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NANOMETROLOGY

DETERMINATION OF THE GEOMETRIC PARAMETERS OF GOLD NANORODS BY PARTIALLY DEPOLARIZED DYNAMIC LIGHT SCATTERING AND ABSORPTION SPECTROPHOTOMETRY

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UDC 535.36

The method of partially depolarized dynamic light scattering is applied to measurements of gold nanorods dimensions in liquids using translational and rotational diffusion coefficients. Compared with the known methods, the new method makes it possible to lower the power of the existing laser radiation and to increase the data set for solving the inverse problem. Nanorod lengths calculated from the diffusion coefficients are in agreement with TEM data. Aspect ratios calculated from extinction spectra in the plasmon resonance domain are in better agreement with TEM.

Keywords: *partially depolarized dynamic light scattering, gold nanorods, aspect ratio, suspension, translational and rotational diffusion coefficients.*

Non-spherical nanoparticles, such as nanorods, nanowire, nanotubes, and nanofibers, are widely used in production of composite materials in various spheres – biomedicine, nanoenergetics, and nanoelectronics. Gold nanorods are used in medicine as nanosensors, probes for cell visualization, and radiation receptors for laser photodynamic therapy. Gold nanorods gained popularity in biosensorics and genomics, as well as in modern nanotechnology, in particular, due to the possibility of tuning the plasmon resonance (PR) in a wide range of wavelengths [1, 2]. Controlled etching proposed by the authors of [2] makes precise tuning of PR and variation of the aspect ratio (length divided by diameter) possible.

Shape and dimensions are the main characteristics influencing the effectiveness of using non-spherical particles for other purposes. The specified characteristics demand priority control at the steps of particle synthesis, implementation into a biosystem, and addition to the material. First of all, control of such geometrical parameters as length, diameter, and aspect ratio is required. Aspect ratio determines the ability of the particles to penetrate biological barriers, which is critical in biomedical applications of the nanoparticles, and in predicting toxicity.

There are various methods for investigating dimensions and shapes of non-spherical nanoparticles: transmission electron microscopy, atomic force microscopy, physicochemical methods. For routine measurements (production control in the manufacturing process, and for compliance with the nanosafety requirements), physicochemical methods, especially optical, have a number of advantages over microscopy methods: possibility of investigating nanoparticle parameters *in situ* in liquid, a large representative sample, relatively inexpensive equipment, and significantly shorter sample analysis times.

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Dynamic light scattering (DLS) is one of the most effective optical methods for measuring nanoparticle dimensions *in situ* in liquids [3]. For non-spherical particles, a modified technique is used – depolarized DLS [4–9]. The DLS method is based on the effect of depolarization of linearly-polarized laser radiation upon scattering by non-spherical particles. The decay rates of scattered light intensity are measured at two polarizations, one of which (co-polarized – *VV* geometry) coincides with the polarization of the radiation exciting scattering, and the other (cross-polarized – *VH* geometry) is perpendicular to it.

These components can be isolated by a polarization analyzer, for example, a Glan–Thompson prism, a scattered light collection system. To determine the decay rates, auto-correlation functions (ACF) of the intensity measured for each of the components of scattered radiation can be used.

For non-spherical systems, such as cylinders, there are two relaxation modes, i.e., two characteristic decay rates that depend on the translational D_t and rotational D_r diffusion coefficients of the nanoparticles. Thus, by determining the values of the coefficients and working backwards (solving the inverse problem) it is possible to determine the geometrical parameters of the nanoparticles.

From the values of D_t and D_r, it is possible to find the length L and the diameter d of the particles using the diffusion model for particles of the given shape. The method of depolarized DLS is used to measure geometrical parameters of gold nanorods [4–6] and carbon nanotubes (CNT) – both single-walled and multi-walled [7–9].

