Precise measurement of gold nanorods by using depolarized dynamic light scattering apparatus*

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A precise and noninvasive method for the size and shape measurement of gold nanorods (GNRs) has been proposed based on depolarized dynamic light scattering (DDLS). A home-made DDLS apparatus has been established. By applying depolarized optical path with precise alignment method, the signal-to-noise ratio (SNR) of this apparatus is highly improved. GNRs with three different diameter and length has been precisely measured by using DDLS method as well as scanning electron microscopy (SEM). The thickness of adsorption layer of cetyltrimethylammonium bromide (CTAB) in solution has been taken into consideration. Results show that size measurement of GNRs by using DDLS method agrees very well with that by using SEM. In addition, it is shown that the extinction spectroscopy strongly limited the application of DDLS method by affecting the effective scattering light intensity. Proper laser wavelength should be chosen before the application of this method.

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Metal and semiconductor materials have become the main target for the development of new functional nanomaterials due to their interesting photoelectric properties on the nanoscale. Potential application of nanorods include new surface coating[1], superhydrophobic coating[2], electrical nanowires[3], and optical metamaterials for long-range imaging with near-field resolution[4]. Gold nanorod (GNR) materials have attracted considerable attention because of their unique properties and latent applications as optical probes. GNRs can strongly absorb or scatter light at specific surface proton resonance wavelengths, exhibiting good optical detectability for bioimaging, biomolecular detection, and photothermal therapy[5-8].

The precise characterization of the physical and chemical behaviors of GNRs in situ solution is crucial for accessing their performance in almost the entirety of the previously mentioned applications. The technique of fluorescence polarization is commonly used for nanoparticle characterization. Fu Feng et al combined radiation pattern with polarimetry analyses and studied the dipolar nature of single objects for a detailed understanding of fluorescent nanostructures[9,10]. Besides, direct imaging techniques are now most widely used method like scanning electron microscopy (SEM) and transmission electron microscopy (TEM). However, due to effect of samples conditions, the results obtained by these methods do not really reveal the situ morphology of GNRs in solution. Moreover, microscopy method requires huge amount of time for characterization and evaluation. Recent years, depolarized dynamic light scattering (DDLS) has been a feasible tool for characterizing non-spherical particles. The method has been applied to optically anisotropic particle such as the tobacco mosaic virus, carbon nanotubes, Ag nanoplatelets and GNRs[11-16]. Since the technique independently provides the rotational diffusion and translational diffusion coefficients of the dispersed particles, the shape and the size of the particles can be estimated. Shetty et al[12] determined the size of single-walled carbon nanotubes based on the DDLS measurement. Part of the obtained values weren't completely consistent with those obtained by the AFM observations and their method is only suitable for the measurement of single-walled carbon nanotubes with a length greater than 300 nm. M Zimbone et al[13] used ultraviolet-visible spectroscopy and DDLS technique to research the morphology and stability of triangular silver nanoparticles and did not consider the effect of the active agent on the sample size measurement. Reece and Gary[14] presented a new analysis of DDLS data to characterize GNRs and diffusion coefficient. However, they only used diffusion coefficient rather than size calculation to evaluate

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DDLS results. Larger errors can be introduced after the calculation of the length and diameters of the sample. In addition, most reported DDLS researches were carried out on the commercial apparatus, many technical details cannot be evaluated and the measurement results can only be received.

In the present work, a depolarized dynamic light scattering apparatus is proposed and established. By adjusting the polarization light path and testing the light intensity signal of the spherical particles and the solvent, the signal-to-noise ratio (SNR) of the particles and the polarization quality of the scattering light are guaranteed. Translational and rotational diffusions of several kinds of GNRs in aqueous solutions are characterized by the DDLS apparatus, and the length and diameter of the GNRs were calculated based on the model proposed by Tirado and Garcia de la Torre[17,18]. Bare sizes of the tested samples have been verified by using scanning electron microscopy, and compared with DDLS results. Thickness of cetyltrimethylammonium bromide (CTAB) is also taken into consideration. The influence of sample dispersity as well as light extinction on the measurement of DDLS has been studied.

