Simulation of the Optical Absorption Spectra of Gold Nanorods as a Function of Their Aspect Ratio and the Effect of the Medium Dielectric Constant

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Gold nanorods with different aspect ratios are prepared in micelles by the electrochemical method and their absorption spectra are modeled by theory. Experimentally, a linear relationship is found between the absorption maximum of the longitudinal plasmon resonance and the mean aspect ratio as determined from TEM. It is shown here that such a linear dependence is also predicted theoretically. However, calculations also show that the absorption maximum of the longitudinal plasmon resonance depends on the medium dielectric constant in a linear fashion for a fixed aspect ratio. Attempts to fit the calculations to the experimental values indicate that the medium dielectric constant has to vary with the aspect ratio in a nonlinear way. Chemically, this suggests that the structure of the micelle capping the gold nanorods is size dependent. Furthermore, comparison with the results obtained for rods of different aspect ratios made by systematic thermal decomposition of the long rods further suggests that the medium dielectric constant is also temperature dependent. This is attributed to thermal annealing of the structure of the micelles around the nanorods.

Introduction

In recent years the interest in the preparation and characterization of nanostructured materials has grown constantly because of their distinctive properties and potential use in technological applications.1,2 Since the electronic, magnetic, and catalytic properties of these particles depend mainly on their size and shape, one of the desired goals is to control the morphology of metal and semiconductor nanoparticles.3–5 Shape control has successfully been demonstrated for platinum nanoparticles4 as well as for metallic carbide nanotubes.5–8 Furthermore, gold nanorods have recently been prepared by electodeposition of gold into nanoporous alumina9–11 and by an electrochemical method with the aid of shape-inducing micelles.12

In addition to the recent interest in the shape control of nanoparticles, the optical properties of noble metal particles with their intense colors have fascinated scientists since the turn of this century.13,14 For example, spherical gold nanoparticles show a strong absorption band in the visible region of the electromagnetic field at about 520 nm. This absorption, called the plasmon absorption,15,16 is absent for very small particles (2 nm and smaller) as well as for bulk gold. It originates from the oscillation of the free electrons (6s-electrons of the conduction band in the case of gold). Mie13 first described this phenomenon theoretically by solving Maxwell’s equations for a radiation field interacting with a spherical metal particle under the appropriate boundary conditions. The only material-related functions and constants in Mie’s theory are the complex dielectric function of the metal and the dielectric constant of the surrounding medium. The plasmon absorption band also depends on the size of the particles and many attempts have been made to experimentally correlate the absorption maximum and the plasmon bandwidth to the actual particle size with overall moderate success.17–20 An inhomogeneous size distribution and different surrounding media in various studies complicate the correlation between theory and experiment.17,18,21 The surrounding medium, often referred to as the capping material, is however of great importance as it prevents aggregation followed by precipitation of gold and other metal particles in solution.

Gans14 extended Mie’s theory to prolate and oblate spheroidal particles averaged over all orientations. For gold nanorods the plasmon resonance then splits into two modes: one longitudinal mode along the long axis of the rod and a transverse mode perpendicular to the first. Maxwell–Garnett theory,16,17,22 an effective medium theory, is also often used to describe the optical properties of metallic nanoparticles. Maxwell–Garnett theory computes the effective (complex) dielectric function of the composite material consisting of the metallic nanoparticles and the surrounding medium (host material). From this dielectric function the refractive index and the absorption can be calculated. The shape of the particles can be included in this theory by a screening parameter. Martin and co-workers9,23–26 have used and modified the Maxwell–Garnett theory to model the absorption spectra of gold nanoparticles with shapes that vary from oblate or pancakelike to prolate or needlelike. The gold nanorods are embedded in a porous aluminum oxide membrane, in which they are well separated and aligned parallel to each other. The optical absorption spectrum shows only one plasmon band, which blue-shifts with increasing aspect ratio in agreement with the theoretical simulations.

We have used Gans’ theory together with the known dielectric function for gold27 and modeled the optical absorption spectra of several colloidal gold nanorod samples with varying aspect ratios. We were able to derive a simple relationship between the absorption maximum of the longitudinal plasmon resonance and the aspect ratio and the medium dielectric constant. A linear dependence of the absorption maximum on the aspect ratio as well as on the medium dielectric constant was found for a constant value of the other parameter. Comparison with experimental results, where the mean aspect ratio was determined by transmission electron microscopy (TEM), indicates...
that the organization of the capping material surrounding the
gold nanorods differs for rods with different aspect ratios.
Furthermore, the fact that the absorption maximum of a certain
rod having a specific aspect ratio is found to depend on its
method of preparation (either by adjusting the conditions of the
method or starting with a distribution of larger rods and
thermally changing it to the distribution required\(^2\)) suggests
that the organization of the micelles around the nanorods is
kinetically and not thermodynamically controlled.

