The study of the geometric parameters and zeta potential of gold nanorods and nanostars based on light scattering methods

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ABSTRACT

Samples of liquid dispersions of gold nanorods and nanostars with different size and shape were synthesized and studied based on dynamic light scattering, polarization measurements, electrophoretic light scattering.

Keywords: nanoparticles, nanorods, nanostars, dynamic light scattering, depolarization, electrophoretic light scattering, zeta potential

1. INTRODUCTION

It is well-known that physical and chemical properties of nanomaterials depend on its size, shape, and composition. Due to various shape-dependent properties anisotropic nanoparticles are of considerable interest in many fields ranging from catalysis to medicine. For example, layer-by-layer coated nanoparticles are used on Ti implants for prevention of implant-associated infections [1] and for fabricate nanofibers containing nanoparticles as future implant materials [2].

Among other particles non-spherical gold nanoparticles, such as nanorods and nanostars, have drawn the most attention because their optical properties can be tuned in the visible and near-IR range, they do not photobleach or blink, and they are chemically inert and biocompatible. Gold nanoparticles could be synthesized using a relatively simple wet chemical methods with fine control over their sizes and size distribution. This features make gold nanorods and nanostars a promising object for biological and medical applications as optical contrast agents for dark field microscopy, two-photon luminescence diagnostic imaging, photothermal therapy of cancer cells, surface enhanced Raman scattering (SERS) etc.

In recent years there has been considerable progress in methods of measurement of the geometric and electrokinetic parameters of nanoparticles. Light scattering methods are the most convenient tool for the analysis of colloidal forms of nanoparticles because they are nondestructive and do not require expensive equipment. Light scattering methods allow rheological and morphological properties of liquid dispersion of nanoparticles to be estimated, which is an additional advantage of these methods.

Presently, devices using static and dynamic light scattering are commercially available. However, in these devices, the data on the size of particles is obtained under the assumption of particle sphericity. The measurement of geometric parameters of nonspherical particles is a more difficult problem that should be solved on the basis of additional research.

The zeta potential (electrokinetic potential) determines the nature and the extent of the interaction between particles and liquid medium. The zeta potential is an important indicator of the colloidal stability of liquid dispersions. The electrophoretic light scattering method is used to measure the zeta potential. However, in existing devices, the data on the zeta potential of particles is obtained under the assumption of particle sphericity.

In this work, the geometric parameters and zeta potential of gold nanorods and nanostars were experimentally investigated.

2. MATERIALS AND METHODS

Several samples of gold nanorods with aspect ratios ranging from 2 to 6 were synthesized by the method described in the literature [3] (fig. 1, a). In addition several samples of gold nanoparticles in the form of stars were synthesized [4] (fig. 1, b). Gold nanostars as the gold nanorods are attractive candidates for SERS spectroscopy due to a lot of hot spots

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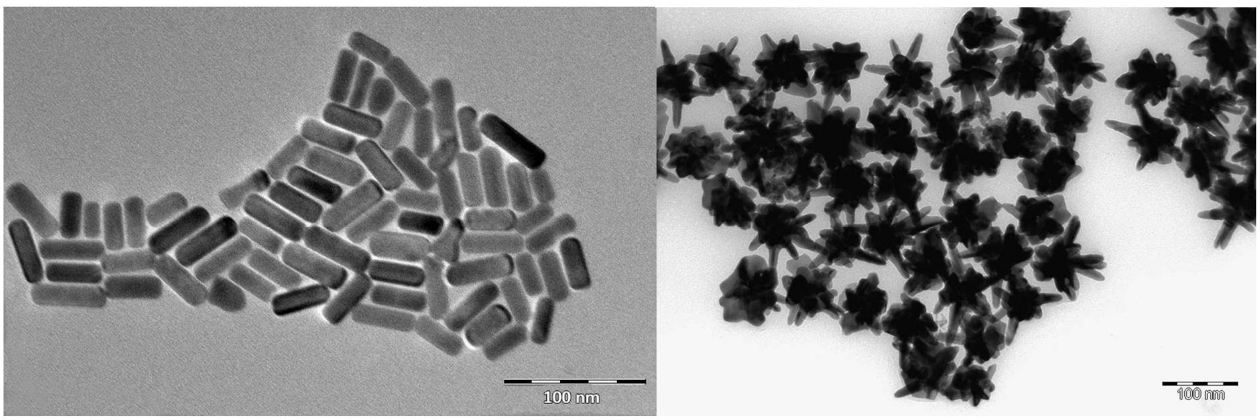
between the branches of nanostars and on the branches' tips. An additional enhancement can be achieved by the hot spots between different particles close to each other, and in this case, the size of particle is of great importance.

One of the ways which allow determining the geometric parameters of non-spherical particles is the measurement of the polarization characteristics of the scattered light.

A model for cylindrical nanoparticles randomly oriented in the liquid dispersion was proposed earlier [5]. This model allows calculating the dependence of the scattered light depolarization ratio (the ratio of depolarized component intensity to common intensity) on the aspect ratio. The model is based on the assumption that each particle has the certain effective area which maintains polarization and the certain effective area which realizes the depolarization. This model allows to find the average aspect ratio of nanorods, if the amount of quasi-spherical impurities is known (for example without impurities). The proposed model also allows to find the number of quasi-spherical impurities, if the average aspect ratio of nanorods is known.



a b

Figure 1. TEM images of synthesized samples of gold nanorods (a) and nanostars (b).

