A Facile Route of Manufacturing of Silicon-Based Nanostructures with Tuned Plasmonic Properties

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Abstract. An environment-friendly method of pulsed laser ablation in liquids is successfully employed for structural modification of silicon nanoparticles leading to a considerable narrowing of their size distribution accompanied with a reduction of the mean size. Contamination-free conditions of synthesis ensure the chemical purity of formed nanostructures that may reduce toxicity issues. Such a laser-induced modification leads to the appearance of plasmonic properties in semiconductor-based nanomaterials. Their spectral position can easily be varied in the whole visible range. Combined in one nanoparticle properties of semiconductors and noble metals can strongly promote applications of composite laser-synthesized nanoparticles for biosensing (using their plasmonic-based surface-enhanced ability) and bioimaging (using their both optical and magnetic abilities) purposes.

1. Introduction
Semiconductor nanomaterials possess unique both linear and nonlinear optical properties that can result to various applications [1-7]. However, it is known that semiconductor nanostructures are characterized by the absence of any plasmonic features that are attributed to noble metal nanomaterials [8]. Such an issue can be overcome by formation of composite nanostructures containing both semiconductor and metal elements [9]. Among different methods of nanoparticle manufacturing, the most promising and facile one is a technique of environmentally-friendly pulsed laser ablation in liquids that provides contamination-free conditions of nanomaterial synthesis [10]. As it has been found lately, this approach is also an effective route of production of ligand-free composite semiconductor-based nanostructures with embedded metal impurities [11-13]. Nevertheless, this type of research is still very challenging being on its early stage requiring many additional studies.

In this work, different types of composite silicon-based nanoparticles with plasmonic properties were formed using femtosecond (fs) laser ablation. For this purpose, silicon wafers of different levels of purity were used for formation of silicon nanoparticle colloidal solutions. Prepared colloids were employed for further laser-induced structural modification by the ablation of various noble metal targets. Afterwards, structural, optical and electronic properties of prepared plasmonic nanocomposites were studied and their possible bioapplications are assessed.
2. Materials and methods
The preparation method is based on a fs laser source emitting light in the infrared spectral range. Its irradiation was focused by a galvanoscaner (162 mm focal distance) into a spot of 50 µm size (experimentally estimated). It also moved the laser beam by a surface of semiconductor and metallic wafers embedded in the deionized water (18 MΩ·cm, 8 mm water level) with 2 m/s velocity. In all experiments, the targets were exposed by the laser irradiation (10 kHz repetition rate and 150 µJ/pulse laser fluence) for 15 minutes. Commercially available wafers of “pure” and “metallurgical-grade” [14] silicon as well as of highly pure noble metals were used. Size distributions and chemical contents of composite nanoparticles were investigated using transmission/scanning electron microscope (TEM/SEM) equipped with energy dispersive X-ray (EDX) spectrometer. Structural properties were examined by means of X-ray methods such as X-ray diffraction (XRD) and X-ray photoemission spectroscopy (XPS). Optical properties were studied using a UV-VIS, Raman and FTIR spectroscopies. An electron paramagnetic resonance (EPR) method was employed to investigate their paramagnetic defect labels with unpaired electrons.

3. Results and discussion
In order to extend functionalities of semiconductor nanomaterials towards plasmonic-enhanced-based applications, a method of pulsed laser ablation was employed for their structural modifications. In this case, it was found that a laser impact on metal targets immersed in a colloidal solution of semiconductor nanoparticles provokes considerable changes of their properties. A typical TEM image of composite silicon-based nanoparticles is shown in Figure 1a. By turn, this treatment also leads to a significant variation of their chemical composition influencing structural and optoelectronic features of nanostructures [11]. In particular, considerable reduction of size distribution of composite semiconductor-metal nanoparticles as compared to initial ones is occurred [11]. One can see that a mean size of silicon-gold nanoparticles is approximately 6 nm with a narrow size dispersion (Figure 1a, inset).

