Designing and Manufacturing of Multifunctional Nanosensors Using Ultrafast Laser Processing

Yury V. Ryabchikov
HiLASE Center, Scientific Laser Applications Department
Institute of Physics of the Czech Academy of Sciences
Dolni Brezany, Czech Republic
e-mail: ryabchikov@fzu.cz

***Abstract*— Ultrafast laser processing is a well-developed model for the nanostructure synthesis as well as for the material modification. Its employment for sensing applications is a facile route of the development of new types of multi-modal nanosensors with required performance whose efficiency can be improved due to their high chemical purity. In particular, pulsed laser deposition is used for the formation of nanosensors requiring complex synthesis conditions in gaseous atmosphere. In this work, pulsed laser ablation in liquids is employed for the easy synthesis of sensing nanoagents. It allows us to form single- and multi-component (also having semiconductor modalities) nanosensors based on different metallic elements, which are successfully used for biosensing (SERS) and nanothermometry applications.**

Keywords-nanosensors; SERS; nanothermometry; laser ablation; ultrafast laser processing.

I. INTRODUCTION

The development of novel multi-modal nanosensors allowing the detection of changes of various parameters is still an important application task. One of the most perspective scientific directions is the creation of highly-sensitive non-toxic multi-functional bionanosensors able to detect slightest modifications in life organisms. Their design and formation is an important objective for the life science being still very challenging due to various complex issues.

Ultrafast laser processing is a very promising appeoach that is an alternative to many chemical synthesis methods providing the extreme purity of the chemical content of the prepared nanosensors. Here, one can highlight the following approaches for their formation:

1) Pulsed Laser Ablation in Liquids (PLAL) allows direct synthesizing of colloidal solutions of composite nanoparticles merging both semiconductor and metallic elements being a facile route to form nanostructures with variable chemical content [1].

2) Pulsed Laser Deposition (PLD) leads to the deposition of nanostructures on a substrate using a high-vacuum or gaseous environment [2].

3) Laser-Induced Forward Transfer (LIFT) allows transferring of nanoparticles (NPs) on a substrate making patterns with required geometric characteristics.

4) Volumetric Modification (VM) can also be performed by irradiating of a material using a high power laser source with ultrashort pulse duration following by further chemical etchning. Such a technique is used for the design and the formation of microfluidic channels, which are very promising for biosensing applications [3].

Thus, the combination of these techniques by employing only one ultrafast laser source used for the different laser processing lets us the design of novel multi-functional nanosensors. In the current research, multi-element nanostructures were prepared and successfully tested for various sensing applications, in particular, for bioimaging using Surface-Enhanced Raman Scattering (SERS) technique due to the presence of a variable content of plasmonic metals as well as for optical or magnetic resonance nanothermometry that can be promising for cell studies.

II. EXPERIMENTS

To produce multi-element nanostructures, which can be employed for sensing applications, ultrafast laser sources (6 ps pulse duration) with variable laser fluence were used. Colloidal solutions were formed by direct laser ablation of a metallic target immersed in an aqueous solution of various semiconductor (Si, C, SiC, Ge) NPs allowing the combination of different elements in one nanoparticle. The deposition was carried out in a high vacuum by irradiating corresponding metallic or semiconductor targets using the same laser sources. The volumetric modification was performed by the laser irradiation of a substrate at various laser parameters followed by their further chemical etching with the hydrofluoric acid [3]. The formed nanostructures were comprehensively investigated by a set of different methods such as UV-Vis, Raman, Photoluminescence (PL) or Electron Paramagnetic Resonance (EPR) spectroscopies, Transmission or Scanning Electronic Microscopy (TEM or SEM) and X-Ray Diffraction (XRD).

III. RESULTS AND DISCUSSION

The ultrafast laser processing leads to significant changes of processed materials reflecting it by changes of their structural and optical properties. As a base for the design of multi-functional nanosensors, colloidal solutions of such semiconductor nanostructures as carbon and silicon were chosen. This choice was substantiated by their successful

 ISBN: 978-1-68558-083-4

applications in bioimaging [4], optical nanothermometry [5], singlet oxygen generation [6][7] or non-linear optical bioimaging [8]. The performed 2-step laser processing considerably modified their properties leading to the appearance of strong plasmonic properties easily controlled by the processing time (Figure 1). Here, semiconductor NPs formed by either laser or chemical methods were successfully used for the design of plasmonic multi-component nanostructures (Figure 1). In the case of C NPs, double-band absorbance was obtained (Figure 1). Besides the achieved plasmonic responses, these nanostructures also revealed strong EPR signals from unpaired electrons due to the presence of certain types of paramagnetic defects [9]. Moreover, X-ray studies of semiconductor-metallic nanocomposites also demonstrated that XRD patterns of semiconductor nanostructures gradually transformed into metallic ones reflecting several crystalline planes corresponded to used for the laser ablation a metallic target.

