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New methodology for anisotropic nanoparticles characterization by Depolarized Light Scattering measurements: length and diameter determination of rod-like nanoparticles

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Biography

Benoit Maxit has got PhD in Chemistry from the University of Bordeaux, France (2007); Clara Catros and Julien Le Mener are currently pursuing their PhD thesis at the University of Bordeaux, France. Florian Aubrit is a research engineer and has got PhD in Chemistry from the University of Bordeaux, France (2017); Olivier Sandre is research director and has PhD I Chemistry from the University of Paris 6, France (2000). David Jacob (CTO of Cordouan Technology) holds a PhD in laser Physics from the University of Rennes, France (1995), and. Sylvain Boj (CEO of Cordouan Technologies since 2015) holds a PhD on guided optics for telecommunication from the University of Paris Saclay, France (1995)

Abstract

Anisotropic nanoparticles (NPs) are often used for wafer polishing purpose in the semiconductor industry. Mastering the characterization of such particles is becoming essential while targeting micrometric electronic components. Moreover, the effective dimensions in the colloidal state as in their final usage (*i.e.* as a slurry at high concentration) can often be different from the dimensions of individual objects observed by electron microscopy in dilute conditions, because attractive interactions between rod-like particles favor bundle formation when they are not balanced by efficient (*e.g.* steric) repulsions^[1]. In this work, we present a new setup and introduce a method for characterization of such nanoparticles using a multi-angle polarization dynamic light scattering technique. This method is based on the measurement of the correlograms of scattered light intensity fluctuations both in the parallel and crossed polarizer configurations, and possibly concomitantly, from which the rotational and translational diffusion coefficients are extracted. By inverting the mathematical expressions of these coefficients, this approach allows the rapid determination of length and diameter of the anisotropic nanoparticles, enabling kinetic measurements. A comparison of experimental results obtained with this multi-angle polarization DLS or depolarized (DDLS) method to classical TEM images is discussed.

Introduction

Indirect optical methods like dynamic light scattering (DLS) measurement exhibit real benefits: limited sample preparation, ease of use, short experimental time, strong statistical relevance of the results, etc.

However, standard DLS analysis assumes that particles are spherical and thus can only provide information on an average hydrodynamic diameter *i.e.* the effective diameter of a sphere

having the same translational coefficient than the NPs. In the case of anisotropic nanoparticles, one can use a refined version of DLS named depolarized dynamic light Scattering (DDLS), which allows size and aspect ratio characterization of very small particles (down to few nanometers).^[2] In this communication, we demonstrate the measurement capabilities of a new and patented commercial DDLS system developed by Cordouan Technologies (named ThetisTM), by presenting experimental results on small gold nanorods. The DDLS results are compared with TEM ones to qualify the relevance and accuracy of the measurements by this non-invasive method.

Principle

The standard DLS system allows to determine the diameter of NPs by measuring their diffusion behavior (Brownian motion) by monitoring - at a given angle of observation θ - the fluctuations of the light scattered by the NP suspensions. More precisely, the autocorrelation function (ACF) calculated from the light intensity fluctuations by baseline subtraction and square root gives access to a translational diffusion coefficient (D_t), which is related to the hydrodynamic radius of the particle by the well-known Stokes-Einstein equation. In the case of anisotropic particles, their dynamics in the liquid are strongly influenced by their size and shape and include both translational and rotational random motions, which are described by a translational diffusion coefficient (D_t) and a rotational diffusion coefficient (D_r), respectively.)

$$D_r = \frac{3k_B T}{\pi \eta L^3} f\left(\frac{L}{w}\right) \quad \text{eq.1}$$

$$D_t = \frac{k_B T}{3\pi \eta L} f\left(\frac{L}{w}\right) \quad \text{eq.2}$$

Using the properties of linearly polarized light it becomes possible to measure D_t and D_r and then in a second step, to deduce, the size and aspect ratio of the anisotropic particles by rather complex numerical inversion of theoretical formulas.^[3]

At first, on the Thetis apparatus described here, a Vertically polarized incident laser beam is focused onto the sample to be analyzed. The scattered light is then collected at different scattering angles (θ) using a compact motorized goniometer. Use of high quality bi-prism polarization splitter enables splitting the scattered beam towards two distinct detection channels set with crossed polarizers allowing the vertical polarized (V-V) and horizontal depolarized (V-H) scattered light beams to be measured separately and possibly simultaneously. In the case of anisotropic particles, the V-V

and V-H detection channels lead to two different ACF, G_{VV} and G_{VH} , calculated from the respective scattered intensity fluctuations of $I_{VV}(t)$ and $I_{VH}(t)$.