Partially depolarized DLS technique. The main limitation of the considered method is the necessity to measure very weak optical signals when detecting the *VH* component of scattered radiation. To eliminate the need to detect this component, the method of partially depolarized DLS has been developed by the authors of the present work [10–13]. The essence of the technique is in measuring scattered light intensity at various positions of the polarization analyzer that are intermediate between the *VH* and the *VV* geometries, i.e., for various ratios of the polarized and depolarized components [10]. From the theory of the technique described in the specified publications, it is possible to obtain a formula for the ACF of the 1st order (i.e., from the amplitude field of the light wave) for an arbitrary angle φ of rotation of the polarization analyzer:

$$g_1(\varphi, \tau) = A(\varphi)\exp(-\Gamma_t\tau) + [1 - A(\varphi)]\exp(-\Gamma_r\tau), \quad (1)$$

where

$$A(\varphi) = A(0)/[1 + A(0)\cot^2(\varphi)]; \quad (2)$$

τ is the delay time (ACF argument); and Γ_t, Γ_r are the decay rates of the rotational and translational radiation components, respectively, which are related to the coefficients D_t and D_r in the following way:

$$\Gamma_t = D_t q^2; \quad \Gamma_r = D_t q^2 + 6D_r. \quad (3)$$

Here, $q = 4\pi n\sin(\theta/2)/\lambda_0$ is the wave vector of scattered radiation; n is the refraction coefficient of the liquid; λ_0 is wavelength of laser radiation in a vacuum.

The values of Γ_t and Γ_r are found by solving the inverse problem, they are selected for (1) and (2) taking into account (3) with the aid of one of the optimization algorithms implementing the non-linear damped least-squares (DLS) method (the Levenberg–Marquardt algorithm). For example, one can use an algorithm based on the function *lsqcurvefit* included in the Curve Fitting Toolbox in Matlab software. This algorithm ensures selection of such values of Γ_t and Γ_r for which the ACF (see (1), (2)) exhibits the best fit to the experimental measurements. Based on the found decay rates, the coefficients D_t and D_r are calculated using (3). The coefficient D_r is calculated for each scattering angle as $(\Gamma_r - \Gamma_t)/6$, then the obtained values are averaged. The coefficient D_t in accordance with (1) is determined as the slope of the linear function $\Gamma_t(q^2)$ calculated using the DLS method, wherein the values of Γ_t obtained for all the scattering angles are used.

In [11], the method of partially depolarized DLS is used to measure the geometrical parameters of multiwalled NT. The purpose of the present work is to investigate the applicability of this method to measuring the geometrical parameters of gold nanorods. Special attention is devoted to selecting an adequate model for the coefficients D_t and D_r. The obtained results are compared with transmission electron microscopy and extinction spectra data.

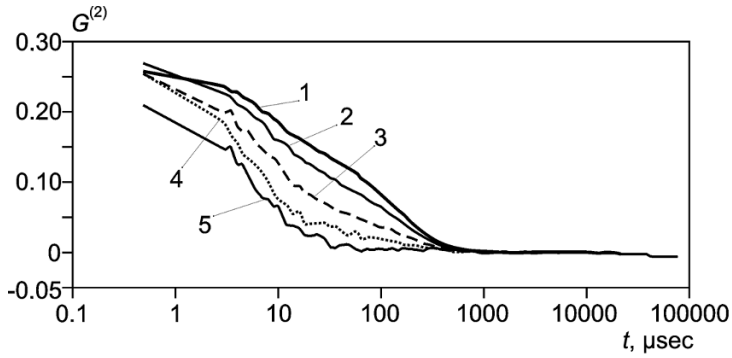

Fig. 1. Auto-correlation functions of gold nanorods GR-2 obtained at Glan–Thompson prism rotation angles of 0, 45, 60, 70, 80° (curves *1–5*); scattering angle 90°.

TABLE 1. Translational D_t and Rotational D_r Diffusion Coefficients Determined by the Partially Depolarized DLS Method

Sample	D_t, μm^2·sec^{-1}	D_r, sec^{-1}
GR-1	15.6	38180
GR-2	8.9	63000
GR-3	9.2	65423

Experimental part. To measure the partially depolarized DLS, a nanoparticle size analyzer ARN-2 developed in VNIIOFI was used. The radiation source was a helium-neon laser (λ_0 = 632.8 nm) with a linearly-polarized radiation (degree of polarization 500:1) and power of 12 mW. An optical diagram of the device is shown in [11–13].

