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# Laser-ablative synthesis of stable size-tunable Bi nanoparticles and their functionalization for radiotherapy applications

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**Abstract.** Nanoformulations of high-Z elements can improve therapeutic outcome in radiotherapy-based treatment of tumors, but current nanomedicine implementations in radiotherapy still need biocompatible, non-toxic nano-agents exhibiting low polydispersity and high colloidal stability. Here, we elaborate methods of femtosecond (fs) laser ablation in water and organic solvents to fabricate stable aqueous colloidal solutions of ultrapure elemental Bi nanoparticles (NPs) and characterize them. We show that fs laser ablation of Bi target leads to the formation of spherical elemental Bi NPs having 25 nm mean size and wide size-dispersion. NPs prepared in water undergo fast conversion into 400-500 nm flake-like nanosheets, while NPs prepared in acetone demonstrate a high colloidal stability. We then employ methods of fs laser fragmentation to control mean size and size dispersion of Bi NPs. Stable aqueous solution of Bi NPs suitable for biomedical applications can be obtained by coating with Pluronic® F-127. We finally show that surface modification of Bi NPs increases its colloidal stability in phosphate buffer saline (PBS) solution by more than 6 fold. Exempt of any toxic synthetic by-products, laser-ablated Bi NPs present a novel appealing nanoplatform for image-guided combination photo- and radiotherapy.

## 1. Introduction

Materials of high atomic numbers (Z) such as Iodine, Hafnium, Gold or Bismuth demonstrate ability to act as an efficient sensitizers of radiotherapy (RT) [1,2,3,4]. From a biomedical perspective, bismuth (Z = 83) has several advantages over other conventional elements for computer tomography (CT) attenuation and RT. First, Bi has the highest Z of all non-radioactive elements which results in its superior radiosensitization properties. Bi has a remarkably high X-ray attenuation coefficient (7.38 cm<sup>2</sup>/g at 90 keV) compared to Au (5.16 cm<sup>2</sup>/g at 90 keV) and I (1.94 cm<sup>2</sup>/g at 90 keV), which leads to its usage in high contrast computed tomography (CT) imaging [5]. Consequently, lower doses of RT are needed to achieve the desired effects [4]. At the same time, X-Ray absorption by photoelectric effect results in the formation of photo- and Auger electrons or characteristic X-Ray radiation leading to intense local ionization of cancer cell and DNA strand breaks. Off target damage is limited, as the range of this effects (1-5µm) is less than the cell size (>10 µm).

Additionally, elemental Bi strongly absorbs light over a broad spectral range extending to NIR. Such an advantage provides a highly localized photothermal heating of elemental Bi NPs by light having



wavelengths in biological transparency window of tissues (650-950 nm). This heating can be used for biovisualization by photoacoustic imaging or for photothermal therapy, which can synergistically enhance RT [3]. Other important advantages of Bi include low toxicity and good biocompatibility [2]. Furthermore, under certain conditions Bi can be easily eliminated from the body due to its favourable reactivity and dissolution properties [6,7]. Bi-based compounds have already been successfully explored in CT imaging and RT [2,3] as well as been used in off-the-shelf medications (e.g., Pepto-Bismol [12]), which confirms their safety. Note that Bi have an exceptionally low price per gram which leads to increased cost effectiveness of Bi in comparison to other high-Z elements. For example, Bi is 570 folds cheaper than Au. Moreover, favourable combination of physicochemical properties of Bi leads to its usage in many areas besides biomedicine: catalysis [8,9], cosmetics [10] and metallurgy [11].

Prospects of Bi-based NPs in the diverse range of applications critically depend on the surface conditions, colloidal stability, size, and purity of the nanomaterials. Traditional synthesis methods based on chemical pathways [13,14,15] are not fully compatible with stringent requirements of biological systems due to the necessity of using potentially toxic solvents and substances. Pulsed laser ablation in liquids (PLAL) provides one of best alternatives to satisfy the above-stated demands. Based on physical mechanisms of nanomaterials formation, fs laser ablation in liquids makes possible fast, scalable, cheap, and reproducible generation of NPs in colloidal state with pure surface and low size dispersion, with almost any composition [16,17,18,19,20,21,22,23]. In particular, we already used fs PLAL for the synthesis of different nanomaterials for biomedical applications, including Au NPs [16,24,25,26], Si NPs [17,18], TiN NPs [19,20] and isotope-enriched  $^{152}\text{Sm}$  oxide NPs [27,28].

