

Hybrid structures based on gold nanoparticles and semiconductor quantum dots for biosensor applications

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Background: The luminescence amplification of semiconductor quantum dots (QD) in the presence of self-assembled gold nanoparticles (Au NPs) is one of way for creating biosensors with highly efficient transduction.

Aims: The objective of this study was to fabricate the hybrid structures based on semiconductor CdSe/ZnS QDs and Au NP arrays and to use them as biosensors of protein.

Methods: In this paper, the hybrid structures based on CdSe/ZnS QDs and Au NP arrays were fabricated using spin coating processes. Au NP arrays deposited on a glass wafer were investigated by optical microscopy and absorption spectroscopy depending on numbers of spin coating layers and their baking temperature. Bovine serum albumin (BSA) was used as the target protein analyte in a phosphate buffer. A confocal laser scanning microscope was used to study the luminescent properties of Au NP/QD hybrid structures and to test BSA.

Results: The dimensions of Au NP aggregates increased and the space between them decreased with increasing processing temperature. At the same time, a blue shift of the plasmon resonance peak in the absorption spectra of Au NP arrays was observed. The deposition of CdSe/ZnS QDs with a core diameter of 5 nm on the surface of the Au NP arrays caused an increase in absorption and a red shift of the plasmon peak in the spectra. The exciton–plasmon enhancement of the QDs' photoluminescence intensity has been obtained at room temperature for hybrid structures with Au NPs array pretreated at temperatures of 100°C and 150°C. It has been found that an increase in the weight content of BSA increases the photoluminescence intensity of such hybrid structures.

Conclusion: The ability of the qualitative and quantitative determination of protein content in solution using the Au NP/QD structures as an optical biosensor has been shown experimentally.

Keywords: quantum dots, hybrid structures, photoluminescence, exciton–plasmon interaction, optical biosensor, proteins

Introduction

The creation of optical biosensors with high sensitivity and resolution is required for the control of biological processes. The combination of different nanoparticles (NPs) with their specific features is one way for creating biosensors with highly efficient methods of transduction.¹ NPs of noble metals have unique optical properties in the visible range of the spectrum due to the excitation of localized surface plasmons. An excitation of plasmon resonance is possible if the radius of an NP is greater than the wavelength. The concepts of bulk and localized surface plasmons and the working principles of both sensing techniques for biosensors were developed.² Currently, gold nanoparticles (Au NPs) have become important component that are widely used in optical bioassays due to their chemical and physical properties as well as

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good biocompatibility.^{3–7} The effect of the exciton–plasmon interaction (an analog of the Purcell effect) that appears as an increase in the rate of spontaneous recombination of excitons in semiconductor materials near metallic structures has a practical interest. This is due to the acceleration of emission in the propagation mode of the surface plasmon polariton along the metal–semiconductor interface or the mode of the surface plasmon localized in a metallic NP. The practical significance of the effect consists of increasing the quantum efficiency of semiconductor light-emitting heterostructures with sufficiently large internal nonradiative losses.^{8,9} The increase of local fields in metal NPs and on their surfaces leads to the improvement of the absorption and luminescence of semiconductor NPs and organic molecules on their surface.^{10–15} The tuning of plasmon resonance is carried out by changing the size, shape and variation of dielectric properties of the metal NPs' surrounding as well as the distance between metal structures.¹⁶ The interaction between metal NPs and semiconductor quantum dots (QDs) continues to attract a considerable attention due to its wide-ranging potential applications from sensing to quantum information processing. The basis of their interaction is the coupling between excitons in QDs and plasmons localized in metal NPs.^{17–21} The decay control of radiative and nonradiative rates as well as the emission intensity in a hybrid structure of metal/QDs using spectrally and spatially tuned plasmonic sources or nano-antennas are crucial in nanophotonics. These processes were used in the creation of solar cells^{22–26} and the light-emitting diode heterostructures.²⁷ Enhanced fluorescence II–VI semiconductor QDs in the presence of a self-assembled Au NPs monolayer was observed.²⁸ Semiconductor QDs have found numerous applications in bioanalysis and bioimaging.²⁹ The dependence of fluorescence enhancement of CdSe/ZnS QDs by local surface plasmon resonance on the amount of Au NPs and pH value of solution was shown.³⁰ Colloidal semiconductor QDs assembled between layers of metal NPs created a highly strong exciton–plasmon interaction.^{31,32}

