Luminescence properties of the hybrid Si-Ni nanoparticles system

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Abstract. The luminescence properties of the colloidal hybrid Si – Ni nanoparticles system fabricated in the pure water by pulsed laser ablation is considered. The redshifted photoluminescence of this system because of the Stark effect in the Coulomb field of the charged Ni nanoparticles has been registered in the blue range of the spectrum.

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1. Introduction

Nanoparticles (NPs) with sizes from a few nanometers to tens of nanometers are artificial materials which exhibit extraordinary optical and electrical properties due to its ultra-small sizes and in particular to quantum confined nature of their energy levels.

The extraordinary properties of size-tunable NPs has given rise to their wide spread applications in nanophotonics, plasmonics, biomedicine, lasing, photovoltaic etc \[1, 2, 3\]. Semiconductor NPs or quantum dots (QDs) are found a number of applications in the biomedical imaging due to the size- dependent flexibility of its luminescent properties. The NPs with the sizes 2-10nm, which is about of the size of small biomolecules, have the great potential for various applications in the modern biomedicine. In difference from organic biological labels, the luminescent QDs have several advantages. At first they have a wide absorption band and can be used with a variety of laser sources having different output wavelengths. On the other side, the luminescence band of QDs can be tuned from UV to IR by changing their sizes and this property allows combining several types of QDs at the one excitation wavelength. It is also important to notice that QDs are more photostable under the long time of laser irradiation. The existence of the mentioned properties of QDs could dramatically improve the use of fluorescent markers in the biological imaging.

During the last decade various methods have been investigated for the synthesis of NPs. Recently, a simple and flexible method of the pulsed laser ablation in liquid media (PLAL) has been demonstrated for the laser synthesis of metal nanoparticles \[4, 5, 6]\. This method also has been applied for synthesis of colloidal solutions of semiconductor QDs \[7, 8, 9]\. Laser ablation in liquids media is especially good-looking for biomedical applications, since NPs could be formed directly in specially prepared bio-conjugated media and such NPs colloidal solution can be exactly tuned for the specific biological target.

The formation of semiconductor nanoparticles via PLAL has been investigated in different experimental conditions, and photoluminescence properties of nanoparticles produced by the PLAL have been found to be strongly dependent as on the physical and chemical properties of liquid environment, as well as on the parameters of the laser irradiation. Laser ablation syntheses of nanoparticles could be explained in terms of the dynamic formation mechanism of the particle growth \[10\]. According this mechanism, a material of target evaporated in the laser plume very quickly aggregate into small embryonic particles, therefore such laser pulse parameters as pulse energy and duration could be highly critical in this process. In the paper \[11\] the influence of a laser beam transverse electromagnetic mode structure on the luminescence properties of laser synthesized GaAs nanoparticles has been studied. In the present work we studied luminescence properties of the Si – Ni hybrid colloidal nanoparticles system fabricated in pure water by the laser ablation method using a nanosecond Nd:YAG laser.
Figure 1. Schematic presentation of the laser synthesis of colloidal nanoparticles in the liquid medium.

2. Experimental arrangements

The pulsed passive Q-switched Nd:YAG laser with wavelength of 1064nm, pulse duration of 8ns and repetition rate of 10Hz was used to synthesize nanoparticles in pure water. The laser beam was focused on the surface of a bulk target (the plate of bulk Si or Ni) allocated in the glass cuvette with distilled water (see Figure (1)). Exposition of the laser irradiation was two hours. To produce hybrid metal-semiconductor system, at first we irradiated a Ni bulk target, then in the same cuvette with water solution of Ni nanoparticles was located the Si bulk target to produce Si nanoparticles. Hybrid nanoparticles system was produced also in similar scheme when Ni and Si nanoparticles were produced separately in different cuvettes and after that mixed in one solution. Note that luminescence spectra of the obtained hybrid nanoparticles were the same in these two experimental approaches. Note also that a luminescence of separately prepared Si nanoparticles was not observed. For luminescence measurements the water solution of nanoparticles was relocated into quartz cuvette with the transparent walls in the UV spectral range. The luminescence of the colloidal QDs was excited by the irradiation at 400 nm wavelength of the continuous wave diode laser with the power of 10mW. The luminescence spectra were analyzed by spectrometer constructed on the base of monochromator LOMO MDR-23-PMT. Electrical signal amplifier was used to enhance output of the PMT. Luminescence spectrum of colloidal Si - Ni QDs is presented in the Figure (2). The considerable blue shift of the photoluminescence has been registered with the location of the maximum at the wavelength of 455nm which is connected with the size-effect and significant difference from the well known
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Figure 2. Photoluminescence spectrum of colloidal Si - Ni nanoparticles.

