Hybrid gold-silicon systems with tuning optical properties

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Abstract. The formation of hybrid silicon-gold NPs as a result of the laser action on a mixed colloidal solution is observed. These hybrid NPs are characterized by the amplification and broadening of the near-field photoluminescence spectra compared to pure silicon NPs. A strong sensitivity of the spectral shape of the emitted light to the intensity of the exciting white light is documented. These results may be used for the realization of functional metasurfaces consisting of randomly distributed resonant NPs. Moreover, as the synthesized NPs emit in red, green and yellow they can be used for fabrication of luminescent color screens.

1. Introduction

One of the most important tasks of modern optoelectronics is the looking for the artificial materials with the most quantum efficiency, which may allow to create high-technology devices on its basis. Silicon is the most attractive material among the semiconductors due to the developed producing technology, cheapness, and the possibility to combine optical and electronic parts in one device [1]. The speed of optical transition in silicon nanoparticles is faster than in bulk material, and the edge of the optical spectral range has shifted to the short-wave area due to quantum-sized effects. The position of the shift depends on the nanoparticle size. One of the way to increase the quantum efficiency is to create nanocomposite structure with metal and semiconductor nanoparticles. Nowadays, there is a great interest to such kind of systems. Nanocomposite layers allow to combine properties of quantum-sized semiconductor and metal systems, and also allow to obtain new properties, untypical to each subsystems separately. Metal nanoparticles distributed between silicon nanoparticles allow to increase the conductivity of the composite layer, providing a more efficient collection of photon carriers. A potential barrier (similar to the Schottky barrier) and a built-in electric field can occur at the border between metallic and semiconductor nanoparticles. This increases the efficiency of separation of photon carriers in such a composite layer and allows us to consider it as a distributed (bulk) metal-semiconductor transition with a large area (analogy with the bulk heterojunction). Localized surface plasmons can be excited in metal particles, which leads to the increasing of the light absorption in the composite layer and as a result to the increasing of the photocurrent.
In the frame of this article, we present the synthesis of gold-silicon NPs by laser action of a colloidal systems [5]. The increase of the optical near field magnitude in the emission of the NPs is observed and interpreted in terms of the redistribution of the near-field scattering intensity due to the nanoantenna action by gold nanoparticles. The spontaneous ordering of NPs in the course of their deposition allows for the formation of thin films that may be used for creation of metasurfaces suitable for controllable manipulation of the transmission and reflectivity of light [6]. These results pave the way to applications of hybrid gold-silicon NPs in optical integrated circuits combining functions transmission and detection of optical signals.

2. Results

2.1. The synthesis of colloidal nanoparticles

In order to synthesize separately silicon and golden NPs we have used the method of the CW-laser ablation, described in work [9]. The application of a moderate intensity CW-laser radiation source enabled us to obtain NPs characterized by a small dispersion of the average size [10]. In our experiments the targets of crystalline monolithic silicon and after that gold were used. To avoid the oxidation of NPs we have conducted the laser ablation experiment in the 99% ethanol solution. The average size and its distribution was varied by the parameters of laser irradiation power [11] and was controlled by dynamic light scattering. The diameters of silicon spherical NPs were chosen at two sizes of 100 nm and 200 nm.

Once the colloidal solution of silicon NPs was obtained we added the solution of gold particles of the 10 nm diameter into it. 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 gold-silicon NPs (Fig. 1).

The most likely mechanism of formation of the hybrid NPs is due to the electrostatic attraction of their constituents. The golden NPs are negatively charged as confirmed by the z-potential measurement [10]. The silicon particles are electrically neutral, initially. However, the non-radiative recombination of optically generated free carriers leads to the break of chemical bonds at the surface of silicon NPs, so that they acquire positive charges. As a consequence, positively charged silicon NPs attract negatively charged golden NPs that results in the formation of hybrid clusters (see Fig. 1).

Figure 1: a) The schematic of the formation of hybrid NPs as a result of the laser irradiation of a mixed Si-Au colloidal solution. SEM-image of hybrid clusters: a central particle of silicon with a diameter of 100 nm (b) and 200 nm (c) is covered by smaller size gold nanoparticles.

