Colloidal quasicrystals based on hybrid nanoparticles

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Abstract. We used laser ablation approach for the synthesis of PbTe nanoparticles (NPs) that allows for the control of the mean size of NPs. The addition of gold particles to the solution results in the formation of hybrid NPs characterized by the amplification and broadening of the near-field photoluminescence spectra compared to initial NPs.

1. Introduction

The possibility of varying the fluorescence wavelength in semiconductor quantum dots, depending on their size, is a principal advantage for the creation of new laser media. Because of the rigid restrictions on the movement of charge carriers in quantum dots, they have an electronic structure similar to atoms.

Colloidal quantum dots are a worthy alternative to traditional organic and inorganic fluorophores. They excel them not only by photostability, but also by the molar extinction coefficient, the quantum yield of fluorescence, and also possess a number of unique photophysical properties. Quantum dots, bonded to the complexes with organic compounds of various kinds can be used in different fields of science and technology, in particular, various sensor systems and optoelectronic devices [1-3]. Quantum dots also find their application in solar batteries, because they have the ability to effectively absorb a sufficiently large range of the solar radiation spectrum [4-5]. The effect of absorption increasing in semiconductor quantum dots is reproduced fairly well in the presence of plasmon nanoparticles, and as a rule, it is accompanied by the effect of amplification of fluorescence [6-7]. In this case, the distance between a quantum dot and a metallic nanoparticle is one of the key factors which determinates the efficiency of the exciton-plasmon interaction between them [8-9].

Particularly complex is the preparation and investigation of hybrid structures based on colloidal quantum dots. The presence of a significant change in the shape and size of quantum dots during the synthesis of such particles leads to the complexity of unambiguous interpretation of their optical properties. For this reason, the methods of laser ablation in a liquid can find wide application in this matter, since it is possible to reliably control the scatter in the sizes of the particles produced and their shape.

In this work, a method for a hybrid-particle PbTe-Au formation, during laser action on a colloidal system consisting of Au and PbTe nanoparticles was used. The dependence of the diameters of the lead particles of lead telluride and the concentration of gold particles, it is possible to vary the luminescence spectrum of the obtained structures.
2. Preparation of hybrid particles in colloidal systems

In order to synthesize separately PbTe and Au NPs we have used the method of the CW-laser ablation, described in work [10, 11]. The application of a moderate intensity CW-laser radiation source enabled us to obtain NPs characterized by a small dispersion of the average size [12, 13]. To avoid the oxidation of NPs we have conducted the laser ablation experiment in the glycerol solution. For synthesis of the hybrid particle were chosen at two sizes of 100 nm and 200 nm.

Once the colloidal solution of lead telluride NPs was obtained we added the solution of gold particles of the 10 nm diameter into it. The concentration proportion in colloidal solution is PbTe:10ml and Gold -1ml. For the irradiation of mixed gold and silicon NP solutions, the Ytterbium fiber laser characterized by the wavelength of 1.06 µm, the pulse duration of 100 ns, the repetition rate of 20 kHz, and laser pulse energy up to 1mJ was then used. The diameter of the laser beam at the focal plane was 30 µm. The laser irradiation of the mixed colloidal system resulted in the formation of hybrid PbTe-Au NPs (Figure 1).

![Figure 1](image)

**Figure 1.** SEM-image of the deposited PbTe-Au hybrid particle.

2.1. Optics of hybrid particles

The absorption spectrum of colloidal systems based on lead telluride particles and hybrid particles shows a maximum absorption at 1490nm, typical for lead chalcogenides, the broadening of the absorption peak can be due to the size effects in nanoparticles [14]. The first maximum at a frequency of 1210 nm is typical for lead telluride material [15]. The addition of golden nanoparticles leads to an increasing of an absorption in the range of 550-870 nm, that dedicates the formation of agglomerates of difficult shapes. There is no significant increase in absorption over the entire wavelength range.
Figure 2. Photoluminescence spectra of the lead telluride particle (black curve) and PbTe-Au hybrid particle (red curve). Inset the absorbance spectra of colloidal system is presented.