Methods of laser ablation have already been explored for the fabrication of Bi-based nanomaterials [21,29,30,31,32]. Most of the articles report that laser ablation of Bi target in organic solutions leads to the formation of stable colloidal solutions of spherical NPs [29,30,31], while ablation in water typically results in formation of unstable solutions of Bi NPs with flake-like morphology [33,34]. This result for NPs obtained in water significantly complicates their further application in biomedicine. Any theranostic agents should be used in the form of aqueous colloidal solutions and have stable structural, dimensional, and morphological characteristics. Bi NPs obtained by laser ablation in organic solvents seem to be the most suitable candidates for use in biomedicine. However, techniques proposed in previous works cannot offer controlled fabrication of Bi NPs colloidal solutions, which are biocompatible and stable in biologically relevant conditions.

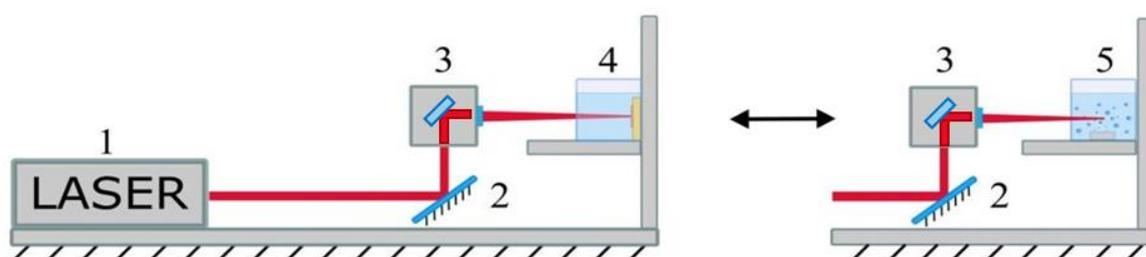
In our previous work, we demonstrated the possibility of synthesizing Bi NPs via ultrashort fs-laser ablation in water and organic solvents [35]. We found that Bi NPs obtained in water rapidly convert into 400-500 nm flake-like nanosheets composed of bismuth subcarbonates, while the NPs prepared in acetone present stable solutions of crystalline elemental Bi NPs having the mean size of 20–40 nm and a low size-dispersion. To transfer spherical NPs of elemental Bi from acetone to water in an unchanged form, we used Pluronic® F68 for surface modification. At the same time, we showed, that due to the relatively high absorption in the infrared range, functionalized biocompatible Bi NPs can act as effective sensitizer for photothermal therapy and photoacoustic bioimaging.

Here, we report on a further elaboration of fs laser-ablative synthesis of size-tunable Bi-based NPs and the characterization of their properties. In particular, we describe a new protocol for the preparation of stable aqueous solutions of Bi NPs covered with Pluronic® F127. We show that surface modification of Bi NPs significantly increases their colloidal stability in biologically relevant conditions, as well as improves their ability to absorb light in the window of biological tissue transparency (650-950 nm). This suggests that a proper surface modification of laser-synthesized Bi NPs is a plausible method to prepare stable, biocompatible, and pure Bi NPs for applications in nanomedicine. We believe that such NPs can also be promising for catalytic and biomedical tasks.

## 2. Materials and methods

### 2.1. Synthesis of NPs

NPs were synthesized by fs laser ablation of the bismuth (Bi) target (GoodFellow, Coraopolis, PA, USA, purity 99,999%) in deionized water (18.2 M $\Omega$  cm at 25 C) or technical grade acetone, under ambient conditions. A schematic of the experimental setup is shown in Figure 1. The target was fixed vertically on the wall of a quartz vessel filled with 50 mL of a liquid. A 3-mm-diameter beam from a Yb:KGW laser (1030 nm wavelength, 250 fs pulse duration, 30 $\mu$ J pulse energy, 100 kHz repetition rate; TETA 10 model, Avesta, Moscow, Russia) was focused by a 100-mm F-theta lens on the surface of the target, through a side wall of the ablation vessel. The thickness of the liquid layer along the laser beam was 4 mm. The focusing conditions were set to obtain maximum productivity from the ablation process (defined as ablated mass per duration of ablation) individually for each solvent. The laser beam was moved over a 25 x 25 mm area on the surface of the target, with 4000 mm/s speed using a galvanometric scanner. This was done to avoid drilling of a hole in the target and to maximize the NPs yield. The duration of each laser ablation experiment was 20 min. The target and the ablation chamber were cleaned after each ablation experiment, by using an ultrasonication step in acetone, followed by ultrasonication in water and isopropanol and, finally, drying under ambient conditions.