The polarization analyzer (a Glan–Thompson prism) was mounted in the intermediate positions corresponding to various angles $0° < \varphi < 90°$ between the linear polarization directions of the incident and the collected scattered beams. Measurements were conducted for the following scattering angles θ = 75, 90, 105°. The investigated sample was placed in a cylindrical cuvette. For each value of θ, an ACF was found for the angles φ = 0, 45, 60, 70, 80°. Based on the measured intensity of the scattered radiation as a function of time, an ACF of the 2nd order $G^{(2)}(\tau)$ was found using a software correlator, i.e., an ACF in terms of intensity. To transition to an ACF of the 1st order, the Seigert ratio was used:

$$G^{(2)}(\tau) = B\{1 + \beta[g^{(1)}(\tau)]^2\}, \quad (4)$$

where $B = \lim_{\tau\to\infty} G^{(2)}(\tau)$ is the baseline of the ACF; β is the instrumental factor that depends on the optical system of the used device (the intercept of the ACF); and $g^{(1)}(\tau)$ are normalized ACF of the 1st order.

Using $g^{(1)}(\tau)$, the inverse problem of identifying the coefficients D_t and D_r was solved according to the Levenberg–Marquardt algorithm.

The extinction spectra were measured using the spectrophotometer-fluorometer SFF-2 Fluoran (developed by VNIIOFI) in two-beam mode relative to the background with a 1 nm scanning step and spectral bandwidth of 5 nm.

The dimensions of the gold nanorods GR-1, GR-2 were determined using a transmission electron microscope (TEM) Libra120 (CarlZeiss, a VNIIOFI product) with the following measurement parameters: accelerating voltage 120 kV, cathode current 3 A, magnification 25000× and 50000×. To determine the dimensions of GR-3, the FEI Tecnai F20 G2 S-TWIN TEM (in Skolkovo Technopark) was used. Imaging was performed using a 200 keV accelerating voltage.

Aqueous suspensions of gold nanorods from the Alfa Asear company (Great Britain) were used to prepare the samples.

TABLE 2. Wavelengths Corresponding to the Plasmon Resonance Peaks, and the Aspect Ratios Calculated Using (5)

Sample	λ_{max}, nm	Aspect ratio
GR-1	694	2.7
GR-2	788	3.6
GR-3	838	4.1

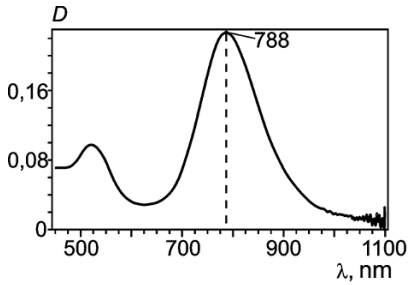

Fig. 2. Extinction spectrum of the GR-2 sample of gold nanorods; plasmon resonance peak at 788 nm; *D* is optical density.

Sample GR-1. Aqueous suspension of gold nanorods No. 46359, batch J18X001. Length 63–73 nm, diameter 19–25 nm, nanorods are positively charged, PR peak at 700 nm. The starting colloid solution was diluted 5-fold with deionized water with the addition of 0.1% aqueous solution of detergent – a stabilized cetyltrimethylammonium bromide (CTAB).

Sample GR-2. Aqueous suspension of gold nanorods No. 46810, batch J18X003. Length 46–56 nm, diameter 9–15 nm, gold nanorods are positively charged, PR peak at 800 nm. The starting colloid solution was diluted 5-fold with deionized water with the addition of 0.1% CTAB.

Sample GR-3. Aqueous suspension of gold nanorods No. 46972, batch L05X008. Length 55–65 nm, diameter 9 to 15 nm, gold nanorods are negatively charged, PR peak at 850 nm. The starting colloid solution was not diluted.

Experiment results and discussion. Figure 1 shows ACF of the 2nd order for the GR-2 sample obtained by the partially depolarized DLS method after subtracting the baseline at Glan–Thompson prism rotation angles of 0–80°. From these ACF, with the aid of the described algorithm the coefficients D_t and D_r (Table 1) were calculated. The extinction spectrum of the GR-2 sample is shown in Fig. 2.

All the extinction spectra have peaks that are due to surface PR. The aspect ratio of the nanorods can be determined from the position of peaks along the wavelengths axis, for example, using the formula from [14]:

$$P = 0.0098\lambda_{max} - 4.12, \quad (5)$$

where λ_{max} is the wavelength of the PR peak.