Fig.1 shows the schematic diagram of DDLS system. In the present system, a 632.8 nm He-Ne laser (21 mW, Thorlabs) beam illuminates the sample after passing through a series of pinholes, a polarizer, a lens and a slit. Pinholes and the slit are used to minimize stray light so that the SNR can be highly improved. Here in this system, Glan Thompson prism (GT1) is used and the incident mixed polarized laser is modulated into vertical polarization state, raising the polarization purity to a nominal ratio of 100 000:1. The laser is then focused by the lens to the center of the sample to limit the scale of scatterer and to increase radiance. As the scatterer is illuminated, an avalanche photodiode detector (APD, Hamamatsu Photonics) arranged by the side of the sample start to receive scattering light from 90° and convert them into pulse signals that can be further processed into auto-correlation functions. A second Glan-Thompson prism (GT2) is used to choose either vertically polarized (VV) or horizontally depolarized (VH) scattered light. The coherence of scattering light is guaranteed by connecting a lens and a monomode optical fiber in front of the APD. A charge coupled device (CCD) camera is used to ensure vertical polarization state of incident light according to the captured photograph. Temperature is maintained at (20.00±0.02) °C by using water cooling system and monitored by using a high resolution platinum resistance thermometer. Method for the adjusting of the incident light into vertical polarization state is shown in Fig.1(a) and (b). As shown in Fig.1(a), sphere polystyrene latex (PSL) was put inside the sample tube. When the polarization direction of the incident laser is not strictly vertical, CCD above the sample tube would capture scattering light from the center of the sample tube due to particle scattering. After introducing and adjusting GT1, vertical polarization state could be assured by minimizing the scattering light at the center, as shown in Fig.1(b). Similarly, at the scattering of 90°, the scattering intensity could be monitored by using an APD. By adjusting GT2, VV scattering state could be achieved by maximize the received light intensity, while rotating GT2 by 90°, little light signals can be detected.

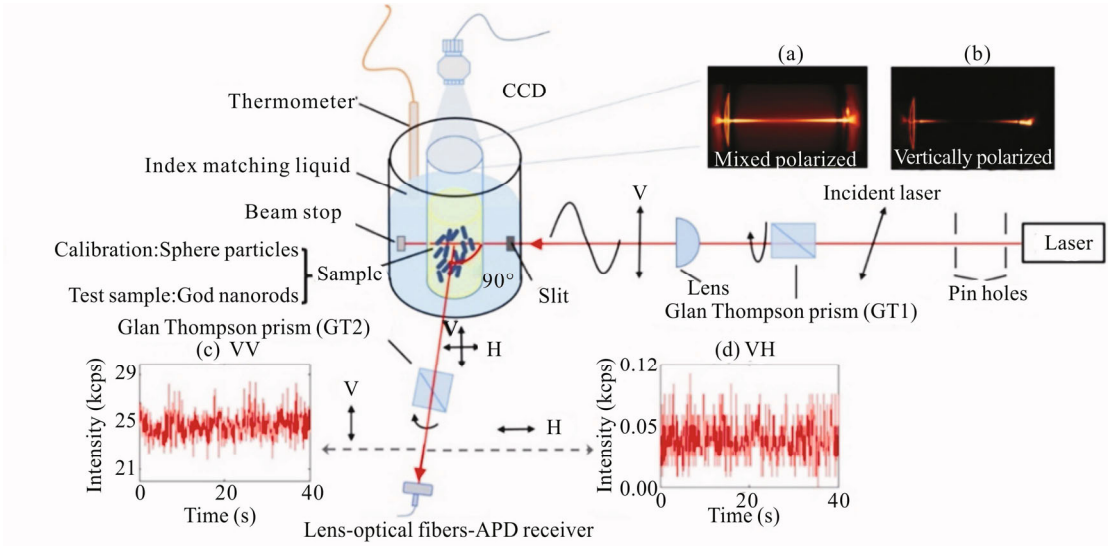


Fig.1 Schematic diagram of DDLS and the adjustment method of polarization state for (a) mixed polarized incident light, (b) vertically polarized incident light, (c) VV scattering light, and (d) VH scattering light

By using the above experimental set-up, VV and VH electric-field time autocorrelation function (EACF) can be obtained from the scattered light, and then analyzed by DDLS method to calculate the diffusion coefficient. The standard VV and VH EACF are as follows[19,20]

$$g_{\mathrm{VV}}(\tau) = S_0(qL)\mathrm{e}^{-q^2D_t\tau} + S_1(qL)\mathrm{e}^{-(q^2D_t+6D_r)\tau} + \ldots, \quad (1)$$

$$g_{\mathrm{VH}}(\tau) = \mathrm{e}^{-(q^2D_t+6D_r)\tau}, \quad (2)$$

where τ is the delay time, $S_0(qL)$ and $S_1(qL)$ are the scattering amplitudes, q is the length of the scattering vector, L is the particle length, and D_t and D_r are the translational and rotational diffusion coefficients of the particle. Here q is given by

$$q = \frac{4\pi n}{\lambda}\sin(\frac{\theta}{2}), \quad (3)$$

where n is the real part of the refractive index of the solvent, λ is the incident light wavelength, and θ is the scattering angle. Research shows that in the regime of $qL<5$ and $5<qL<10$, $g_{VV}(\tau)$ can be treated as only containing the first term and the first two term, respectively.