**Figure 1.** Schematic representation of the experimental setup for laser ablation and fragmentation in liquids. 1 - a fs Yb:KGW laser; 2 - a mirror; 3 - a galvanometric scanner with focusing F-theta lens; 4 - the ablation chamber with the target submerged in liquid; 5 - the laser fragmentation chamber with magnet stirrer.

As an additional control over the NPs size, we applied the technique of fs laser fragmentation by generation of white light supercontinuum in Kerr media, which was developed in our previous work [28]. Briefly, a solution of Bi-based NPs obtained by the laser ablation was illuminated by the same laser in the absence of the target. The laser beam was focused into the solution 1 cm behind the entrance glass. The solution was continuously homogenized by a magnetic stirrer during the fragmentation process.

### 2.2. Surface modification of Bi NPs

Bi NPs ablated in acetone were successfully transferred to water using a surface coating by Pluronic® F127 (Sigma-Aldrich, St. Louis, MO, USA). To achieve this surface coating, the polymer F127 was added to colloidal solution of Bi NPs in 4:1 ratio by mass and then vortexed until polymer dissolution. After this step the solution was centrifuged 10 min at 10000 RCF and the supernatant was discarded to remove the rest of the polymer. The formed pellets were resuspended in 1 mL of deionized water or PBS to produce a stable dispersion. Functionalized NPs were stored at RT for further use.

### 2.3. Characterization of NPs

Morphology, structure, size, and composition of the synthesized NPs were characterized by a scanning transmission electron microscopy (STEM) system (MAIA 3, Tescan, Czech Republic) operating at 0.1-

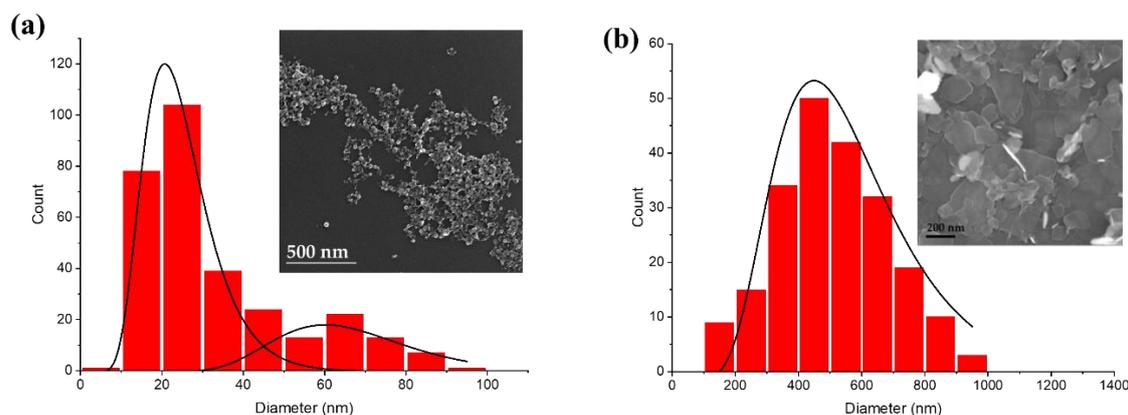
30 kV coupled with an EDS detector (X-act, Oxford Instruments, High Wycombe, UK). Samples for electron microscopy were prepared by dropping 1  $\mu\text{L}$  of the NPs solution onto a cleaned silicon substrate and subsequent drying at ambient conditions.  $\xi$ -potential and DLS measurements were performed using a Zetasizer ZS instrument (Malvern Instruments, Orsay, Paris, France). The concentration of NPs solution was determined by measuring the target weight before and after the ablation step and dividing this mass difference by the ablation liquid volume. Optical properties of the obtained NPs were characterized using a spectrophotometer (SOL Instruments, 330-1100 nm spectral range, Belarus) in cuvettes with 10 mm optical path.