Looking at the equations,^[5] one can notice that both ACFs contain the same “mixed relaxation mode” combining the translational decay rate Γ_t and the rotational decay rate Γ_r .

$$G_{VV}(\tau) = A_1 \exp^{-(\Gamma_t + \Gamma_r)\tau} + A_2 \exp^{-\Gamma_t \tau} + B \quad \text{eq.3}$$

$$G_{VH}(\tau) = A_3 \exp^{-(\Gamma_t + \Gamma_r)\tau} + B' \quad \text{eq.4}$$

$$\Gamma_t = D_t \times q^2 \quad \text{eq.5}$$

$$\Gamma_r = 6 \times D_r \quad \text{eq.6}$$

Thus, one method to determine D_t and D_r from DDLS measurements consists in plotting the two relaxation decay rates (the mixed mode and the pure translational mode) as a function of the square of the wave vector q^2 and to determine the slope of the linear fit, which theoretically should be the same for both curves.

The wave vector q is defined by:

$$q = \frac{4\pi n}{\lambda} \times \sin(\theta/2) \quad \text{eq. 7}$$

With n the liquid phase refractive index, λ the laser wavelength, and θ the detection/scattering angle.

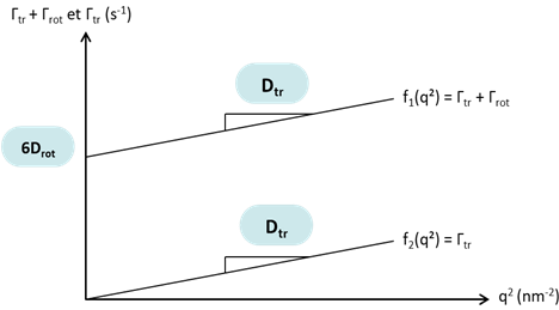


Figure 1

Experimental results

To evaluate Thetis instrument performances, three model suspensions of gold nanorods (NR) were used: Au-NR1 and Au-NR2 synthesized using protocol reported in literature,^[4-6] and Au-NR3 commercial sample from NanoComposix (Product n° GRCN980 – batch n° ASP0002). A first estimate of the size and aspect ratio of these NPs was achieved by the analysis of transmission electron microscopy (TEM) images.

Then the samples were analyzed by DDLS for comparison purpose. In each case, the measurements were performed by varying the scattering angle θ from 30° to 150°, acquiring both V-V and V-H data for each detector position.

Figure 2 shows the normalized ACFs measured on sample Au-NR1 at seven different scattering angles for V-V ACFs (Fig. 2a) and V-H ACFs (Fig. 2b) respectively.

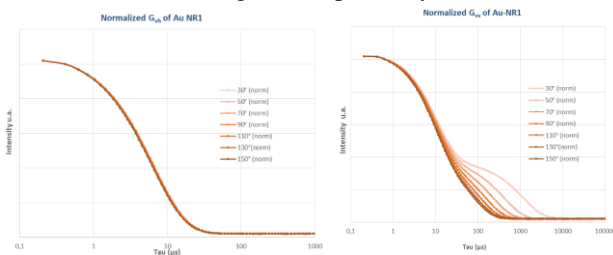
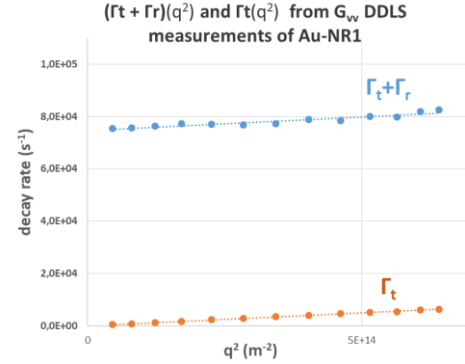


Figure 2a

Figure 2b

Using the SBL (Sparse Bayesian Learning) multimodal algorithm designed by Cordouan, the ProTheta[®] software extracts the different decay rate values from each ACFs and plots them as a function of q^2 .



Finally, using the model of De La Torre et al. for cylindrical shapes,^[5] the hydrodynamic dimensions of Au-NR1/2/3 were calculated by inversion of the measured diffusion coefficients:

		Au-NR1	Au-NR2	Au-NR3
TEM sizes *+ CTAB bilayer thickness	L (nm)	44.8 *	28.3 *	59.9
	w (nm)	26.2 *	14.5 *	10.1
	L/w	1.7(1)	1.9(5)	6.0(0)
DDLS measurement	D_t (nm ² ·s ⁻¹)	9.93 10 ⁶	1.89 10 ⁷	1.37 10 ⁷
	D_r (s ⁻¹)	1.24 10 ⁴	7.19 10 ⁴	1.37 10 ⁴
	L (nm)	46.0	28.3	70.7
	w (nm)	34.8	16.9	14.2
	L/w	1.32	1.70	4.97

The table above clearly shows that the particle size measurements obtained with the DDLS Thetis setup are consistent with those from the TEM analysis, especially for Au-NR2 nanorods for which both the length and the aspect ratio were accurately determined within the accuracy of the measurement.

Conclusion

These results highlight the relevance and robustness of the multi-angle DDLS method for characterizing the size and aspect ratio of anisotropic nanoparticles in suspension. The setup can also be used to discriminate in a simple way and without ambiguity anisotropic nanoparticles from a polymodal sample of isotropic particles.

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