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Depolarized light scattering from colloidal gold nanoparticles

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ABSTRACT

We present a study of depolarized light scattering from gold nanoparticles of various shapes and heterodispersity in aqueous solutions. The light scattering anisotropy for particles with average aspect ratio ~1.2 and above 1.5 was measured experimentally and modelled theoretically. For elongated particles the anisotropy reaches the minimum value of about 0.5 in the spectral region 550–750 nm and its position corresponds to the maximum of the scattering component in the extinction spectra. Our work demonstrates the potential to distinguish plasmonic scattering from gold nanoparticles from the background Rayleigh scattering that is important for applications in sensing and imaging in turbid media.

1. Introduction

There is growing interest in extraordinary size-dependent optical properties of noble metal nanoparticles. These nanoparticles exhibit a strong UV–visible extinction band that it is not present in the bulk metals. This extinction band is a result of the fact that electrons in nanometer sized metallic particles may undergo a resonance of the incident photon frequency with a collective excitation of the conduction electrons known as a localised surface plasmon resonance (LSPR), which makes them excellent scatterers and absorbers of visible light [1–4]. LSPR excitation results in wavelength-selective absorption with extremely large molar extinction coefficients ($\sim 3 \times 10^{11}$ M^{-1} cm^{-1}) [5] and intense resonant Rayleigh scattering with the efficiency equivalent to that of 10^6 fluorophores [6,7]. Gold nanoparticles, in addition to their enhanced absorption and scattering, have other attractive properties such as: resistance to photobleaching or chemical/thermal degradation and good biocompatibility [8]. These properties, combined with relatively simple synthesis [9] and the possibility of conjugation to a variety of biomolecules, antibodies or biological targeting moieties [10,11] make them suitable for biochemical sensing and detection [12–14].

Recently, we reported depolarized light scattering from colloidal silver solutions [15,16]. We observed that, in contrast to scattering by dielectric particles, light scattered by metallic nanoparticles was partially depolarized within the spectral range coinciding with the high extinction region of the silver colloidal solution and that the scattering component was responsible for the depolarization effect. As shown in several experimental reports [1,17–19] the extinction cross-section, and the relative contribution of scattering to the extinction, is strongly dependent on the nanoparticle size for both gold [18] and silver [1,6] and the spectral position of the resonance depends on the particle chemical composition, size and shape. With increasing nanoparticle size both the extinction coefficient as well as relative contribution of scattering are also increased. In general, in the case of small nanoparticles (below 30 nm) the absorption dominates over scattering, whereas the plasmonic scattering plays a significant role for larger nanoparticles (above 50 nm).

In our previous report, we presented a theory of depolarized light scattering, based on the interference of two surface plasmon resonances in the same particle [20] that is strongly dependent on shape and particularly the aspect ratio for the non-spherical particles.

This work investigates depolarized scattering of gold nanoparticles and is motivated by non-toxicity, chemical stability and the potential of gold nanoparticles to extend depolarized light scattering into the 600–800 nm spectral range. These properties are important for biosensing without the use of dyes and visualization of objects hidden in a scattering/absorbing dielectric medium including imaging inside the tissue.

In the course of this study we have synthesized the range of colloidal gold nanoparticles with varying average particle size and shape and investigated the effect of nanoparticle size on the extinction and depolarized scattering. We also present the results of theoretical modelling of the observed phenomena.

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2. Materials and methods

2.1. Preparation of colloidal gold nanoparticles

The following materials were purchased from Sigma-Aldrich and used as received: $HAuCl_4 \cdot 3H_2O$, trisodium citrate dehydrate and concentrated HCl, HNO_3, H_2SO_4, Ludox SM-30 (30% by weight colloidal silica suspension in water), methanol, and 30% H_2O_2. Nanopure water (>18.0 MΩ), purified using the Millipore Milli-Q filtration system, was used in all experiments. The Au colloid was synthesized according to the Frens' method with slight modifications [21,22]. All glassware used in the synthesis was thoroughly cleaned in aqua regia (HCl:HNO_3, 3:1), rinsed with Milli-Q water and oven dried prior to use. The stock solutions of 1% $HAuCl_4$ and 38.8 mM sodium citrate were prepared in advance. Other solutions were made freshly as needed. During preparation of various sizes and varying heterodispersity Au colloids, 100 mL of 0.01% $HAuCl_4$ was brought to a rolling boil with vigorous stirring in a 500 mL three-neck round bottom flask with a condenser. Various amounts: 1.5, 1, 0.75, 0.5 and 0.3 mL of 38.8 mM sodium citrate and with varying injection speed was added to the vortex of the solution, respectively, to produce gold colloids with various nanoparticle sizes, size distributions and particle shape. Boiling was continued for about 10 min before the heating mantle was removed with vigorous stirring until the solution reached room temperature.