Experimental Section

The gold nanorods were prepared in micelles using an
electrochemical method described previously.\(^1\) The electro-
chemical cell consisted of a gold (anode) and a platinum plate
(cathode). An additional silver plate is placed behind the Pt
electrode. The electrolyte solution consisted of a hydrophilic
cationic surfactant, hexadecyltrimethylammonium bromide, and
a hydrophobic cationic cosurfactant, tetradecylammonium bro-
mide or tetraoctylammonium bromide. The ratio between these
surfactants controls the average aspect ratio of the gold nanorods.
The electrolysis was carried out for 45 min with an applied
current of 5 mA at a temperature of 42 \(^\circ\)C and under constant
ultrasonication. The nanorods were separated from spherical
nanoparticles by centrifugation.

The UV–vis absorption spectra were recorded on a Beckman
DU 650 spectrophotometer. The size and shape distributions
of the nanorods were determined from the TEM images of the
evaporated solutions on carbon-coated copper grids. A Hitachi
HF-2000 field emission TEM operating at 200 kV was used.
Normally, 300 particles were counted in determining the
distributions for each sample.

Results

Figure 1 shows the absorption spectrum and a TEM image
of one of the prepared samples. The average aspect ratio of
these nanorods is 3.3 and they have two absorption maxima at
525 and 740 nm corresponding to the transverse and longitudinal
mode, respectively. This sample was also used for the thermal
reshaping studies presented elsewhere.\(^2\) Seven more gold
nanorod samples were prepared by the method described in the
Experimental Section. Their average aspect ratio was controlled
by the ratio of surfactant molecules to cosurfactant molecules.
The average aspect ratios and the absorption maxima of their
longitudinal plasmon resonance are listed in Table 1.

Using an extension of the Mie theory it is attempted here to
explore theoretically the relationship between the aspect ratio
of the gold nanorods and the position of this absorption
maximum. According to Gans,\(^1\) the extinction coefficient \(\gamma\)
of randomly oriented particles in the dipole approximation is

\[
\gamma = \frac{2\pi N V \epsilon_m^{3/2}}{3\lambda} \sum_j \left( \frac{1}{P_j^2} \right) \frac{(1/P_j^2) \epsilon_2}{\epsilon_1 + \frac{1 - P_j}{P_j} \epsilon_m^{3/2}} + \epsilon_2^2
\]

where \(N\) is the number of particles per unit volume, \(V\) the
volume of each particle, \(\epsilon_m\) the dielectric constant of the
surrounding medium, \(\lambda\) the wavelength of the interacting light,
and \(\epsilon_1\) and \(\epsilon_2\) are the real and complex part of the material
dielectric function. The latter one is frequency dependent, while
\(\epsilon_m\) is assumed to be a constant. \(P_j\) are the depolarization factors
for the three axes \(A, B, C\) of the rod with \(A > B = C\). They are
defined as

\[
P_A = \frac{1 - e^2}{2e^2} \ln \left( \frac{1 + e}{1 - e} \right) - 1
\]

\[
P_B = P_C = \frac{1 - P_A}{2}
\]

where

\[
e = \sqrt{1 - \frac{B^2}{A^2}}
\]

The ratio \(A/B\) is the aspect ratio \(R\).

With the known values for the complex dielectric constant of
gold,\(^2\) eq 1 is plotted in Figure 2 for different aspect ratios
while the medium dielectric constant was fixed to a value of 4.
It can be seen that two maxima are present in the simulated
absorption spectra corresponding to the transverse and longi-
tudinal resonances. The absorption maximum of the transverse
mode shifts to shorter wavelength with increasing aspect ratio.
This trend for the transverse mode of the surface plasmon

Figure 1. Left: Experimental UV–vis absorption spectrum of a gold nanorod sample with an average aspect ratio of 3.3. The band at 525 nm is
taken to be the transverse plasmon resonance, while the one centered at 740 nm is called the longitudinal plasmon absorption. Right: TEM image
of the same solution.
TABLE 1: Absorption Maximum of the Longitudinal Plasmon Resonance $\lambda_{\text{max}}$ and Average Aspect Ratio $R$ of the Electrochemically Prepared Gold Nanorod Samples and the Respective Values Obtained by Thermal Reshaping