The luminescence of a bulk Si material located in the near infrared region. The peak on the 400nm is the excitation laser wavelength. The bandwidth of the luminescence spectra on the halfheight was about 40nm that demonstrates the narrow size distribution of laser generated QDs, which is achieved without application of any size selection schemes. Possible contributions to the luminescence from a quartz material of the cuvette and water has been eliminated by a comparison with the photoluminescence from the same cuvette filled with the clean water or with the solution of Coumarin 120 organic dye (see Figure (3)). The long-term stability of the luminescence properties of the produced QDs was observed during the one year.

3. Theoretical consideration and discussion

Here we give some interpretation of the results of our experiment by estimations based on the known properties of silicon nanoparticles and quantum confinement effect, as well as the effect of the charged nickel nanoparticles on luminescence spectra of the colloidal Si quantum dots.

As is known [12], metallic nanoparticles generated in diverse media by the method of a laser ablation carry a positive or negative electrical charge. In our case, the charged Ni nanoparticles within the Si – Ni hybrid system induce a static electrical field which causes Stark shift of the electron-hole energy levels in the silicon QD. In the following, we consider a point charge at a certain distance from the surface of the silicon QD (see Figure (4)). The assessment of the Si nanoparticles luminescence spectrum shifting under the influence of a static electric field of an external charge allows us to explain
Figure 3. Photoluminescence spectrum of the Coumarin 120 organic dye (water solution).

The experimental results by the Stark effect in the inhomogeneous (Coulomb) field.

The external point charge \( q \) on the distance \( R_q \) from the center of the silicon quantum dot creates a screened electrostatic field at the point \( r \) inside the QD, potential of which can be given in the following form [13]:

\[
\Phi (r) = q \sum_{n=0}^{\infty} \frac{2n+1}{\epsilon n + n + 1} \frac{r^n}{R_q^{n+1}} P_n(\cos \vartheta),
\]

where \( P_n(\cos \vartheta) \) is the Legendre Polynomial, \( \epsilon \) -screening dielectric constant of Si QDs, \( \vartheta \) -angle between the vectors \( r \) and \( R_q \). The shift of the energy levels of an exciton caused by an external electrostatic field can be evaluated using the wavefunction \( \Psi_0(r_e, r_h) \) of the electron-hole system:

\[
\Delta E = \int d\mathbf{r}_e d\mathbf{r}_h [\Phi (\mathbf{r}_h) - \Phi (\mathbf{r}_e)] |\Psi_0 (\mathbf{r}_e, \mathbf{r}_h)|^2.
\]

(2)

Taking into account the form of the potential of the external field (1), the energy shift (2) can be represented in the form of the sum

\[
\Delta E = \sum_{n=0}^{\infty} \Delta E_n,
\]

(3)

where

\[
\Delta E_n = \frac{eq}{R_q} \int d\mathbf{r}_e d\mathbf{r}_h \left\{ \frac{2n+1}{\epsilon n + n + 1} \right\}.
\]
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\begin{equation}
\times \frac{(r^n_h P_n (\cos \vartheta_h) - r^n_e P_n (\cos \vartheta_e))}{R^n_q} |\Psi_0 (r_e, r_h)|^2 \right). \tag{4}
\end{equation}