### 3. Results and discussion

#### 3.1. Synthesis and characterization of Bi-based NPs

Laser ablation of the Bi target in technical acetone (LAA) and in deionized water (LAW) resulted initially in dark-brown colloidal solutions. However, 100 minutes after the end of the synthesis water-based colloidal solution became substantially turbid, changed their color to milky-white and precipitated. The morphology of LAW Bi NPs changed from strictly spherical to flake-like form. Meanwhile LAA Bi NPs converted their coloration during the entire storage period (6 months) under ambient conditions, which indicates their high colloidal stability. Such a stability can be explained by the electrostatic stabilization of the NPs in solution. This assumption is confirmed by measurements of the zeta potential: -20 meV for LAA Bi NPs. This result coincides with the stability threshold for colloidal solutions [36].

As a result, we found that LAA leads to the formation of strictly spherical Bi NPs with bimodal size distribution. The distribution peaks are at 20–30 nm and 60–70 nm. At the same time, LAW leads to the formation of 400–500 nm flake-like nanosheets with sharp edges, different thickness, and wide size dispersion. Typical STEM images and size distributions of Bi NPs obtained by LAA and LAW are shown in Figure 2.

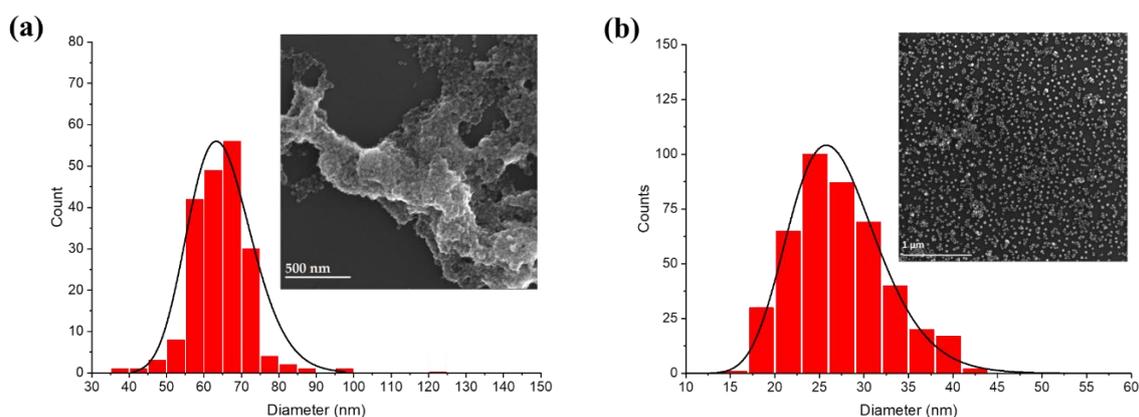


**Figure 2.** Size distributions and typical scanning transmission electron microscopy (STEM) images of Bi NPs after fs laser ablation in (a) acetone and (b) water.

In addition to morphology, size characteristics and optical properties, NPs obtained by LAW and LAA also differ in chemical composition. In our previous work we showed that flake-like nanosheets obtained by LAW are mostly composed of Bi subcarbonates, while NPs prepared by LAA composed of pure elemental Bi [35]. Effective atomic number is the defining parameter in terms of nano-radiotherapy. Higher  $Z$  guarantee more effective RT due to the larger photoelectric effect cross-section. Therefore, it is critically important for applications in RT that the particles consist of pure bismuth. To improve the efficiency of distribution and accumulation of NPs in targeted sites, nano-agents should have a size of

several tens of nm, narrow size, and morphology distribution. Incorrectly chosen NPs parameters can noticeably reduce the circulation time, worsen the distribution of the nano-agent in the body, and, as a result, dramatically reduce the effectiveness of therapy. In this case, Bi NPs obtained by LAA are the most favorable candidate for biomedical applications in the field of RT sensitization.

