

AN IMPACT OF THE LASER IRRADIATION TIME ON PROPERTIES OF COLLOIDAL SOLUTIONS OF SILICON NANOPARTICLES

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The design of semiconductor-metallic nanostructures using pulsed laser ablation in liquids (PLAL) is a very demanding task for biomedical applications being at an early stage of its development. Only few recent papers show the possibility of such a synthesis of composite nanoparticles as well as their perspectives for biosensing applications. However, mechanisms of the laser-stimulated formation of semiconductor-metallic nanoparticles involving several processes are not clarified yet being considerably depended on experimental conditions. In this work, we demonstrated an impact of the laser irradiation of colloidal solutions of silicon nanoparticles at different exposure time in the presence/absence of a gold target. In particular, longer ablation of the metal led to a stronger plasmonic maximum in silicon nanoparticles at around 520 nm. It also decreased the hydrodynamic size from 165 nm to 85 nm as well as the ξ -potential from -46 mV to -30 mV by increasing the ablation time from 0 s to 600 s. At the same time, the lowest electrical conductivity value (~ 1.5 $\mu\text{S}/\text{cm}$) of the plasmonic nanocomposites was detected at 120 s irradiation time. The highest concentration of synthesized composite nanoparticles ($\sim 3 \cdot 10^{11}$ NPs/mL) was achieved at 180 s ablation time. Another purpose of the paper was to reveal an influence of the used laser irradiation on properties of the colloidal solutions of silicon nanoparticles themselves. It was found a considerable decrease of their absorbance with the increase of the laser exposure time that can be associated with the change of their properties (e.g. concentration, size, oxidation state etc.). Thus, the laser irradiation strongly affects properties of colloidal solutions of silicon nanoparticles that must also be taken into account considering possible mechanisms of the formation of composite nanostructures. Presented in the paper fast optical diagnostic can help to determine properties of colloidal solutions of nanocomposites formed by PLAL prior their biomedical or catalytic applications.

KEYWORDS

Laser ablation, silicon nanoparticles, silicon-gold nanoparticles, composite nanoparticles, optical properties, Dynamic light scattering

1 INTRODUCTION

A distinct feature of nanostructured materials is a dependence of their physico-chemical properties on size, shape and surface chemistry differing from macroscopic counterparts due to the quantum confinement effect. It leads to a possibility for synthesized nanoparticles (NPs) to be applied in a wide range of

various applications such as catalysis [Lysyakova 2015], photovoltaics [Furasova 2018], medical diagnostics [West 2003] or pharmaceuticals [Ma 2011]. Many efforts were also made to improve nanomaterials' functionality by merging plasmonic, magnetic and semiconductor materials in one multifunctional nanopatform that demonstrates promising features for biomedical applications [Zhao 2020], [Chen 2020]. Moreover, metallic-semiconductor composite nanostructures exhibited multiple functionalities that exceed properties of individual components due to the variation of the chemical content of their core and shell [Ahmed 2020], [Morsi 2019]. In spite of the fact that the vision of scientific researchers to create composite nanomaterials with unique characteristics differing from the individual components has been considered for many years [Kanda 2018], [Menazea 2020], [Morsi 2019], [Shoueir 2020] there is still a lack of studies of such materials.

Usually, multicomponent nanostructures are formed by complex chemical methods that rules out applications required ultra-high purity of synthesized materials (e.g., catalysis, biosensing, theranostics etc.). It stimulates the development of new simple and efficient techniques of contamination-free manufacturing of composite nanostructures with easily controlled specific properties. One of the most promising synthesis can be performed in the biocompatible liquid environment by using "green" laser-based method - pulsed laser ablation in liquids (PLAL). It allows considerable widening of nanomaterials' applications towards many new fields such as sensor, drug delivery, imaging or theranostics [Amendola 2021], [Waag 2021]. Thus, this technique attracts recently more and more attention for the fast and easy production of colloidal solutions of single- and multicomponent nanoparticles with outstanding purity and controlled physico-chemical properties [Timofeev 2023], [Gurbatov 2022], [Lee 2022], [Nyabadza 2022], [Sadrolhosseini 2016], [Khashan 2016], [Dahl 2007].

The formation of composite nanostructures using PLAL is a complex procedure stimulated by the high power laser irradiation and usually taken place in a stirred or recirculated liquid. It involves several processes simultaneously such as the emission of nanoclusters from a solid target, the decomposition of the liquid, the formation of plasma, the interaction with dissolved oxygen or the fragmentation of the dispersed in the liquid NPs by post irradiation [Schwenke 2011]. All these aforementioned processes can provoke a shielding effect of the incoming laser beam reducing the energy deposited on the target surface. Thus, the formation of nanocomposites can be significantly influenced by numerous experimental parameters that can affect the mentioned above processes in considerably different ways. It will lead to the continuous variation of nanoparticle properties (concentration, size, oxidation etc.) offering a great possibility to control their performance by a proper choice of the irradiation conditions [Sadrolhosseini 2016], [Khashan 2016].