The first term in the sum (3): \( \triangle E_0 = 0 \). We will estimate only the term corresponding to \( n = 1 \) taking into account the smallness of the other terms. Thus,

\begin{equation}
\triangle E_1 = \frac{eq}{R_q} \int dr_e dr_h \frac{3}{\epsilon + 2} \frac{r_h \cos \vartheta_h - r_e \cos \vartheta_e}{R_q} |\Psi_0 (r_e, r_h)|^2 , \tag{5}
\end{equation}

which can be written in the following form:

\begin{equation}
\triangle E_1 = \frac{D_{eq}}{R^2} \frac{3}{\epsilon + 2} \left( \langle z_h \rangle - \langle z_e \rangle \right) , \tag{6}
\end{equation}

where \( D \) is the size of an exciton, \( \langle z_{h,e} \rangle = \int |\Psi_0 (r_e, r_h)|^2 z_{h,e} dr_e dr_h \) are the mean values of the charge distribution density of the hole and the electron, respectively. To calculate the energy spectral shifting in accordance with the conditions of the above described experiment, let us estimate \( |\triangle E_1| \).

As is shown in [14], the emitted photon energy depends on silicone nanocrystallite size. With the decreasing of the size of nanoparticles the quantum confinement affects on the band gap of the exciton thereby increasing emission energy. During the experiment with the solely silicon nanoparticles the luminescence had not been observed in the visible spectrum at the irradiation by the wavelength of 400 nm. This fact evidences that bandgap energy of the Si QDs is more than 3 eV, which is agreed with the results of the work [15]. According to the work [14], such energies corresponds to silicon nanoparticles with diameter less than 1.4 nm. To determine the other parameters we will take for screening dielectric constant \( \epsilon = 6 \), which corresponds to the diameter \( D = 1.3 \) nm of Si quantum dots at the passivation with the hydrogen atoms, according to the paper [16].

As we consider Si nanoparticles generated in a liquid medium (pure water in our case), dangling bonds of the silicon atoms on the dot surface should be saturated mostly by the hydrogen atoms. Note that in the process of the laser ablation hydrogen molecules are produced due to water molecules dissociation in the surroundings of the laser plume. As is shown in the work [16], in the case of the hydrogen passivated Si nanoparticles the size of the exciton is approximately equal to the diameter of the QD.

Since we consider the nickel nanoparticles in close proximity from the silicone QDs, then \( R_q - R \ll R \), and Coulomb potential is strong enough to pull the hole away from the electron. In this case, the quantity \( |\langle z_h \rangle - \langle z_e \rangle| / D \) can reach as large as 0.5 [17]. Then, we have \( |\triangle E_1| = 0.207 \) eV. This shift of bandgap energy corresponds to a red shift of Si quantum dot luminescence spectrum by about 30 nm (it is clear that depending on the distance of the point charge from the surface of silicon QD this shift will be changed). This shift can explain the observation of blue luminescence in the case of hybrid Si-Ni nanoparticles system in opposite to the case of the solely Si nanoparticles in the colloidal solution.

Summarizing, by the luminescence picture of the mixed metallic-semiconductor nanoparticles in the colloidal solution one can define the sizes of quantum dots.
The Si colloidal QDs in liquids can be used in a number of optical applications, in particular, as luminescent markers in the biomedical imaging in vivo and in vitro. The knowledge of peculiarities of their luminescent properties is very important for such kinds of biomedical applications. More complex assemblies of nanocrystals can be easily constructed by the presented technique of laser synthesis of colloidal QDs including complexes of nanoparticles of different materials. These complex artificial structures will exhibit new physical and chemical properties that require further investigation and could be applied in the optical nanotechnologies. The results of this study may have far-reaching consequence for nanoparticles applications.

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