We found that the presence of water played a decisive role in the final morphology and composition of Bi NPs: even the addition of 1% v/v of water to LAA Bi NPs resulted in a change of NPs shape from spherical to flake-like nanosheets. The morphological alterations were accompanied by a change in chemical composition of NPs: elemental Bi turned into Bi subcarbonates  $(\text{BiO})_2\text{CO}_3$  and  $(\text{BiO})_4\text{CO}_3(\text{OH})_2$  [35]. However, if the solvent for LAW NPs is quickly changed from water to acetone, the NPs conserve their spherical shape, which is shown in Figure 3a. The size dispersion of such re-suspended NPs becomes narrower and monomodal, but the mean size of the NPs is still difficult to control. To further narrow down the size dispersion and vary the mean size of the NPs, we used the method of fs-laser fragmentation with white light supercontinuum. In this case, after fragmentation of initial bare NPs prepared by LAA at 100  $\mu\text{J}$  pulse energy for 1 hour we obtain colloidal solution of strictly spherical NPs with narrow and controllable size distribution with the mean size of about 25 nm (Figure 3b).



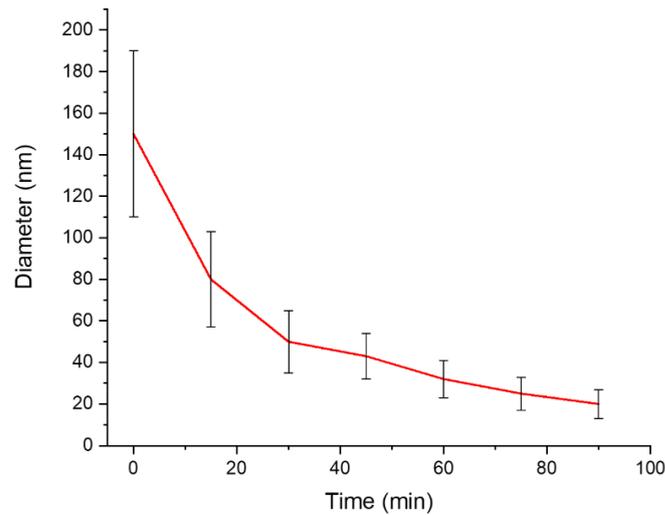
**Figure 3.** Size distributions and typical scanning transmission electron microscopy (STEM) images of Bi NPs obtained by (a) fs laser ablation in water and subsequent re-dispersion in acetone and by (b) fs laser fragmentation at 100  $\mu\text{J}$  pulse energy for 1 hour.

It was found that mean size and size dispersion of Bi NPs during the fragmentation process have a clear tendency to decrease with increase the laser irradiation time. To determine the dependence of the Bi NPs size characteristics on the duration of the fragmentation process, the hydrodynamic size of NPs was recorded during the fragmentation process. The results of DLS hydrodynamic size measurements are shown in Figure 4. White light supercontinuum fragmentation in liquids is an easy and fast technique, which makes possible to obtain stable colloidal solutions of Bi NPs with precise size control from 150 to 20 nm.

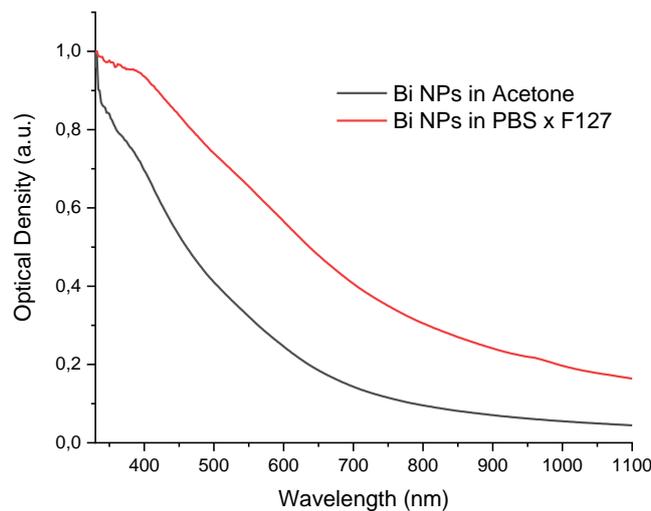
### 3.2. Optical properties of Bi NPs

Due to vanishing band gap the Bi NPs, exhibit remarkable absorption in the infrared range, which can be extremely useful in another therapeutic modality - in photothermal therapy. To increase biocompatibility, colloidal stability, and circulation time in bloodstream of fabricated NPs we elaborated an easy and cheap method to cover Bi nanostructures with Pluronic® F127, described as in Materials and Methods section. The main parameter that determines the ability of particles to act as effective sensitizers for photothermal therapy and photoacoustic imaging is their optical absorption in the relative transparency window of biological tissues (650-900 nm). In our previous work devoted to Bi NPs, we

