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THE CdSe/CdS QUANTUM DOTS LUMINESCENCE ENHANCEMENT NEAR SILICA LAYER WITH THE ION-SYNTHESIZED SILVER NANOPARTICLES

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Abstract Photoluminescence characteristics of hybrid quantum dots CdSe/CdS deposited on the surface of silica containing the layer of ion-synthesized silver nanoparticles were studied. The quenching or enhancement of the luminescence depending on distance between silver nanoparticles and quantum dots layers was detected. The optimal spacer layer and excitation waveleghth for the highest intensity of their photoluminescence in the plasmon field of metal nanoparticles was defined.

1. Introduction

Recent years some interest was significantly increased in different luminescent materials due to their wide use in various light-emitting and optoelectronic devices, as well as in bio- and chemosensors. Considerable attention was attracted to quantum dots (QDs) based on metal chalcogenides, resulting in their photostability and size-dependent luminescence in the wide visible region [1]. The optical characteristics of the QDs depend on the presence in their vicinity of noble metal nanoparticles (MNP). Strong local plasmon field near MNP as result of conduction electron oscillations in external electromagnetic field could significantly increase the intensity of the QD luminescence [2]. The feature of MNP plasmon influence on the luminescence of QDs is determined by a combination of various factors such as the distance between MNP and QDs, their sizes, shape, type of chemical composition, the excitation wavelength etc [3–5].

Among different approaches for obtaining of MNP, such as chemical vapor deposition, vacuum deposition et al., the ion implantation is one of most interesting technology. This method allows to fabricate composite materials based on different dielectric matrices (silicate glass, polymers, crystals) containing in the surface layer ion-synthesized MNP of certain sizes [6]. Structures with MNP formed by ion implantation can be used to improve luminescence efficiency of different materials. For example, recently it was demonstrated the luminescence enhancement of thin ZnO films, deposited on the surface of silica containing ion-synthesized silver nanoparticles [7].

In present paper, we report on the designing a new system organized by a combination of a layer of silver nanoparticles produced by ion implantation in the surface region of the silica covered by thin film of chemically synthesized hybrid core-shell CdSe/CdS QDs, and a study an influence MNP plasmon field on the photoluminescence of QDs in such system.

2. Experimental Procedure

CdSe and CdSe/CdS QDs were obtained by colloidal method in an aqueous-organic media [8]. A solution of 0.72 g NaOH in 2 ml of bidistilled water was added 30 ml of glycerol and 10 ml of oleic acid. Further, the mixture was introduced 266 mg (1 mmol) of cadmium acetate dihydrate in 2 ml of water, after which the reaction mixture was heated up to 190 ºC. At this temperature 1 mmol selenosulfate was added to a solution, and the mixture was stirred for 15 min. After cooling the reaction mixture obtained CdSe QDs were extracted with n-hexane.

Hybrid CdSe/CdS core/shell QDs were obtained in water-ethanol medium containing 1 mmol of cadmium acetate dihydrate and CdSe QDs, which was introduced into a solution of thioacetamide (1 mmol) at a temperature of 50 ºC. These nanoparticles CdSe/CdS were purified by reprecipitation.

Plasmon structures on the base of silica (SiO_2) with the silver nanoparticles were prepared by low energy implantation by Ag^+ ions with an energy of 30 keV, a dose of $4 \cdot 10^{16}$ ion cm^{-2} at current density 8 μA cm^{-2} with ILU-3 accelerator by the technique described in detail in [6].

The photoluminescence and photoluminescence excitation spectra of QDs were detected by the Cary Eclipse (Varian) fluorescence spectrophotometer. Optical absorption spectra were measured with a two-beam spectrometer Perkin Elmer Instrumental LAMBDA 35. QDs size were evaluated by dynamic light scattering with Malvern Zetasizer Nano which was equipped with a narrow filter at 632.8 nm. The average size of the QDs was estimated to be of ~ 9.3 nm.

Thin films of QDs with a thickness about 35 nm were deposited by spincoating equipment from solution in n-hexane on the surface of blank silica and silica with ion-synthesized silver nanoparticles.

For same samples, between a glass surface with MNP and film with QD separating polymethylmethacrylate (PMMA) layer from a polymer solution in chloroform of various thicknesses was deposited.

3. Results and Discussion

In present paper the influence of the plasmon field of silver nanoparticles on the optical properties of CdSe/CdS QDs was studied in comparison with control samples with QD layers of the same thickness (about 35 nm) deposited on the surface of the blank silica. Figure 1 shows the absorption spectra of a control sample (SiO_2 + QD) and a test sample (Ag:SiO_2 + QD) consisting of the superposition of the contributions from absorption layers of silver nanoparticles and QDs in transparent region of silica from 340 to 800 nm. The wide selective band with a maximum at 400 nm appears as result of the surface plasmon resonance in the silver nanoparticles [9].

The effect of the plasmon electromagnetic field of MNP on the QD luminescence in the samples was studied when the luminescence was exited at the wavelength of 400 nm, corresponding to maximum plasmon absorption (figure 2). It is seen that the test sample with silver nanoparticles has the luminescence intensity of QD layer approximately twice lower compared with the control sample. The observed luminescence quenching is obviously explained due to nonradiative electron transitions or energy transfer from the QD to the MNP which happens in the case of a relative close space position to each other MNP and QDs [4].