After D_t and D_r are calculated by fitting the EACF, the length (L) and diameter (D) of nanorods are solved with the inversion model of diffusion coefficient and size of nanorods. Tirado and Garcia de la Torre (TG) model is suggested to be applied to nanorods with an aspect ratio $m=L/D$ of $2<m<30$[17,18]. TG model may be summarized in the following equation.

$$D_t = \frac{kT}{3\pi\eta L}(\ln(\frac{L}{D}) + 0.312 + 0.565\frac{D}{L} - 0.1\frac{D^2}{L^2}) \quad , \quad (4)$$

$$D_r = \frac{3kT}{3\pi\eta L^3}(\ln(\frac{L}{D}) - 0.662 + 0.917\frac{D}{L} - 0.05\frac{D^2}{L^2}), \quad (5)$$

where k is Boltzmann's constant, T is the absolute temperature, and η is the solvent viscosity.

Four different sized GNR samples were supplied by Beijing Zhongkeleiming Technology Co. Ltd with nominal lengths × diameters of 40 nm×16 nm, 78 nm×13 nm, 80 nm ×25 nm and 300 nm×20 nm, respectively. All the samples were observed by using SEM again so that the size could be re-confirmed. The GNR suspensions were diluted 1-2-fold with deionized water containing CTAB as stabilizing agent. The solvent was filtered through 0.22 μm PTFE syringe filters before dilution. Each DDLS test was carried out for 60 s—120 s with the minimum sampling time of 1 μs, according to the scattering intensity. For some special case where the scattering light intensity was very low, test duration was extended up to 180 s. Each test was repeated at least 6 times to ensure the repeatability and reliability of the results.

Tab.1 shows the scattering light intensity of GNRs and deionized water. It can be seen that the scattering light intensity of GNRs with the size of 80 nm×25 nm is much greater than that of GNRs sized of 78 nm×13 nm and 300 nm×20 nm. Except for the reason of particle number concentration, the effect of light extinction may be another main reason for the difference of scattering intensities. For the case of GNRs sized of 40 nm×16 nm, almost no effective scattering light can be recorded for DDLS measurement. One alternative method for further measurement might be changing laser wavelength.

The background scattering intensity of deionized water has also been measured and shown Tab.1. It can be seen that the scattering light intensity of deionized water is much weaker than that of GNRs, in both VV and VH mode. So, the original SNR can be satisfied for DDLS measurement. Additionally, it is obvious that the ratios of VV and VH light intensity of different GNR samples are different, which reflects the nature of size and shape of different GNR samples so that DDLS method can be applied.

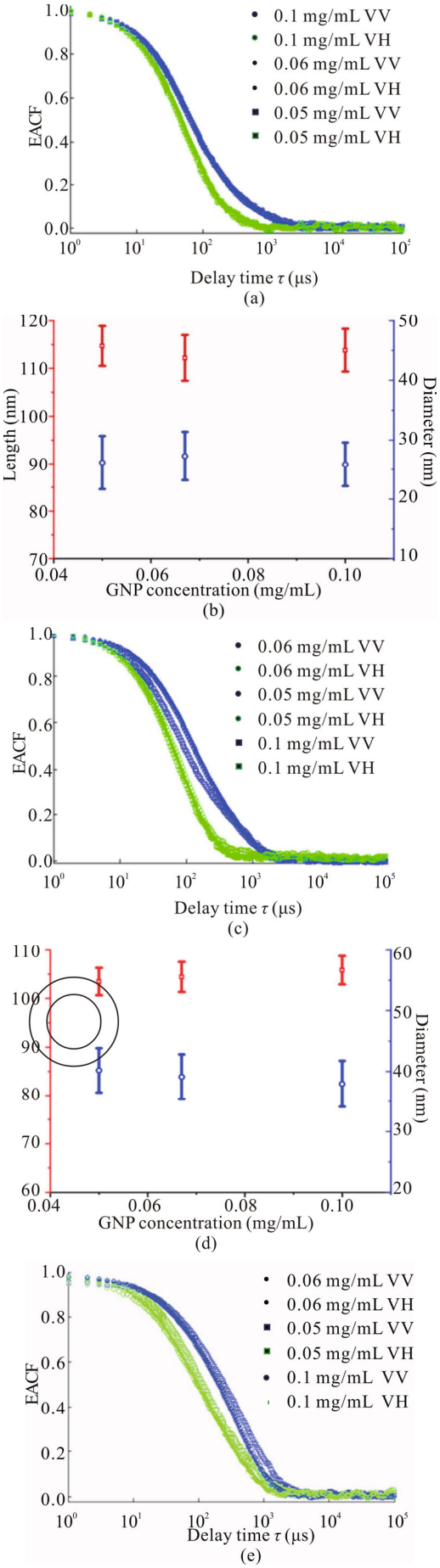
Tab.1 Average scattering light intensity of different GNRs and deionized water, where the mixed polarized scattering light is the scattering light received without GT2