Silicon nanostructures are one of the most promising and well-studied materials suitable for designing of composite nanoparticles. Their properties are also considerably influenced by used synthesis methods. In particular, nanostructures prepared by the electrochemical etching of a bulk silicon have an efficient photoluminescence in the visible spectral range due to the quantum confinement of photoexcited charge carriers that can be employed for various applications such as nanothermometry [Ryabchikov 2013], [Ryabchikov 2014], singlet oxygen generation [Ryabchikov 2007], [Konstantinova 2006] or optical bioimaging [Osminkina 2006], [Zabotnov 2020]. Contrary, the laser ablation of the same silicon wafer forms much larger NPs showing no any emissions. However, they can be employed for non-linear optical bioimaging due to such

strong non-linear optical properties as second harmonic generation (SHG) and two-photon excited luminescence (TPEL) [Kharin 2019]. It is worth noticing that their physico-chemical properties can be significantly changed due to the laser-assisted synthesis of nanocomposites such as silicon-gold nanoparticles (Si/Au NPs) [Ryabchikov 2019], [Ryabchikov 2020], [Kutrovskaya 2017].

However, manufacturing of composite semiconductor-based nanoparticles doped with different metallic elements using pulsed laser ablation is still very challenging task being unexplored field in the modern nanotechnology. Main difficulties here are related to the presence of several chemical elements in a liquid medium whose different properties will be continuously changed during the laser impact. Moreover, the variation of the irradiation conditions will also affect individually their properties. Furthermore, there is a great lack in the literature related to the pulsed laser ablation formation of semiconductor-metallic nanostructures. All these reasons strongly complicate the design of nanocomposites with defined properties requiring understanding of the contribution of all processes occurred during the synthesis. Additionally, an important point is the development of fast diagnostic techniques that can identify properties of nanocomposites prepared at different experimental conditions prior their applications.

In this paper, we show an impact (i) of the duration of the laser irradiation of colloidal solutions of Si NPs as well as (ii) of the presence of a gold target on their properties using multi-angle dynamic light scattering (MA-DLS) and UV-Vis spectroscopy techniques. We demonstrate the appearance of the plasmonic absorbance in Si NPs due to the formation of composite nanostructures whose efficiency increases with the time of the ablation of the gold target. The maximum Si/Au NPs concentration in the colloidal solution is achieved at 180 s ablation time while their minimum conductivity is found at 120 s irradiation time. Larger ablation time leads to the decrease (i) of the hydrodynamic size of composite nanoparticles as well as (ii) of their ξ -potential. It is important to mention that a longer irradiation of Si NPs colloidal solutions without any targets provokes a considerable decrease of their absorbance efficiency. Our findings demonstrate the strong dependence of the properties of colloidal solutions of Si-based NPs on the laser irradiation time as well as on a used ablated target and will help to choose appropriate parameters for the synthesis of composite nanoparticles with required properties.

2 EXPERIMENTAL METHODS

To irradiate colloidal solutions of silicon nanoparticles, we used 1030 nm wavelength radiation from a pulsed (6 ps pulse duration, 10 kHz repetition rate) Yb:KGW laser (Pharos, Light Conversion, Lithuania). The laser energy fluence was controlled by a half-wave plate fixed at 5 J/cm² being choosing well above the laser ablation threshold for silicon and gold in water in order to compensate energy losses during nanoparticle synthesis. The position of the laser beam, focused on the sample surface into a 50 μ m diameter spot, was controlled by a galvanoscanner with 2 m/s velocity scanning speed in order to minimize influences of the cavitation bubble and emitted nanoparticles. The distance between lines was 50 μ m within a 10x10 mm² area of in order to minimize untreated surface. For nanoparticle synthesis we used commercially available wafers of pure silicon (99,99%) as well as of a highly pure gold (99,99%). Firstly, pure silicon nanoparticles (Si NPs) were prepared by ablating a silicon target in deionized water. Subsequently, Si/Au NPs were obtained by the laser ablation of

a gold target in the presence of Si NPs (0.1 mg/L concentration, 30 nm mean size) in the solution. In both cases, the targets were placed under 10 mm water level. In order to establish effects of the laser impact on Si NPs themselves, the colloidal solutions of Si NPs were also irradiated without any targets using the same experimental conditions. Additionally, the gold target was treated at the same conditions in deionized water forming pure Au NPs. All these experiments were performed at nine different times (30, 60, 90, 120, 150, 180, 300, 420 and 600 s). To observe changes in optical properties of Si NPs due to the aforementioned laser treatments, absorbance spectra of both bare Si NPs and Si/Au NPs were measured in the spectral range of 300–800 nm by means of a UV-Vis double-beam spectrophotometer (Shimadzu UV – 2600). In order to estimate the hydrodynamic size, the particle concentration, the conductivity and the ξ -potential of prepared nanoparticles we used Multi-Angle Dynamic Light scattering (MA-DLS) (Zetasizer Ultra, Malvern) system.

