New Compositions of Cadmium Selenium Nanoparticles and Dye Molecules with Cyclodextrin Inclusion Complexes

M.M. ASIMOV[1*], S.S. ANUFRIK[2], V.V. TARKOVSKY[2], H.H. SAZONKO[2]
[1]Institute of Physics National Academy of Science of Belarus, Minsk, Belarus
[2]Yanka Kupala State University of Grodno, Grodno, Belarus
m.asimov@dragon.bas-net.by

***Abstract* — Spectroscopic properties of new heterogeneous multicolor compositions based on cadmium selenium (CdSe/ZnS) nanocrystal and inclusion complexes of dye molecule with β – cyclodextrin are presented. Spectral florescence of proposed compositions investigated in thin films. Signals from multicolor fluorescence of proposing compositions may be combined to definite spectral codes that could be used for tracking or verification of different objects. Calibration bar of signal within spectral codes guarantee high reliability in practical application of proposed multicolor compositions. Express analysis the size of nanoparticles during their synthesis and purification by spectroscopic methods is suggested. Application of Cyclodextrin molecules as target delivery systems is considered.**

Key Words: **Cadmium Selenium, β – cyclodextrin, dye molecule, fluorescence, multicolor composition.**

I. INTRODUCTION

Arising interest to nanoparticles like CdSe is based on photophysical and spectroscopic properties that are determined by their size. Nanoparticles are widely used in spectroscopic and biological investigations, in particular, as fluorescence marking substances of biological structures [1-4]. Nanoparticles also investigated as laser material for multicolor generation.

Spectroscopic properties of nanoparticles are depended on their size. This phenomenon gives the possibility for creation variety of compositions with new spectral-luminescence properties in combination of dye molecules. Such materials are interesting for a different application such as spectral coding, active laser medium etc.

As it well-known dye molecules are widely used in printing industry and informational technologies [5, 6] due to their unique spectroscopic properties. Development of new type of inks and dye molecules increases the level of document protection.

Technological progress in this direction significantly improves reliability and efficiency of this kind of document protection and verification method.

One of the perspective approaches in developing above mentioned direction is synthesis of compositions using achievements of modern nanotechnologies. In present the most interest is connected with the CdSe nanoparticles as the component of composition materials with dye molecules.

Combination of spectral-luminescent properties in wide spectral range extends the choice of creation unique multicolor compositions with nanoparticles. Interesting compositions, systems and methods for tracing and/or identifying a library of elements using signals from one or more semiconductor nanoparticles combined to define spectral codes are proposed.

Fluorescence quantum yield of nanoparticles can reach about 90% and narrow symmetrical emission spectral bands practically dose not overlap. Therefore it is possible to obtain clean and bright colors in wide spectral diapason. The size of nanoparticles should be taken into account using it as component of compositions with dye molecules. So combination of nanoparticles with defined size and different dye molecules allow create compositions of matter with predicted spectral properties. In this paper the results of spectral-luminescence investigations of new compositions of CdSe nanoparticles and the molecules of Rhodamine 6G with β - Cyclodextrin.

II. MATERIALS AND METHODS

For investigations of spectral-luminescence characteristics of compositions nanoparticles of CdSe synthesized at the Institute of physics and chemical problems of Belorussian State University has been used. Initial concentration of CdSe nanoparticles in water solution was $2*10^{-4}$ M/l. For prevention of aggregation processes all solutions stored at reduced temperature about $+5^0$C. This precaution guaranteed stability of solution during the measurements of spectroscopic characteristics of investigating compositions. The chemical structure of the molecule of Rhodamine 6G [7] is presented in fig. 1.

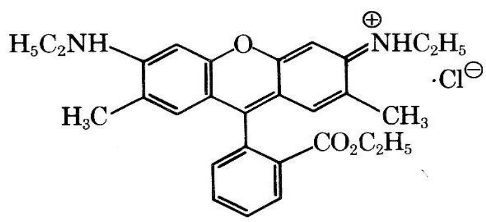

Fig.1 – Chemical structure of Rhodamine 6G

Spectral-luminescent characteristic of Rhodamine 6G molecules has been modified by formation of inclusion complexes with β – Cyclodextrin. In fig.2 the chemical structure of cyclodextrin molecule is presented [8].