Nominal size (nm)	Average scattering light intensity (kcps)		
	Mixed polarized	Vertically polarized	Horizontally depolarized
40×16	0.82	0.55	0.16
78×13	220	120	24
80×25	854	491	80
300×20	785	582	65
Deionized water	0.33	0.29	0.035

Fig.2 shows the normalized VV and VH EACF of three kinds of GNRs at the scattering angle of 90° and the corresponding size calculation based on TG model. Three different sample concentration has been tested within the range of 0.05—0.1 mg/mL. Generally speaking, for all the tested samples, the decay of VH correlation function is faster than that of the corresponding VV function. And within the range of the three sample concentrations, DDLS measurements of each sample have good agreement.

For GNRs sized of 78 nm×13 nm shown in Fig.2(a) and (b), the repeatability of EACF as well as the corresponding size calculation results is quite satisfied. The deviation of average size of L and D at different sample concentration is less than 4.7 nm, indicating the uniformity of particle size distribution and the stability of the present method. Similarly, results of GNRs sized of 80 nm×25 nm also show satisfied repeatability. However, unlike the above GNRs, the larger GNR sample sized of 300 nm×20 nm shows visible deviation in the EACFs, as shown in Fig.2(e). And the measurement results can be more sensitive to the changing of sample concentration[19].

In order to further explain the nature of the above differences of DDLS results, all the GNR samples were characterized by using SEM so that the nominal dimensions claimed by the supplier could be re-confirmed. Fig.3 shows the SEM micrographs of the GNR samples sized of 78 nm×13 nm, 80 nm×25 nm and 300 nm×20 nm, respectively. More than 500 particles had been measured to obtain a statistical length and diameter for each GNR sample. And the results are compared with the nominal dimension provided by the supplier as shown in Tab.1. There are large deviations between SEM measurement results and the nominal value. So in the following analysis, SEM measurement results are used as the true reference value of the GNR samples.



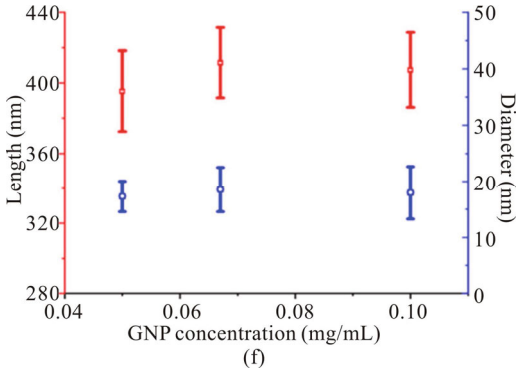


Fig.2 Autocorrelation function and size measurement of GNRs sample: (a,b) 78 nm×13 nm; (c,d) 80 nm×25 nm; (e,f) 300 nm×20 nm