3 RESULTS AND DISCUSSION

To reveal an impact of the laser irradiation at different conditions on properties of Si NPs, we treated them at various exposure time in the presence/absence of a gold target. Such a treatment leads to considerable changes of properties of colloidal solutions of Si NPs that are reflected in strong variations of their colors (Figure 1). In particular, one can see a significant difference in the color of colloidal solutions treated with and without a gold target. It indicates a facile possibility of changing of their properties using an appropriate ablated material. Firstly, the irradiation of the colloidal solutions by the laser beam focused on the gold target leads to the appearance of a pink shade at a lower exposure time that becomes deep red at a longer duration (Figure 1a). It can indicate changes of the structure of Si NPs due to the formation of composite Si/Au NPs reported recently [Flimelova 2023], [Ryabchikov 2019]. Similar to Si/Au NPs, pure Au NPs also have a trend in the change of their color with the laser ablation time (Figure 1c). Moreover, the laser exposure time also strongly influences the color even if Si NPs colloidal solutions were treated without any targets. In this case, it changed from brownish (0 s) to almost transparent (600 s). Evidently, such a treatment also considerably affects properties of semiconductor nanostructures that must be taken into account considering mechanisms of the formation of semiconductor-metallic nanostructures. These results point out a strong interaction between silicon nanoclusters (due to the possible fragmentation of Si NPs) and gold ones (due to the ablation of a gold target) whose properties are affected by the laser irradiation duration. Darker color of Si/Au NPs colloidal solutions prepared at a larger irradiation time can indicate a higher concentration of nanoparticles in solutions that is supported by direct particle concentration measurements and UV-Vis absorbance data shown below.

To establish changes in optical properties of Si NPs treated at different exposure time, we measured their absorbance spectra by means of UV-Vis spectroscopy. One can see that the laser irradiation significantly modifies absorbance of Si NPs colloidal solutions depending on its duration and the presence of a metallic target (Figure 2). In particular, a plasmonic maximum at around 520 nm appeared at 30 s of the laser irradiation becoming \sim 5-times stronger at 600 s ablation time (Figure 2a) that is typical for nanostructured gold due to collective oscillations of free electrons [Liu 2017]. At the same time, the laser treatment at the identical conditions without any targets provoked the decrease of the absorbance of Si NPs without any

plasmonic features (Figure 2b). Contrary, pure Au NPs formed at different ablation time showed various intensity of the plasmonic absorption being similar to the case of Si/Au NPs (Figure 2c). Thus, plasmonic properties of Si NPs can be associated with incorporated in them gold nanodomains.

The observed intensity variation of the plasmonic absorption can be caused by the modification of the chemical content of NPs due to a larger amount of the ablated gold. Indeed, as it is known, the absorbance intensity of a solution linearly depends on the concentration of a matter in the solvent and can be given by the following formula [Mayerhöfer 2018]:

$$A = \epsilon \cdot c \cdot l \quad (1)$$

where A is absorbance, ϵ is molar extinction coefficient [$L/(\text{mol}\cdot\text{cm})$], c is concentration [mol/L], l is path length [cm]. Hence, a higher concentration of Si/Au NPs in colloidal solutions can increase their absorbance efficiency. It is worth noticing that a larger absorbance value can also be associated with a higher content of nanostructured gold in studied silicon nanoparticles without any changes of their concentration in the colloidal solution. However, in our case one can also expect a variation of the molar extinction coefficient of Si/Au NPs due to their time-dependent chemical composition. It is important that the position of a plasmonic peak is significantly affected by a used metal and can be changed in the visible spectral range [Ryabchikov 2020], [Flimelova 2021]. Moreover, the intensity, the spectral position and the width of the plasmonic peak also depend on such particle characteristics as morphology, dielectric medium and surface-absorbed molecules [Phuoc 2007]. Thus, these aforementioned properties of plasmonic features of composite nanoparticles can also be influenced by their structure depending on the laser ablation time. The determination of the structure and the chemical composition of Si/Au NPs prepared at different laser irradiation time is out of the scope of the current paper and will be performed separately using a couple of techniques such as energy-dispersive X-ray spectroscopy (EDX), inductively coupled plasma mass spectroscopy (ICP-MS), X-ray photoelectron spectroscopy and X-ray diffraction (XRD).

