A comparative study of classical approaches to surface plasmon resonance of colloidal gold nanorods

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Abstract We report the errors in the evaluation of the surface plasmon resonance of gold nanorods by three classical approaches: the Gans model, the Discrete Dipole Approximation and the Surface Integral method. Using these methods, which are based on the propagation of an electromagnetic wave through a composite medium with different refractive indices, might result in an inaccurate prediction of absorption maxima. For test samples of nanorods prepared by a seed-mediated method, whose homogeneity and quality were also fully demonstrated in this study, the mismatches in the wavelengths of absorption maxima $|\Delta\lambda_{\max}|$ between experimental and theoretical data were observed to be greater than 50 nm. In general, the observed surface plasmon resonances exhibit two distinctive bands corresponding to the transverse and longitudinal modes. The weak transverse mode was located in the region from 510 to 518 nm and varied slightly with the aspect ratio of the rods. In contrast, the longitudinal mode showed a strong dependence on aspect ratio and ranged from 658 to 768 nm. We demonstrated that the mismatches may be sufficiently reduced if the interdependence between these two modes is taken into account.

Keywords Gold · Nanorods · Plasmon · Gans · Discrete Dipole Approximation · Surface Integral

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Introduction

Colloidal gold nanostructures have great potential for application in nanomedicine, photonics, and optoelectronics owing to their surface plasmon resonance (SPR) properties [1, 2]. SPR is an optical phenomenon that arises from the interaction between an incident electromagnetic field and conduction electrons in metals. Under light irradiation, the conduction electrons are driven by the electric field to collectively oscillate at a resonant frequency relative to the energy of the incident light. At this frequency, the incident radiation is strongly absorbed, inducing a particular resonance behavior in a given nanostructure. This effect is of great interest for both analytical sensing and nanostructure functionalization in modern nanomedicine. The SPR cross-section generally depends strongly on the shape and size of a given gold nanostructure, as well as on the dielectric constant of the surrounding medium. There are two ways to understand SPR. At a low level theory, SPR is caused by the absorption of conduction electrons circulating in the delocalized molecular orbitals (MOs) at the surface of a metallic nanostructure. Because a number of valence band MOs are always available, there are also plenty of possible circulation routes around the nanoparticle surface. This appears to be a natural explanation for multipole resonance in metallic nanoclusters. The specific geometry of gold nanorods usually induces two main circulation paths, one corresponding to the transverse and the other to the longitudinal SPR mode. The modes are interdependent, and both vary with the aspect ratio (which is defined as the ratio of the length to the diameter of a rod). Qualitative evaluation may be performed using a technique such as time-dependent density functional theory (TD-DFT). Recent theoretical predictions of SPR based on the aspect ratio (AR) rely on Maxwell's theory of wave propagation through a composite medium with two different refractive indices. Absorption

occurs at the interface where the refractive index of metallic nanoclusters abruptly changes to the value of vacuum (or that of the surrounding medium). The loss of momentum is one reason why absorption occurs. In this study, the SPR phenomenon of anisotropic gold nanostructures, gold nanorods prepared by a modified seed-mediated method, was investigated. We first discuss the careful characterization of sample quality and size homogeneity and show that both the transverse and longitudinal modes depend on the AR. Whereas a minor change in the transverse mode induced no observable shift in color, the large variation in the longitudinal mode (approximately 10 times larger) shifted the color of the colloids from green to bright red. The experimental results were then compared to the predictions made by classical approaches to show that within the framework of Maxwell's theory (where no correspondence between the two modes is taken into account), the deviation between theory and experiment might be large. The failure of classical theory lies in its fundamental assumption of a unique refractive index for an entire nanostructure, whereas it is clear that the density of the electronic cloud surrounding a metal nanostructure varies with position; thus, if SPR is being interpreted in terms of the refractive index, then one should take into account the variation of refractive index across the surface of a particular nanostructure.

Material preparation and characterization

Gold nanorods are commonly prepared by the seed-mediated method, which was first introduced by Jana et al. [3] and later modified and improved by Nikoobakht et al. [4]. A recent modification of the method to improve the reproducibility of gold nanorods in terms of their shape and size was reported in ref. [5]. Briefly, seed gold nanoparticles were prepared by adding an ice-cold aqueous solution of sodium borohydride (NaBH_4 , Kanto) to a mixed aqueous solution of cetyltrimethylammonium bromide (CTAB, Aldrich) and hydrogen tetrachloroaurate hydrate (HAuCl_4 , Sigma-Aldrich), resulting in the formation of a brownish-yellow solution containing seed gold nanoparticles. All chemicals used were of a high grade of purity. The age of the seed solution is an important factor in reproducing gold nanorod samples. In our experiments, the seed solution was used within 5 to 10 min of preparation, whereas in the original procedure, the solution was used within 2 to 5 h. A small amount of the gold seed solution was then added to a growth solution containing CTAB, HAuCl_4 , silver nitrate (AgNO_3 , Merck, 99.9 %), and ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, Kanto, 99.5 %; silver nitrate was used as a growth catalyst and an agent for controlling the aspect ratio of the nanorods). The color of the solution changed over time depending on the final size of the gold nanorods. The nanorods were allowed to grow overnight