<table>
<thead>
<tr>
<th>Preparation</th>
<th>Thermal Reshaping</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$R$</td>
</tr>
<tr>
<td>780</td>
<td>3.7</td>
</tr>
<tr>
<td>749</td>
<td>3.5</td>
</tr>
<tr>
<td>740</td>
<td>3.3</td>
</tr>
<tr>
<td>709</td>
<td>3.0</td>
</tr>
<tr>
<td>673</td>
<td>2.7</td>
</tr>
<tr>
<td>660</td>
<td>2.65</td>
</tr>
<tr>
<td>656</td>
<td>2.5</td>
</tr>
<tr>
<td>610</td>
<td>2.1</td>
</tr>
</tbody>
</table>

*The medium dielectric constant $\epsilon_m$ was calculated as outlined in the text.

Figure 2. Calculated absorption spectra of elongated ellipsoids with varying aspect ratios $R$ using eq 1. The medium dielectric constant was fixed at a value of 4. The inset shows a plot of the maximum of the longitudinal plasmon band determined from the calculated spectra as a function of the aspect ratio. The solid line is a linear fit to the data points. The dotted line is a plot of eq 8 with a medium dielectric constant of 4.

Figure 3. Calculated absorption spectra of elongated ellipsoids with varying medium dielectric constant $\epsilon_m$ using eq 1. The aspect ratio was fixed at a value of 3.3. The inset shows a plot of the maximum of the longitudinal plasmon band determined from the calculated spectra as a function of the medium dielectric constant. The solid line is a linear fit to the data points. The dotted line is a plot of eq 8 with a aspect ratio of 3.3.

The relationship between the absorption maximum of the longitudinal mode and the aspect ratio and the medium dielectric constant can be regarded as linear for the range examined in Figures 2 and 3. (The fit in Figure 2 has a regression coefficient of $r = 0.99928$, and in Figure 3 $r = 0.99989$). This is an important conclusion because it cannot be seen directly by considering eqs 1−4. It especially shows that the effect of the medium dielectric constant should not be underestimated.

If these linear dependencies hold, then it would further be interesting to derive an equation which allows us to predict the absorption maximum of the longitudinal mode for a certain aspect ratio and dielectric constant instead of calculating the whole absorption spectrum. This can be done by considering that the resonance condition for the longitudinal mode is roughly fulfilled if

$$
\epsilon = -\frac{(1 - P_A)\epsilon_m}{P_A} = \epsilon_1
$$

The real part of the gold dielectric function $\epsilon_1$ is wavelength dependent. However, a plot of $\epsilon_1$ vs the wavelength of the interacting light in the interesting range between 500 and 800 nm is found to be nearly linear, and a fit gives the following values for the intercept and slope with a regression coefficient of 0.99956:

$$
\epsilon_1(\lambda) = 34.66 - 0.07\lambda
$$

Similarly, plotting $(1 - P_A)/P_A$ as a function of the aspect ratio $R$ between 2 and 4 and linearizing yields

$$
\frac{1 - P_A}{P_A} = -3.40 + 2.45R
$$

with a regression coefficient of 0.99846. Combining eqs 5−7 then gives

$$
\begin{align*}
\lambda_{\text{max}} &= 33.34\epsilon_m R - 46.31\epsilon_m + 472.31 \\
&= (33.34R - 46.31)\epsilon_m + 472.31
\end{align*}
$$
can be described by a linear relationship (eq 8 are also plotted in Figure 4. Indeed, the experimental data points are given in Table 1 and TEM and the absorption maximum for the eight different resonance was of great interest to us. The values of the average aspect ratios and the absorption maxima for the eight different samples prepared electrochemically are given in Table 1 and are also plotted in Figure 4. Indeed, the experimental data points can be described by a linear relationship ($\lambda_{\text{max}} = 392.11 + 103.70R$ with $r = 0.999676$) in general agreement with other experimental results.11,12 Also included in Figure 4 are the experimental data points obtained after thermal reshaping of the sample shown in Figure 1 ($R = 3.3, \lambda_{\text{max}} = 740 \text{nm}$). They follow a linear trend as well ($\lambda_{\text{max}} = 547.29 + 58.9R$ with $r = 0.999519$).

