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# Scattering response of Au and Ag nanoparticles with different sizes embedded in azopolymer matrix

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In this article we analyze the scattering response of a realistic model of thin azopolymer film (synthesized in Institute of Optical Materials and Technologies) with embedded Au and Ag spheres with mean radius 45 nm and 20 nm. The refractive index of the polymer matrix at 473 nm is 1.628, as determined by spectrophotometric measurement. This wavelength is commonly used for recording holographic gratings in such materials. Single particle optical behavior is analyzed using the exact vector equations of the scattering theory. Computer program was developed for estimation of scattered fields in terms of expansion coefficients. The particles are considered as ensemble of non-aggregated spheres with normal distribution of sizes, characterized by the mean radius $<r>$ and its standard deviation which is taken as $\sigma_r = <r>/4$. We ignore multiple scattering by individual particles. Based on these approximations, the angular dependences of all the matrix elements describing the optical response of the investigated nanocomposite film are calculated.

**Keywords:** light scattering, metal nanoparticles, nanocomposite films, azopolymer

## INTRODUCTION

The problem of light scattering by particles has attracted the attention of many researchers. In optical particle characterization, mainly scattering by some basic particle shapes such as spheres, spheroids, ellipsoids, cubes and cylinders have been investigated. In some early works special cases for certain types of particles have been resolved using various approximations [1-3]. Pioneering work of Gustav Mie and Lorenz provides more comprehensive view of the problem of scattering of particles [4].

Perhaps the most important, analytically solved problem in the theory of scattering by small particles is that of a sphere of arbitrary radius and refractive index [4, 5]. The Mie solution was obtained applying Maxwell's electromagnetic theory to the problem of light scattering from a homogeneous spherical particle with separation of variables.

Herein we present a numerical analysis of the scattering response of thin azopolymer film (synthesized in Institute of Optical Materials and Technologies) with embedded Au and Ag spheres with mean radius 45 nm or 20 nm by calculations of the scattering matrix.

This study is related with recently reported results for the enhanced photoinduced birefringence in composite materials [6, 7]. One of the suggested mechanisms that assist the reorientation of the azomolecules in presence of nanoparticles is connected with the light scattered from the nanoparticles at the recording wavelength, namely 473 nm.

## THEORY

The scattering of electromagnetic radiation by any material is related to its heterogeneity. Each material is in some sense heterogeneous, and for this reason all materials scatter electromagnetic radiation.

When a particle is illuminated by light, the nature of the particle – its shape, size and material – determine how much light will be scattered, what is its angular dependence, as well as how much light will be absorbed by the particle [8]. The process of scattering from a particle can be described as follows: A particle with a certain shape, size and optical properties is illuminated by monochromatic plane wave with arbitrary polarization. In order to determine the electromagnetic field inside and outside the particle, vector Maxwell's equations are solved by separation of variables, within and

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outside the particle, so that they fulfil the boundary conditions between the particle and the surrounding environment. Naturally, these equations are solved for the various separate areas, namely inside the particle, near and far from the particle.

The connection between the incident ($i$) and scattered ($s$) electric field is presented in a matrix form as follows:

$$\begin{pmatrix} E_{\parallel s} \\ E_{\perp s} \end{pmatrix} = \frac{e^{ik(r-z)}}{-ikr} \begin{pmatrix} P_2 & P_3 \\ P_4 & P_1 \end{pmatrix} \begin{pmatrix} E_{\parallel i} \\ E_{\perp i} \end{pmatrix} \tag{1}$$

where the elements $P_j\left(j = 1, 2, 3, 4\right)$ of the amplitude scattering matrix are complex variables and depend in general on the angle of scattering $\theta$ and the azimuth angle $\varphi$ and $k$ is the wave vector. Eq. (1) is valid for polar coordinate system $\left(r, \theta, \varphi\right)$ and the $z$-axis is defined as the direction of propagation of light ahead (forward direction). The scattering angle $\theta$ is counted from the centre of the particle and is equal to zero for backscattering (i.e. in direction opposite to the incident light) and 180° for forward direction.