without stirring at 24 °C. The resulting solution was centrifuged to remove the surfactants and possible by-products such as large particles and cubes. For comparison, spherical gold nanoparticle samples were synthesized using the citrate reduction method [6]. This method, pioneered by Turkevich et al. [6], is one of the most popular and environmentally friendly ways to synthesize gold nanospheres. We modified the original procedure to improve the control over the size and size distribution of the resultant gold nanoparticles. Briefly, an aqueous mixture composed of hydrogen tetrachloroaurate hydrate (HAuCl_4 , Sigma-Aldrich, 99.9 %) and sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, Scharlau, 99.5 %) in a certain molar ratio was heated to boiling under vigorous stirring. At 72 ± 1 °C, within a few minutes, the solution first became colorless, then turned dark blue, and finally became brilliant red or purple, depending on the molar ratio between the precursors. The gold nanoparticle sample was then left to cool naturally to room temperature. The average particle diameter can be tuned over a wide range (from approximately 10 to 100 nm) by varying the concentration ratio between the Au salt and sodium citrate.

The crystal structure and morphology of the synthesized samples were characterized using a Siemens D5005 XRD diffractometer and JEOL JEM-1010 transmission electron microscope (TEM), respectively. The absorption spectra of the samples were measured at room temperature using a Shimadzu UV-vis-2450PC spectrometer.

Figure 1a, b shows the typical XRD patterns of the synthesized gold nanorods and nanospheres, respectively. The pattern exhibits well-resolved (111) and (200) diffraction peaks, which could be well indexed to the face-centered cubic (fcc) phase of metallic gold (PDF 04–0784, ICDD). It is worth pointing out that for the nanorods, the ratio of the intensity of the (200) diffraction peaks to the (111) diffraction peaks is substantially higher than both the standard value (0.53) given in PDF 04–0784 (ICDD) and that of the gold nanospheres shown in Fig. 1b. A sum of two Gaussians representing the XRD peaks and a decaying exponential function simulating the background was fitted to the XRD data. As a result of the fit, for the gold nanorods, the relative intensity ratio of the (200) and (111) diffraction peaks was found to be approximately 2.29. The (200) diffraction peak became the most prominent peak, which may indicate anisotropic growth of the crystal along the [100] direction, resulting in the formation of rod-like particles. In case of the spherical gold nanoparticles, the ratio of intensity between the (200) and (111) diffraction peaks is considerably lower than the standard value (0.39 versus 0.53). This observation supports the theoretical prediction [7] and the results of HRTEM analysis described elsewhere [8] that suggest that noble-metal nanocrystals are exclusively composed of the lowest-index crystal planes and, in general, the thermodynamic equilibrium shape is a truncated octahedron bound by {111} and {100} planes.

Fig. 1 The typical XRD patterns of the prepared gold nanorods (a) and gold nanospheres (b)

The morphology of the synthesized gold nanorods and particles was examined using TEM images with the help of the image processing program ImageJ [9]. Figure 2 shows the absorption spectrum of the gold nanospheres with a representative TEM image (the inset). As shown, the absorption maximum occurs only at 522 nm, which signifies a single resonance mode. The TEM image shown in the set demonstrates that the particles were well dispersed, with a narrow size distribution. The nanoparticles appeared to be spherical in shape, and their average size was determined to be 15.4 nm with a standard deviation of 2.3 nm. A total of six nanorod samples were produced: CR658, CR687, CR696, CR726, CR745, and CR768; TEM images of the samples are shown in Fig. 3a. The samples mostly consist of relatively well-dispersed gold nanorods, although by-products such as large particles and cubes were not negligible, especially in the case of samples CR695 and CR726. As was revealed by TEM, the synthesized gold nanorods are somewhat spherically or ellipsoidally capped cylinders. The average ARs of samples CR658, CR687, CR696, CR726, CR745, and CR768 were estimated from their corresponding TEM images to be 2.3 ± 0.1 , 2.8 ± 0.1 , 2.9 ± 0.1 , 3.1 ± 0.1 , 3.40 ± 0.15 , and 3.8 ± 0.2 , respectively. Sample CR768, shown in the lower-right corner of Fig. 3a, which exhibited the highest AR (3.8 ± 0.2), showed a broad AR distribution,

Fig. 2 The absorption spectrum of the gold nanospheres; the inset shows the corresponding TEM image

leading to a large standard error. However, compared with the results reported by other authors, the errors obtained in this study are quite smaller, which indicates that good size and shape homogeneity were achieved.

