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Technology of introduction of nanoparticles of silver in green leaves and research of processes of photoradiation

This paper presents the results of a study of the spectral characteristics of the green leaves of houseplants, «enriched» with silver nanoparticles. The dimensions of nanoparticles corresponded to 80 nm, the shape — spherical. Studies of the absorption spectra in the range of 350–650 nm showed that the nanoparticles are «embedded» in the amount of green leaf. Analysis of the absorption spectra obtained from measurements with silver nanoparticles solution, also confirmed the results. The findings may contribute to understanding Photoprocesses in organic and biological objects. The practical part is due to the ability to create photo-biological sensors and biosensors.

Key words: chlorophyll, silver nanoparticles, the absorption spectra, luminescence, green leaves, biosensors, sorption, absorption, fluorescence, phosphorescence, radiation, a quantum of light, the photon.

Research of photoprocesses with participation of nanoparticles which are a part of the different natural structural organizations is an actual task. Interest in such researches is bound to a possibility of their application in devices which treat biosensors, biosensors, etc.

One of efficient methods is the luminescent method because it is characterized by high sensitivity, effectiveness and informational content of the obtained data. The luminescent method falls into categories of the most efficient non-contact research techniques of organic matters. The chlorophyll is a substance thanks to which plants can use solar energy for synthesis of organic matters. The chlorophyll is capable to absorb light and gives it. But intensity of a luminescence in this case is very weak and cannot be to be applied in practice. At the same time in scientific literature there is information that existence of nanoparticles of some metals (for example, silver and gold) can lead to strengthening of such luminescence [1–3]. Effectiveness of use of particles of silver in this case is higher, than gold particles.

The purpose of this work is development of technology of introduction (implantation) of nanoparticles of silver in cages of green leaves then to investigate effects of a reradiation of the absorbed energy. In work processes of absorption and a photoluminescence of green leaves of house plants with the introduced silver nanoparticles are considered.

In the course of work methods of synthesis of nanoparticles (Turkevich method, borohydride method, and biosynthesis of nanoparticles) were used and photometric measurements are taken.

It is known that the higher plants contain two forms of chlorophyll: chlorophyll *a* and chlorophyll *b*. The structure of chlorophyll *a* (Fig. 1) is established by Vilyptetter and Fischer and confirmed in 1960 to Woodward who carried out the complete synthesis of chlorophyll *a* [4].

Chlorophyll *a* and *b* differs on color: chlorophyll *a* has blue-green color, and chlorophyll *b* — flavovirent color. The maintenance of chlorophyll *a* in a leaf of a plant is approximately three times more in comparison with chlorophyll *b*. Absorption spectra of both forms are given in Figure 2 in which it is visible that crests of bands of absorption of chlorophyll *a* lie in areas of lengths of waves of 440 nanometers and 700.

The maximal intensity of the sunlight reaching a terrestrial surface falls on blue-green and green areas length of waves (450–550 nanometers). And in these areas absorption light molecules of chlorophyll is minimum.

In Figure 3 the scheme of the first energy levels of a molecule of a chlorophyll is shown and. In the ground state such molecule has a zero spin. All excited states with a zero spin are called singlet (*S*). Excited states with the spin equal to unit are called triplet (*T*).

