] and is often assumed to be close to 1. The classic effective mean free path of electrons in spherical particles varies from $L_{eff}=a$ (isotropic scattering) to $L_{eff}=4a/3$ (diffusive scattering).[27] The size-limiting effects in metal nanoshells, unlike those in homogeneous particles of various shape,[27,37] have not been studied with proper exactness (see, however, a series of papers by Prodan and Nordlander[38–40] on the first-principle calculations). In this work, we use a formula derived by Kachan and Ponyavina[29] for the effective mean free path of electrons in the case of isotropic scattering

$$\varepsilon'' = \varepsilon_b'' + \Delta\varepsilon(a) = \varepsilon_b'' + iA_L \frac{\lambda_p}{L_{eff}} \left(\frac{v_F}{2\pi c} \right) \left(\frac{\lambda}{\lambda_p} \right)^3 \qquad (1)$$

$$L_{eff} = a\left[\frac{1}{1+x^2} - \frac{x}{2} - \frac{(1-x)(1-x^2)}{4(1+x^2)} \ln\frac{(1-x)}{(1+x)} \right], \quad x = \frac{a-s}{a} \qquad (2)$$

where a and s are the outer radius and the shell thickness, respectively. Granqvist and Hunderi in their pioneering work[28] used the following analytical expression for L_{eff}:

A - 2.5/Ag, 4/Sil, 3.5/Ag

B - 3.25/Ag, 3.25/Sil, 3.5/Ag

C - 3.5/Ag, 3.5/Sil, 3/Ag

D - 4.25/Ag, 2.75/Sil, 3/Ag

E - 4/Ag, 4/Sil, 2/Ag

F - 4.5/Ag, 2.5/Sil, 2/Ag

G - 5/Ag, 3/Sil, 2/Ag

H - 4.75/Ag, 2.75/Sil, 2.5/Au

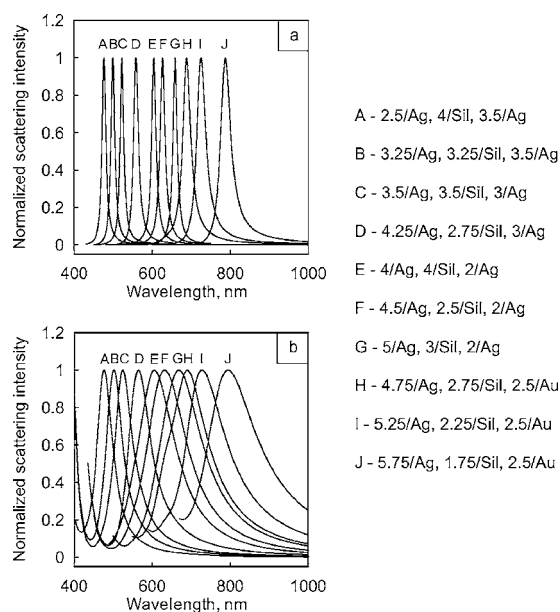I - 5.25/Ag, 2.25/Sil, 2.5/Au

J - 5.75/Ag, 1.75/Sil, 2.5/Au

Fig. 3 Resonant light-scattering peaks of three-layer nanospheres calculated without (a) and with (b) a size correction of the dielectric function. The overall radius of nanostructures with a variable relative dimension of the core versus the shells is fixed (10 nm). The MDM structure is designated in the legend as (core radius)/(core material), (thickness of shell 1)/(material of shell 1), (thickness of shell 2)/(material of shell 2). All dimensions are in nanometers.

$$L_{\text{eff}} = s\sqrt[3]{2(a/s) - 1} \qquad (3)$$

to simulate optical properties of a glass containing silver particles with dielectric cores by using the Maxwell Garnet rule and the dipole polarizability of core/shell particles.[15] For thick shells, Eqs. (2) and (3) give close results ($L_{eff} \sim s$), whereas, for thin shells Eq. (3) gives overestimated L_{eff}-values.

The spectral dependence of the bulk gold refractive index $n_g(\lambda)$ was obtained from a spline by analogy with Ref. 16. Specifically, for wavelengths of 210.4–469.9 nm, the spline nods were taken from Irani et al.;[41] for those of 480–640 nm,

from Otter;[42] and for those of 657.4–1605 nm, from Johnson and Christy.[43] The bulk refractive index of silver was obtained from Johnson and Christy's[43] data.