In this work, we investigated the enhancement of photoluminescence (PL) as a result of exciton–plasmon interactions of semiconductor CdSe/ZnS QDs with an Au NP array on a glass wafer and used the resulting hybrid structures for testing proteins. With the help of optical microscopy, the structure of the Au NPs array surface was studied, depending on the number of the spin coating layers and their baking temperature. The absorption spectra of both the Au NP arrays and their hybrid structures with QDs were recorded and compared. The PL spectra of QDs in such hybrid structures were

studied. The influence of the processing temperature of Au NP layers on the PL spectra of QDs in the hybrid structures is discussed. Changes in the spectra of PL hybrid structures during protein testing have been shown.

Materials and methods

NPs and reagents

The solution of Au single particles with a size range of 3–5 nm, purchased from UT Dots, Inc. (Champaign, IL, USA), in p-Xylol solvent (99.5%, Sigma-Aldrich) were used to obtain NP arrays. Hydrophobic spherical CdSe/ZnS QDs of core/shell type with a core diameter of 5.0 nm were obtained from Belarusian State University (Minsk). The surface of the CdSe core was covered with two monolayers of ZnS and a layer of surface-active trioctylphosphine oxide molecules. We used bovine serum albumin (BSA) lyophilized with a purity of greater than 98% in a phosphate buffer 20 times, with a preservative (0.1% sodium azide) with a pH of 6.8 purchased from BioloT (St. Petersburg, Russia) as a target protein analyte. All the reagents were used without any further purification process.

Preparation of hybrid NP structures

The Au NP arrays were fabricated on a glass wafer using a spin coating process with a rotation speed of 1,000 rpm. To obtain an even distribution of Au NPs in the layer, we used a low-concentration solution of NPs in p-Xylol. Each Au NPs layer after deposition was baked using a hotplate to remove the solvent in 1 or 2 minutes. The several samples of Au NP arrays on a glass wafer were fabricated with different baking temperatures of 50°C, 100°C, and 150°C. CdSe/ZnS QDs were deposited on the Au NPs array surface from toluene solution by the spin coating method. To investigate the interaction of hybrid structures with proteins, BSA in PBS was deposited on their surface using the spin layer method.

Characterization of the prepared structures

The absorption spectrum of Au NPs in p-Xylol was recorded using a spectrophotometer (U200, Jena, Germany), as shown in Figure 1A. The intensive peak at 542 nm is associated with plasmon resonance in Au NPs. Weak peaks at 892 nm, 924 nm, and 1032 nm correspond to p-Xylol (Figure 1A). The absorption spectra of Au NP arrays on a glass wafer obtained at different baking temperatures as well as the hybrid structures with QDs were recorded using a spectrophotometer