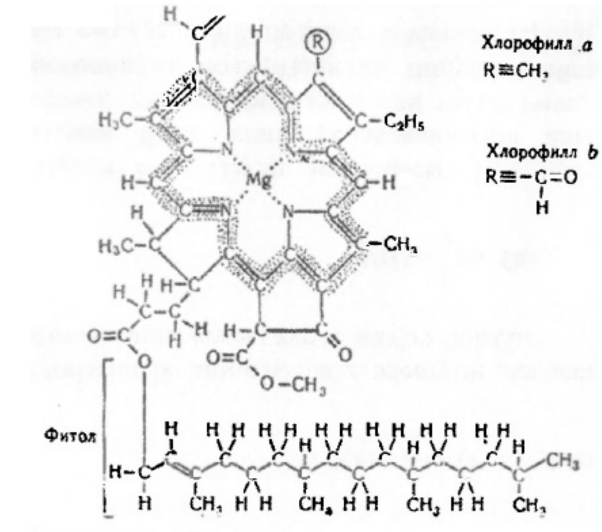

Figure 1. Constitutional formulas of chlorophyll *a* and chlorophyll *b*

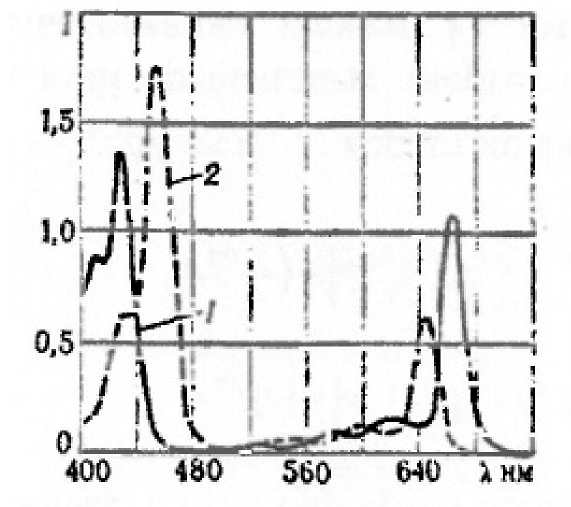

Figure 2. Light absorption spectra a chlorophyll *a* (curve 1) and a chlorophyll *b* (curve 2)

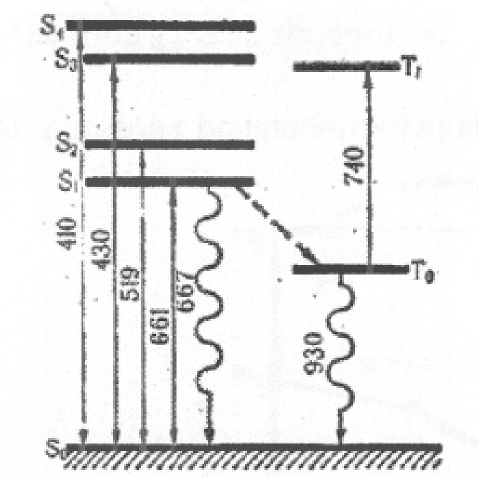

Figure 3. Scheme of singlet and triplet energy levels of a molecule of a chlorophyll and direct pieces correspond to absorption, wavy shooters — blooms. Figures specify a wavelength in nanometers

The luminescence arises when transforming energy to sunlight when energy is absorbed by atoms, molecules or ions of some substances. Not all substances have ability to luminesce. Particles of the luminescing substance, having absorbed energy quantum, turn into excited state which lasts very short time, and then, reverting to the original state, they give excess of energy in the form of a luminescence. Energy, necessary for exaltation of a luminescence, can be reported to particles of luminescent substance in the different paths: it is possible to direct to it a stream of light rays or it is possible to reach exaltation of particles in blows of electrons etc.

Now one type of a luminescence of plants — a bloom is known. A bloom of green plants was opened by Stokes [4]. Today many works are devoted to research of this phenomenon [5,6]. It is established that the chlorophyll of leaves fluoresces.

Intensive bloom of leaves of plants is caused by chlorophyll *a* and has a maximum approximately at 682 nanometers. Besides, weaker strip with a maximum at 656 nanometers caused by chlorophyll *b* and two weak strips from a chlorophyll a with a maximum is found at 740 nanometers and 812 nanometers.

Intensity of fluorescent radiation of alive leaves makes about 0,1 % of amount of the absorbed light; in chlorophyll solutions intensity of a bloom in ten times more. The belief that the obtained data can supply with the direct information on use mechanism plants of light energy at photosynthesis was the main incentive to studying of a bloom.

According to works [5, 6] there are bases to consider that irrespective of a wavelength of the absorbed light the exited molecule of a chlorophyll almost instantly moves to more low energy level which corresponds to energy of «red» quantum. From this state various paths of transformation of excitation energy are possible. On the basis of the received results authors do the conclusion that observed long-lived afterglow is bound to enzymatic chemical reaction and, therefore, cannot be explained with purely physical phenomena — a delayed bloom or a phosphorescence.