We would also like to highlight an important point that can be fully missed considering mechanisms of the formation of semiconductor-metallic NPs investigating them by methods mentioned above. For this purpose, "fast" optical techniques such as UV-Vis spectroscopy and MA-DLS are good techniques for the fast visualisation of properties of Si NPs colloidal solutions irradiated without any targets. Our study by means of the UV-Vis spectroscopy reveals a considerable reduction of the absorbance of Si NPs colloidal solutions being irradiated without the gold target. For instance, one can observe 40-times decrease of the Si NPs absorbance at 520 nm wavelength by irradiating the colloidal solution for 10 minutes. Hence, taking into account the equation (1), these absorbance properties of Si-based NPs irradiated at different conditions can indicate the variation of their concentrations. Similar to the aforementioned case of Si/Au NPs, the lower absorbance of fragmented Si NPs (fr-Si NPs) can be associated with the decrease of their concentration due to the prolonged laser exposure. In order to check this statement, direct measurements of the concentration of composite nanoparticles were performed using DLS (Figure 3a). Ablation of the gold target immersed in colloidal solutions of Si NPs leads to the considerable (20-fold) change of the amount of nanoparticles during the laser irradiation. The concentration of Si/Au NPs increases from $\sim 1.4 \cdot 10^{10}$ NPs/mL (initial Si NPs) to $\sim 3.0 \cdot 10^{11}$ NPs/mL during the first 180 s (Figure 3a). Nevertheless, longer (> 180 s) laser ablation provokes slight (3-fold) decrease of the nanoparticle concentration from $\sim 2.9 \cdot 10^{11}$ NPs/mL to $\sim 1.2 \cdot 10^{11}$ NPs/mL

(Figure 3a). Possible reasons of such a decrease can be associated with higher losses of the laser energy in the colloidal solutions due to the presence of silicon and gold nanoclusters whose size and concentration can depend on the irradiation time. Hence, continuous emission of gold nanoclusters can provoke a higher absorbance of the laser energy leading to the lower laser fluence on the target's surface. It reduces both the amount of the emitted from the gold target nanoclusters and the efficiency of the fragmentation of silicon nanoparticles located close to the focal position of the laser beam. Thus, smaller amount of nanoclusters of both types interact each other leading to the decrease of the concentration of synthesized composite nanoparticles.

Moreover, the deposition of some smaller NPs on the surface of bigger ones can also take place in order to reach thermodynamic stable state (Ostwald ripening) that can provoke additional reduction of the concentration of nanoparticles detected by DLS. At the same time, the laser irradiation of Si NPs colloidal solutions without any targets slightly increases their concentration to $\sim 3 \cdot 10^{10}$ NPs/mL that remains almost constant at a larger duration (Figure 3a). One can assume that this treatment can change the structure of nanoparticles, e.g., their oxidation state. In the case of synthesized Au NPs, one can observe a growth of their concentration with the laser ablation time (Figure 3a). Furthermore, laser-induced sintering of some composite nanoparticles can also take place at larger (>180 s) ablation time reducing their concentration. The estimation of their energy losses in our case is quite complicated because of continuous changes of the properties of the colloidal solutions due to: (i) the increase of the amount of gold nanoclusters, (ii) the variation of the amount, size, oxidation state of Si NPs, (iii) the formation of composite Si/Au NPs with possible time-dependent properties. Thus, a computer simulation is required in order to distinguish a time-dependent contribution of each processes in the laser energy losses and to estimate their values at a certain time.

To define the hydrodynamic size of aqueous colloidal solutions of nanostructures, we performed measurements of nanoparticles prepared at different laser exposure time using DLS system. The measured hydrodynamic size includes the diameter of the inorganic core of NPs and the thickness of the solvation shell around them being depended on the interaction between nanostructures and a liquid medium. In our case, we found a linear decrease of the hydrodynamic size of Si/Au NPs from 165 nm (Si NPs, 0 s) to 85 nm (Si/Au NPs, 600 s) (Figure 3b). The polydispersity index (PI) of Si/Au NPs increases from ~ 0.15 to ~ 0.24 for Si/Au NPs formed at 30 s and 600 s, respectively. However, the colloidal solutions irradiated without any targets show some increase of the hydrodynamic size of Si NPs (Figure 3b). Their PI value varies between 0.25 and 0.37 indicating non-homogeneous size distribution. At the same time, pure Au NPs formed due to the laser ablation of the gold target in deionized water reveal the reduction of their hydrodynamic size (Figure 3b) having PI in range of 0.18 – 0.28. These results show complicated processes occurred during the synthesis of Si/Au NPs being depended on the type and amount of participated materials.

Here, different mechanisms can be responsible for the obtained changes due to the interaction of NPs with the laser light. Firstly, the solvate shell thickness can be reduced due to a lower surface charge (Figure 4a). Secondly, the physical size of the core can also be decreased due to the possible laser fragmentation of nanoparticles (planned to be studied separately by means of electronic microscopy). Such a laser-

induced fragmentation of bigger NPs into smaller ones is occurred immediately after the formation of composite nanoparticles [Al-Jumaili 2018] via inverse Ostwald ripening [Sadrolhosseini 2016], [Hamad 2014], [Onwudiwe 2014].