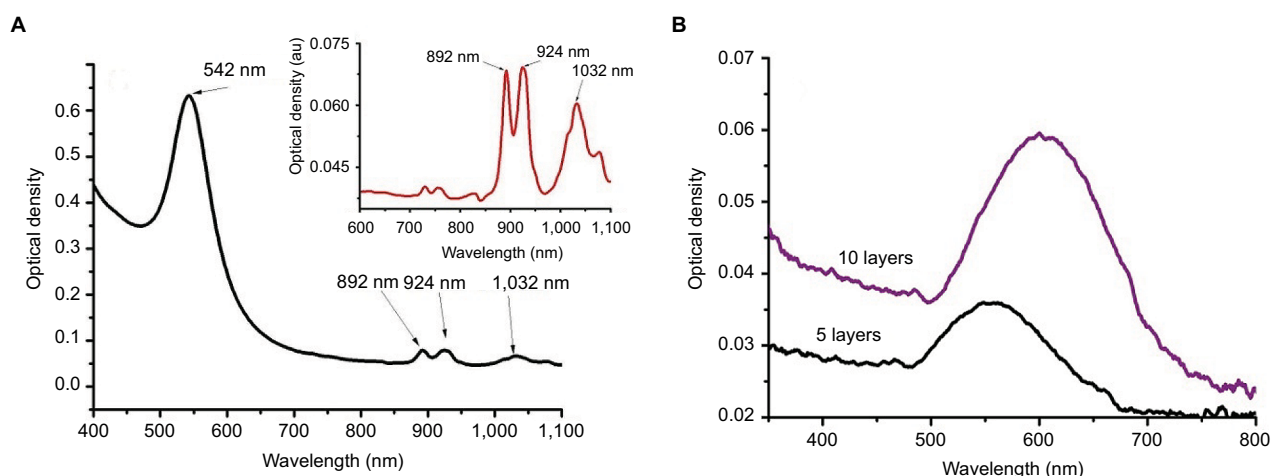


Figure 1 (A) Absorption spectra of a solution of Au NPs with a size range of 3–5 nm in p-XyloL. The inset shows the absorption spectrum of p-XyloL. (B) Absorption spectra of Au NP arrays on a glass substrate, obtained by the deposition of 5 and 10 layers with a baking temperature of 100°C for each layer for 1 and 2 minutes, respectively. **Abbreviation:** Au NPs, gold nanoparticles.

(Shimadzu, Duisburg, Germany). Figure 1B shows the absorption spectra of Au NP arrays, consisting of 5 and 10 layers, prepared with a baking temperature of 100°C for 1 and 2 minutes, respectively.

Images of the Au NPs structure on a glass wafer surface were obtained using an optical microscope (Carl Zeiss, Oberkochen, Germany). The gold particles' sizes and their area were analyzed using the ToupView software. The average NPs aggregate area (mathematical expectation) was defined as

$$\langle S \rangle = \frac{\sum_{i=1}^k S_i}{k},$$

where S_i – the area of i th NPs aggregate, k – the number of NP agglomerates.

The filling fraction was calculated as the ratio of the sum of particles areas to the sample area. The results of statistical analysis of particles in the Au NP arrays are given in Table 1. To study the luminescent properties of Au NPs/QDs hybrid structures and to test proteins, a confocal laser scanning microscope LSM 710 (Carl Zeiss) with the excitation light wavelength of 405 nm at room temperature was used.

Results and discussion

Optical properties of Au NP arrays

The three main plasmonic structures, as nanohole arrays, diffraction gratings, and nanoslit arrays, that can provide transmission surface plasmon resonance were utilized to improve the detection limits, sensitivity, selectivity, and dynamic range of biosensors.³³ We used the Au NP

Table 1 Results of statistical analysis of Au NPs array images

| Parameters | Temperature | | |
|-------------------------------|-------------|-------|-------|
| | 50°C | 100°C | 150°C |
| S_{min} , μm^2 | 0.01 | 0.02 | 0.07 |
| S_{max} , μm^2 | 13.72 | 49.54 | 55.2 |
| Average area, μm^2 | 1.32 | 2.16 | 5.02 |
| Filling fraction, % | 49.8 | 56.2 | 75.7 |

Abbreviation: Au NPs, gold nanoparticles.

arrays on a glass wafer, obtained by sequentially depositing several layers of NPs with a spin coating process and baking each layer to remove the solvent. With an increase in the numbers of deposited Au NP layers from 5 to 10, the red shift of the maximum of the plasmon peak in the absorption spectra was observed, as shown in Figure 1B. The spectral shift to longer wavelengths is explained by the modification of the resonance frequencies of plasmon oscillations in Au NPs.

The images of Au NP aggregates on a glass surface are shown in Figure 2. An increase in the area of the particles and the filling fraction was observed with increasing baking temperature. The average area of particles increased from 1.32 μm^2 to 5.02 μm^2 with an increase in temperature from 50°C to 150°C, respectively (Table 1). The filling fraction increased from 49.8% to 75.7% at these temperatures. This indicates a decrease in the distance between Au NP aggregates.