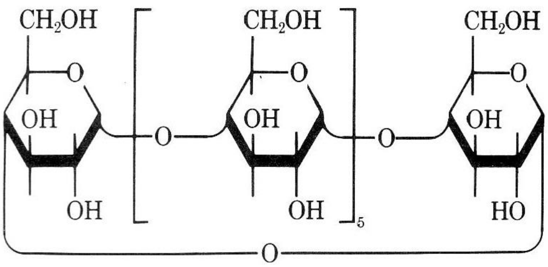

Fig.2 – Chemical structure of Cyclodextrin

Cyclodextrins are cyclic, non-reducing oligosaccharides consisted from six, seven or eight glucopyranose units. The most important and readily accessible of this group is β – Cyclodextrin. This molecule is able to include into inner cavity different dye molecules. An attractive properties of β – Cyclodextrin is it high water solubility. Cyclodextrins are able to form "host-guest" complexes with hydrophobic molecules given the unique nature imparted by their structure. As a result, these molecules have found a number of applications in a wide range of fields. Other than the above mentioned pharmaceutical applications for drug release, cyclodextrins can be used in environmental protection: these molecules can effectively neutralize inside their rings variety of toxic compounds, like heavy metals and hazard chemicals – ecotoxicants. Cyclodextrins also can form complexes with stable substances, like trichlorfon (an organophosphorus insecticide) or sewage sludge, enhancing their decomposition [9, 10].

Cyclodextrins are water-soluble due to all of hydroxyl groups are located on the outer surface of the ring and the internal cavity of the doughnut-shaped molecule is slightly apolar.

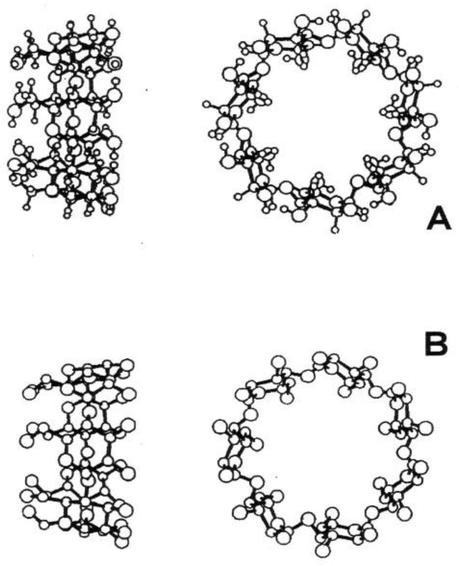

Fig.3 – Spherical rode model of β - Cyclodextrin: (A) - view from side and top; (B) - from side and bottom

Cyclodextrins attracts by their photo technological ability to modify photochemical and photophysical properties of big amount of different organic molecules.

Cyclodextrins are transparent in visible spectral range and do not introduce additional absorption and/or fluorescence bands to the spectroscopic characteristics of dye molecule "host -guest" inclusion complexes [11, 12].

The formation of the inclusion compounds greatly modifies the physical and chemical properties of the guest molecule, mostly in terms of water solubility. This is the reason why cyclodextrins have attracted much interest in many fields, especially pharmaceutical applications: because inclusion compounds of cyclodextrins with hydrophobic molecules are able to penetrate body tissues, these can be used to release biologically active compounds under specific conditions.

In most cases the mechanism of controlled degradation of such complexes is based on pH change of water solutions, leading to the cleavage of hydrogen or ionic bonds between the host and the guest molecules. Alternative means for the disruption of the complexes take advantage of heating or action of enzymes able to cleave α-1,4 linkages between glucose monomers [13, 14].

Cyclodextrins are typical "host" molecules and may trap a great variety of molecules. They may include "guest" molecules totally, or in part, only by physical forces, i.e. without covalent bonding.

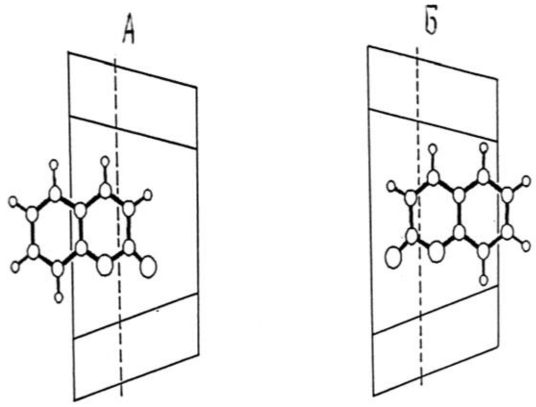

Fig.4 – Direct and reverse inclusion of dye molecule into cavity of Cyclodextrin

Investigations of spectroscopic characteristics of created new compositions were carried out in thin film by using Methyl Isobutyl Ketone $\{(CH_3)_2CHCH_2OH)\}$ that used as a solvent in inkjet printers. Fluorescence and excitation spectra of investigating composition were measured using spectrofluorimeter SFK1211A ("Solar", Minsk).