Thus, our results highlight an important role of a gold target during the irradiation of colloidal solutions of Si NPs leading to the synthesis of composite nanoparticles with ablation time-dependent gold content in Si NPs.

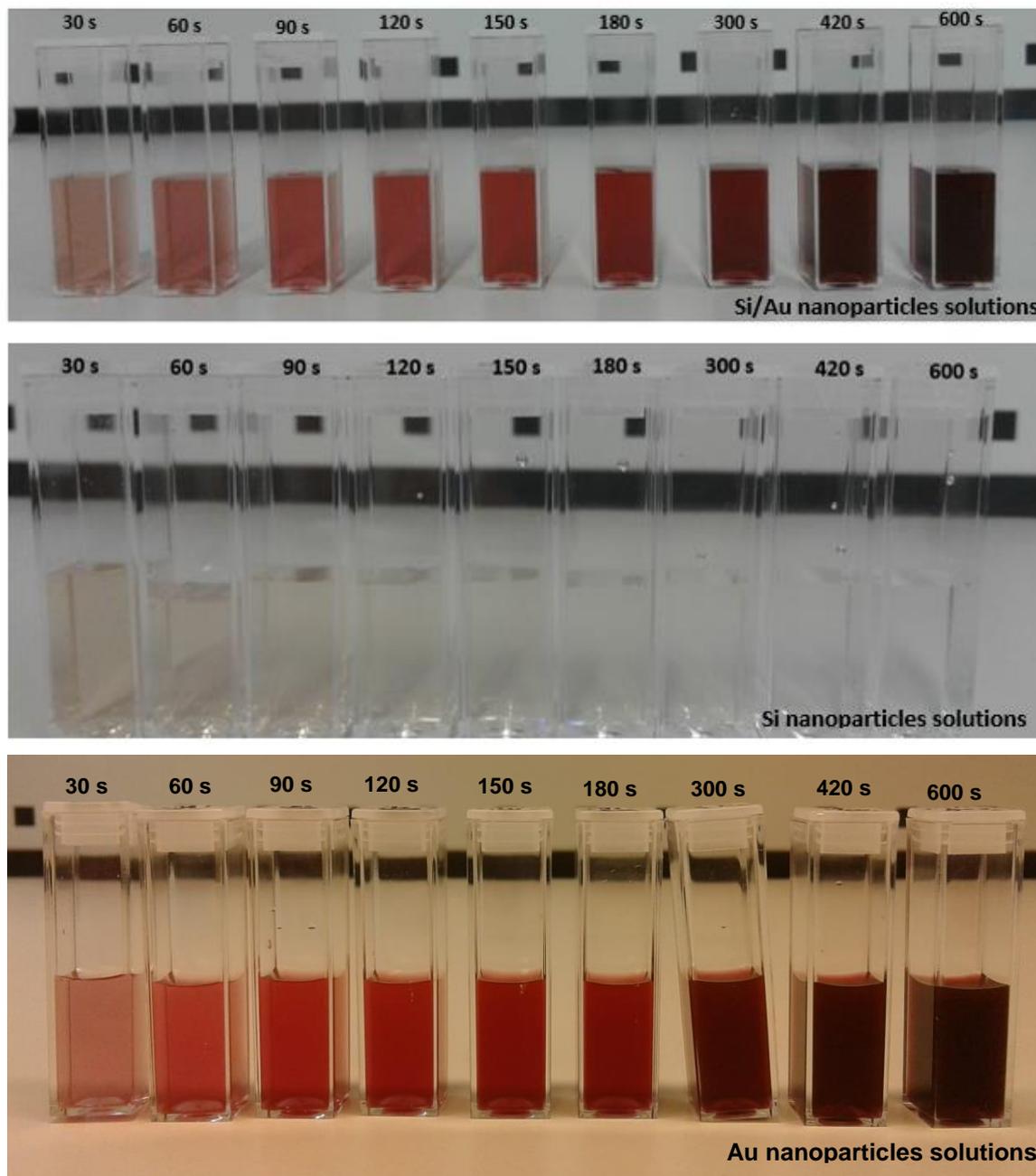


Figure 1. Colloidal solutions of Si/Au NPs, Si NPs, Au NPs treated by a pulsed laser with (Si/Au NPs) and without (fr-Si NPs) a gold target at different exposure time.