To obtain the maximum red shift of the plasmon peak, three Au NP arrays on a glass wafer were fabricated at different baking temperatures of 50°C, 100°C, and 150°C. The

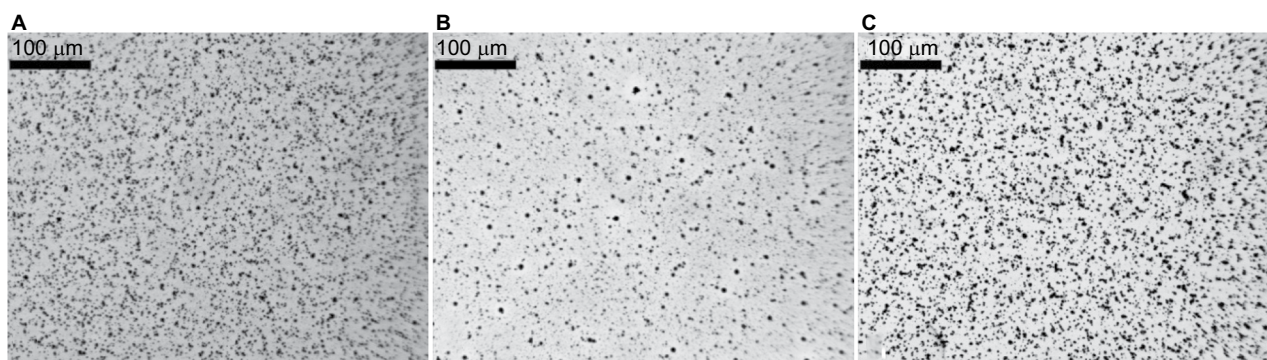


Figure 2 Images of Au NP arrays on a glass wafer obtained using an optical microscope. Samples were prepared using a spin coating process followed by baking at 50°C (A), 100°C (B), and 150°C (C) within 1 minute to remove the solvent.

Abbreviation: Au NPs, gold nanoparticles.

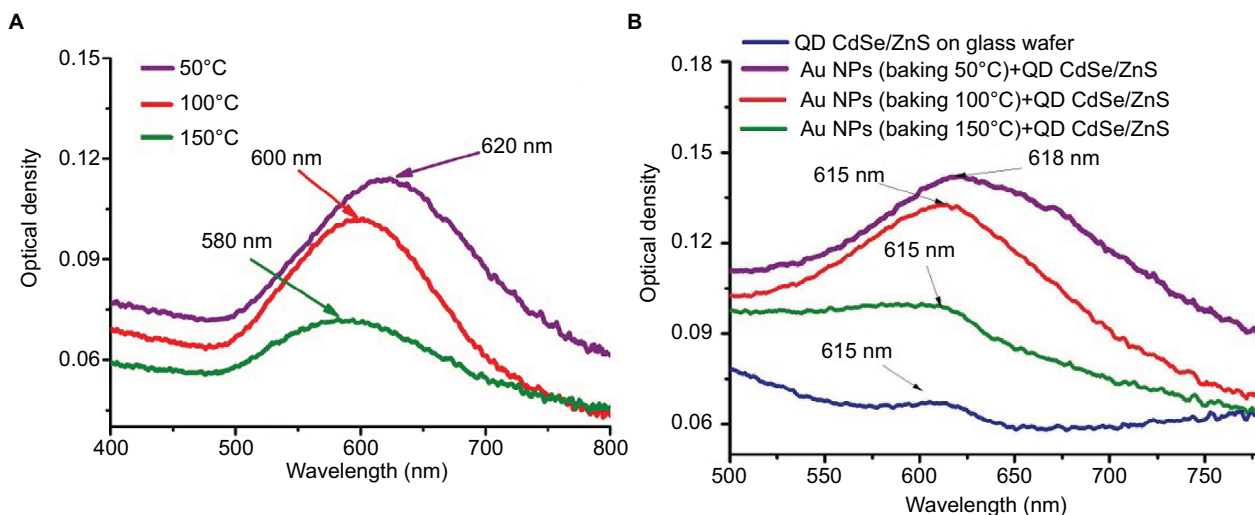


Figure 3 (A) Absorption spectra of Au NP arrays on a glass wafer with a processing temperature of 50°C, 100°C, and 150°C. (B) Absorption spectra of the same samples of Au NP arrays on a glass wafer with CdSe/ZnS QDs deposited on their surface from toluene solution by spin coating.

