Carbon nanoparticles. Preparation and specially formed optical properties

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ABSTRACT

The work is devoted to the study of the optical properties of carbon nanoparticles synthesized by the method developed during our experimental studies. The optimal conditions for the creation of carbon nanostructures with predetermined properties are defined. Nanoparticles of the size of about 80-1000 nm were obtained in our experimental approach, the maximum of absorption of which is localized at wavelengths in the violet-blue region of the spectrum (420 nm and the maximum of luminescence in the green region (530 nm). The absorption index at the wavelength of 633 nm, which is used for the diagnosis of optical speckle fields, is estimated. The assumption is made about the possibility of using the obtained particles for correlation diagnostics of optical speckle fields.

Keywords: carbon nanoparticles, luminescence, absorption, speckle field

1. INTRODUCTION

The relevance of the study of the carbon nanomaterials properties is related to the unique features of these structures, namely, their specific optical manifestations, fluorescence in the visible region of the spectrum, anomalous absorption, chemical passivity, and non-aggressiveness to biological systems.

According to the existing classification[1], fluorescent nanoparticles are divided into four classes, among which carbon nanoparticles are notable due to their size of about one hundred nanometers. Such structures are rather attractive because they exhibit luminescence at wavelengths in the yellow-green and red regions of the spectrum.

The analysis of the methods[2] for creating carbon particles distinguishes between top-down and bottom-up methods. In the top-down methods, carbon particles are typically formed from larger carbon materials such as graphite, carbon nanotubes, soot, activate carbon, graphite oxide. At the same time the bottom-up one works with a subset of molecular precursors that allows obtaining a particle in one cycle.

Top-down methods include laser ablation and laser based synthesis, oxidation, electrochemical release, while the *bottom-up ones* include pyrolysis, ultrasound assisted synthesis, microwave synthesis, electrochemical synthesis, synthesis without physical treatment, hydrothermal synthesis. Without considering the disadvantages and advantages of each method, we chose hydrothermal synthesis of carbon nanoparticles to produce nanoparticles of about hundreds of nanometers in size. The properties of the created particles[3,4] significantly depend on the surface structure of the shell and on the structure of the nucleus, the location of polar groups, and their active centers. The mechanism of carbon nanoparticles synthesis, the nature of the reagents, and the peculiarities of the electronic transitions of the basis of the substance determine the set of photo-induced redox reactions of electron exchange between the active centers of donors and acceptors, and therefore the properties of the obtained nanoparticles. The method we choose allows us to isolate nanoparticles with stabilized carboxyl and amino groups, with predetermined optical properties.

Much research work has been devoted to the study of carbon structures[5]. But the isolation and creation of carbon structures, which are predetermined and whose properties are foreseen, is a separate task that was successfully solved in the course of the work, and is an intermediate stage of the problem of the diagnostic nature of the analysis of random optical fields.

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Therefore, the purpose of this work is to develop and extend the technique of creating carbon nanoparticles with predictable properties, namely, controlled sizes, strong optical absorption at wavelengths of 405 nm, and emission in the visible region at wavelengths of about 530 nm. The creation of such particles will allow the diagnostics of speckle fields, by moving these particles along the intensity gradient by optical fluxes with their localization in the singular regions[6-16]. Such diagnostic approaches extend the existing correlation-singular methods of processing complex inhomogeneous optical fields[17-21].

2. FUNDAMENTALS OF APPROACHES FOR OBTAINING CARBON NANOPARTICLES. SIZE ESTIMATION

Among the existing techniques for the creation of carbon nanoparticles[5], in our experimental approach, as it was previously mentioned, the bottom-up method is used. Citric acid (0.2 g) and urea (0.2 g) were selected as reagents[3] in equal proportions. In a plastic tube, the mixture is dissolved in 5 ml of distilled water to form a clear solution. Then the solution is poured into a porcelain crucible (10 ml in volume) and has been heated in the oven at t = 190°C for 2 hours. The heat treatment results in the formation of a precipitate consisting of carbon nanoparticles. After cooling, the latter is dissolved in 10 ml of distilled water within 3 hours. Particles dissolved in water are removed into a separate flask. To obtain an aqueous solution of carbon nanoparticles of the same size, a magnetic stirrer MicroMed 35-40 minutes is used. In 2 hours at rest after mixing, a solution is obtained, which is used for further centrifugation to separate particles of different sizes[22].