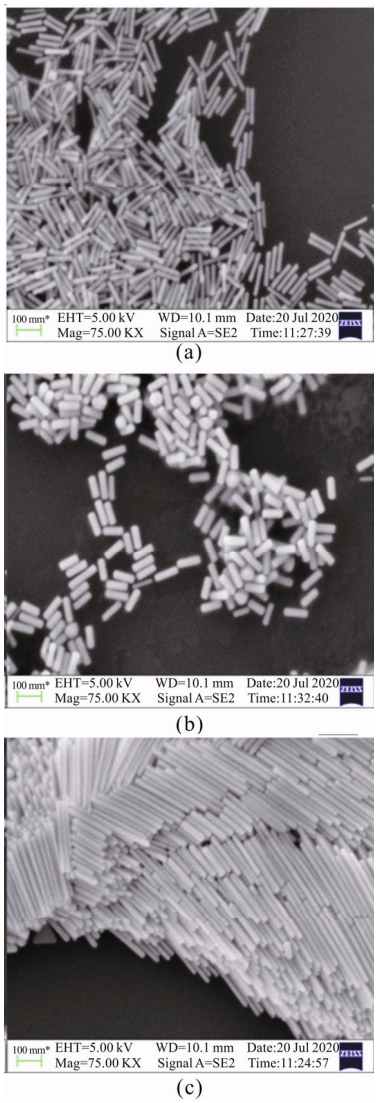


Fig.3 TEM micrographs of GNRs: (a) 78 nm×13 nm; (b) 80 nm×25 nm; (c) 300 nm×20 nm

Length and diameter measured by using DDLS were generally larger than that obtained from SEM graphs. Since GNRs in aqueous solution were usually surrounded by surfactants or capping agents to maintain a stable state, the thickness of adsorption layer should be

taken into consideration when applying DDLS method. In the present work, CTAB was used as the surfactant. Research shows that generally the thickness of CTAB layer around the particle (at the concentration of 1mM) is about 3 nm[21]. Based on the above theoretical study, the calculated length and diameter from DDLS measurement were corrected. Results before and after correction are summarized in Tab.2 and compared with that obtained from SEM measurements.

As is shown in Tab.2, for the two smaller GNRs samples sized of 100.1 nm×19.6 nm and 92.6 nm×31.2 nm, the average lengths and diameters obtained by DDLS before correction are basically 8% and 17% larger compared to the corresponding reference values determined by using SEM, respectively. There are mainly two factors needed to be taken into consideration: firstly, all the particle dimensions calculated by dynamic light scattering method are hydrodynamic ones; secondly, CTAB absorption layers will naturally increase the particle size. Despite this, size distributions obtained by DDLS are similar to that obtained by SEM measurements.

Tab.2 TEM measurement and DDLS measurement before and after correction

SEM measurement		CTAB layer (nm)	DDLS measurement		Corrected size	
L (nm)	*D* (nm)		*L* (nm)	*D* (nm)	*L* (nm)	*D* (nm)
100.1±6.5	19.6±4.7		113.2±4.5	26.7±4.2	107.2±4.5	20.7±4.2
92.6±6.4	31.2±3.5	3	104.9±2.9	38.9±3.7	98.9±2.9	32.9±3.7
366.2±34.9	15.6±4.9		408.3±21.7	19.7±3.8	402.3±21.7	14.1±3.8

For the GNRs sized of 366.2 nm×15.6 nm, the average length and diameter error obtained by DDLS before correction are about 12% and 15%. From the SEM measurement, one can easily tell that the dimension distribution of this sample is much larger than that of the other two samples. So the corresponding DDLS measurement also shows considerable dimension deviations. In addition, during the calculation of particle size from EACF, one tradeoff between the solution of D_t and D_r should be considered. If the calculated value of D_t has positive deviation, D_r will be smaller. And the corresponding consequence is that the calculated L is much larger while D is much smaller. This is especially true when the size distribution is wide.

From overall view in Tab.2, standard deviations of the calculated particle sizes from DDLS method are smaller than those by SEM measurements. This is because DDLS is a statistical method and the total number of particles counted by using DDLS method is much larger than that by using SEM. From Ref.[21], the thickness of CTAB absorption layer for the present solution system can be treated as 3 nm. After correction of the DDLS results by subtract the thickness of CTAB, final dimension deviations of GNRs measured by using DDLS method are within 8% compared to SEM results. Considering that all DLS measurements contains the nature of hydrodynamic effects, leading to approximately 7%—8% larger than the naked particle size[22], the present work gives satisfied measurement results.

With the increasing application demand of different nanorods materials, the requirement of fast, non-invasive and precise measurement has been growing. In the present work, based on a home-made depolarized dynamic light scattering apparatus with detailed precision analysis, an effective method for the characterization of GNRs is presented. Firstly, the calibration of each parameter of the apparatus and the validity of scattering signal acquisition have been studied thoroughly to assure measurement accuracy. Secondly, the effect of CTAB absorption layer on DDLS results has been considered. And the corrected length and diameter obtained from DDLS results show very good agreement with that from SEM measurements. In addition, proper laser wavelength needs to be pre-chosen before applying DDLS method by testing the extinction spectrum of the corresponding sample.

In the future, multiple laser wavelengths can be selected to further research the appropriate waveband for GNRs measurement and improve the accuracy of measurement.

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