Concentration of CdSe nanoparticles and "inclusion complexes" of Rhodamine 6G molecules with β – cyclodextrin in thin film was $1 \cdot 10^{-5}$ M. Spectral - luminescent characteristics of the component of composition of matter were measured also separately in order to compare with the characteristics of latter. All measurements were carried out in thin film covered on quartz plate.

III. METHOD OF THERMAL ACTIVATION

For obtaining inclusion complexes the method of thermal activation in distilled water is used. Organic molecule and cyclodextrin dissolves in water (a mixture of water and ethanol) in the ratio of 1:1 or 1:5. This solution is slowly heated to a temperature of 60^0 C under continuous stirring until ingredients completely dissolves. Then solution is then slowly cools to room temperature. It is possible some of the sediment, which indicates the excess of cyclodextrin in the mixture. The resulting solution must be filtered.

Obtained solution is slowly heated up to the temperature of 60^0 C at continuous stirring until ingredients completely dissolves. Then solution is slowly cool down to room temperature. It is possible some deposition of excess of cyclodextrin in the mixture. Prepared by this methods solution must be filtered.

The formation of the inclusion complexes with of organic molecules is controlled by a comparison of the maxima of fluorescence spectrum with the original components of organic compounds and their complexes. Maximum fluorescence spectrum of the complexes shifts to a long wavelength spectral range by few a nanometers. Another method of controlling the formation of the inclusion complexes is a comparison of the life time of fluorescence of original molecule with the original organic compounds.

IV. METHOD OS MECHANICAL ACTIVATION

The most effective way of obtaining an inclusion complexes is the method of mechanical activation in planetary - centrifugal mill with water-cooled (type AGO-2) in centrifugal acceleration of 20 g and time of the mechanical processing of 20 minutes. The typical molar ratio of mixture components (organic molecule and β – cyclodextrin) vary in the range of 1:1 - 1:5, respectively.

When using this process, to obtain complexes enable to monitor the impact of disaggregation on the change of physical and chemical properties of the investigated organic compounds.

Mechanical processing of a mixture of organic compounds and β – cyclodextrin lasted not less than 40 minutes with selection of probe samples for analysis in every 5 minutes. Analysis of samples was carried out using the methods of IR and NMR spectroscopy for the controlling any structural changes (oxidation, polymerization, etc.) in the organic molecule.

For the effective formation of inclusion complexes it is necessary penetration of molecule or its part that is complementary to β – cyclodextrin plane (see Fig. 3). Included molecule is oriented in such a way as to achieve maximum contact between the hydrophobic part of the "guest" and low-polarity internal cavity of β – cyclodextrin. Hydrophilic part of the "guest" molecule is as far as possible remains outside of the cavity providing maximum contact with the solvent and hydroxyl groups of β – cyclodextrin [15].

V. RESULTS AND DISSCUTIONS

Before the investigation of spectral-luminescence characteristics of multicolor compositions spectral properties of it component was measured. A fluorescence spectrum of CdSe nanoparticles in thin film under the excitation wavelength at λ = 360 nm is presented in fig. 5.

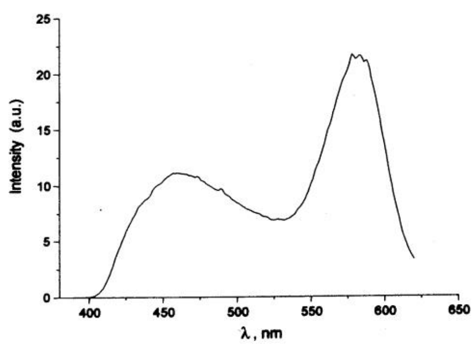

Fig.5 – Fluorescence spectra of CdSe in thin film under excitation at λ = 360 nm

As it seen fluorescence spectrum of CdSe nanoparticles consist from two bands with maximum at λ_1^{max} = 460 nm and λ_2^{max} = 580 nm. The intensity of long wavelength band is approximately two times higher than shortwave one.