Eight centrifuge tubes are used in the centrifugation process. The centrifugation frequency can vary from 500 rpm to 13000 rpm. Centrifugation time is also regulated. In the first stage, the centrifugation frequency was set to 500 rpm, the time of centrifugation varied from 1 to 8 minutes. During this time interval the composition of the solutions does not change visually, i.e. the deposition of particles did not occur. The next step consisted in mixing the solutions in one container for stirring with a MicroMed stirrer and continuing the centrifugation of the resulting solution, starting from 9 minutes. This is the time period of centrifugation that enabled to obtain a precipitate of large particles and a residual working solution with suspended particles. Obtaining a precipitate allows to conclude the separation of carbon particles in the residual liquid. The time of centrifugation in the production of particles was being increased. To determine the end time when the concentration of nanoparticles in the working solution did not change with increasing centrifugation time, optical approaches for estimating the optical density of the solutions were used. Diluted in distilled water, the dried precipitate, in our case, is called sample.

The optical density was measured using[6] the setup shown in Fig. 1. The main components of the setup are a filament lamp of iodine cycle with stabilizer (1), monochromator MUM 01 (6), cuvette with prepared sample (7) and photodiode FD-288B (8). The use of a stabilizer allows you to maintain the voltage level and to ensure the stability of the radiation intensity of the incident beam. Radiation of a filament lamp of iodine cycle is in the wavelength range of 90-2200 nm, from which the monochromator emits a working wavelength corresponding to the maximum absorption of the obtained carbon nanoparticles (405 nm). FD-288V germanium photodiode acts as a radiation receiver, with a working wavelength range of 190-1100 nm, a dark current of 40 nA.

Sample preparation for optical density measurement was as follows. The resulting working solution for different time intervals of centrifugation was dried; to compare the set of samples obtained, the latter were dissolved in an equal volume of distilled water (2 ml).

The optical density was estimated as:

$$D = -\ln(I_\tau / I_0) = kl\,, \tag{1}$$

where I_τ – the intensity of the transmitted radiation, I_0 – the intensity of the radiation incident on the cuvette, k - the extinction index, l - the thickness of the cuvette (10 mm).