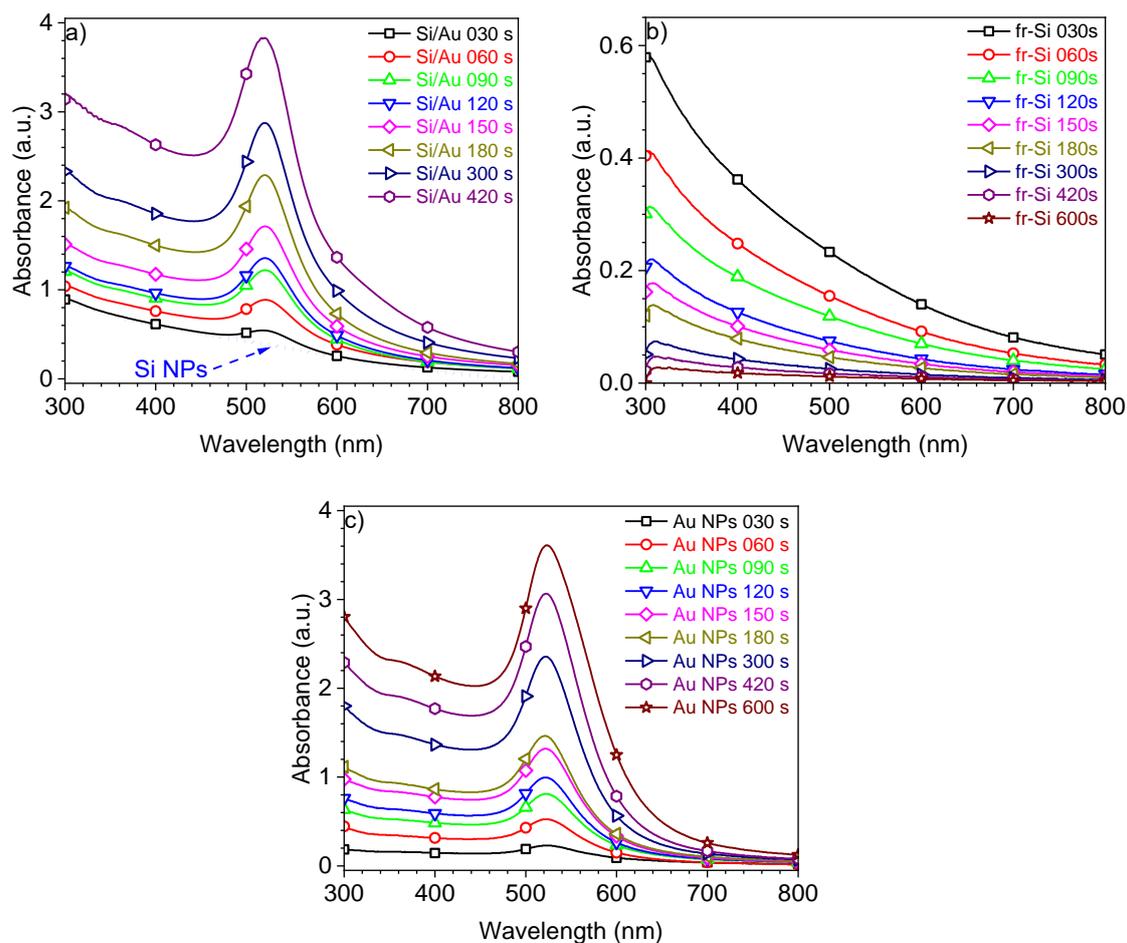


Figure 2. Absorbance spectra of colloidal solutions of Si/Au (a), Si NPs (b), Au NPs (c) treated by a pulsed laser with (Si/Au NPs) and without (fr-Si NPs) a gold target as well as of a gold target in deionized water at different exposure time.

