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NANOSTRUCTURES

Bi@SiO_2 Core@Shell Composites Formation Based on Laser Synthesized Bi Nanoparticles

A. V. Skribitskaya[a,*], N. A. Korotkova[b], P. A. Kotelnikova[b], G. V. Tikhonowski[a], A. A. Popov[a], S. M. Klimentov[a], I. N. Zavestovskaya[c], and A. V. Kabashin[d]

[a] *National Research Nuclear University MEPhI, Moscow, 115409 Russia*

[b] *Shemyakin–Ovchinnikov Institute of Bioorganic Chemistry, Russian Academy of Sciences, Moscow, 117997 Russia*

[c] *Lebedev Physical Institute, Russian Academy of Sciences, Moscow, 119991 Russia*

[d] *LP3, Aix Marseille University, CNRS, Marseille, 13288 France*

** e-mail: sav1998@list.ru*

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Abstract—Present article provides a method of Bi@SiO_2 core@shell nanocomposites obtaining via surface modification of laser-synthesized bismuth nanoparticles with tetraethoxysilane. The SiO_2 shell coating on Bi nanoparticles was demonstrated to form spherical nanoformulations with the mode of size distribution at 250–300 nm. The developed approach is a novel perspective alternative to the traditional methods that allows designing biocompatible Bi-based nanocomposites for the sensitization of multimodal theranostics.

Keywords: nanoparticles, bismuth, surface modification, nanocomposites, laser ablation in liquid

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1. INTRODUCTION

Over the past decade, the quantity and quality of basic research in biomedicine has reached a new level, where Bi-based nanomaterials occupy a special place. The highest atomic number among stable elements ($Z = 83$) and unique optical properties motivate the use of Bi-based nanoparticles (NPs) for sensitization of computed tomography and photoacoustic imaging [1, 2], chemotherapy and radiotherapy [3, 4], inhibition of bacterial infections [5], and drug delivery [6, 7]. Traditionally, bismuth NPs are synthesized via complex multi-step chemical reactions using toxic precursors, which often contaminate the NPs surface [8–11]. In this context, pulsed laser ablation in liquid (PLAL) appears to be an attractive alternative approach to produce ultrapure and colloidally stable NPs with controllable properties. High productivity, flexibility, and simplicity of the method determine its wide use in biomedicine, nanophotonics, and power engineering [12–14]. Clinical application of such nanomaterials requires surface modification of NPs with biocompatible compounds to reduce their toxicity and increase accumulation in target areas [12]. The use of silicon dioxide is one of the most effective methods for solving this problem [15]. The uniformity of the morphological and dimensional identity of NPs is a key factor in the synthesis of compounds with a SiO_2 shell [16]. Under such conditions, the PLAL method, which makes it possible to produce NPs with spherical morphology and specified dimensional properties, seems to be an optimal approach [17]. Nanocomposites based on laser-ablated Bi NPs with a biocompatible SiO_2 shell are a new promising compound for sensitizing multimodal theranostics of oncological diseases.

2. MATERIALS AND METHODS

Silicon dioxide shells on Bi NPs were grown using the Stöber method [18]. This method is a widely used sol–gel technique that allows the synthesis of SiO_2 nanoparticles of controllable size and morphology. For the Stöber reaction tetraethoxysilane (TEOS) $(C_2H_5O)_4Si$ (Komponent-reaktiv, Russia), 30% ammonium hydrate (NH_4OH) (Chimmed, Russia), 95% ethyl alcohol (C_2H_5OH), and deionized water (18.2 MΩ cm at 25°C) were used. Bismuth nanoparticles were synthesized by femtosecond pulsed laser ablation in liquid, developed in our previous work [19]. A 3-mm diameter beam from a Yb:KGW laser TETA-10 (Avesta, Russia; wavelength of 1030 nm, pulse duration of 270 fs, pulse energy of 30 μJ, and rep-