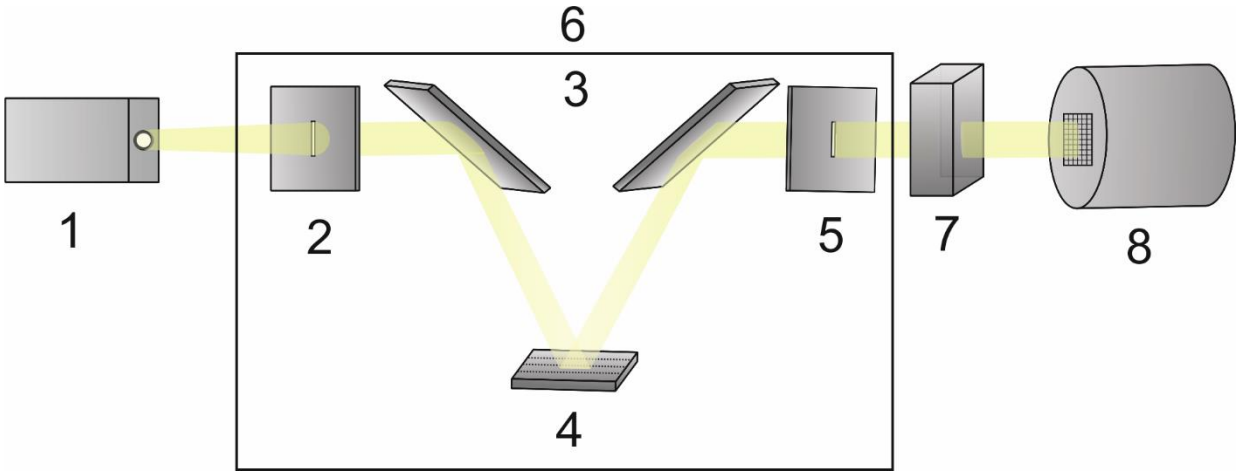

Fig. 1. Setup for measuring the optical density of the samples: 1 - filament lamp of iodine cycle with a stabilizer, 2 - the entrance slit, 3 - the system of rotating mirrors, 4 - the diffraction mirror, 5 - the output slit, 6 - monochromator MUM-01, 7 - cuvette with the sample, 8 - radiation receiver[22]

For example, the results of calculations of the optical density for the centrifugation frequency of 500 rpm (405 nm) for different centrifugation times are shown in Fig. 2.

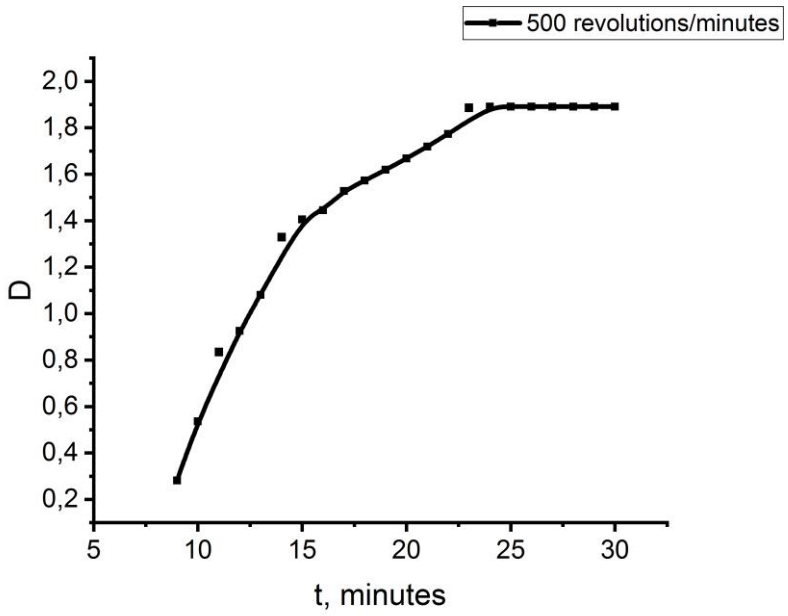

Fig. 2. Dependence of the optical density of the samples on the centrifugation time for centrifugation frequency of 500 rpm[6]

In particular, for the centrifugation frequency of 500 rpm (Fig. 2), at time interval from 9 to 20 minutes, the particle concentration increased, respectively, with the decrease in the signal at radiation receiver (8) (Fig. 1). The increase in particle concentration is accompanied by an increase in the extinction of the samples and a corresponding decrease in the intensity of the transmitted radiation. This change results in the increase in the optical density.

From the 21st minutes, the signal at the output of the sample remained constant. The optical density of the samples did not change, which enables to conclude about the time, which under the selected conditions determines the formation of a final solution with working nanoparticles.

To check and control the conditions found, the working solutions obtained for different time intervals of centrifugation are merged into one tank, then this solution is mixed with the MicroMed stirrer for further centrifugation for 21 minutes with subsequent control of the optical density. The result of the optical density is confirmed, thus a conclusion can be made that for 500 rpm, 21 minutes is the exact time that reproduces the condition of obtaining carbon nanoparticles. It was the obtained working solutions that we used to study the luminescence spectra.

Working solutions for different centrifugation frequencies are obtained and controlled similarly. It should be noted that the gradual increase in the centrifugation frequency causes a decrease in the time at which a constant (unchanged) concentration of carbonic particles in the working solution is observed (Fig. 3).

