Physico-chemical properties of nanocomposites based on multi-component hybrid quantum dots

Zarangiz Islomova, Alisher Ishankulov*, Kadriddin Khalilov, Radik Shamilov, Nurali Mukhamadiev, and Yuriy Galyametdinov

1 Samarkand state university, Samarkand, Uzbekistan
2 Kazan National Research Technological University, Kazan, Russia

Abstract. Composites of inorganic nano objects such as quantum dots (QDs) and organic materials such as luminescent or polymers can be developed based on them for special applications such as optical devices, electro-optical devices and computing. In the study, nanocomposites based on multi-component quantum dots were obtained and nanocomposites were obtained by inserting them into polymethyl methacrylate (PMMA). First, core/shell hybrid quantum dots were synthesized, then core/shell/shell systems were obtained, and their absorption, luminescence spectra and sizes were obtained. In this work, information is presented about the opening of wide opportunities for the use of semiconductor nanocrystals related to obtaining new hybrid nanocomposite systems for nanomedicine and biomedicine.

1 Introduction

© The Authors, published by EDP Sciences. This is an open access article distributed under the terms of the Creative Commons Attribution License 4.0 (https://creativecommons.org/licenses/by/4.0/).
various fields of science and technology: in micro and optoelectronics, Polymer nanocomposites, for example, as new optical and light-emitting devices with high intensity, in optics and laser technologies [4,5]. When such nanostructured composites are used as active layers of light-emitting diodes, it is possible to combine and combine the radiation of both components in one device. Thus, new organic-inorganic light sources are created, which makes them the material of the future.

Quantum dots have unique optical and chemical properties, together with high photostability and the use of powerful excitation sources in a wide spectral range. Nanostructures have great potential for functional applications. However, the use of these materials is still very limited due to the difficulty in tuning their properties by controlling their morphological or structural properties. In addition, since the general properties of nanoscale systems are very different from the properties of individual particles, the special topology implemented in the nanocomposite material is another way to modulate the functional properties [6-8].

One of the most common methods for the synthesis of quantum dots is the chemical deposition method, which is based on reactions between metal ions and organic compounds [9]. Various organic compounds can be used as surfactants in the synthesis of quantum dots. Synthesis of CdSe/ZnS quantum dots using natural compounds, including flavonoids, quercetin as a surfactant is one of the current problems.

Currently, worldwide research activities in the field of nanostructured materials are mainly focused on metal and semiconductor nanoparticles. Due to their very small size, metal and semiconductor nanostructures are difficult to process, store and use.

2 Methods

The All QDs syntheses were carried out in a 15 mL quartz flask on a magnetic stirrer under an inert (argon) atmosphere. A fluoroplastic plug with a thin slot was used to supply and expel argon and tracers into the reaction medium. A variable power ceramic heater was used to heat the reaction mixture. The temperature was controlled using a chrome-aluminum thermocouple. During the synthesis, the Ar pressure was controlled by a traditional reducer.

To obtain a nanocomposite of quantum dots with PMMA-based nanocomposites, the following were used: ready-made CdSe/ZnS quantum dots (luminescence peak 515 nm) and CdSe/CdS (luminescence peak 600 nm) stabilized with oleic acid; polymethyl methacrylate (Sigma Aldrich); toluene (analytically pure, KhimReaktiv), sodium hydroxide (analytically pure, GOST 4328-77); distilled still water (pH = 7) (GOST R 58144-2018), L-cysteine (Sigma Aldrich), citric acid (GOST R 53040-2008). All reagents were used without further purification.

Synthesis of core/shell hybrid CdSe/ZnS quantum dots

To grow the ZnS shell around the CdSe core, the authors used the method presented in [10-12]. By growing a shell on the surface of the CdSe core, the core diameter, extinction coefficient and concentration were determined.

The absorption of a monochromatic light flux by a homogeneous medium obeys the Buger-Lambert-Ber law (1):

\[ \frac{1}{I_0} = 10^{-\varepsilon cl} \]

where \( I_0 \) is the intensity, energy (or number of quanta) of the monochromatic light falling on the front surface of the material layer per unit of time; \( I \) - intensity, energy of the light that passed through the substance layer within a unit of time; \( l \) - layer thickness, cm; \( s \) - substance concentration, mol/l; \( \varepsilon \) - is the molar absorption coefficient, l/(mol·cm). The absorption coefficient depends on the nature of the substance, the wavelength of the light, etc.
property. The dependence of the optical density on the wavelength (\(\lambda\) nm, cm) or frequency (\(v, cm^{-1}\)) of the absorbed light represents the absorption spectrum of a given substance. 

Electron-optical properties of quantum-sized structures depend on the size of the crystal in the direction in which the movement of charge carriers is limited (quantum-sized effect).

