Spectral manifestations of the exciton-plasmon interaction of Ag$_2$S quantum dots with silver and gold nanoparticles

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Abstract

The purpose of our study was to develop methods for creating hybrid nanostructures based on colloidal Ag$_2$S quantum dots, pyramidal silver nanoparticles, Au nanorods, and to determine the spectral-luminescent manifestations of exciton-plasmon interactions in these structures. The objects of the study were Ag$_2$S quantum dots passivated with thioglycolic acid (Ag$_2$S/TGA QDs) and 2-mercaptopropionic acid (Ag$_2$S/2-MPA QDs), gold nanorods (Au NRs), silver nanoparticles with pyramidal geometry (Ag NPs), and their mixtures. The spectral properties were studied using a USB2000+ with a PMC-100-20 photomultiplier system (Becker & Hickl Germany). The article considers the transformation of the luminescence spectra of colloidal Ag$_2$/TGA QDs and Ag$_2$/2-MPA QDs in mixtures with pyramidal Ag NPs and Au NRs. The study demonstrated the presence of the effects of the contour transformation of the luminescence spectra due to the Fano effect, as well as the luminescence quenching following direct contact between QDs and NPs.

Keywords: silver and gold nanoparticles, silver sulfide quantum dots, hybrid nanostructures, luminescence spectrum

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1. Introduction

Metal nanoparticles (NPs), semiconductor quantum dots (QDs), and hybrid structures based on them can be used to solve certain basic and applied science problems in biology, medicine, chemistry, optoelectronics, photocatalysis, etc. [1–10]. Most of these spheres require sensors which can be used for various purposes. These sensors include fluorescent thermometers, pH sensors, fluorescent indicators of impurity ions, and biosensors based on the luminescence of QDs and dyes as well as on light scattering from plasmonic NP, etc. It is possible to control the spectral position of the plasmon resonance of metal NPs using their size [5, 4], shape [11], and dielectric environment [12], as well as by changing the structure of their interface. Thus, NPs can be decorated with semiconductor QDs, whose luminescence spectra partially or completely overlap with the plasmon peak of the extinction spectrum. Creation of hybrid structures with plasmon-exciton coupling based on plasmonic NPs and semiconductor QDs, may result in the high sensitivity of the structures’ spectra to impurities, the environment, and the properties of the surrounding solution or matrix. As a result, hybrid nanostructures demonstrate both the additive properties of their components and novel unique sensory properties arising from direct interaction between the components and their close proximity to each other [6–18]. Variations in the regime of exciton-plasmon coupling (weak, intermediate and strong) enable resonance spectral-luminescent effects in the weak (Purcell effect), intermediate (Fano effect), and strong (Rabi splitting) regimes of exciton-plasmon coupling [14, 19–21]. The type of interaction and the distance between the components are crucial for such hybrid nanostructures. Of vital importance is to predict the spectral-luminescent properties of hybrid nanostructures. This problem has not been thoroughly studied yet. It is thus important to study the optical properties of synthesised nanostructures. To solve this problem, it is necessary to develop approaches to the synthesis of hybrid nanostructures based on technologies that allow for various regimes of exciton-plasmon interaction of metal NPs with QDs and dye molecules, as well as for the tuning of the optical resonance of the components of hybrid nanostructures.

The purpose of our study was to develop methods for creating hybrid nanostructures based on colloidal AgS quantum dots (AgS QDs), pyramidal silver nanoparticles (Ag NPs), gold nanorods (Au NRs), and to determine the spectral-luminescent manifestations of exciton-plasmon interactions in these structures.

2. Experimental

2.1. Samples

Colloidal AgS QDs, passivated using molecules of thioglycolic acid (AgS/TGA QDs) and 2-Mercaptopyruvic acid (AgS/2-MPA QDs) with an average size of 2.0 nm and 2.8 nm respectively, were synthesised using a one-step method. The method involves using TGA and 2-MPA molecules in the crystallisation both as the sources of sulphur and as passivators of QDs interfaces [22,23]. The approach involves mixing the initial reagent AgNO₃ (2.4 mM) and TGA (2-MPA) (4.8 mM). When TGA was used to passivate the QDs interfaces, distilled water was used as a solvent. When 2-MPA was used, the synthesis was performed in viscous medium (ethylene glycol).

The method of synthesising pyramidal Ag NPs was based on a combination of two methods: reduction of Ag with trisodium citrate (Na₃C₆H₅O₇) and reduction of Ag with sodium borohydride (NaBH₄). To do this we subsequently poured 0.5 ml of PVP (0.003 М), 3 ml of Na₃C₆H₅O₇ (0.03 М), 0.2 ml of H₂O₂ (30%), and 0.5 ml of NaBH₄ (0.05 моль) into the AgNO₃ (50 мл, 0.02 М) aqueous solution with constant stirring at room temperature. At this stage the formed particles were predominantly spherical. When the constantly stirred colloidal solution was subjected to optical radiation with a wavelength of 520 nm, pyramidal Ag NPs were formed.