The obtained carbon particles, which are suspended in aqueous solutions, are subject to careful size measurement and analysis. In particular, for the particle size measurements an optical setup was used consisting of a biological immersion microscope Biolam 70 and a CCD camera (DCM-500 SCOPE Video Glass). The video eyepiece is supported on OS Windows 2000 / XP / 2003/7 (32 and 64 bit). ScopePhoto software was used. To measure the size of the nanoparticles, the software scale was calibrated. At this stage it was possible to determine the average particle sizes from 920 nm for centrifugation frequency from 500 rpm to 456 nm for a centrifugation frequency of 5000 rpm[6].

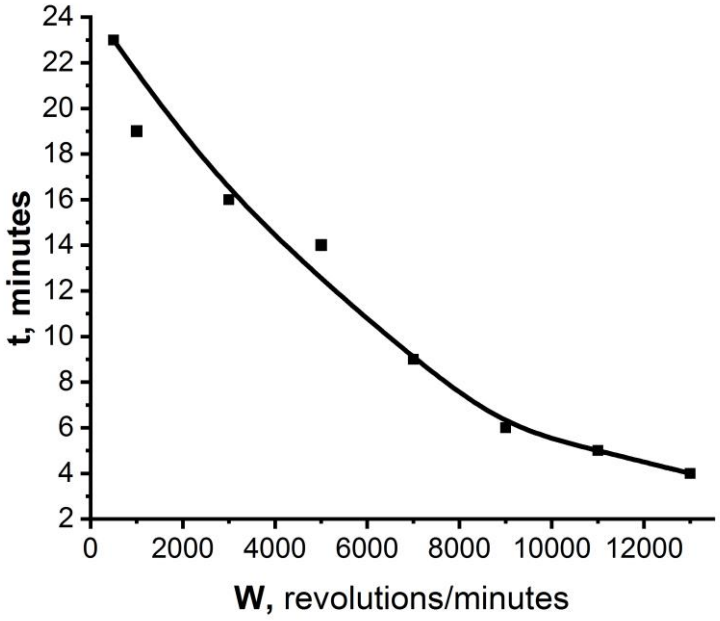

Fig. 3. Dependence of the deposition time of the particles on the rotation speed of the centrifuge[22]

For more accurate measurements, atomic force microscopy approaches were used. Specially prepared specimens[23] were carefully analyzed, which allowed the determination of carbon nanoparticle sizes up to 89 nm for centrifugation frequency of 13,000 rpm. It is the aqueous solutions of such carbon nanoparticles that will enable to diagnose optical fields, to observe the movement of these particles by internal optical fluxes[21, 24-29], and to perform spatial-frequency processing and reproduction of phase distributions over a spatial recorded picture, visualized by luminescence. The mobility of the investigated objects, the spatial displacement of optical fields can be studied through the analysis of the skeleton of the optical field[21], the reproduction of phase information using mathematical processing of Hilbert transform, in particular. In addition, the use of particles with new properties determines the expansion of approaches and methods for recording information, i.e. in bistable elements and memory systems[30-32].

3. SPECTRAL ANALYSIS OF CARBON NANOPARTICLES (ABSORPTION, TRANSMISSION, FLUORESCENCE)

The use of carbon nanoparticles to diagnose the scalar optical field scattered by the studied object (speckle field) involves the measurement and evaluation of the absorption of these particles at a wavelength λ = 633 nm of He - Ne laser radiation. Speckle field is formed at a given wavelength, and optical flows formed here act on nanoparticles changing their location, moving them into the region of minimum intensity with singularities.

Determination of the absorption index is carried out on the scheme shown in Fig. 1. Here ensure the following conditions:

1. the thickness of the cuvette is 1 cm;
2. the volume of the sample in the cuvette does not exceed 2 ml;
3. the signal at the outlet of the cuvette with the sample must be the same for all centrifugation frequencies of 500 - 13000 rpm at an absorption maximum of carbon particles (420 nm).

