Plasmonic enhancement of photoluminescence from cadmium sulfide and lead sulfide quantum dots

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Abstract. Plasmonic core/shell nanoparticles Ag/SiO$_2$ with different shell thicknesses were synthesized. Localized plasmon resonance was investigated by UV-vis spectroscopy. Arranged layers of plasmonic nanoparticles and quantum dots were obtained on a quartz substrate using a spin-coating technique. Plasmon-enhanced photoluminescence excited by 405 nm laser corresponding to the plasmon resonance was studied on CdS and PbS quantum dots structures. The possibilities of twofold and fourfold intensity increase are demonstrated for CdS and PbS quantum dots respectively.

1. Introduction
In metallic nanoparticles, where the electrons are confined in the three dimensions, the electron density oscillations (plasmons) induce an electric field around the nanoparticle that can be much larger than the incident light one [1]. Such plasmonic particles open the possibility to amplify, concentrate and manipulate electromagnetic field at the nanoscale and enhance light absorption and luminescence of organic fluorophores [2, 3, 4] or inorganic quantum dots (QDs) [5, 6, 7] located near the metallic nanoparticles. Moreover, the metallic particle can modify the ratio of radiative and non-radiative QD decay rates and alter its quantum efficiency [8].

However, luminescence can be strongly quenched when a distance between plasmonic and emitting particles is small [9]. One of the reasons is that a charge carrier from an electron-hole pair photoexcited in an emitting particle can tunnel and be captured by metallic nanoparticle, so radiative recombination won’t happen (Figure 1, the leftmost piece). In this case, the luminescence is undesirably reduced in comparison with a system consisting only of radiating particles. To avoid this effect, it is necessary to suppress tunneling by creating a barrier between the particles. Such a barrier is usually made by a dielectric [10] or polyelectrolyte [5] spacer between plasmonic and emitting layers. The spacer thickness is typically ones or tens of nanometers, and there is some optimum thickness of the layer whereby maximal enhancement is observed. On the one hand, spacer thickness must be thick enough to suppress charge carriers tunneling, on the other hand, spacer thickness should be thin enough so the metal particle electromagnetic field can effectively impact the emitting particle.

In this paper, we propose instead a specially created layer between metal and semiconductor nanoparticles layers, use metal/dielectric nanoparticles containing a spacer as a shell of the structure. Possible ways to specify the distance between plasmonic and emitting particles in such way are shown in Figure 1. For instance, the metallic nanoparticle can be covered by SiO$_2$
shell while emitting nanocrystals can be covered by wide-bandgap semiconductor material shell to obtain type-I heterojunction nanostructures. In the most general case, the spacer may be distributed between the plasmon and quantum dot nanoparticles, so both types of particles can be coated. In this article emitting particles are semiconductor nanocrystals of cadmium sulfide CdS and lead sulfide PbS, covered with non-conducting oleic acid molecules. Plasmon particles are Ag/SiO$_2$ — silver core particles coated by silica layer of different thickness. All of these particles types are obtained by colloid chemistry techniques.

2. Experiment

Synthesis of 20 nm in diameter monodisperse silver nanoparticles was produced by the known procedure [11]. For the coating of silver nanoparticles by silica, it was applied a modified Stober technique, described earlier for gold nanoparticles [12]. Different shell thickness $h_s$ was achieved using different tetraethoxysilane (TEOS, silica precursor) concentrations. The following formula was derived of geometric and chemical reasons to determine TEOS amount $V_p$ needed to add into a given volume of the sol $V_{sol}$ of silver core particles to obtain specified $h_s$:

$$V_p = \frac{\eta_c}{\eta_s} \cdot \frac{M_c M_p}{M_s} \cdot \frac{\rho_s}{\rho_c \rho_p} \cdot \frac{V_{cs} - V_c}{V_c} \cdot C_c \cdot V_{sol},$$  \hspace{1cm} (1)

where $p$, $c$, $s$ are indices correspond to the precursor shell, shell material and the core material, respectively, $\eta$ — chemical yields of reactions for the formation of core and shell, $M$ — molar masses, $\rho$ — densities, $d_c$ — core diameter, $C_c$ — concentration of core nanoparticles. The average diameter of the silver core particles $d_c$ was calculated by following linear equation [13]:

$$d_c = \frac{\lambda_{\text{max}} - 382.6}{1.18}$$  \hspace{1cm} (2)

The results obtained from formula (1) are in agreement with atomic force microscopy data for Ag/SiO$_2$ nanoparticles deposited separately on an atomically smooth silicon surface.

Absorption spectra of Ag/SiO$_2$ particles are shown in Figure 2. As it is evident from spectra, shell-covered particles retain their monodispersity. The thicker a shell, the more red-shifted plasmon resonance peak due to the environment dielectric constant alteration (Figure 2, b). With such thin shells environment, the dielectric permittivity can be considered as combined dielectric permittivity of silicon dioxide and an aqueous medium. Particles were synthesised with the same core diameter $d_c = 20$ nm and different shell thickness $h_s = 15, 25, 35$ and 40
nm. These shell thicknesses were chosen because we expected the maximum enhancement when the spacer is less than 50 nm due to our preliminary work.

![Graph](image1.png)

**Figure 2.** (a) Absorption spectra of Ag/SiO$_2$ particles with different shell thickness and (b) the same spectra on a larger scale near the plasmon resonance maxima ($T = 300$ K)

Materials of quantum dots were selected as significantly differ in their optical properties, but rather similar in chemical nature. Absorption and photoluminescence (PL) spectra of colloidal quantum dot solutions are shown in Figure 3.