The colloidal synthesis of Au nanorods was performed in the presence of a surface-active substance (SAS), cetyltrimethylammonium bromide (CTAB), whose aqueous solution forms cylindrical micelle, thus creating anisotropic environment for the growth of NRs. Au NRs were formed in several stages, which included subsequent preparation and mixing of the seeds and growth solutions. As a seed solution we used spherical Au NPs (3 nm), obtained by means of the
chemical reduction of HAuCl₄ (7 μl, 0.36 M) with a NaBH₄ solution (1.0 ml, 5mM) in the presence of CTAB (20 ml, 0.02 mM). The growth solution was a mixture of HAuCl₄ (28 μl, 0.36 M), CTAB (50 ml, 0.1 mM), AgNO₃ (100 μl, 0.02 M), and C₆H₈O₆ (5 ml, 0.05 μM). After adding the seed solution to the growth solution, the reaction mixture gradually becomes blue, purple, or brown-red depending on the ratio of the length of the Au NRs to their diameter. By adding variable concentrations of AgNO₃ to the growth solution we could regulate the ratio of the length of the Au NRs to their diameter. The obtained Au NRs were purified from reaction products by means of several cycles of centrifugation and dispersion.

Hybrid structures were formed by mixing colloidal solutions of Au NRs (pyramidal Ag NPs) and Ag₂S QDs/TGA (or Ag₂S QDs/2-MPA) with a molar ratio of [\(n(\text{NPs})] : [\text{[QDs]}] \sim 10^{-4} \text{ mole fraction (m.f.).}

2.2. Methods of experimental studies

The size and morphology of Ag₂S/TGA QDs, Ag₂S/2-MPA QDs, pyramidal Ag NPs and Au NRs were determined by means of a Libra 120 transmission electron microscope (TEM) (Carl Zeiss, Germany). The absorption properties were studied using a USB2000+ spectrometer (Ocean Optics, USA) with a USB-DT light source (Ocean Optics, USA). The luminescence spectra and the luminescence decay kinetics of Ag₂S/TGA QDs, Ag₂S/2-MPA QDs, and their mixtures with plasmonic NPs were studied using the USB2000+ and a TimeHarp 260 system for time correlated photon counting (PicoQuant Germany) with a PMC-100-20 photomultiplier tube (Becker&Hickl Germany) with a time resolution of 0.2 ns. A diode laser NDV7375 (Nichia, Japan) with a wavelength of 405 nm (200 mW) was used to stimulate the luminescence.

3. Results and discussion

Figure 1 presents TEM images of pyramidal Ag NPs and Au NRs. The analysis of TEM images demonstrated that pyramidal Ag NPs are formed with an average edge length of 19 nm (Fig. 1a). The photo-induced transformation of Ag NPs from spherical to pyramidal, followed by a growth in size, results in the shift of the extinction peak to longer wavelengths, from 480 nm to 590 nm (Fig. 2a, dotted line).

The described approach to the synthesis of Au NRs allowed us to obtain Au NRs with a size from 20÷9 nm to 25÷9 nm (Fig. 1b) and regulate their average size (ratio of the length to the diameter) by adding 100 μl and 70 μl of AgNO₃ (0.02 M) to the growth solution of Au NRs. The increased length of Au NRs results in the shift of the extinction peak to longer wavelengths, from 640 to 690 nm respectively (Fig. 2b, dotted line).

According to the results of TEM, the suggested methods of synthesising Ag₂S QDs and Ag and Au NPs provided for the compatibility of the components and the formation of hybrid structures. TEM images demonstrate that the largest number of QDs are observed next to Ag and Au NPs (Fig. 1).

The spectra of optical absorption of Ag₂S/TGA QDs and Ag₂S/2-MPA QDs shifted to shorter wavelengths relative to the edge of the fundamental absorption of single crystals of silver sulphide (1.09 eV). This happened due

Fig. 1. TEM images demonstrating the formation of associates of Ag₂S QDs with pyramidal Ag nanoparticles (a) and Au nanorods (b)
to the quantum size effect. In the absorption spectrum of colloidal Ag₂S/TGA QDs, we observed a specific feature in the 590 nm region, which was characteristic of the most probable excitonic transition in the absorption spectrum. When colloidal Ag₂S/TGA QDs were excited at the wavelength of 405 nm, we observed recombination luminescence, with the absorption band peak at 615-620 nm (Fig. 2a, b).

The absorption spectrum of colloidal Ag₂S/2-MPA QDs has a prominent peak at about 690 nm, corresponding to the most probable excitonic transition in the optical absorption spectrum. For colloidal Ag₂S/2-MPA QDs a recombination luminescence was observed with the peak at 820 nm (Fig. 2c).