The estimation of the absorption index of the samples is carried out in accordance with (1). The results of calculations of the absorption index spectrum of samples for the centrifugation frequency of 500, 5000 and 13000 rpm are shown in Fig.4.

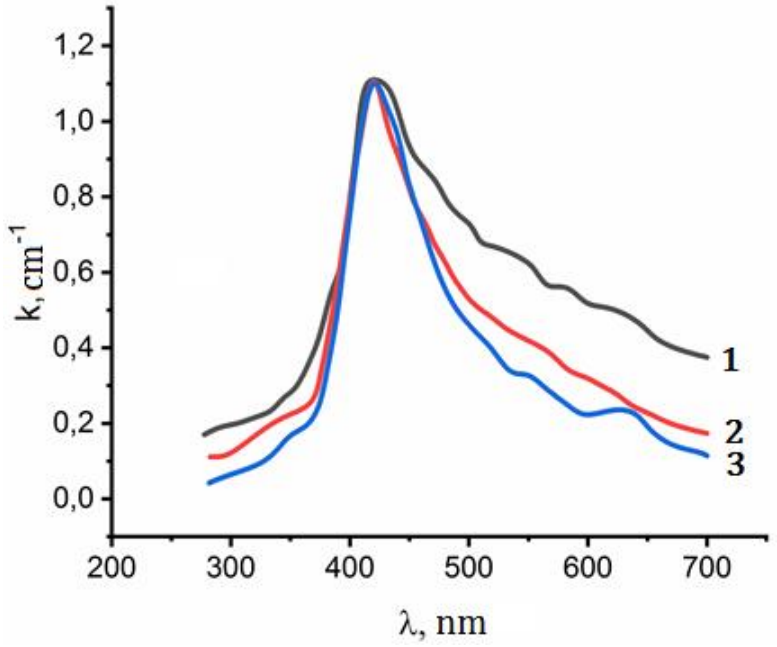

Fig. 4. Dependence of the absorption index of the samples on the wavelength for the centrifugation frequency: 1) 500 rpm, 2) 5000 rpm, 3) 13000 rpm

Analysis of Fig. 4 demonstrates that under the mentioned above conditions, the maximum of absorption spectrum for all samples is at wavelength of 420 nm, with an absorption index k_λ= 1.1 cm^{-1}. The absorption index of the samples for the wavelength of 633 nm for different centrifugation frequencies are as follows: for example, for particles of size 920 nm (500 rpm) k_λ= 0.10 cm^{-1}, 456 nm (5000 rpm) k_λ= 0.06 cm^{-1} and 89 nm (13000 rpm) k_λ= 0.04 cm^{-1}.

The absorption index at a wavelength of 633 nm are used to calculate the components of the resulting optical force acting on the nanoparticles, namely the gradient component, the scattering and absorbing components.

The obtained values of absorption index allow us to calculate the transmission spectra. In accordance to

$$\tau_\lambda = e^{-k_\lambda l}, \quad (2)$$

where k_λ is the spectral absorption index, l is the thickness of the cuvette (in our case 1 cm).

For example, the following figure 5 presents the transmission spectra for particles of 920 nm, 456 nm and 89 nm, obtained for the centrifugation frequency of 500, 5000 and 13000 rpm, respectively.