The SPR phenomenon of gold nanorods was monitored using standard UV–vis–NIR spectroscopy. The normalized absorption spectra of the gold nanorods produced in this study are shown in Fig. 3b. While symmetric gold nanospheres exhibit a single SPR peak at approximately 522 nm, anisotropic nanoparticles such as rods, cubes, triangular plates, and pyramids exhibit multiple SPR peaks due to highly localized charge polarizations at corners and edges [1, 2]. In all six spectra, there are two distinctive SPR bands corresponding to the oscillations of conduction electrons along and perpendicular to the long axis of the rods. The weak transverse surface plasmon resonance (TSPR) peak occurs in the region from 510 to 518 nm and does not depend strongly on the aspect ratio of the rods. However, the peak is clearly blue-shifted from the value of 522 nm observed for the nanospheres. The longitudinal surface plasmon resonance (LSPR) mode shows a strong resonance peak at longer wavelengths and depends strongly on the aspect ratio of the rods. As the average AR increases from 2.3 to 3.8, the LSPR peak is red-shifted from 658 to 768 nm, leading to an increase in the brightness of the colloid. By varying the AR, the LSPR peak can be effectively tuned over a wide wavelength range from the visible to near-infrared region, making gold nanorods very attractive candidates for applications in photonics, optoelectronics, and biotechnology [1, 2]. It is evident from Fig. 3b that the measured shifts, blue for the transverse mode and red for the longitudinal mode, appear to increase in magnitude with the aspect ratio.

Fig. 3 The TEM images of the nanorod samples CR658, CR687, CR696, CR726, CR745 and CR768 (a) and the corresponding normalized absorption spectra (b)

Discussion

The experimental results regarding the dependence of the position of the LSPR peak on the aspect ratio were compared to the theoretical predictions made by the Gans model [10], Discrete Dipole Approximation (DDA) [11], and the Surface Integral (SI) approach [12]. As an extension of Mie's theory, the Gans model predicts how the LSPR wavelength λ_{LSPR} varies with AR for small ellipsoids suspended in water (high dielectric constant of approximately 80.1 at

20 °C). The experimentally measured SPR peaks appear to be red-shifted from the values predicted by the Gans model, as shown in Fig. 4. There are a number of factors that account for this disagreement, but first and foremost, the Gans model treats particles as ellipsoids suspended in water, which is not the case for the studied samples.

The discrepancy between the experimental data and theoretical predictions is well-known, and several groups have tried to use computational methods such as the DDA [11] and SI [12] approaches to solve the problem. Taking into

Fig. 4 The comparison of experimental longitudinal SPR peak positions with the results of Gans and DDA simulations for various shapes of gold nanorods

account the actual shapes and sizes of rods, Prescott and Mulvaney [11] demonstrated that the AR alone cannot be used to accurately predict λ_{LSPR} . In addition, the position of the LSPR peak is very sensitive to the end-cap geometry of rods. Detailed analysis and discussions can be found in [11]. Figure 4 shows two theoretical simulations for two different morphologies of gold nanorods, a flat-end cylinder and a spherically capped cylinder, suspended in a medium with a refractive index of 1.33 [11]. The latter appears to be a more appropriate model, as shown in Fig. 4. It is also reasonable to treat the synthesized rods as spherically capped cylinders, as suggested by TEM analysis. However, overall, the DDA approach still does not accurately predict the experimental data. Moreover, the predicted rate of change of λ_{LSPR} with the AR is too high compared with the experimental data.

Using the SI approach, Pecharroman et al. [12] recently concluded that not only the AR but both the end-cap geometry and surface roughness of rods play an important role in determining the extinction spectrum. Detailed analysis and discussions are reported in [12]. Fig. 5 compares the experimental data from this analysis with the results of the SI calculations reported by Pecharroman et al. [12] for smooth rods with an end-cap geometry featuring different degrees of flatness. The flatness can be modeled by using the parameter $\text{exc} = z/a$ (z and a denoted in the figure). As shown, the best fit to the experimental data is obtained when exc is between 0.4 and 0.6: that is, when the rod is treated as neither a flat-end nor spherically capped cylinder but something in between. In Fig. 6, we compare the experimental data with the SI predictions for spherically capped rods with different degrees of surface roughness $\rho = r/a$ [12]. The roughness ρ was considered to be smaller than 10 % of the nanorod diameter. It is clear that the experimental data, spread over

Fig. 5 The comparison of experimental longitudinal SPR peak positions with the results of SI calculations for various end-cap geometries of smooth gold nanorods

the range of ρ from 0.02 to 0.08, and the rate of change of λ_{LSPR} with AR were not well modeled.