An obtained result demonstrates domination of two sizes in synthesized CdSe nanoparticles. According the fluorescence spectrum of CdSe nanoparticles in thin film the maximum wavelength of shorter band correlates with size of particles few nanometers.

Fluorescence band in long wavelength spectral range is due to particles with size of tens nanometers. At the same time in introduced into thin film CdSe nanoparticles consisted number of amount particles with different sizes but at very low concentrations. That why fluorescence spectrum of synthesized CdSe nanoparticles dominantly consists of two intensive bands.

Fluorescence spectra of compositions of CdSe nanoparticles with inclusion complexes of Rhodamine 6G with β – cyclodextrin molecules are presented in fig. 4.

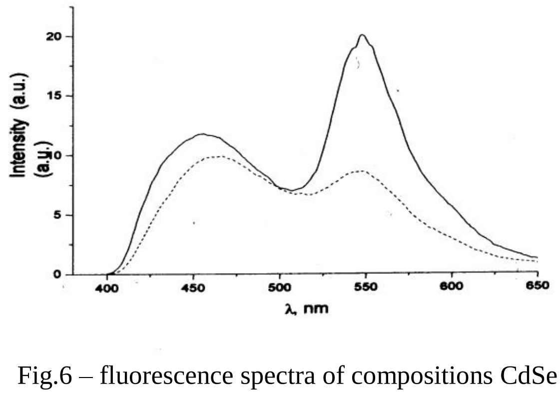

Fig.6 – fluorescence spectra of compositions CdSe quantum dots with inclusion complexes of Rhodamine 6G and β – Cyclodextrin

As it seen from fig. 6 under the excitation of investigating compositions at λ = 350 nm dual fluorescence is observed. Moreover long wavelength band is twice intensive than short-wave band of fluorescence. At the same time under the excitation at λ = 380 nm intensity of long wave fluorescence decreases more than the short-wave one. The maximum of short-wave fluorescence is slightly shifts towards long wave spectral region.

These results also demonstrate perceptivity developing unique multicolor compositions on the base of nanoparticles and different inclusion complexes of dye molecules with cyclodextrins for many practical applications.

The obtained results of investigation of spectroscopic properties of CdSe nanoparticles in thin film is interesting in practical application due to dual spectrally separated fluorescence bands.

Different spectral bands from one or more nanoparticles open possibility in creating new compositions for spectral coding and other different applications. Such compositions may be used as original markers that easily could be visually controlled by the color emission.

New compositions on the base of cadmium selenium nanoparticles and "inclusion complexes" of Rhodamine 6G with β – cyclodextrin demonstrate potential possibility of their practical application in spectral coding.

An obtained result demonstrates domination of two sizes in synthesized CdSe nanoparticles. According the fluorescence spectrum of CdSe nanoparticles in thin film the maximum wavelength of shorter band correlates with size of particles few nanometers. Fluorescence band in long wavelength spectral range is due to particles with size of tens nanometers.

Cadmium selenium nanoparticles with two separated fluorescence bands in thin films on the base of Methyl Isobutyl Ketone may be considered as compound for tracking and verification of different materials including documents and books.

Obtained results shows perceptivity of developing this approach in creating grate number of original multicolor heterogeneous compositions with different nanoparticles, dye molecules and cyclodextrins.

Proposed approach may be applied in clinical practice as well as developing an effective laser active medium for multicolor generation. Cyclodextrin inclusion complexes are very promising substances for application in target drag delivery systems.

VI. CONCLUSION

Spectral-luminescence characteristics of new compositions of matter on the base of cadmium selenium nanoparticles and "inclusion complexes" of Rhodamine 6G with β – cyclodextrin demonstrate potential possibility of their practical application in spectral coding.

Cadmium selenium nanoparticles with two separated fluorescence bands in thin films on the base of Methyl Isobuthil Ketone may be considered as compound for tracking and verification of different materials including documents and books.

Optical method of express analysis the size of nanoparticles at the process of synthesis and purification based on their fluorescence excitation spectra is proposed. Developing approaches are promising in creating great number of original multicolor compositions with different nanoparticles, dye molecules and cyclodextrins.

Proposed approach may be applied in developing an effective laser active medium for multicolor generation.

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