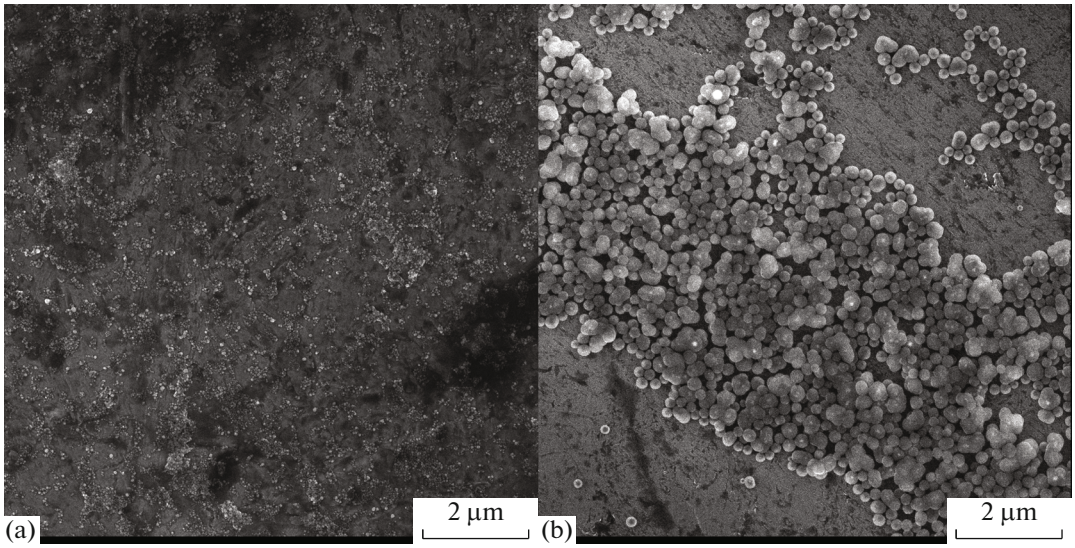

Fig. 1. SEM images of (a) Bi nanoparticles synthesized by PLAL and (b) core@shell structured Bi@SiO_2 nanocomposites.

etition rate of 100 kHz) was focused by a flat-field (F-theta) lens on the surface of a Bi target (GoodFellow, USA, purity 99.5%) immersed in chemically pure acetone. Morphological, dimensional, and structural properties of Bi NPs were studied by using scanning electron microscopy (SEM) (MAIA 3, Tescan, Czech Republic) and energy-dispersive spectrometry (EDS) (X-Act, Oxford Instruments, UK). The hydrodynamic size distribution was obtained by dynamic light scattering (DLS) (Zetasizer ZS, Malvern Instruments, France).

After synthesis in acetone, Bi NPs were transferred to ethanol by centrifugation and solvent exchange. Next, 140 μg of Bi NPs was dissolved in 9 mL of ethanol. Then, 600 μL of deionized water and 500 μL of ammonia hydrate were added to the colloid. Under the constant stirring, 1 mL of 45 mM tetraethoxysilane was added dropwise to the resulting solution with NPs. The final colloid was placed in a laboratory rotator for 16 hours at the room temperature, after that the nanocomposites were washed in ethanol by triple centrifugation for 15 min at 5000*g*.

3. RESULTS AND DISCUSSION

Analysis of SEM data clearly indicates the formation of Bi NPs and Bi@SiO_2 nanocomposites with close-to-spherical morphology, which is typical of PLAL (Fig. 1). Also, SEM images of Bi@SiO_2 nanocomposites display a clearly visible core@shell structure, where bright centers correspond to the cores of Bi nanoparticles, and the less contrasting surface layer corresponds to the SiO_2 shell (Fig. 1b).

The results of characterization of dimensional properties of laser-ablated Bi NPs and Bi@SiO_2 nanocomposites are presented in Figs. 2a and 2b, respectively. Size distributions of the prepared nanomaterials conforms to the lognormal law. The size distribution mode of the original bismuth NPs is in the range from 30 to 40 nm, while the distribution mode of nanocomposites is in the range from 250 to 300 nm. Differences in the distributions of the Feret diameter and hydrodynamic diameter are due to the specifics of the DLS measurements. The DLS method is not able to separate the presence of small NPs from the background of larger ones, which affects the broadening of the size distribution and a shift of the mode towards larger sizes.

In addition, the Stöber reaction produced both composites with Bi NPs core and SiO_2 shell and pure SiO_2 NPs. These nanoformulations cannot be completely separated from Bi@SiO_2 nanocomposites. However, individual SiO_2 nanoparticles are easily identified using SEM. This circumstance made it possible not to take SiO_2 NPs into account when plotting the size distribution of nanocomposites with SEM images, but it affected the results of DLS measurements. To confirm the formation of SiO_2 shell on the surface of laser-ablated Bi NPs, we additionally analyzed the chemical structure of nanocomposites using energy-dispersive spectroscopy. The results of EDS analysis of Bi NPs and Bi@SiO_2 nanocomposites are presented in Fig. 3. The data were normalized to the signal from Bi. The study of the compositional char-