To verify the proposed model a series of experiments was carried out. The depolarization ratio of light scattered in water dispersion of gold nanorods with different aspect ratios was measured. The measurements were carried out using the particle size analyzer "Photocor Complex" (Photocor Ltd., Russia).

The geometric parameters of gold nanostars were study by classical dynamic light scattering (DLS) method.

The electrophoretic light scattering method was used to measure the zeta potential of nanoparticles. However, in existing devices, the data on the zeta potential of particles is obtained under the assumption of particle sphericity. A calculation the zeta potential of non-spherical particles especially in the case of nanorods by the formula for spherical particles can lead to erroneous conclusions about colloidal stability of liquid dispersions of nanoparticles.

Therefore, an accurate expression for zeta potential of nanorods in liquid dispersions was obtained. A spheroidal model for a description of geometric shape of nanorods was used. The following expressions can be obtained for zeta potential of spheroids, based on expressions for the capacitance and the diffusion coefficient of spheroids [6, 7]. The zeta potential for prolate spheroid with semi-axes $a > b = c$ and aspect ratio $p = a / b > 1$, moving along the axis a, is

$$\zeta_{pe} = \frac{v}{E}\frac{\eta}{\varepsilon}\frac{4\ln\left(p+\sqrt{p^2-1}\right)}{-\frac{2p}{\sqrt{p^2-1}}-\left(1+\frac{p^2}{p^2-1}\right)\ln\frac{p-\sqrt{p^2-1}}{p+\sqrt{p^2-1}}}, \quad (1)$$

the zeta potential for oblate spheroid with semi-axes $a = b > c$ and aspect ratio $p = c / a < 1$, moving along the axis a, is

$$\zeta_{oe} = \frac{v}{E}\frac{\eta}{\varepsilon}\frac{4\arccos\left(p\right)}{\left(\frac{1}{1-p^2}+2\right)\left(\frac{\pi}{2}-\text{arctg}\frac{p}{\sqrt{1-p^2}}\right)-\frac{p}{\sqrt{1-p^2}}}, \qquad (2)$$

where v is velocity, E is electric field intensity, η is the medium viscosity, ε is the permittivity.

Note that the zeta potential of cylindrical and spheroidal particles is determined by the functions, which depends only on the aspect ratio, not on the particle size.

3. RESULTS

Samples of gold nanorods water dispersion with aspect ratios ranging from 2 to 6 were studied. In experiments, the registration of the scattered light intensity was carried out for the scattering angle of 90° with VV-polarization and VH-polarization. The experimental and calculated values of aspect ratio were in good agreement if the quasi-spherical impurities were assumed into the proposed model and were in disagreement in the opposite case.

Samples of gold nanostars water dispersion with different core and branch sizes were studied. As a result of the study, it was found that there was a bimodal particle size distribution for samples of nanostars water dispersion. There were translational and rotational modes in distribution. The translational mode allows to estimate the average hydrodynamic radius of the particles. The rotational mode depends on the branches length. For more accurately measure of nanostars properties such as core size, the number of branches and branch size further researches are required.

The zeta potential of nanorods with different aspect ratios can be calculated using expressions (1, 2). Fig. 2 shows the dependence of the zeta potential on the particles aspect ratio (v = 12 μm/s, E = 2 kV/m, η = 0,9 mPa·s, ε_r = 78,5). It was considered that the spheroid orientation changes in the transition from $p < 1$ to $p > 1$.

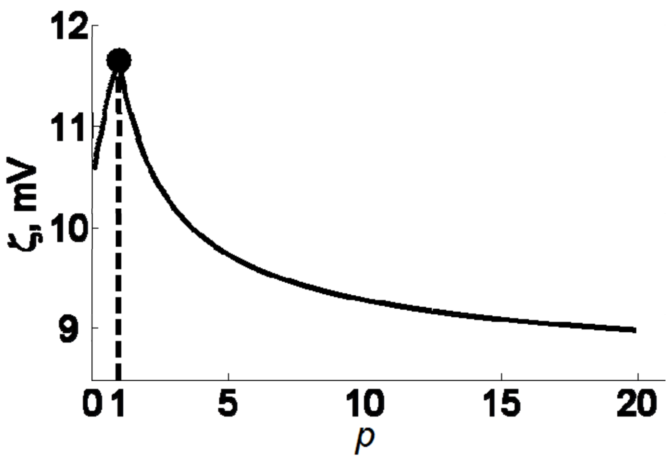


Figure 2. The dependence of the zeta potential ζ on the aspect ratio p for spheroidal and spherical (p = 1) particles.

4. CONCLUSIONS

Samples of gold nanorods and nanostars with different size and shape were synthesized and studied on the base of light scattering methods – DLS, polarization measurements, electrophoretic light scattering.

The possibility to find the average aspect ratio of nanorods or the number of quasi-spherical impurities in the sample of nanorods suspension by depolarization measuring was shown. For nanostars, the average hydrodynamic radius and branches length can be estimated based on the bimodal particle size distribution obtained by DLS.

Accurate expressions of zeta potential of nanorods in liquid dispersions were obtained. It was shown that the zeta potential of nanorods is determined by the functions, which depends only on the aspect ratio, not on the particle size. Dependence of the zeta potential for spheroidal particles on the aspect ratio was calculated. Dependence on Fig. 2 can be useful for analysis of liquid dispersions of nanorods with different aspect ratio.

The obtained results can be used to study colloidal systems of non-spherical nanoparticles and to develop new devices for biological applications.

5. ACKNOWLEDGMENT

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