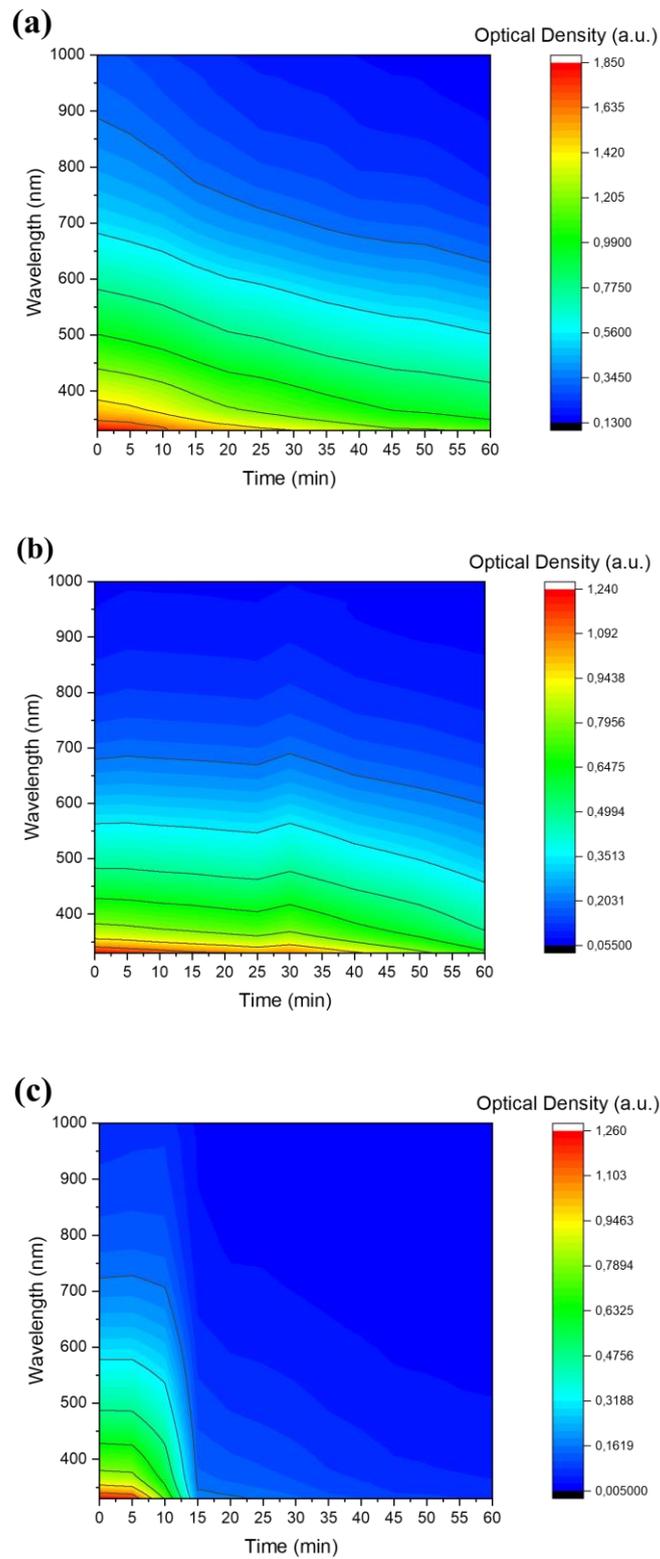
found that NPs with the surface modification by Pluronic® F68 have a higher photoconversion ability, which was confirmed by photothermal tests upon excitation with an 800 nm continuous-wave laser [35]. Here we obtained the optical extinction spectra of functionalized and bare elemental Bi NPs. Coated NPs exhibit stronger IR absorption compared to bare particles obtained by LAA (Figure 5). This observation confirms the previously obtained results. Coated NPs of elemental bismuth have higher biocompatibility, less toxicity and show a better ability to act as a sensitizer for photothermal therapy and photoacoustic imaging.