For an explanation of the received results authors do the assumption that in the common reaction sequence of a photosynthesis some of early reactions are reversible before highlighting of the absorbed light quantum.

Technique and technology of measurements

Scientific and applied interest in nanoparticles of silver was connected by a possibility of their application as a highly dispersive basis for strengthening of a signal of molecules of organic compounds in a spectroscopy of a Raman Effect. In addition, antibacterial preparations on the basis of the colloid silver well proved to be in medicine. Now a large number of traditional methods of receiving nanoparticles of silver [7] is known. In the work we used the most prime method of receiving nanoparticles — a so-called method of «green chemistry» [8]. This method differs in simplicity, availability and lack of toxic influences. It combines the low cost of starting materials, biocompatibility, availability of natural reagent reducer, superficially the active materials which play a role of stabilizers and complex — all this promotes receiving in total stable nanoparticles of silver. In work silver particles which sizes made about 80 nanometers were used. The aqueous solution of the prepared particles found a weak red luminescence even at visual supervision. Research of absorption spectra was carried out on a spectrophotometer of SF-46 which is intended for measurement of transmittances and absorption of fluid and solid transparent matters in a spectral range from 190 to 1100 nanometers.

Results and their discussion

Before experiment work on scheduling of stages of realization of experiment was carried out. Further stages of the plan were strictly kept. First, the houseplant which leaves could serve as objects for experiments was chosen. There are data [1–3] that plants of which excess «aquosity» of leaves is characteristic have the greatest resistance to external influences. Appearance of the chosen houseplant is presented in Figure 4.

The green leaf after outer inspection, was subjected to dusting and other pollution by washing under running water, and then under a stream of distilled water. The cleared leaf by means of a copper mortar turned into the homogeneous mass after which filtering the saturated solution of a chlorophyll used for research of absorption spectra turned out.

Figure 4. Photo of a houseplant

At first measurements of absorption spectra of green leaves without the introduced silver particles were taken. These data were necessary for identification of absorption bands during the scheduling and realization of further works, the bound to studying of a photoluminescence.

For an exception of processes of aggregation (formation of the composite couples) of molecules of a chlorophyll the aqueous solution of weaker concentration was prepared (Figure 5, a curve 4). Filing of an absorption spectrum of a saturated solution showed that the range consists of two main absorption bands, in violet (420 nanometers) and red (680 nanometers) spectral ranges.

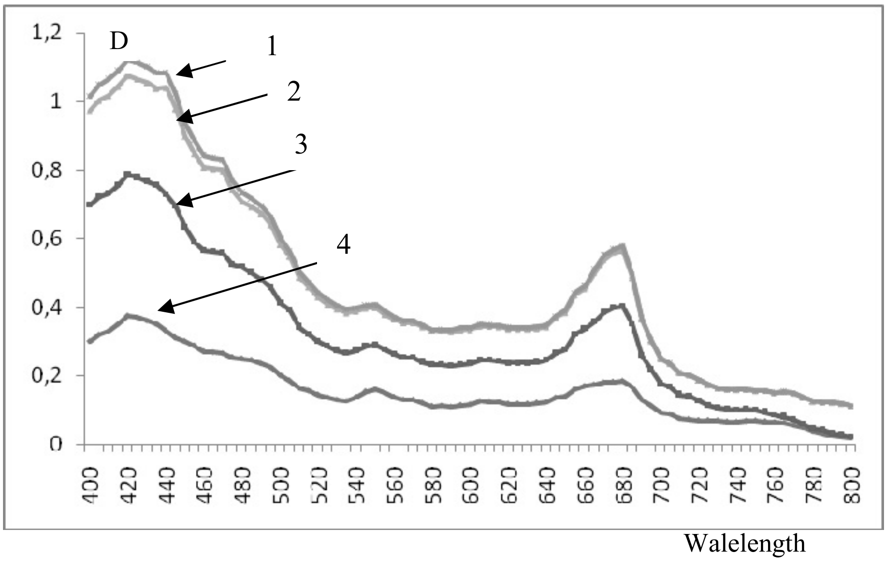

Figure 5. Absorption spectra of solutions of a green leaf at different concentration of chlorophyll.
Increase of concentration of chlorophyll comes from a curve 3 to a curve 1