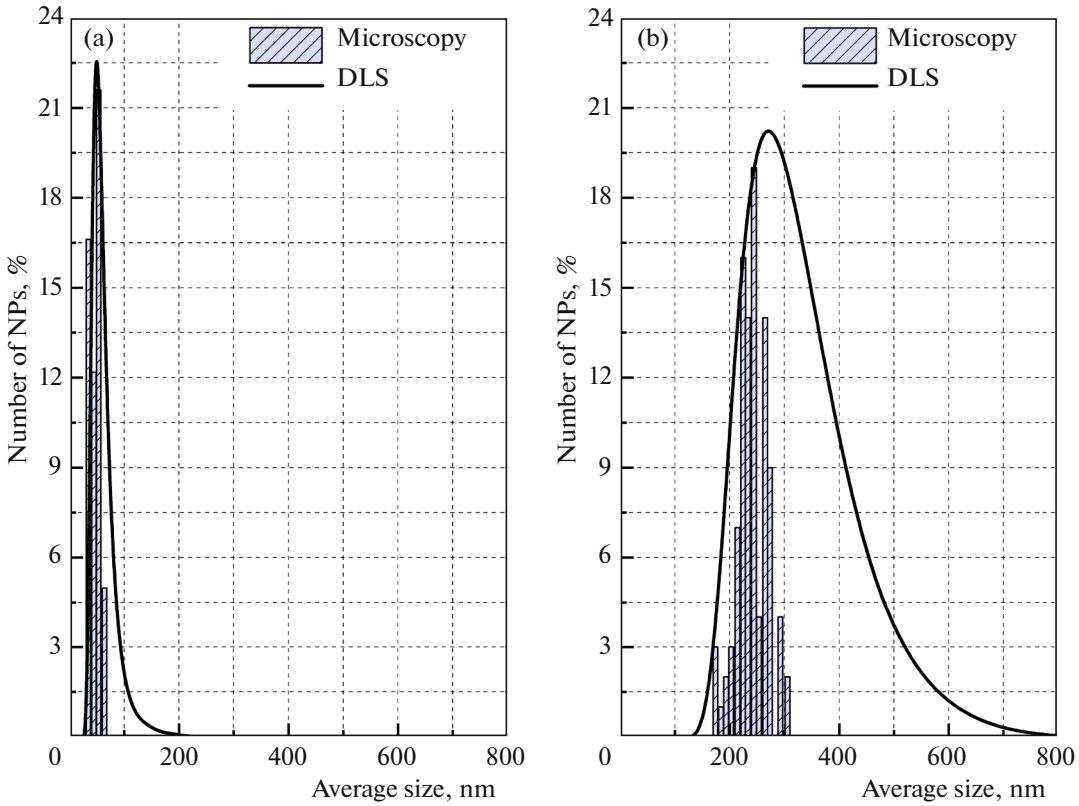

Fig. 2. Size distributions of (a) laser-ablated Bi nanoparticles and (b) Bi@SiO_2 nanocomposites.

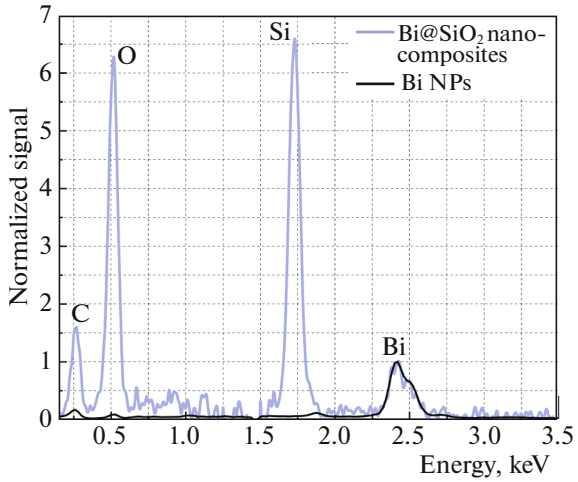

Fig. 3. Results of EDS analysis of laser-ablated Bi nanoparticles and Bi@SiO_2 nanocomposites.

acteristics of the synthesized NPs reliably confirmed the presence of Bi in both types of nanomaterials. The presence of Si and O in the composition of nanocomposites, which are the main elements of the shell, was also detected. The presence of oxygen in the composition of the initial Bi NPs is due to weak oxidation of the NPs surface during laser ablation, while the presence of carbon for both types of NPs can be due to organic contamination of the SEM vacuum chamber.

The EDS analysis together with the obtained SEM images confirms the formation of core@shell structured nanocomposites with core of laser-synthesized Bi NPs and shell of SiO_2.

4. CONCLUSIONS

Core@shell structured nanocomposites were prepared by chemical modification of laser-synthesized Bi NPs surface using tetraethoxysilane. The use of the PLAL method made it possible to obtain Bi NPs with relatively uniform morphological and size characteristics and with a size distribution mode in the range of 30–40 nm. The synthesized NPs acted as nucleation centers for biocompatible SiO_2 shells during the Stöber reaction. Using SEM and EDS, the formation of Bi@SiO_2 nanocomposite structures with close-to-spherical morphology and size distribution mode in the range from 250 to 300 nm was reliably demonstrated. The use of a biocompatible SiO_2 modification will not only reduce the toxicity of the Bi core, but also preserve all the original multimodal theranostic properties.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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