The hybrid nano-system we have obtained in this way allows to combine the properties of such prospective materials as gold and silicon [12]. It may be used for the amplification of the photoluminescence efficiency and the enhancement of the photoluminescence bandwidth in comparison to silicon NPs. The optical hybrid metasurfaces composed by golden and silicon NPs and emitting in the visible spectral range are expected to have a broad range of applications in optoelectronics and photonics.
2.2. *Optical properties of hybrid particles: a dark-field microscopy study*

To control the deposition of the NPs from a small colloidal drop we have taken an advantage of the methods described in [9, 10]. Namely, we have deposited hybrid clusters using the technology of sputtering small colloidal drops on the surface of the transparent substrate [11]. The conclusions of the above section on the geometry of the deposited NPs are confirmed by the Raman spectroscopy data (Fig. 2).

![Image of deposited hybrid gold-silicon NPs](image)

Figure 2. A dark-field (scattered light) image of the deposited hybrid gold-silicon NPs for different pump intensities: the white light intensity increases from 1000 lm (a) to 2000 lm (c). There are hybrid clusters consist of 100 and 200 nm hybrid particles. At high pumping, the cluster demonstrates the wide scattering spectra that clearly show green, yellow and red components at the highest pump intensity (c). The scattering spectrum of this large cluster is clearly larger than one taken from the 100 nm particle (a, b, c). The Raman spectra of Si NPs and of the laser irradiated Si-Au colloidal solution are shown in (d) by black and red curves, respectively.

The optical spectroscopy studies of the synthesized colloidal systems demonstrate a significant modification of the light absorption spectra as a result of the association of silicon and gold nanoparticles. The Raman spectra from the initial colloidal system (the red curve in Fig. 2) shows a peak at the wavelength of 520 cm\(^{-1}\) that corresponds to the crystalline phase of silicon and a broad shoulder (440-480 cm\(^{-1}\)) corresponding to the amorphous phase of silicon. After the laser irradiation of the mixed Si-Au colloidal solution, the intensity of the peak corresponding to the crystalline phase (black curve in Fig. 2(d)) is increased, and the shoulder corresponding to the amorphous phase is reduced. The hybrid gold-silicon nanoparticles are characterized by a wide amplitude peak at about 500-580 nm on the background of the exponential tail. This spectrum is indicative of a strong variation of the near field response of the hybrid nanoparticles compared to silicon nanoparticles in the range of 500-520 nm.

It is important to underline that at a high optical pumping intensity the hybrid silicon-gold clusters of the larger size clearly show scattering of green, yellow and red light (see Figure 2(c)) that is promising for their applications in luminescent screens.

![Image of optical density of colloidal solutions](image)

Figure 3. The optical density of colloidal solutions, which contain Si NPs (black curve) and hybrid gold-silicon NPs (red and blue curves).
In order to have a deeper insight to the optical properties of the synthesized hybrid NPs we have recorded the dark field microscopy images [13], where only the scattered light is collected. As one can see from Fig. 3 a, b, NPs fabricated from the crystalline Si targets with addition of gold particles resonantly scatter light in a wide spectral range: from red to blue color. It is important to note that a large part of Si NPs does not provide any resonant optical response in the visible range, because of their low refractive index. After the laser irradiation that led to the merging of Si and gold NPs and formation of clusters we detected a much stronger scattering signal from the deposited NPs.

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).

![Figure 4. The AFM (a, c) and SNOM images (b, d) of the deposited 100 nm (top panels) and 200 nm (bottom panels) Si-Au clusters.](image)

Figure 4 compares the AFM and SNOM images of hybrid gold-silicon clusters. One can see that in both cases 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 (see also the SNOM profiles at the panels (c, d)). The hybrid nanoparticles are larger than the pure silicon ones [11], because of that the diameter of the crown demonstrated by the hybrid particles is approximately twice larger than the size of the crown in the SNOM image of pure silicon particles. The dramatic 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 510 nm.

3. Conclusion

We have developed a method of the synthesis of hybrid silicon-gold nanoparticles whose optical properties may be efficiently tailored by varying the characteristic sizes and concentrations of constituent gold and silicon nanoparticles. To synthesize silicon and gold NPs we use CW-laser ablation in ethanol. In order to fabricate hybrid NPs we have irradiated colloidal gold and silicon 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 nano-clusters that yielded a direct access to tailoring their optical properties. In the solutions containing hybrid gold-silicon NPs, the strong electric and magnetic multipole resonances have been observed. The possibility of a near-field control by the control of the Si-Au hybrids size is demonstrated. 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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