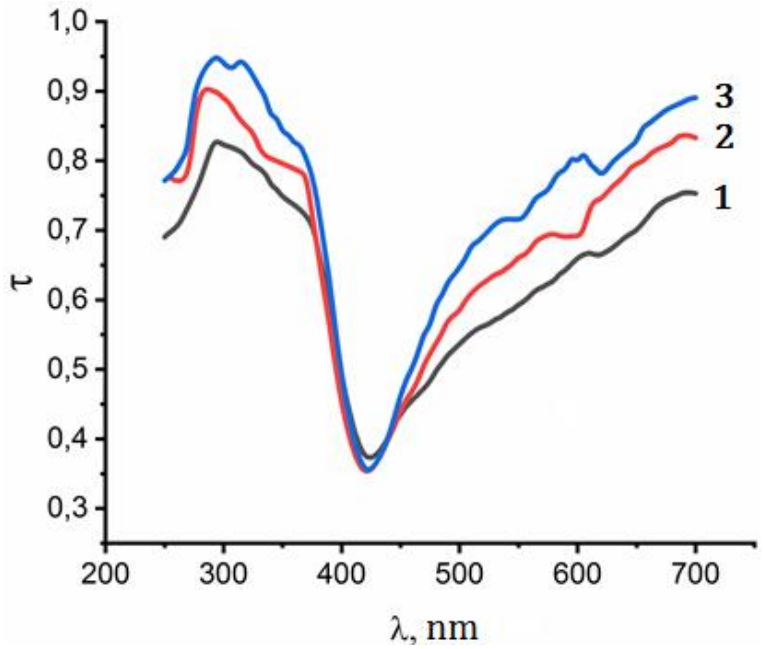

Fig. 5. The dependence of the transmittance of the samples on the wavelength for particles of different size: 1) 920 nm, 2) 456 nm, 3) 89 nm

Visualization of the skeleton by carbon nanoparticles becomes possible if the fluorescence of the nanoparticles can be fixed. For that the results of measuring the luminescence of the obtained carbon nanoparticles on the setup, the scheme of which is shown in Fig. 1, are presented. The sample under study is placed in front of the monochromator. In order to eliminate the effects of scattered laser radiation (maximum radiation of 405 nm, which corresponds to the maximum absorption (420 nm) of carbon nanoparticles) from the radiation source to the photodetector, a light filter with bandwidth of 650 nm is placed behind the monochromator. In order to avoid the manifestation of temperature changes, the temperature regime and the exposure time are controlled. So, the laser source used in our experimental approach is Laser 303 (maximum radiation at a wavelength of 405 nm and power of 5 mW).

The sample is prepared in a special way: to measure the luminescence of aqueous solutions of carbon nanoparticles obtained for different centrifugation frequency under the same conditions, the optical density of the solutions is estimated. The uniformity of optical density values, that is, the equal absorption of solutions, is chosen as the criterion of readiness of the samples for measuring the luminescence. Figure 6 shows the luminescence spectra for the samples obtained for centrifugation frequency of 500 rpm, 5000 rpm, and 13000 rpm. As far as it is seen from the obtained results, the luminescence maximum corresponds to the wavelength of 530 nm (Fig. 6)[22].