As appears from the received results, increase in maintenance of chlorophyll in solution leads to body height of an optical density and width of absorption bands (Figure 5, curves 1–3). At the same time observed maxima are not displaced. The absorption spectra received by us coincided with the results which are available in other references [8, 9].

At the following stage of researches silver nanoparticles took root into the chosen leaf. For this purpose the leaf heated up. Authors recognized from the fact that when heating a leaf its time as it happens, for example, to a time human skin at temperature increase will extend. At the same time, if the leaf is located in solution with silver nanoparticles, then it is probable that particles of silver «will get» into the formed time and will remain there. Strengthening by nanoparticles of silver of a weak luminescent emission of leaves is as a result possible.

Beforehand temperature tests of green leaves during which it was established that heating of leaves in water differently influences leaves of different plants were carried out. In certain cases within one hour at rather low temperatures (to 50 ºC) leaves in subsequent devitalized. In some cases their stability up to temperature of 90–100 ºC was observed. Green leaves of the studied plant kept viability when heating to 50 ºC.

Procedure of introduction of nanoparticles of silver was carried out in the following sequence. Beforehand capacity with the thermometer for control over temperature and with a drain cock at the bottom was prepared. The sizes of capacity allowed installing a vessel with solution of nanoparticles of silver inside. The unimpaired green leaf was carefully lowered in this solution. Gradually added heated water to an outside storage tank. At achievement of temperature in +50 degrees Celsius, process of warming up was slowed down a path of drainage of heated water. Thus, water temperature was maintained in an outside storage tank at a temperature of +50 degrees Celsius. At the same time, naturally, as solution with nanoparticles, and a green leaf about +50 degrees Celsius got warm too.

For an assessment of effectiveness of the method used in work, that is for definition of a share of the particles introduced in leaf cages, and shares of the particles which remained on its surface the following experiment was made. Processed and beforehand the leaf which is dried up within 10 clocks was crushed. Drying of a leaf was necessary in order that green material did not influence results of experiment. Then the crushed leaf was diluted with distilled water and the received solution was filtered. Visual survey of solution showed that solution took more turbid form in comparison with the similar solution received from a leaf, not exposed silver particles, and after his endurance under sunshine the weak luminescence appeared. To exclude effect of scattering of sunshine absorption spectra of the received solution were measured. Measurement of absorption spectra was taken in the range of 350–650 nanometers. The received range is presented in Figure 6 (curve 1). From drawing it is visible that the range consists of an absorption band in the field of 420–430 nanometers. Comparison with literary data confirmed a truth of the received results. The received result also confirmed our hypothesis of a possibility of introduction of nanoparticles in cages of green plants. Value of the registered optical density of initial solution (Figure 6, a curve 2) showed that it is possible to draw a conclusion that the quantity of particles of silver in solution considerably decreased (curves also show it in drawing).

But still early to speak about an absolute accuracy of this method without the subsequent researches, application of opportunities of a submicroscopy and careful measurements of a luminescent emission.