3 Results and Discussion

All the nanostructures examined in this paper correspond to those studied by Chen et al.[24] Figure 1 shows the scattering spectra of solid gold nanospheres, two-layer structures, and three-layer structures. The spectra were calculated by using size-corrected dielectric functions (solid lines) and bulk optical constants (dashed lines). Evidently, the size-limiting correction of the optical constants leads to dramatic changes in the FWHM values and in the absolute maxima, whereas the resonance spectral positions coincide in both cases. We emphasize that the size-limiting correction of the optical constants is an important factor that allows one to bring the measured and calculated spectra into satisfactory agreement for suspensions of solid spheres[16,44] and gold nanoshells[25] as well as for single spherical particles.[45] On the other hand, it has been reported that the calculations with the bulk dielectric function reproduce the experimental light scattering spectra of individual gold nanoshells[46] and nanorods.[47] Thus, one needs further studies of the issue because the nanorod size and shell thickness in the cited reports[46,47] were too large for noticeable size-correction effects.

Following the argumentation in Ref. 24, we discuss further the optical properties of MDM structures only in terms of the normalized (to the resonance peak value) scattering spectra and FWHM, without consideration of the absolute resonance values. In accord with earlier experimental observations and theoretical simulations,[17,23] Fig. 2 shows the normalized scattering spectra of two-layer silica/Au (or Ag) particles that are tuned to the VIS-NIR resonance position by varying the core/shell ratio at a constant external diameter of 20 nm and at a constant dielectric/metal composition. Note that our non-corrected spectra are in full agreement with the data of Chen et al.[24] However, after appropriate correction for the size-limiting effects, all spectra become essentially broadened and their peak-to-baseline ratio approaches the range from 3 to 5, which is close to that of the solid nanosphere resonances. In the case of three-layer MDM structures (Fig. 3), we obtained
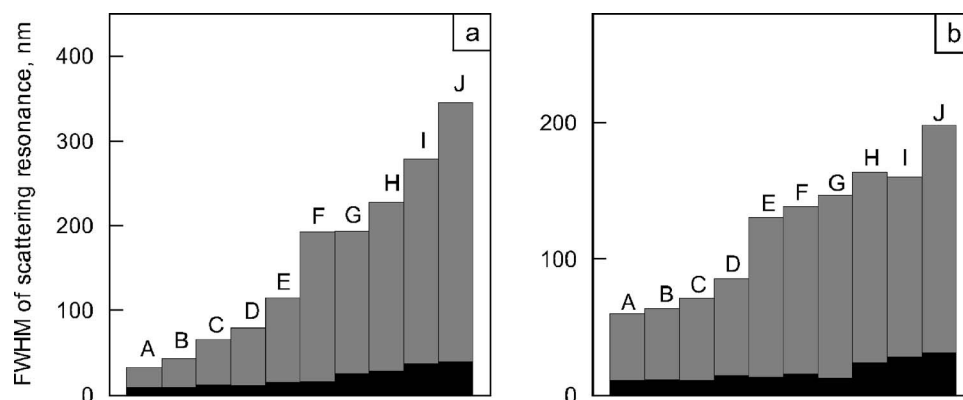

Fig. 4 Dependence of the FWHMs of the resonance peaks of two- (a) and three-layer (b) nanoshells. The gray area corresponds to the data from calculations using L_{eff} according to Eq. (2). The solid area corresponds to calculations without a size-limiting correction. Denotement from A to J corresponds to the structures shown in Fig. 2(a) and Fig. 3(b).

similar results; therefore, no additional comments are needed.

Figure 4 presents a summary of Figs. 2 and 3 in terms of the FWHM values for structures designated by the letters A–J in Figs. 2 and 3. The solid and gray columns correspond to the noncorrected and size-corrected calculations, respectively. The corrected FWHM values lie within the range of 50–300 nm, depending on the resonance peak position. Clearly, these resonance widths are close to the solid-sphere FWHM values.

4   Conclusions

In this work, we have examined the same dielectric/metal and MDM spherically symmetric nanostructures that were studied previously by Chen et al.[24] The only difference between the two studies was the use of bulk or size-corrected dielectric functions for metal shells, whereas the computational algorithm was based on the same recurrence scheme, suggested by Wu and Wang.[33] We have shown that scattering of electrons at the metal shell surface is accomplished by a decrease in the resonance peak value and by a dramatic increase in the FWHM values. By contrast with the previous conclusions,[24] we did not find any significant differences in the scattering resonances of the usual silica/metal nanoshells and three-layer MDM nanostructures. We did not consider particle-size polydispersity because it is clear without any calculations that the resonance scattering spectra of a polydisperse sample is simply the sum of monodisperse spectra weighed with a particular fraction content. Evidently, polydispersity will result in the well-known, size-dependent broadening of spectra, caused by different resonance positions of different species. To summarize, we have not found any significant advantages of three-layer MDM spherical structures for applications to OCT and to light-scattering spectroscopy imaging.

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