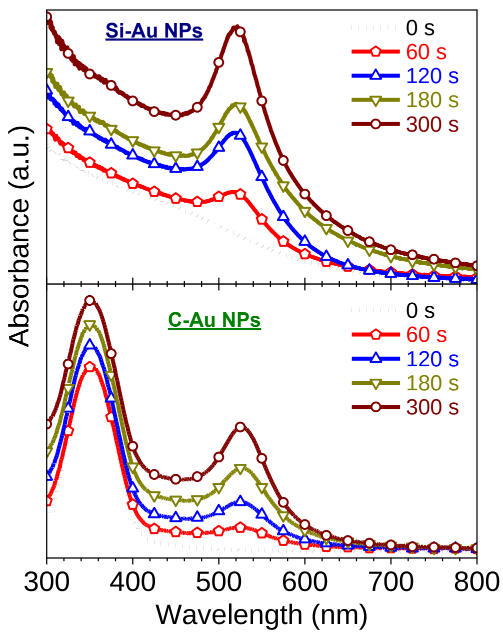

Figure 1. Laser-induced appearance of variable plasmonic sensing modalities in silicon (on the top) and carbon (on the bottom) nanoparticles.

These important modifications opens up a new important niche for semiconductor nanomaterials in the field of nanoplasmonics allowing their implementation in SERS biosensing additionally to the aforementioned applications [10]. Moreover, using the photoluminescence response of semiconductor NPs one can apply them for optical nanothermometry whose efficiency will be significantly affected by embedded noble metal elements acting as either (i) plasmonic resonance enhancers or (ii) metallic quencher of the fluorescence. Furthermore, paramagnetic defects of semiconductor nanostructures can also be employed at the same time as temperature nanosensors for magnetic resonance nanothermometry.

In summary, the design of novel nanosensors based on single- and multi-element nanostructures formed by ultrafast laser processing was demonstrated and their sensing performance was assessed. In particular, PLD technique was used to deposit different plasmonic nanostructures with variable size on a substrate. LIFT technology was employed to design sensors whose performance was considerably influenced by the size and composition of NPs and the distance between them. Moreover, composite NPs with features affected by PLAL conditions were also deposited on a substrate or were used as a concentrated colloidal solution. These nanosensors were used for the detection of (i) bacteria using SERS technique showing 10^5 cfu/mL detection limit for *L.innocua* and *E.Coli* [10], (ii) environment temperature by magnetic or optical nanothermometry showing 0.75 %/°C sensitivity. Thus, such nanosensors can be promising for biosensing, bioimaging and nanothermometry applications.

ACKNOWLEDGMENT

Yu. V. R. acknowledges the funding from The European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Actions Individual Fellowship (grant agreement No 897231, LADENTHER); the European Regional Development Fund and the state budget of the Czech Republic (Project No. BIATRI: CZ.02.1.01/0.0/0.0/15_003/0000445) and also thanks Prof. J. Behrends (FU, Berlin, Germany) for the financial and experimental support of the EPR measurements as well as Dr. A. Zaderko (ILM, Lyon, France) for carbon nanodots.

REFERENCES

[1] Yu. V. Ryabchikov, “Facile Laser Synthesis of Multimodal Composite Silicon/Gold Nanoparticles with Variable Chemical Composition”, J. Nanopart. Res., vol. 21(4), pp. 85, April 2019.

[2] M. J. Lo Faroa et al., “Surface-enhanced Raman scattering for biosensing platforms:a review”, Radiat. Eff. Defect S, vol. 177, pp. 1209–1221, October 2022.

[3] K. Sugioka et al., “Femtosecond laser 3D micromachining: a powerful tool for the fabrication of microfluidic, optofluidic, and electrofluidic devices based on glass”, Lab Chip, vol. 14, pp. 3447–3458, June 2014.

[4] A. Kasouni, T. Chatzimitakos, and C. Stalikas, “Bioimaging Applications of Carbon Nanodots: A Review”, C, vol. 5, pp. 19, April 2019.

[5] Yu. V. Ryabchikov, S. A. Alekseev, V. Lysenko, G. Bremond, and J–M. Bluet, “Photoluminescence thermometry with alkyl–terminated silicon nanoparticles dispersed in low–polar liquids”, Phys. Status Solidi–R, vol. 7(6), pp. 414–417, May 2013.

[6] Yu. V. Ryabchikov et al., “Dependence of the Singlet Oxygen Photosensitization Efficiency on Morphology of Porous Silicon”, Phys. Status Solidi A, vol. 204(5), pp. 1271–1275, April 2007.

[7] E. A. Konstantinova et al., “Electron Paramagnetic Resonance and Photoluminescence Study of Si Nanocrystals – Photosensitizers of Singlet Oxygen Molecules”, J. Non–Cryst. Solids, vol. 352(9–20), pp. 1156–1159, June 2006.

[8] A. Yu. Kharin et al., “Bi-modal nonlinear optical contrast from Si nanoparticles for cancer theranostics”, Adv. Opt. Mater., vol. 7(13), pp. 18011728, April 2019.

[9] Yu. V. Ryabchikov, and J. Behrends, “Expedient Paramagnetic Properties of Surfactant-Free Plasmonic Silicon-Based Nanoparticles”, Opt. Quan. Electron., vol. 52, pp. 177, March 2020.

[10] M. Kögler et al., “Bare Laser–Synthesized Au–Based Nanoparticles as Non–Disturbing SERS Probes for Bacteria Identification”, J. Biophotonics, vol. 11(7), pp. e201700225, February 2018.