The intensity and polarization of light are usually characterized in terms of the Stokes vector $S = \left(I, Q, U, V\right)$. The Stokes parameters of light scattered by a single particle are found from the electromagnetic field inside and outside the particle. A scattering matrix with 16 elements converts the Stokes parameters of the incident light $\left(I_i, Q_i, U_i, V_i\right)$ into the Stokes parameters of scattered light $\left(I_S, Q_S, U_S, V_S\right)$, as seen below [8]:

$$\begin{pmatrix} I_S \\ Q_S \\ U_S \\ V_S \end{pmatrix} = \frac{1}{k^2 r^2} \begin{pmatrix} P_{11} & P_{12} & P_{13} & P_{14} \\ P_{21} & P_{22} & P_{23} & P_{24} \\ P_{31} & P_{32} & P_{33} & P_{34} \\ P_{41} & P_{42} & P_{43} & P_{44} \end{pmatrix} \begin{pmatrix} I_i \\ Q_i \\ U_i \\ V_i \end{pmatrix} \tag{2}$$

This matrix is also sometimes referred to as phase matrix. The phase matrix in the case of spherical isotropic particles has much simpler form, and it is described by only four parameters – $P_{11}$, $P_{12}$, $P_{33}$ and $P_{34}$:

$$\begin{pmatrix} P_{11} & P_{12} & 0 & 0 \\ P_{12} & P_{11} & 0 & 0 \\ 0 & 0 & P_{33} & P_{34} \\ 0 & 0 & -P_{34} & P_{33} \end{pmatrix} \tag{3}$$

Hence, if we find these four parameters ($P_{11}$, $P_{12}$, $P_{33}$ and $P_{34}$) of the scattering matrix, we will know the scattering response of the system.

So far we considered a single particle. Recently, materials composed of several nanosized components, known as nanocomposite materials, have attracted considerable attention. They consist of a matrix in which nanoparticles are embedded. When we have an ensemble of particles, each particle in addition to the external field is excited by the resultant field of the scattered waves from all other particles. This complex case is usually simplified by two main approximations. The first is that the density of particles is small enough and they are at sufficiently large distance from each other, so that in the vicinity of each particle the total scattered field from all the other particles is less than the external field. Then each particle is affected only by the external field. The second approximation assumes an incoherent scattering by particles in the ensemble.

## RESULTS AND DISCUSSION

Our model considers a homogeneous spherical metal (Au or Ag) particle embedded in azopolymer matrix. The complex refractive indices of gold and silver are taken from Ref. 9. The calculations are made for mean radius of the metal spheres 45 nm and 20 nm, respectively, the ensemble of particles having a normal distribution of sizes. The azopolymer used for the matrix of the nanocomposite material is synthesized in the Institute of Optical Materials and Technologies. The refractive index of the polymer matrix is estimated to be 1.628 at 473 nm based on spectrophotometric experimental data. This wavelength corresponds to the one commonly used for recording holographic gratings in such materials. Single particle optical behavior is analyzed using the exact vector equations of the scattering theory. Far-field scattered and near-field electromagnetic fields are calculated by the method of separation of variables.

Computer algorithm was developed for calculation of the scattered fields in terms of expansion coefficients. The particles are considered as ensemble of non-aggregated spheres. Further, we have ignored multiple scattering by individual particles. We also assume that the spheres, incorporated in the azopolymer samples, have normal distribution of sizes, characterized by the mean radius $\langle r \rangle$ and its standard deviation $\sigma_r$.