Equation 8 is plotted in the insets of Figures 2 and 3 as the dotted line for a fixed dielectric constant of 4 and a fixed aspect ratio of 3.3, respectively. Very good agreement is found with the data points calculated by the full expression of eq 1 even after the two simplifications in eqs 6 and 7 were made. This therefore suggests that the assumptions made in the derivation of eq 8 are acceptable.

Discussion

The theoretical calculations were carried out in order to compare them with experimental data. Especially the relationship between the average nanorod aspect ratio determined by TEM and the absorption maximum of the longitudinal plasmon resonance was of great interest to us. The values of the average aspect ratios and the absorption maxima for the eight different samples prepared electrochemically are given in Table 1 and are also plotted in Figure 4. Indeed, the experimental data points can be described by a linear relationship ($\lambda_{\text{max}} = 392.11 + 103.70R$ with $r = 0.999676$) in general agreement with other experimental results.11,12 Also included in Figure 4 are the experimental data points obtained after thermal reshaping of the sample shown in Figure 1 ($R = 3.3, \lambda_{\text{max}} = 740 \text{nm}$). They follow a linear trend as well ($\lambda_{\text{max}} = 547.29 + 58.9R$ with $r = 0.999519$).

Surprisingly neither of the two experimental lines can be matched by eq 8 for a single value of the medium dielectric constant. Varying $\epsilon_m$ can reproduce the right slope for either line, but the intercept also depends on $\epsilon_m$. The broken line in Figure 4 is a plot of eq 8 with a medium dielectric constant of 4.2. This value of $\epsilon_m$ was chosen in order to match the experimental absorption maximum of the nanorods. The points in Figure 5 were calculated by solving eq 8 with the experimentally determined absorption maxima and aspect ratios for the different samples as listed in Table 1. These values of the medium dielectric constant are also included in Table 1. The solid lines are obtained setting eq 8 equal to the linear regressions in Figure 4 and solving for $\epsilon_m$ as a function of the aspect ratio $R$. This yields the following equations:

$$\epsilon_m = \frac{103.70R - 80.20}{33.34R - 46.31} \quad (9)$$

$$\epsilon_m = \frac{58.99R - 75.02}{33.34R - 46.31} \quad (10)$$

A dependence of the medium dielectric constant on the nanorod aspect ratio means in more chemical terms that the structure of the surrounding micelle is different for different nanorod sizes. The micelle consists of two surfactant molecules, hexadecyltrimethylammonium bromide and tetracetylammonium bromide or tetradecylammonium bromide, and prevents the nanorods from aggregation and precipitation. Their respective ratio controls the length of the gold nanorods suggesting a different environment for each prepared sample due to a different composition of the micelles. The exact arrangement of the molecules within the micelle and their interaction with the gold surface are however not known at the moment. The assumption that the organization of the molecules at the gold surface might differ for rods of different length seems very reasonable and this in turn would lead to a variation in the effective medium dielectric constant. Values between 3 and 7 for $\epsilon_m$ are also very reasonable when compared to other organic chemicals with structures similar to the surfactants used in this study.30

From Figures 4 and 5 it is also obvious that the thermal reshaping of the nanorods alters the structure of the micelle surrounding the smaller rods, which stay in solution. A reorganization of the micelle structure due to an elevated temperature causes the gold nanoparticles to have a different effective environment characterized by a higher value for its dielectric constant as monitored by the longitudinal surface plasmon oscillation of the nanorods. This suggests that the structure of the capping micelles of a certain rod at room temperature prepared by thermal reshaping is different from the
one of a freshly prepared sample with the same average aspect ratio. Heating the micellar solution could anneal the structure of the micelles capping the gold nanorods. This suggests that the originally synthesized sample has a micellar structure that is kinetically, rather than thermodynamically, controlled. Heating the solution anneals the structure toward the more stable thermodynamic structure with a higher value of the dielectric constant.

Equation 8 is an excellent approximation for the region considered here (aspect ratio ranging from 2 to 4 and a wavelength range of 500 to 800 nm), but applying this simple theory (dipole approximation) to an inhomogeneously broadened sample and proposing a change of the medium dielectric constant which is usually applicable to sizes of less than 1/10 the wavelength of the interacting light. Our particles have a typical length of about 60 nm and a width of 20 nm and are therefore just within the limit of the dipole approximation. The question however arises if multipole terms have to be considered for larger particles with the same aspect ratio and if the absorption spectrum might change for much smaller particles of the same aspect ratio.

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References and Notes