Experimental values of the wavelengths corresponding to PR peaks and the aspect ratios calculated using (5) are given in Table 2.

Images of the GR-2 gold nanorods obtained using TEM are shown in Fig. 3. Image processing was performed using image processing and analysis software ImageJ that made it possible to determine the average dimensions of the gold nanorods (Table 3).

To determine *L*, *d* of the nanoparticles using the partially depolarized DLS method, it is necessary to use the model for diffusion coefficients of particles suspended in a liquid. Several such models for cylindrical particles are known. In practicality, the formulas for the coefficients D_t and D_r in all the models can be reduced to the following [15]:

TABLE 3. Geometrical Parameters of Gold Nanorods Determined by Various Experimental Methods

Sample	Length, nm		Diameter, nm		
	DLS	TEM	DLS	DLS, PR	TEM
GR-1	60.7	57.5 ± 1.2	8.6	22.6	22.4 ± 0.8
GR-2	35.7	40.7 ± 1.5	18.5	9.9	16.1 ± 1.0
GR-3	35.6	44.4 ± 1.8	18.1	8.7	11.6 ± 0.4

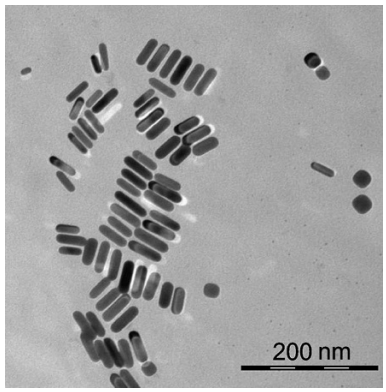

Fig. 3. Image of the GR-2 sample obtained by TEM.

$$D_t = kT[\ln P + C_t(P)]/(3\pi\eta L), \quad (6)$$

$$D_r = 3kT[\ln P + C_r(P)]/(\pi\eta L^3), \quad (7)$$

where k is the Boltzmann constant; T is the absolute temperature; η is dynamic viscosity of the solvent; $P = L/d$ is the aspect ratio; $C_t(P)$, $C_r(P)$ are the correlation functions that take into account the effect of the ends of cylindrical samples on translational and rotational diffusion, respectively (referred to as the "end effect terms" in [15,16]). In [15,16], for $C_t(T)$, $C_r(T)$ various expressions in the form of quadratic trinominals of $1/P$ are given. There are several theoretical models, each of which offers coefficient values for these trinominals [16]. Analysis of the models and equations (6), (7) shows that the length calculated using the coefficients D_t, D_r is less dependent on model inaccuracy and experimental values of the coefficients than on the diameter and the aspect ratio. Even for the nanoparticles with an ideal cylindrical shape the models are approximate. The shape of real gold nanorods as a rule is not cylindrical. The ends of such rods are not flat surfaces but hemispheres, which is confirmed by the electron microscopy data, including the results shown in Fig. 3. As a result, in this work the proposed theoretical dependences for the correlation function were not considered, but instead an earlier Kirkwood model was used, which can be obtained by substituting $C_r(P) = C_t(P) = 0$ into (6) and (7). Note that precisely this model was used to estimate the geometrical parameters of MWNT from D_t, D_r coefficients in [9]. The length and diameter of gold nanorods calculated using the TEM and partially depolarized DLS methods are given in Table 3. Rod diameters were determined using the equation $d_{DLS+TEM} = L_{DLS}/P_{PR}$, where L_{DLS} is the length calculated from the coefficients D_t and D_r, and P_{PR} is the aspect ratio estimated from the PR peak location in experimental extinction spectra.

From the data in Table 3, it follows that rod lengths determined using the DLS and TEM methods correlate better than diameters. This confirms the analysis of Eqs. (6) and (7) for the coefficients D_t, D_r.

Conclusion. By the partially depolarized DLS and absorption spectrometry methods, the length and diameter of gold nanoparticles were calculated. The length calculated from the diffusion coefficients is less affected by inaccuracies of the

l experimental values of the coefficients, than the diameter and the aspect ratio. Differences in the values of the rod lengths calculated from the experimentally determined diffusion coefficients using the simple model not taking into account the effects on the ends of the rods for the investigated samples reach 6-20%. The aspect ratios calculated from the peak location wavelengths of plasmon resonance are more accurate.

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