Thus, neither DDA simulations nor the SI approach accurately predicted the experimental results. It is crucial to determine whether the discrepancy between the experimental results and theoretical predictions is due to physical effects or some inadequacy in the experimental measurements. The fact that gold nanorods synthesized via the seed-mediated method are believed to be coated with a thin layer of surfactant CTAB should be taken into account when modeling the refractive index of the rods' surrounding medium. Moreover, the problems of polydispersity and plasmon coupling between rods may also play a non-negligible role. These problems, however, should introduce

Fig. 6 The comparison of experimental longitudinal SPR peak positions with the results of SI calculations for spherically capped gold nanorods with different values of surface roughness ρ

a systematic error that affects the overall estimation accuracy, but this is not the case. Therefore, the only remaining reason seems to lie in the inadequacy of the formulation of SPR by classical theory, but because a discussion of this subject extends beyond the scope of this article, we only show that, if we take into account the interdependence between the two SPR modes, we are able to sufficiently reduce the discrepancies listed above.

Recall that the shifts in both λ_{TSPR} and λ_{LSPR} scale with the AR; thus, by extension, λ_{TSPR} may be used to linearly scale λ_{LSPR} to an expected value. Assuming the simplest case, the relation may be written as follows.

$$\lambda_{\text{LSPR}}^{\text{Expected}} = \left(\frac{\lambda_{\text{TSPR}}^{\text{Measured}}}{\lambda_0} \right) \lambda_{\text{LSPR}}^{\text{Measured}}, \quad (1)$$

where λ_0 is a constant. Within the narrow range of experimental ARs (Figs. 4–6), we may safely consider the expected values of λ_{LSPR} to scale linearly with the AR, that is, $\lambda_{\text{LSPR}}^{\text{Expected}} = ka_r$ (where k is a scaling constant and a_r is an aspect ratio). Substituting this expression into (1) yields

$$\lambda_0 = \lambda_{\text{TSPR}}^{\text{Measured}} \left(\frac{\lambda_{\text{LSPR}}^{\text{Measured}}}{ka_r} \right). \quad (2)$$

Therefore, each measured value $a_r(i)$ ($i=1, \dots, 6$ in our case) provides one value $\lambda_0(i)$. If the physical correspondence between the two SPR modes really exists, then λ_0 will be determined with high accuracy. The temporal, incomplete numerical evaluation indeed showed that the relative error of the estimation of λ_0 was less than 5 %, and λ_0 had a value of 514.13 nm, which is very close to the mean value of λ_{TSPR} (514.33 nm). The predicted values $\lambda_{\text{LSPR}}^{\text{Expected}}$ obtained from (1) using the λ_0 calculated for our samples showed that the relative error $|\Delta\lambda_{\text{LSPR}}/\lambda_{\text{LSPR}}| \times 100 \% < 0.65 \%$. For the accuracy obtained, we believe that some physical correspondence between the two resonance modes truly exists. A full discussion of this conclusion in the light of density functional theory will be presented elsewhere; to date, TD-DFT has been used only for small clusters with a few atoms (less than 20, e.g., Ref. [13] for $\text{Ag}_3\text{Au}_{10}$ cluster, Ref. [14] for Ag_mNi_p , $m+p \leq 8$, and Ref. [15] for Au_{20} single chain clusters). Because TD-DFT calculations are still difficult for clusters large enough to provide meaningful results (such as the Ag clusters with diameters of up to 9 nm in Ref. [16] and [17]), the interpretation of the interplay between the SPR modes according to relation (1) can provide a rough, phenomenological estimate of this coupling effect.

Conclusion

The optical properties of gold nanorods are dominated by the SPR phenomenon. As anisotropic particles, gold

nanorods exhibit two characteristic SPR peaks corresponding to the transverse and longitudinal SPR modes. There is clearly a discrepancy between the experimental results and theoretical predictions made by Gans model, DDA and SI calculations. In our opinion, the Gans model is too simple, whereas the Surface Integral approach appears somewhat arbitrary when modeling surface topology and roughness; thus, the Discrete Dipole Approximation is the most appropriate method for SPR simulation at the classical theory level. Furthermore, the refractive index of the surrounding medium, as well as the problems of polydispersity and plasmon coupling between nanorods, might sufficiently account for the discussed discrepancies. We suggest that the interdependence between the two resonance modes might play an important role and should be taken into account.

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