Thus, the geometry and size of pyramidal Ag NPs (19 nm) and Au NRs (20÷9) nm ensured a significant overlap between their extinction spectra and the luminescence spectra of Ag₂S/TGA QDs (620 nm) (Fig. 2a, b). The mixture of Au NRs (25÷9) nm and Ag₂S/2-MPA QDs (820 nm) did not yield any significant overlap between their extinction spectra and the luminescence spectra of Ag₂S/2-MPA QDs (Fig. 2c).

Mixtures of Ag₂S/TGA QDs and Ag₂S/2-MPA QDs with plasmonic pyramidal Ag NPs and Au NRs demonstrated complex bands in the extinction spectra, which were not simply a sum of the spectra of mixtures components. It was also noted that the optical density increased over the whole extinction spectrum, when QDs and NPs were mixed. The difference in the location of the stop band peaks of the components and redistribution of the intensity within the resulting contours indicate the presence of exciton-plasmon interaction between the components.

Fig. 2. The extinction spectra of pyramidal Ag NPs (a) and Au NRs with size of (20÷9) nm (b) and (25÷9) nm (c), the luminescence spectra of Ag₂S/TGA QDs (a and b), Ag₂S/2-MPA QDs (c), and their mixtures with NPs.

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The most interesting patterns, however, were observed in luminescence spectra of QDs mixed with plasmonic NPs. Mixtures of Ag$_2$S/TGA QDs (luminescence peak at 620 nm) with Ag NPs (light extinction peak at 590 nm) demonstrated a decrease in the luminescence intensity of QDs by 8 times (Fig. 2a) together with a decrease in the luminescence lifetime by 5–7 %. The observed patterns indicate that the effects of exciton-plasmon coupling are dominated by the carrier phototransfer between the components of the associates. The phototransfer blocks QDs luminescence, when the overlap between the extinction peak of Ag NPs (nanoresonator mode) and Ag$_2$S/TGA QDs luminescence is not complete [10, 24].

On the contrary, when the overlap between the luminescence spectra (620 nm) and the plasmon peak (640 nm) was greater, mixtures of the same samples of Ag$_2$S/TGA QDs with plasmonic Au NPs (20÷9 nm), demonstrated an increase in luminescence quantum yield by 1.5 times (Fig. 2b). At the same time, the intensity of QDs recombination luminescence fell below the luminescence level of the initial QD sample after a 20-second exposure to luminescence excitation. The initial increase in the intensity of Ag$_2$S/TGA QDs luminescence is accounted for by the Purcell effect, which presumes greater probability of optical transition in proximity to the nanoresonator [25]. However, the following significant decrease in the luminescence intensity may be caused by the photo-stimulated charge transfer between the components of the studied associates, which, as we know, blocks the luminescence [10, 24]. Incomplete luminescence quenching indicates that some of QDs are not in full contact with NPs, which is necessary for the injection of photostimulated charge carriers.

Mixtures of Au NRs (25÷9 nm, extinction peak at 690 nm) and Ag$_2$S/2-MPA QDs demonstrated a decrease in QDs luminescence intensity at the band peak (820 nm). In this case, a dramatic transformation of the spectral contour of Ag$_2$S/2-MPA QDs luminescence band was registered. However, the peak intensity grew in the region with the wavelengths shorter than 700 nm (Fig. 2b). Apparently, such a behaviour of the luminescence spectrum is connected with the quantum interference (Fano antiresonance) during exciton-plasmon interaction [26]. At the same time, the average luminescence lifetime increased from 94 to 115 ns at the wavelength of 750 nm and decreased from 94 to 16 ns at the wavelength of 820 nm. This also indicates the presence of exciton-plasmon interaction. The enhancement of luminescence at 700 nm may be accounted for by the Purcell effect, when there is direct contact between a plasmonic nanoparticle and quantum dots. A slowdown in the luminescence decay is explained by a decrease in the effectiveness of the non-radiative recombination caused by the difference in the immediate environment of the QDs.

4. Conclusions

The article suggests a new method for synthesising hybrid associates based on Ag$_2$S/TGA QDs, Ag$_2$S/2-MPA QDs, pyramidal Ag NPs, and Au NRs. The study determined the transformation effects of the luminescence spectra contours resulting from the quantum interference (the Fano effect), and the luminescence quenching occurring when there is direct contact between QDs and NPs. The observed interaction between Ag$_2$S QDs and plasmonic NPs indicates the possibility to regulate the spectrum and the quantum efficiency of QDs IR luminescence. However, the results of the latest experiments definitely indicate the complexity of exciton-plasmon interaction in the studied systems, as several effects are observed at the same time, including the Purcell effect, the Fano effect, and the photo-induced charge transfer between QDs and NPs.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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