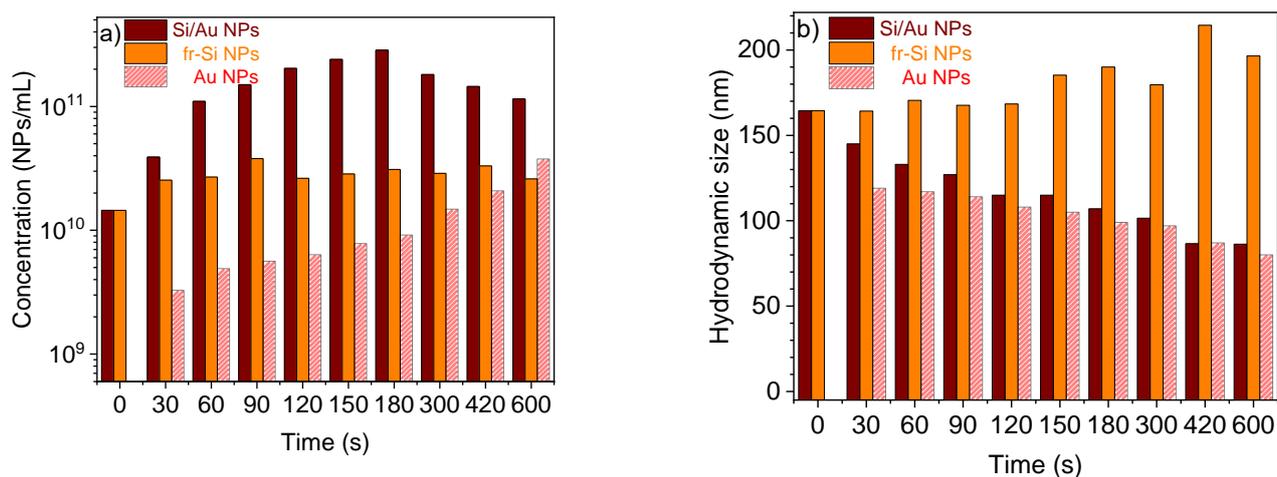


Figure 3. Particle concentration (a) and hydrodynamic size (b) of NPs treated by a pulsed laser without (fr-Si NPs) and with (Si/Au NPs) a gold target (Au NPs) as well as of a gold target in deionized water at different exposure time.

To study the stability of colloidal solutions irradiated at different conditions, we performed the measurements of their ζ -potential. Its value for initial Si NPs (-46 mV) shows a good chemical stability of the colloidal solution influenced by the

laser exposure (Figure 4a). By increasing the irradiation time from 30 s to 600 s in the presence of the gold target immersed in this colloidal solution, one can observe $\sim 30\%$ decrease of the ζ -potential from -42 mV to -30 mV (Figure 4a). Taking into

account the dependence of the hydrodynamic size of Si/Au NPs on the laser ablation time (Figure 3b), we can conclude that larger composite nanoparticles have better stability due to higher ξ -potential values that is a similar trend shown for gold nanoparticles of different sizes [Coradeghini 2013].

As it is known, ξ -potential is the electrical potential at the slipping plane located at the interface between the mobile fluid of a colloidal solution and a solvate shell attached to the particle surface. Thus, its value can depend on the amount of charge carriers located in the solvate shell. Experimentally detected lowering of the hydrodynamic size of Si/Au NPs can be caused by the decrease of the shell thickness that will reduce the number of charges diminishing ξ -potential of nanoparticles. Another reason can be related to a larger concentration of gold nanostructures in composite nanoparticles formed at larger laser ablation time that can induce additional decrease of the ξ -potential value. These results indicate that the stability of colloidal solutions of composite nanoparticles can be affected by different parameters such as size of nanoparticles and their chemical composition.

To detect any changes in the electrical properties of semiconductor nanoparticles due to the laser irradiation in the presence of the gold target, we checked the electrical conductivity of Si/Au NPs prepared at different laser ablation time using DLS system. We detected 35 % decrease of the conductivity value (from 2.35 $\mu\text{S}/\text{cm}$ to 1.53 $\mu\text{S}/\text{cm}$) for composite nanoparticles formed during the first 120 s followed by the further increase up to 2.39 $\mu\text{S}/\text{cm}$ for 600 s (Figure 4b). At the same time, pure Au NPs demonstrated a continuous increase of the electrical conductivity value from 3.7 $\mu\text{S}/\text{cm}$ to 4.8 $\mu\text{S}/\text{cm}$ with the laser ablation time (Figure 4b). Thus, the presence of Si NPs in water provokes ~ 2 -fold decrease of the conductivity value also changing its time-dependent behaviour (Figure 4a). However, the laser irradiation of Si NPs without any targets slightly modified their conductivity (Figure 4b). The initial decrease of the conductivity value of Si/Au nanostructures can be a consequence of the reduction of the size of nanoparticles due to the laser-induced fragmentation. Moreover, the interaction between gold and silicon nanoclusters can provoke the formation of multiple nanodomains inside the reduced nanoparticles. Therefore, it can lead to the quantum confinement of charge carriers in these areas lowering their mobility in the nanostructures that provokes smaller conductivity values (Figure 4b). Further increase of the electrical conductivity of Si/Au NPs formed at a longer laser ablation time (> 120 s) can be attributed to considerable changes of their chemical composition. Starting from 120 s, the amount of nanostructured gold incorporated in Si NPs can be relatively high ensuring better mobility of charge carriers that can provide the growth in the conductivity of Si/Au NPs. In order to establish a relationship between the electrical conductivity of composite nanoparticles and their content, a detailed investigation of the chemical composition of Si/Au NPs using EDX and ICP-MS techniques is required and will be carried out separately.