Abbreviations: Au NPs, gold nanoparticles; QDs, quantum dots.

layers of Au NP array were baked for 1 minute. At the baking temperature of 50°C, the absorption band maximum associated with the excitation of localized surface plasmons in Au NP arrays was found at a wavelength of 620 nm. At higher baking temperatures, a significant reduction in absorption was observed, as shown in Figure 3A. The observed blue shift of the maximum in the absorption spectra was associated with the melting of single Au particles and the formation of Au NP aggregates of large dimensions (Table 1).

Optical properties of Au NPs/QDs hybrid structures

The lifetime of the exciton changes due to the coupling with the radiative and nonradiative plasmon modes, which can lead to attenuation or amplification of the radiation. The PL amplification in metal–semiconductor structures is associated with the resonance interaction of dipole radiators with the modes

of localized surface plasmons in metallic NPs.^{17–19} The quantum efficiency of the emitting electron–hole pair increases in the near optical field of the plasmon mode excited in the gold structures. The process of Förster resonance energy transfer (FRET) between semiconductor NPs in the presence of metal nanocrystals can become faster. The enhancement of FRET occurs due to the effect of plasmon-assisted amplification of electric fields inside the nanoscale assembly. Simultaneously, metal nanocrystals can lead to an increase of energy losses during the FRET process.^{34,35}

To enhance of the PL intensity of CdSe/ZnS QDs as a result of the exciton–plasmon interaction, we deposited the QDs on the surface of Au NPs array. The efficiency of exciton–plasmon interactions depends on the relative sizes of metallic NPs and QDs, their spatial distribution, the spectral overlap of the QDs radiation, and the surface plasmon resonance of Au NPs. Figure 3B shows the absorption spectra