The further insight into the structural properties of the synthesized colloidal solution is provided by the spectra of photoluminescence excitation detected with use of the Horiba Fluorolog-3 spectrofluorimeter with an 8 nm spectral width slit. The pump wavelength is 514 nm for realization of plasmon illumination of semiconductor particle covered with gold nanoparticle. As one can see, the maximum of the luminescence has a Stokes shift relative to the pump wavelength. In the case where lead telluride particles are coated with gold, the intensity of their luminescence increases substantially and additional local maxima are observed. So, the lifetime of the luminescence is reduced by an order of magnitude, which allows us to detect the Parsel effect realization.

To reveal the optical properties of the synthesized hybrid NPs we have compared the images provided by the atomic force microscope (AFM) with those of the scanning near-field optical microscope (SNOM).

2.2. AFM and SNOM investigation of hybrid particles

Figure 3 compares the AFM and SNOM images of hybrid clusters consists of a lead telluride center and golden noncontinuous shell. One can see that the SNOM spectra are characterized by a strong peak at the center of the particle surrounded by a weaker intensity crown corresponding to the field of the surface localized Mie mode. The increase of the near field emission of the hybrid nanoparticles is a signature of a sizeable nanoantenna effect of the metallic shell. The near-field emission amplification is observed in the case of pumping at the wavelength of 514 nm.
2.3. Modeling of the optical properties of a single hybrid particle

We have modelled the optical properties of hybrid NPs using the Wave Optics modulus of the commercial software COMSOL Multiphysics 5.2a. As a model system we have considered a 100 nm PbTe sphere, covered with periodically arranged 10nm NPs of gold and attached to a BK7 glass surface. We have assumed that this structure is illuminated by a plane monochromatic Y-polarised wave propagating along the structure axis Z from the surface side and having the wavelength of $\lambda=514$ nm. The calculated distribution of the electromagnetic field intensity has been normalized to enable the direct comparison with the experimental data. Figure 4 shows the calculated distribution of the field intensity in the planes separated from the surface by 50 nm that corresponds to the center of the nano-cluster and 120 nm that is 10 nm below the top point of the hybrid nano-particle.

Figure 4. The results of numerical modelling: images of near-filed distribution in the planes separated by $z=50$nm (a) and $z=120$nm (b) from surface of the glass substrate.
The calculated near field intensity distributions certify the significant enhancement of the electromagnetic radiation at the wavelength corresponding to the plasmon resonance in gold. The areas of near field enhancement visible in the plane passing by the center of the nanocluster are localised around the gold NPs extending by about the radius of the PbTe NP. This field geometry certifies of the combined effect of gold and lead telluride constituents of the cluster on the localised near-field. The scattering and enhancement of light is governed by the entire cluster rather than by individual metallic NPs. The strong enhancement of the scattered field is observed in the polarisation plane of the incident light. At the level of the top-point of the nanocluster, the field distribution shows the local maximum corresponding to the center of the cluster surrounded by strong dips that are followed by the peaks of the field at the shell of the nanocluster. These features are clearly visible in the experimental SNOM images shown in Figure 3b. Some quantitative differences between the experimental and simulated images may be caused by the detection method. As the aperture of the near-field detector is of the order of nanometers, it necessarily averages the optical signal over an area comparable with the characteristic size of the cluster. This leads to a loss of signal coming from the shell areas of the cluster, while the signal coming from its central part is detected with a higher accuracy. Nevetherless, the qualitative agreement of the SNOM images and the simulation confirms the size able nano-antenna effect, focussing of radiation and the strong field enhancement by hybrid nanoparticles.

3. Conclusion
We have developed a method of the synthesis of hybrid PbTe-Au nanosystems whose optical properties may be efficiently tailored by varying the characteristic sizes and concentrations of constituent gold and semiconductor nanoparticles. To synthesize PbTe and gold NPs we use CW-laser ablation in glycerol. In order to fabricate hybrid NPs we have irradiated colloidal gold and lead telluride NPs with the nano-second laser pulses at the wavelength of 1.06 micrometers. The addition of the gold NPs to the solution and the subsequent laser irradiation modifies the optical response of the system. In particular, it starts featuring broad and intense resonances. We have demonstrated an efficient control over the size of hybrid nanoclusters that yielded a direct access to tailoring their optical properties. The possibility of a near-field control by the control of the PbTe-Au hybrids size is demonstrated. The distribution of the near-field intensity calculated by COMSOL Multiphysics is nicely corresponding to the experimental results. These results pave the way to the realization of optical metasurfaces characterized by a controllable variety of functional properties and the strong optical response in the visible spectral range.

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