The presence of various content in nanoparticles is confirmed by EDX studies (Figure 1b) revealing several maxima corresponding to different elements. Their relative intensities determine ratios between these elements. In this case, signals from the copper can be neglected arising from a used TEM grid. It worth noting that in order to study Si-Cu NPs, nickel or gold grids were used. The responses attributed to gold and silicon justify the presence of both species in a nanoparticle reflecting a mass contribution of the corresponding elements. The aspect ratio between them strongly depends on used experimental conditions [11].

![Figure 1](image.png)

**Figure 1.** a) A transmission electron microscope image of composite nanoparticles formed by laser ablation of a gold target immersed in a colloidal solution of bare silicon nanoparticles. A corresponding size distribution is shown in inset. b) An energy-dispersive X-ray spectrum of composite silicon-gold nanoparticles.
The formation of composite nanoparticles can be caused due to an interaction between metal nanoclusters emitted from a target and silicon ones appeared due to laser-induced decomposition of silicon nanoparticles [15]. Possible mechanisms of the nanocomposite synthesis are described in more details in the work [12]. The presence of different types of nanoclusters in the laser plume leads not only to a significant reduction of their mean size but also to a change of the chemical composition of newly formed nanoparticles (Figure 1b).

Such a modification of the structure of nanoparticles provokes remarkable changes of their optoelectronic properties (Figure 2a and 2b) [10]. First of all, one can find significant alteration of optical transmission spectra caused by laser-induced actions on various metal targets in the presence of silicon nanoparticles (Figure 2a). In these cases, strong minima are appeared in the spectra of composite nanoparticles significantly depending on a used metal (Figure 2a). Indeed, each element has its own plasmonic frequency that allows us to tune spectral position in overall visible range (400 nm for Si-Ag NPs; 522 nm for Si-Au NPs; 613 nm for Si-Cu NPs). Recent studies show that laser-synthesized silicon-gold nanocomposites are promising for bacteria detection [16] using surface-enhanced Raman scattering (SERS) as well as for the identification of spoilage in the food industry [17] due to their significant plasmonic properties.

At the same time, composite silicon-gold nanoparticles reveal remarkable paramagnetic properties due to a great number of paramagnetic defects with unpaired electrons that can be detected using EPR spectroscopy. Figure 2b represents a typical experimentally observed EPR spectrum (derivative) of these kinds of nanoparticles. A performed calculation gives a following value of the defect states (in comparison with an etalon sample [12]) – 0.5·10¹⁹ spin/g that is less than that of the initial bare silicon nanoparticles. Proposed mechanisms of these changes can be associated with the interaction between silicon and gold nanoclusters in the laser-induced plasma plume leading to charge redistribution. Additionally, possible strong localization of unpaired electrons may provoke fast dissipation of energy of the excited defects. A calculated value of g-factor (2.0055) corresponds to dangling bonds in amorphous silicon [12].

Thus, laser-synthesized composite nanoparticles combine in one nanoparticle modalities of semiconductor (silicon) and metallic (gold, silver, copper) nanostructures ensuring possibility to solve simultaneously several tasks in various applications. One of the most important one is related to nanomedicine where such nanoparticles can be served for bioimaging, biosensing, hyperthermia etc. at the same time using specific experimental conditions.

Figure 2. a) Optical transmission spectra of composite nanoparticles formed by laser ablation of the metallic targets (silver, gold, copper) immersed in a colloidal solution of bare silicon nanoparticles. b) Electron paramagnetic resonance response of composite nanoparticles formed by laser ablation of a gold target immersed in a colloidal solution of bare silicon nanoparticles: an experimental derivative curve (open points), its computer simulation (lines) and an absorption curve (closed points).
4. Conclusions
Pulsed laser ablation in liquids technique is shown to be a very effective and promising versatile route to synthesize composite nanostructures with various chemical content and different plasmonic and magnetic resonance properties. Laser-induced structural modification of silicon nanoparticles leads to a strong change of their size distribution and chemical content that can be controlled by experimental conditions. A combination of semiconductor and metallic materials in form of one nanoparticle provokes the appearance of considerable plasmonic features in silicon nanostructures with paramagnetic labels that can potentially be employed for biosensing and bioimaging (including magnetic resonance imaging) applications at the same time. The obtained results show high further perspectives of laser-synthesized composite nanostructures for solving multipurpose tasks in biomedical applications.

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