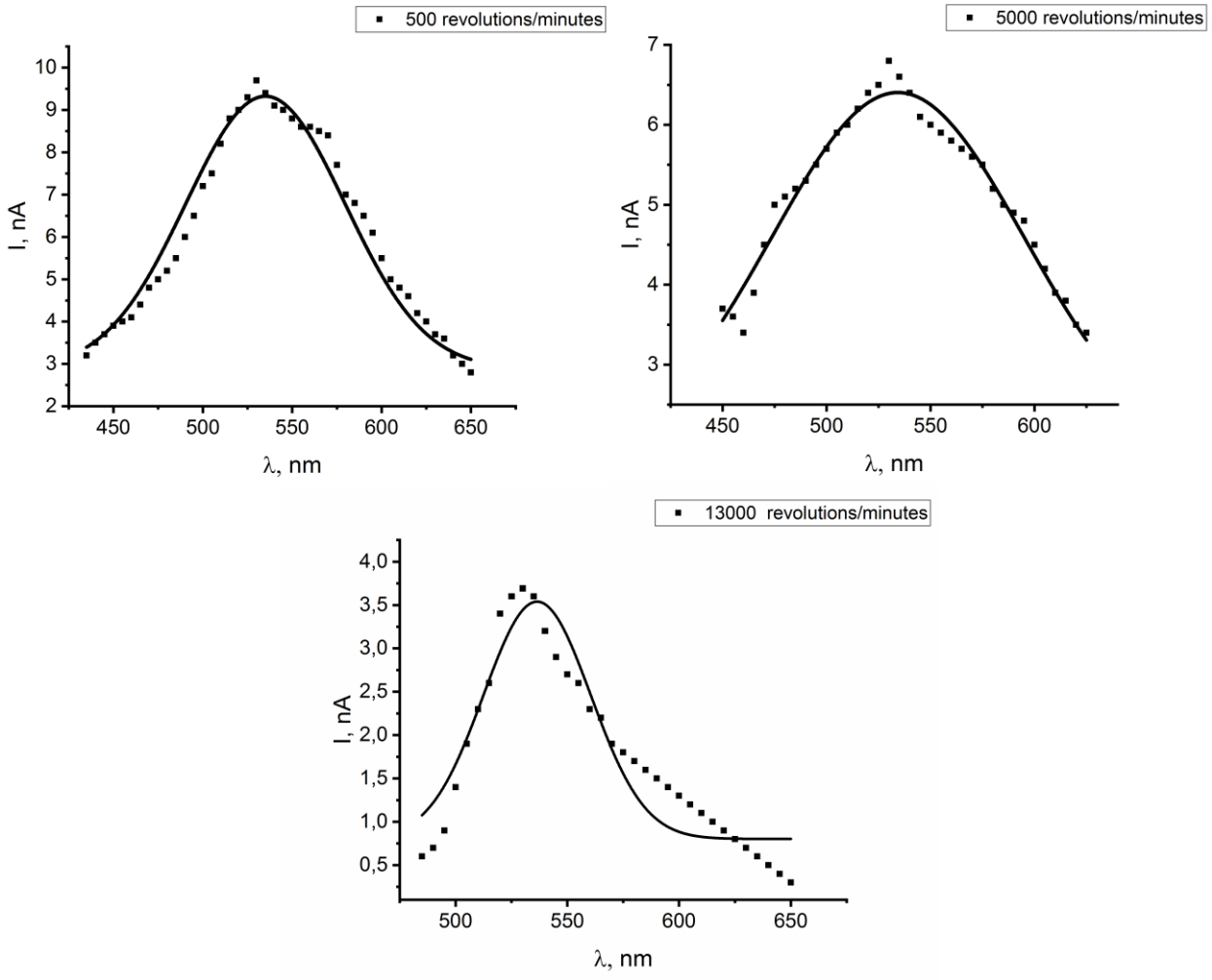

Fig. 6. Spectrum of luminescence for different rotation speed of the centrifuge[22]

The radiation of carbon nanoparticles at this wavelength is also used to study complex optical fields. Gradient optical forces determine the movement of carbon nanoparticles in the areas where the localization of nanoparticles occurs. The optical speckle field is modeled by a set of spatially distributed carbon nanoparticles in the areas of the intensity gradient, thereby reproducing the structure (skeleton) base of the optical field, followed by mathematical processing of this structure, restoring the phase map in real time and obtaining information about the state of the object.

A distinctive feature of this approach using carbon structures is that the probability of error in the diagnostics of amplitude zeros is reduced, since gradient optical forces are directly related to the magnitude of internal energy flows and their spatial distribution in the analyzed speckle field.

The structure of the optical speckle field is visualized with the following fixation of this structure by a CCD camera. The prospects of studying optical fields with carbon nanoparticles prove to be a promising mechanism for conducting structural analysis of speckle fields with the recovery of phase information about an object, the reproduction of information about spatial changes in the structure of nano- and macroobjects.

CONCLUSIONS

As a result of the research the carbon nanoparticles of the predicted sizes of about 80-1000 nm with predetermined properties, including the absorption maximum in blue region at a wavelength of 420 nm and luminescence maximum in the green region of the spectrum at wavelength of 530 nm were obtained. The absorption index of the investigated carbon nanoparticles at wavelengths of 633 nm for different their sizes is estimated. Complex diagnostics of optical speckle fields can be organized in this case with complex reproducing of the phase map of an object, and then – the amplitude distributions of micro- and macroobjects, the states of which change over time.

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