In this approach, states for electrons (slots) are obtained analytically by solving the Schrödinger equation (2) for the orbital quantum number (s-state) for a potential well with infinitely high walls:

\[
E_n^{\text{eff}}(h^+) = \frac{\hbar^2 \pi^2 n^2}{2m^*_e(h^+)} R^2 
\]

Here

\(\hbar\) - Planck's constant;

\(m^*_e\) - effective mass of an electron (slit);

\(R\) - QD radius;

\(n\) - principal quantum number.

Corrections to the size of the closed region of a massive crystal are distinguished according to the nature of matter within the energy distribution of the lowest electron and slit states (3):

\[
E_{\text{eff}} = E_{\text{mass}} + E_{1.0}^{\text{mass}}(R) + E_{1.0}^h
\]

Here

\(E_{\text{eff}}\) - Values of effective closed region for QD;

\(E_{\text{mass}}\) - the size of the closed area of a massive crystal;

\(E_{1.0}^{\text{mass}}\) and \(E_{1.0}^h\) - are the energy values of the first level of size quantization for electron and slit, respectively.

Methodology for obtaining nanocomposites of quantum dots

Preparation method of CdSe/ZnS QD nanocomposite with PMMA. Polymethylmethacrylate was chosen as the base polymer due to its superior photoluminescence properties.

A solution of quantum dots with a concentration of 2 mg/ml was obtained in toluene. Next, PMMA was also dissolved in toluene (2 mg/ml). The resulting solutions are mixed in different proportions of KN + PMMA: 1/1; 7/3 and 2/8. Nanocomposite films were obtained by spin coating from a solution in toluene using a Spin Coater Laurell WS-400-6NPP-LITE rotating at 1000 rpm. As a substrate for composite films, transparent quartz glass was used in the UV and visible regions of the spectrum. The resulting films were then dried in a vacuum device to completely remove the toluene.

Results and Discussions

Oleic acid was used as a stabilizer, and CdSe/ZnS CNs were synthesized at high temperature in octadecene environment. In the luminescence spectrum of the obtained CdSe/ZnS nanoparticles, the relative intensity range corresponds to the wavelength of 500-600 nm (Fig. 1). Hybrid CdSe/ZnS KNs have a narrow and symmetrical intensity range of the luminescence spectrum. "Core-shell" hybrid CdSe/ZnS quantum dots obtained by organic synthesis in an inert atmosphere show the maximum of luminescence intensity in the range of 576 nm.
During the study, a microscopic image of quantum dots was also obtained by doping on polymethyl methacrylate (Fig. 2). It was found that the shape of multi-code spheres is spherical.

With an increase in the concentration of luminophores, the intensity of radiation at wavelengths $\lambda = 465$ nm and $545$ nm for CdS/ZnS and ZnSe/CdS/ZnS quantum dots does not increase uniformly, and due to the decrease in concentration in the PMMA matrix, the maximum KN content is 20% (Fig. 3).
After determining the luminescence and absorption spectra of CdSe/ZnS quantum dots, the average hydrodynamic size distribution histogram of the nanoparticle was also obtained.

The average hydrodynamic (GD) size of the synthesized CdSe/ZnS CNs was 9.3 nm, taking into account the stabilizer shell (Fig. 4).

The main reason for this increase in the overall size is the growth of the ZnS shell on the surface of the CdSe core. Because the size of the ZnS shell monolayer is 0.35 nm. As can be seen from the hydrodynamic measurement, we can see that the monodispersity of nanoparticles is reduced by the growth of the shell on the surface of the core.

Fig.4. Number-weighted distribution of the hydrodynamic size of the CdSe (a) and CdSe/ZnS (b) nanoparticles.

4 Conclusions

The luminescence properties of thin films of nanocomposites based on CdSe/ZnS and CdSe/CdS QDs with polymethylmethacrylate were obtained and studied. The luminescence spectra of the composites were found to be significantly dominated by the PMMA peak; An increase in QD concentration causes a slight shift of the PMMA emission peak to the region of shorter wavelengths. It has been shown that up to 50% mass uniformity can be achieved in composites with PMMA.

A technique for obtaining hydrophobic nanocomposite microparticles containing CdSe/ZnS QDs, i.e., sulfur-containing surfactant particles, has been developed. It was found that the intense luminescence of QDs in microparticles is preserved, the position of the peak is slightly shifted to longer wavelengths. It has been shown that polymer particles tend to aggregate and gradually settle out of the aqueous phase.

References


Murray C.B., Norris D.J., Bawendi M.G.  

Gutsev L. G., Dalal N. S., Gutsev G. L.  

Arif S. Amin B., Ahmad I., Maqbool M., Ahmad.  

Ishankulov A. F., Halilov Q. F., Muxamadiev N. Q., Shamilov R. R., Galyametdinov, Y. G.  

Leontyev A.P., Yaroshchuk I.O., Smirnov S.V., Kosheleva A.V., Pivovarov A.A., Samchenko A.N., Shvyrev A N.  

Khalilov K.F. et all.  

Speranskaya E. S., Goftman V. V., Goryacheva I. Y.  