The control of the conductivity of semiconductor nanoparticles can have tremendous relevance for various biomedical applications, for example, biocompatible-sensing materials [Hamza 2017]. Laser-synthesized silicon nanoparticles have an important role in biomedicine for cancer theranostics or nonlinear optical bioimaging [Kharin 2019] due to their biocompatibility and biodegradability [Ryabchikov 2020]. However, their applications are obstructed in some biomedical fields where the translation of biological responses into electrical signals is needed due to the low electrical

conductivity of Si NPs. Unique chemical and physical properties of specially designed nanoparticles could help to transfer electrons from the bio specific layer to the electrode surface [Hamza 2017]. However, the laser synthesis in aqueous-containing medium additionally decreases the conductivity of Si NPs due to their unavoidable oxidation. To overcome this issue, one can perform the laser-induced change of the chemical composition of semiconductor nanoparticles by embedding metallic nanodomains of highly conductive metals (e.g., silver, gold, copper) [Ryabchikov 2020], [Flimelova 2021]. Evidently, larger concentration of these metallic elements should increase the conductivity of synthesized composite nanoparticles that can depend on occurred laser-induced physico-chemical processes and exact structure of formed nanoparticles. Among aforementioned metals, gold is the most promising one due to great perspectives of gold nanostructures in the field of biomedicine [Elahi 2013]. They also show the increase of the sensitivity of biochemical detection of electrochemical biosensors [Hamza 2017]. Moreover, we hypothesize that the conductivity of Si NPs could additionally be increased due to the decrease of their oxidation that can be easily carried out during laser synthesis [Ryabchikov 2018]. Thus, our findings indicate that embedding of the metallic nanostructures into Si NPs can potentially enlarge their applications towards bioelectrochemical sensing.

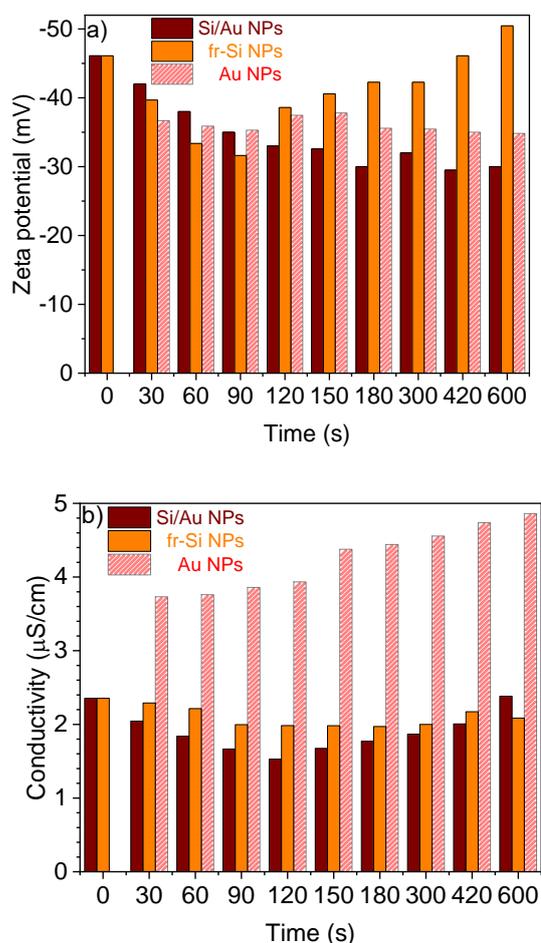


Figure 4. Zeta potential (a) and conductivity (b) of NPs treated by a pulsed laser without (fr-Si NPs) and with (Si/Au NPs) a gold target as well as of the gold target in deionized water (Au NPs) at different exposure time.

4 CONCLUSION

In summary, changes of properties of colloidal solutions of Si NPs under the laser irradiation at different conditions are shown by fast diagnostic optical techniques. The appearance of plasmonic properties in Si NPs with the laser ablation time-dependent efficiency is observed due to the formation of composite Si/Au NPs. All prepared colloidal solutions of silicon-gold nanostructures demonstrate good chemical stability with ζ -potential reduced from -46 mV for initial bare Si NPs to -30 mV for Si/Au NPs prepared at 600 s. The concentration of composite nanoparticles in colloidal solutions increases during the first 180 s of the laser ablation followed by the further slight decrease of their amount at a larger irradiation time (>180 s). At the same time, longer ablation time provokes ~ 2 -fold linear decrease of the hydrodynamic size of nanocomposites as compared to the initial bare silicon nanoparticles (from 165 nm to 85 nm). The reduction of the conductivity of Si/Au NPs during the first 120 s of the laser treatment (from 2.35 $\mu\text{S}/\text{cm}$ to 1.53 $\mu\text{S}/\text{cm}$) can be associated with lower sizes of nanoparticle and the possible formation of separated gold and silicon nanodomains. Further growth of the conductivity value (from 1.53 $\mu\text{S}/\text{cm}$ to 2.39 $\mu\text{S}/\text{cm}$) can be caused by both a higher concentration of Si/Au NPs and a larger metallic content in them. Longer irradiation of colloidal solutions of Si NPs without any targets decreases their absorbance that can be associated with the variation of their properties. The presented in the paper results can help (i) to get an idea about processes occurred during the laser irradiation of colloids at different conditions as well as (ii) to obtain fast detection of properties of colloidal solutions of semiconductor-metallic nanocomposites prior their biomedical or catalysis applications.

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