In order to eliminate QD luminescence quenching in systems with MNP it is proposed in the literature to use some organic or inorganic spacer layers for increasing the distance between MNP and QDs [9, 10]. Therefore, we formed special samples, in which between the QD thin film and the surface of the silica with silver nanoparticles a thin layer of PMMA was introduced.

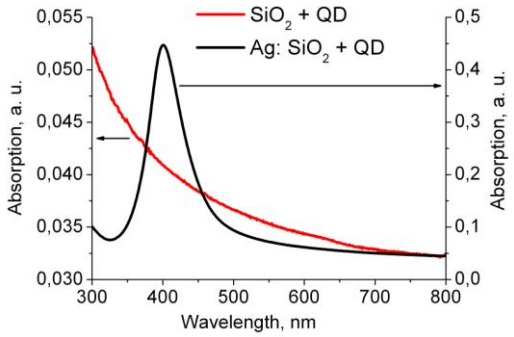

Figure 1. The absorption spectra of the samples.

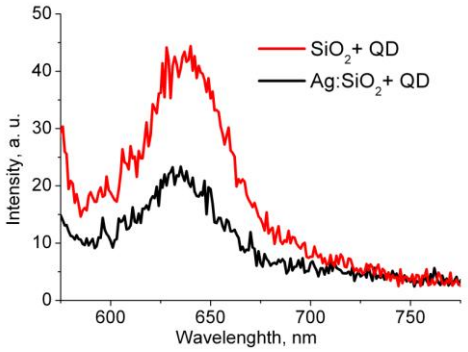

Figure 2. Photoluminescence spectra of the samples at an excitation wavelength of 400 nm.

The different thicknesses of the spacer layer were selected to estimate the impact of surface plasmon resonance of MNP on the QD luminescence intensity. Introduction a thin PMMA layer (~ 35 nm) in the structure of the sample lead to a decreasing of luminescence quenching. With increasing thickness of the spacer layer to 100 nm a luminescence quenching is replaced by a luminescence enhancement. The maximum increasing of the QD emission was defined for a layer with thickness of about 150 nm. Further increase in the thickness of the spacer layer results in a monotonic reduction of enhancement factor to 1.0 and the presence of silver nanoparticles in the such sample did not change the luminescence intensity of QDs.

As example, in figure 3 shows luminescence spectra of a test sample Ag:SiO_2 + PMMA + QD with a thickness of separation layer of 150 nm in comparison with a control sample SiO_2 + QD which were excited at a wavelength of 400 nm, as in case of figure 1. It is clear seen that the intensity of the QD photoluminescence at wavelength of 640 nm was increased by ~ 50 % at present case.

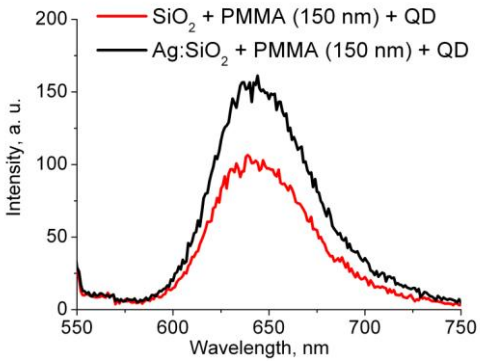

Figure 3. Photoluminescence spectra of the samples with the PMMA layer of 150 nm at an excitation wavelength of 400 nm.

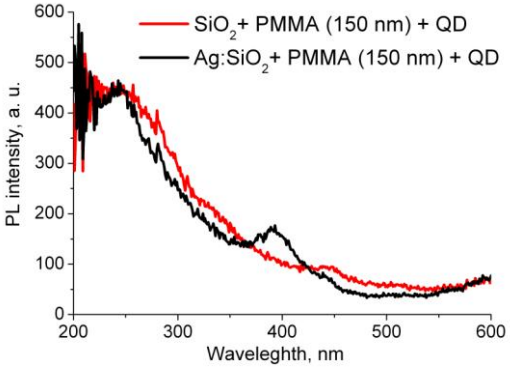

Figure 4. PLE spectra of the samples with the PMMA layer of 150 nm at a photoluminescence wavelength of 640 nm.

Thus in dependence on the distance between QD and MNP two competing processes could be occurred. First, it is nonradiative energy transfer from the QDs to the silver nanoparticles, which is possible only at very small distances between them. The second opposite effect is the luminescence enhancement of QDs located in a field near MNP, which decreases exponentially with a distance from the surface of MNP.

It is should be mention that the intensity increasing of QD luminescence is observed only when it is excited in the spectral region of the plasmon absorption of silver nanoparticles, as it is confirmed by

the spectral dependence of the photoluminescence excitation (PLE) for a test sample Ag:SiO_2 + PMMA + QD (figure 4). The PLE spectrum of this sample presents a selective band, which is matching in spectral position with the surface plasmon resonance band of silver nanoparticles (figure 1).

4. Conclusion

The multilayer systems consisting of CdSe/CdS quantum dots deposited on the surface of the silica containing ion-synthesized silver nanoparticles exhibiting surface plasmon resonance were formed. The effect of plasmon field of metal nanoparticles on photoemission characteristics of quantum dots layer depending on their distance was studied. The optimal spacer layer and excitation waveleghth for the photoluminescence enhancement of the quantum dots were determined.

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5. References

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