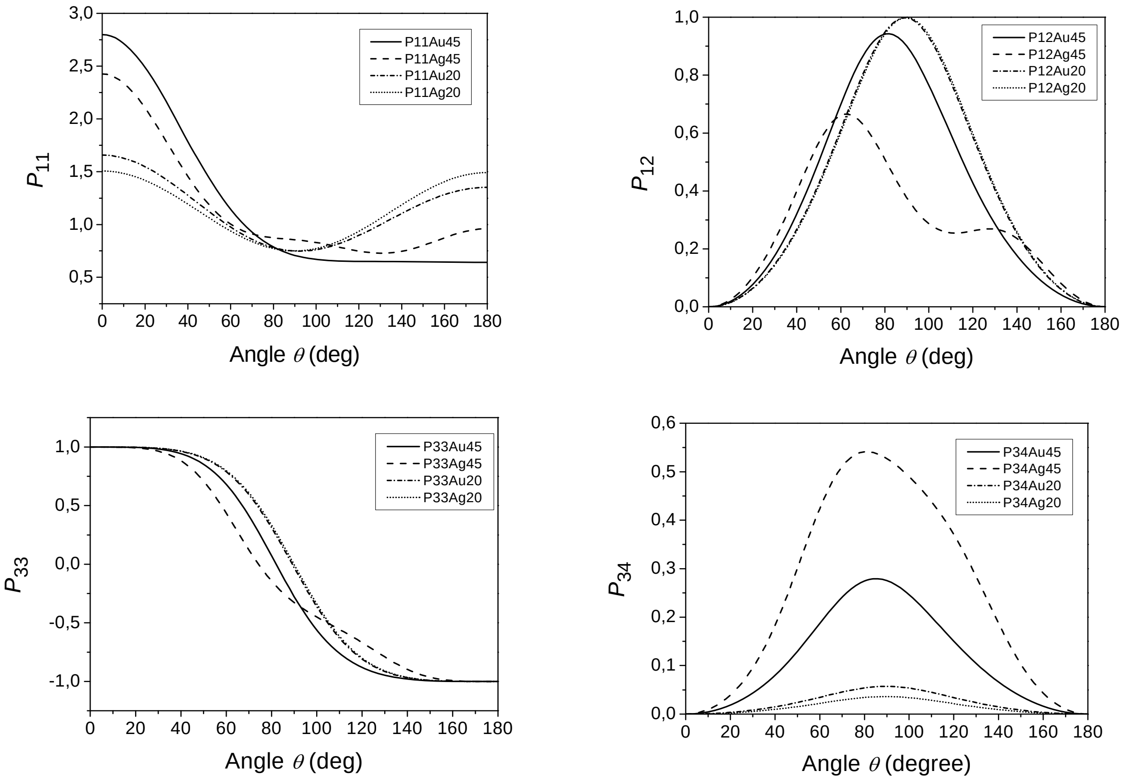


**Fig. 1.** Angular dependence of the scattering matrix elements $P_{11}$, $P_{12}$, $P_{33}$ and $P_{34}$.

Calculations were done for Au and Ag nanoparticles with $<r> = 45$ nm and $<r> = 20$ nm. In both cases the value of the standard deviation is taken to be $\sigma_r = <r>/4$.

The angular dependences of all the matrix elements $P_{11}$, $P_{12}$, $P_{33}$ and $P_{34}$ describing the scattering response of the investigated nanocomposite film are calculated and graphically presented in Fig. 1.

As seen in Fig. 1, the behavior of all four scattering matrix elements for both the gold and silver particles with radius 20 nm is similar. This is because they are within the approximation for small particles. On the other hand, the angular scattering dependences of the 45 nm sized gold and silver particles are different.

## CONCLUSION

The scattering matrix elements are calculated and compared for nanocomposite layers consisting of Au or Ag nanoparticles with two different sizes (20 and 45 nm) embedded in dielectric azopolymer matrix. In such a way, the scattering response of the system can be defined. The angular dependences of the four scattering matrix elements in the case of spherical isotropic particles are presented. It is seen, that the obtained values for gold and silver particles with size 20 nm are very close, which is explained by the approximation for small particles. Hence, for particles with radius 20 nm or below, the scattering response does not depend on the composition of the particle.

For particles with radius 45 nm however, the scattering of the system is different for gold and silver, and depending on the desired optical properties, one of these materials can be selected.

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# РАЗСЕЙВАНЕ ОТ АЗОПОЛИМЕРЕН СЛОЙ С ВГРАДЕНИ Au И Ag ЧАСТИЦИ С РАЗЛИЧНИ РАЗМЕРИ

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(Резюме)

Анализирано е разсейването на реалистичен модел на тънък азополимерен слой (синтезиран в ИОМТ) с вградени Au и Ag сферични наночастици с радиуси 45 нм и 20 нм. Показателят на пречупване на полимерната матрица за 473 нм е 1,628 и е определен от спектрофотометрични експериментални данни. Тази дължина на вълната е подходяща за холографски запис в изследваните материали. Поведението на единична частица е анализирано посредством точните векторни уравнения на Максуел.

Разработени са компютърни програми за пресмятане на ъгловата зависимост на разсеяната светлина. Частиците се разглеждат като ансамбъл от неагрегирали сфери като се пренебрегват многократните отражения между частиците. Приемаме също, че частиците имат нормално разпределение по размери и се характеризират със средния си радиус $<r>$ и стандартно отклонение $\sigma_r = <r>/4$. Направените изчисления са за Au и Ag наночастици с $<r> = 45$ нм и $<r> = 20$ нм. Представени са ъгловите зависимости за 473 нм на четирите матрични елемента, определящи разсейването на изследвания нанокомпозитен слой.