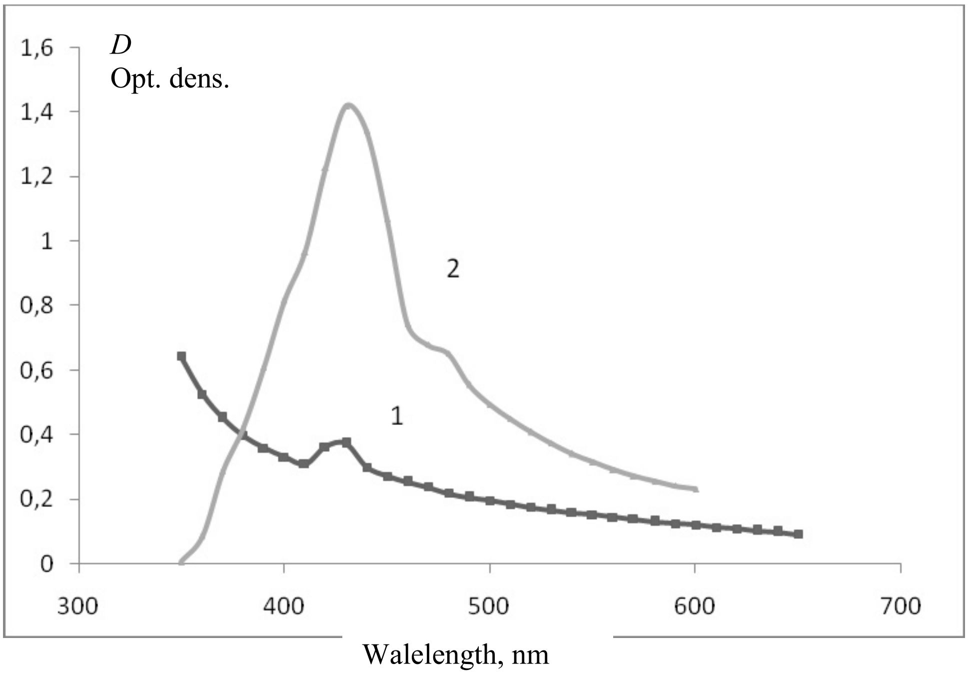

Figure 6. Absorption spectrum of nanoparticles of silver: after repeated disolution (1),
in initial solution before introduction of particles of silver (2)

Conclusion

On the basis of the received results it is possible to draw a preliminary conclusion that the method of introduction of nanoparticles of silver offered in this article in green leaves of house plants is rather effective. It is possible to assume that nanoparticles of silver «are built in» the extended time of cages, the results received at measurements of absorption spectra testify to it (Figure 6, a curve 1).

During further experiments research of luminescent properties of the green leaves «enriched» with nanoparticles of silver of various dimension is supposed. In particular it is expected that when using nanoparticles dimension to 15 nanometers, the effect of strengthening of a photoluminescence of green leaves will increase several times.

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Жасыл жапырақтарға күміс нанобөлшектерін енгізу технологиясы және фотошағылу үрдістерін зерттеу

Мақалада күміс нанобөлшектерімен «байытылған» бөлмеде өсетін өсімдіктердің жасыл жапырақтарының спектрлік сипаттамаларын зерттеу нәтижелері келтірілген. Нанобөлшектердің өлшемдері 80 нм сәйкес келеді, ал пішіні бойынша олар сфера тәрізді. Жұтылу спектрлеріне 350–650 нм диапазонында жүргізілген зерттеу жұмыстары нанобөлшектердің жасыл жапырақ көлеміне «енгенін» көрсетті. Күміс нанобөлшектері енгізілген ерітіндісіне жүргізілген талдау алынған нәтижелерді дәлелдеді. Ол мәліметтер органикалық объектілердегі фотопроцестерді тереңірек түсінуге үлес қосады. Практикалық жағынан жұмыс нәтижелері фото-биологиялық сенсорлармен сезгіштерді жасауға қолданылуы мүмкін.

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Технология внедрения наночастиц серебра в зеленые листья и исследование процессов фотоизлучения

В данной работе представлены результаты исследования спектральных характеристик зеленых листьев комнатных растений, «обогащенных» наночастицами серебра. Размеры наночастиц соответствовали 80 нм, форма — сферическая. Отмечено, что исследования спектров поглощения в диапазоне 350–650 нм показали, что наночастицы «встроились» в объеме зеленого листа. Анализ спектров поглощения, полученных при измерении раствора с наночастицами серебра, также подтвердил полученные результаты. Полученные данные, подчеркнуто авторами, могут способствовать пониманию фотопроцессов в органических объектах. Определено, что практическая часть исследования обусловлена возможностью создания фото-биологических сенсоров и датчиков.