2.2. Instrumentation and measurements

Transmission electron microscopy (TEM) was performed using a Zeiss EM910 electron microscope at a 100 kV acceleration voltage and acquiring images at a magnification of 31 500×. 10 μl of each gold colloidal solution as prepared were applied to a 200-mesh Formvar/carbon coated nickel grid (Ted Pella, Inc.) and allow to settle for 5 min before the liquid drop was carefully removed with a piece of filter paper. The samples were left to dry out completely before the measurements. The TEM images were analysed using ImageJ software [23] by fitting an ellipse to each particle projection outline. The following parameters were extracted and analysed: number of particles, their projection area, perimeter, major and minor axis and aspect ratio. Some image areas were showing strongly agglomerated nanoparticles and an automatic fitting procedure using watershed processing (division of agglomerates into individual particles) produced highly inaccurate results. Such areas were manually removed and not included in the data analysis.

The extinction of the gold colloidal solutions was measured as synthesized using a Cary 50 spectrometer (Varian, Inc.). The scattering of the colloidal gold nanoparticles and silica solution (Ludox) was examined over a range of wavelengths using an Eclipse spectrofluorometer (Varian, Inc.) equipped in manual polarisers and in a right angle excitation–emission geometry. The spectrofluorometer was carefully calibrated and corrected for instrumental and geometrical factors (G-factor) in the entire wavelength range from 350 nm to 800 nm using silica solution (Ludox). G is an instrumental factor which corrects for the polarization bias in the detection system and is given by

$$G = I_{HV}/I_{HH}$$

where I_{HV} is the fluorescence intensity when the excitation polarizer is kept horizontal and the emission polarizer vertical and I_{HH} is the fluorescence intensity when both polarizers are kept horizontal.

The intensities of the scattered light were measured under parallel (I_{VV}) and orthogonal (I_{VH}) polarizer conditions and the experimental scattering anisotropy (R_e) was calculated according to Eq. (1)

$$R_e = \frac{I_{VV} - G * I_{VH}}{I_{VV} + 2G * I_{VH}} \quad (1)$$

The gold colloid particle dimensions data were used to calculate the expected anisotropy according to the theoretical model developed in our previous study [15,19] and compared with experimental data.

The potential of the gold nanoparticles for imaging by using depolarized scattering was demonstrated by placing a 0.5 cm square cuvette containing the solution of gold nanoparticles inside a larger 1 cm × 2 cm cuvette containing a Ludox solution. The concentrations were adjusted to ensure that the scattering intensity from both solutions was comparable. A vertically polarized 655 nm diode laser beam was directed through both cuvettes, and light scattered from the gold and Ludox particles was observed at a 90° angle through a polarization analyser parallel and orthogonal to the polarization of the incident light.

3. Results and discussion

The average nanoparticle size of a range of colloidal gold nanoparticles synthesized here measured by TEM was between 20 and 147 nm, and similar to the values demonstrated by Frens [21]. This size was controlled by varying the ratio of reducing/stabilizing agents (the trisodium citrate-to-gold ratio). In this work we concentrated only on presenting results for the selected four gold colloidal solutions, which have shown the weakest and the strongest light depolarization effect. For these solutions the large numbers of TEM images (68 in total) were collected to provide reliable statistics of the size and shape distributions. Representative TEM images for two significantly different colloidal gold nanoparticles are presented in Fig. 1 and the results of size distribution analysis for these colloids are presented in Fig. 2.

Both colloids are not monodisperse and their estimated averaged particle size and average aspect ratios (Fig. 2) are: 16 nm and 1.19 for colloid (a) and 80 nm and 1.59 for colloid (b), respectively. Most of the particles have a spherical shape, but especially for the colloid with larger average particle size a significant number of particles have an aspect ratio of more than 2. Since light scattering efficiency is proportional to the square of the volume of the particle [6], even a small fraction of particles with the aspect ratio above 2 can contribute significantly to depolarized light scattering. From the analysis of the TEM images of gold particles for two other colloids (data not presented here) the estimated average size and aspect ratio were: 130 nm and 1.21 (956 particles counted) for the third and 100 nm and 1.53 (329 particles counted) for the fourth colloid, respectively.

Furthermore we studied absorption/ scattering properties of these two groups of gold nanoparticles with predominantly spherical (up to 1.21 average aspect ratio) and with significant contribution of non-spherical (above 1.5 average aspect ratio) particles. Each gold colloidal solution before measurements was diluted to the concentration yielding a comparable optical density of ~0.2 and the obtained normalized extinction spectra are presented in Fig. 3.

The shape of the extinction spectrum for colloidal gold nanoparticles with average particle sizes of 16 and 130 nm, presented in Fig. 3A and 3B is in good agreement with theoretical extinction spectra based on the Mie theory for spherical particles for these average sizes. It supports our previous observation based on the analysis of a large number of TEM images that particles from these colloids are predominantly spherical. In contrast, the shape of the extinction spectrum measured experimentally for colloidal gold nanoparticles with average sizes of 100 nm and 80 nm presented in Fig. 3C and 3D is significantly different than that calculated theoretically for spherical particles. We observe a noticeable long