The PL maximum is Stokes-shifted from the first exciton peak in the absorption spectrum. In the case of CdS QDs besides narrow fundamental luminescence band, the wide PL band is observed in the long-wavelength region, related to unpassivated surface states in the core material, which also display radiative recombination. Spectral characteristics shape and peak positions stay the same for quantum dots, applied on the substrate.

![Graph](image2.png)

**Figure 3.** Absorption (---) and photoluminescence (-----) spectra of (a) cadmium sulfide and (b) lead sulfide quantum dots ($T = 300$ K)

QDs absorption spectra have the extensive nature, and optical density increases when wavelength decreases. Thus, the same short-wave emission source can be used for PL excitation in all the samples. In all experiments described below we used a low power (10 mW) laser 405
nm, corresponding to the simultaneous excitation of the plasmon resonance in Ag/SiO$_2$ particles and efficient PL excitation of semiconductor nanocrystals.

![Diagram of structures for study of the plasmon luminescence enhancement](image)

**Figure 4.** The scheme of structures for study of the plasmon luminescence enhancement

The general view of structures produced for the study of plasmon-enhanced luminescence is in Figure 4, where Ag/SiO$_2$ — nanoparticles with different shell thickness (0 — no shell, 15, 25, 35 and 40 nm) and QDs — quantum dots of different material (CdS or PbS). For obtaining these structures the following procedure was carried out: 20 $\mu$l of plasmonic nanoparticles aqueous solution was deposited on a quartz substrate by spin-coating. Then the substrate was placed in a furnace at 200$^\circ$C for 5 min. to remove a solvent. To achieve a continuous uniform layer of plasmonic particles described procedure was repeated 5 times. Then the procedure was repeated for QDs solutions, but the solvent removal was carried out at 100$^\circ$C temperature. Control samples were layers of quantum dots on quartz glass substrate without the underlayer plasmonic particles.

The obtained structures further were investigated by PL spectroscopy. The excitation of the samples PL was carried out by 405 nm laser from above through a thin layer of quantum dots. The spectra were measured by fluorescence spectrometer based on a diffraction grating and a silicon photodiode. Laser beam falls at 45$^\circ$ angle, but excited PL from QDs is normal to the input slit of monochromator. Polarization of incident and emitted light was not studied in this paper.

3. Results and discussion

For describing luminescence enhancement let’s preliminarily introduce the concept of the enhancement factor:

$$K = \frac{\text{max}(I(\lambda))}{\text{max}(I_0(\lambda))}$$

where $I(\lambda)$ and $I_0(\lambda)$ — structure photoluminescence spectra in the presence and absence of plasmonic particles correspondingly. Photoluminescence spectra of CdS and PbS structures in compose with different shell thickness Ag/SiO$_2$ nanoparticles are shown in Figure 5.

As it can be seen from CdS photoluminescence spectra luminescence associated with defect states also enhances. The largest enhancement factors (Figure 5, right) $K = 1.9$ for CdS and $K = 4.2$ for PbS are observed at $h_s = 35$ nm for both types of QDs. However, it should be taken into account that the thickness of the shells had discrete values and the optimum thickness can vary for different types of particles. Shapes of enhancement factor curves are also similar for both types of particles, despite their different PL wavelength region. CdS QDs show low quantum efficiency compared to PbS QDs and substantially their PL is determined by defect states on the surface, so we see that wide PL band related to those states is strongly enhanced. The sharp nature of the amplification curve is most likely due to the fact that both tunneling effects and plasmon field amplification effects are nonlinearly dependent on the distance. As
Figure 5. The photoluminescence spectra of CdS (top) and PbS QDs in the presence of plasmonic particles with different shell thickness. Right plots illustrate the dependence of the enhancement factor on the shell thickness.

follows from the absorption spectra of semiconductor and metallic nanoparticles (Figures 2 and 3), the techniques used to synthesize nanoparticles make it possible to obtain monodisperse nanocrystals, so we do not observe broadening of the gain characteristics that could be observed with an appreciable dispersion of particle diameter and shell thickness.

We assume that maximizing the effect on some optimal thickness is explained not only by considerations described in the introduction (the competition the tunneling of charge carriers and enhancing the electromagnetic field) but also by factors such as the total change of light scattering when using thicker shells (Figure 2). Some impact can be affected by changing the diameter ratio plasmonic nanoparticles and quantum dots. In addition, quantum dots of cadmium sulfide and lead sulfide have significantly different dielectric constants, which as we noted earlier affects the plasmon resonance of particles. This diversity of effects requires a clear theoretical consideration, but in this short paper, we only show the experimental fact of the enhancement effect itself.

4. Conclusions
The effect of the plasmon enhancement of photoluminescence was investigated for CdS and PbS nanoparticles in the presence of plasmon nanoparticles Ag/SiO₂ with different thickness of the dielectric coating (15 – 40 nm). Increasing of PL intensity for all the studied QDs is observed at some optimum spacer thickness, which is consistent with the results of the literature review.
The greatest gain for investigated photoluminescence quantum dots are observed at $h_s \approx 35 \text{ nm}$ with maximal enhancement coefficients: $K = 4.2$ for PbS and $K = 1.9$ for CdS quantum dots.

This approach, when instead of a system of metal particles layer/insulator layer, we used the composite particles of metal/insulator simplifies the process of creating structures with quantum dots, where it required the plasmonic enhancement of the absorption of light or luminescence. Our research shows that this enhancement can be very significant but it depends on the quantum dots, their optical properties, and quantum efficiencies.

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