**Figure 4.** Dependence of Hydrodynamic diameter of Bi NPs obtained by LAA on duration of fs-laser fragmentation.



**Figure 5.** Extinction spectra of initial Bi NPs, prepared by LAL in acetone, and functionalized with Pluronic® F127 Bi NPs.



**Figure 6.** Dependence of extinction spectra of (a) functionalized with Pluronic® F127 Bi NPs in deionized water or (b) in PBS, and (c) initial LAA Bi NPs in PBS on time of storage obtained by the optical spectrometry method.

### 3.3. Stability test on Bi NPs

For biomedical applications, besides the fact that the NPs should be biocompatible and non-toxic, they should also be stable in biologically relevant conditions. PBS, which osmolarity and ion concentration correspond to relative parameters in the human body, is one of the most widespread isotonic solution used in biomedicine. The presence of a high salt content in the PBS negatively affects the colloidal stability of NPs, significantly increases their tendency to aggregation and change surface chemical composition. The protective shell in the form of a non-toxic polymer not only improve the biocompatibility and circulation time of NPs in the bloodstream, but also significantly increases their colloidal stability.

To determine the effect of surface modification of NPs on their colloidal stability in PBS and water, we detected the kinetics of changes in the optical spectra of coated and uncoated NPs. All the samples were taken at the same initial concentration. The results are shown in Figure 6. It was found that functionalized Bi NPs have a 6.2-fold lower tendency to aggregation in PBS (time of decrease in optical density by  $e$  times), in contrast to bare NPs, which is a clear marker of success surface modification of NPs. The most stable were covered Bi NPs in deionized water. The absence of free ions in the solution and the neutral pH of the medium has a favorable effect on the colloidal stability of NPs.

## 4. Conclusion

We elaborated the technique of fs laser ablation and fragmentation in liquid ambient to fabricate colloidal solutions of Bi-based NPs suitable for applications in radiation nanomedicine, photothermal therapy and photoacoustic imaging. We found that laser-ablation of the bare Bi target in technical grade acetone leads to the formation of spherical Bi NPs with bimodal size distribution and peaks in the region of 20-30 nm and 60-70 nm. The NPs prepared in water experienced a rapid conversion into 400-500 nm flake-like nanosheets, composed of bismuth subcarbonates ( $(\text{BiO})_2\text{CO}_3$  and  $(\text{BiO})_4\text{CO}_3(\text{OH})_2$ ), having a low colloidal stability, while the NPs obtained by LAA demonstrated high chemical and colloidal stabilities. We also found that a rapid re-dispersion of LAW Bi NPs from water to acetone leads to the formation of spherical NPs with narrow and monomodal size distribution and the mean size of 60-70 nm. To obtain an additional control on size characteristics of Bi NPs, we elaborated a technique of fs-laser fragmentation in liquids. The laser fragmentation step opens an avenues for precise size-tunable NPs synthesis with high control on mean size and size dispersion of obtained NPs. It was shown that only 1-hour fragmentation at an energy of 100  $\mu\text{J}$  and a repetition rate of 10 kHz made possible the fabrication of stable colloidal solutions Bi NPs with an average size of  $25 \pm 10$  nm and wide and bimodal size distribution. Fragmented NPs have spherical morphology and low size dispersion.

We finally introduced a procedure to obtain a stable aqueous solution of elemental Bi NPs suitable for biomedical applications, based on the surface modification of NPs with Pluronic® F127 and their subsequent transfer to the PBS solution in unchanged form. We also showed that the covered Bi NPs have higher ability to act as efficient sensitizers of photothermal therapy and contrast agents in photoacoustic imaging than initial Bi NPs prepared by LAA. At the same time, we showed that surface modification increases colloidal stability in a biologically relevant media - PBS solution by 6.2 fold. Based on obtained physico-chemical characteristics and exceptional purity, laser-synthesized elemental Bi NPs promise a major advancement of current methods for photo- and radio-nanomedicine.

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