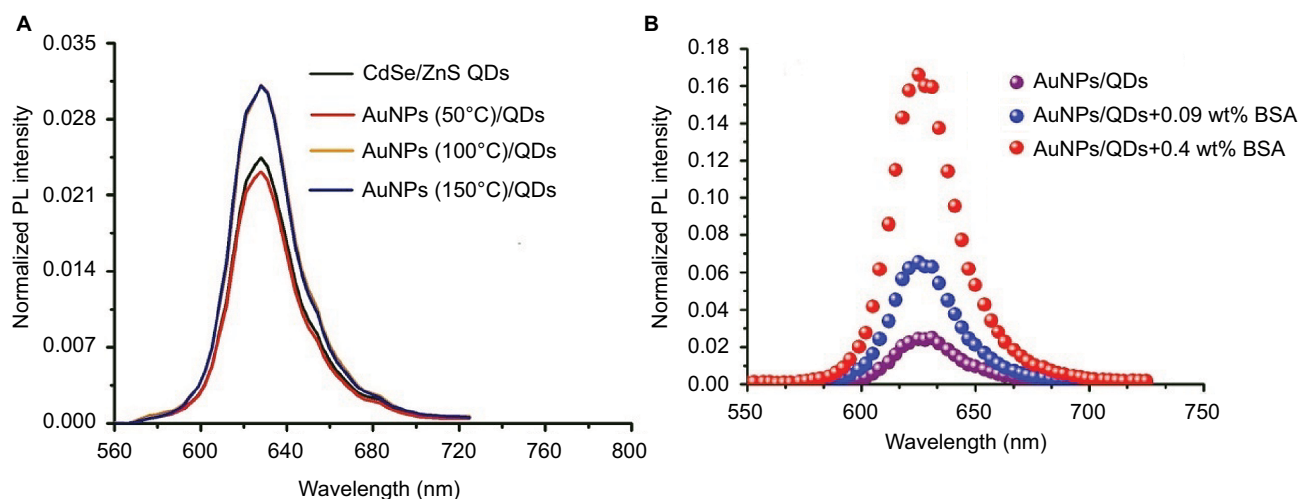


Figure 4 (A) PL spectra of CdSe/ZnS QDs with a core diameter of 5 nm deposited on the surface of Au NP arrays on a glass wafer, obtained at the temperatures of 50°C, 100°C, and 150°C. (B) PL spectra of the Au NPs/QDs hybrid structure without and with 0.4 wt% and 0.09 wt% BSA in a PBS, deposited using the spin coating technique. **Abbreviations:** Au NPs, gold nanoparticles; BSA, bovine serum albumin; PL, photoluminescence; QDs, quantum dots.

of hybrid structures of Au NP arrays baked at 50°C, 100°C, and 150°C with CdSe/ZnS QDs. The absorption spectrum of CdSe/ZnS QDs on a glass wafer is given in Figure 3B for comparison. The exciton–plasmon interaction between QDs and Au NPs led to changes in the absorption spectra of the samples. The maximum of the QDs absorption band corresponds to a wavelength of 615 nm. With an increase in the baking temperature of Au NP layers, a decrease in the intensity of the absorption was observed. These changes correlated with the increase in the Au NPs area and the filling fraction (Table 1).

The PL spectra of the CdSe/ZnS QDs deposited on the Au NPs surface of samples obtained at different baking temperatures are shown in Figure 4A. The CdSe/ZnS luminescence in the hybrid structures with Au NPs was observed in the wavelength range of 575–700 nm at room temperature (Figure 4A). The PL spectra of samples with Au NP arrays treated at temperatures of 100°C and 150°C coincide in Figure 4A. The PL intensity of QDs on a surface of the Au NP arrays increased by 60% compared to the QDs intensity on a glass wafer. This can be explained by the incomplete overlap of the QDs and the Au NP arrays of the absorption spectra (Figure 3A and B) without which it is impossible to enhance the intensity of PL.

Interaction of Au NPs/QDs hybrid structures with protein

The biosensor should basically consist of a transducer and a recognition element for a specific analyte. Hybrid solid

structures of Au NPs/QDs on a glass wafer have been studied as a possible biosensor of protein analyte. On the surface of hybrid structures with Au NP layers baked under 150°C was precipitated bovine serum albumin in a phosphate buffer saline. Figure 4B shows the luminescence spectra of Au NPs/QDs hybrid structures with BSA and without it. We used solution with 0.09 wt% and 0.4 wt% BSA. The intensification of PL intensity was observed with an increase in the BSA weight content (Figure 4B). These results indicate the promising use of the studied hybrid structures as optical biosensors for qualitative detection and quantitative determination of protein content in solutions.

Conclusion

In this paper, the hybrid structures based on gold particle arrays and CdSe/ZnS QDs with a core diameter of 5 nm were experimentally investigated. Au NP arrays were fabricated on a glass wafer using the spin coating technique, and their microscopic structure and absorption spectra were studied. It has been shown that the baking temperature of the Au NP layers influenced their structure and absorption spectra. With increasing baking temperature, the agglomerates' area and the filling fraction of the Au NPs increased. The blue shift of the plasmon peak in the absorption spectra was observed at the same time. The increase in absorption and a red spectral shift of the plasmon peak as well as the enhancement of PL intensity in the hybrid structures spectra of CdSe/ZnS QDs on the surface of the Au NPs array were observed. When testing the BSA using the prepared hybrid structures, it was found out

that its weight content affects the intensity of the PL of these structures. The experimental results obtained in this work allow us to state that such structures can serve as an optical biosensor for the qualitative and quantitative determination of protein content in solutions. Further studies of such structures, aimed at enhancing the exciton–plasmon interaction of the Au NPs array with QDs, can increase their effectiveness.

Acknowledgment

We greatly acknowledge the support provided by the German Research Foundation under grants LU 605/16-1 and HI 1261/5-1.

Disclosure

The authors report no conflicts of interest in this work.

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