

PLASMON AND OPTICAL PROPERTIES OF METAL NANOPARTICLES AND THEIR APPLICATION TO HIGH-SENSITIVITY RAMAN SPECTROSCOPY AND BIOPHOTONICS

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PROJECT GOALS

The objects of investigations in this project were the mechanisms and effects of interaction between the electromagnetic field and noble metal nanoparticles and nanostructures. The main efforts were directed to a detailed description of the optical properties of these structures in the near- and far-field zones. The interest was also focused on two applications of these structures: gold-nanoparticles-assisted cancer-cell photothermal therapy and design of structures for surface enhanced Raman spectroscopy (SERS).

RESULTS

The main results of the activities performed under the project can be summarized as follows:

- theoretical models were developed and applied to the description of the main characteristics of the plasmon resonance of noble metals for wide ranges of geometries, system parameters and incident irradiation. The critical parameters that influence significantly the optical properties of noble metal nanoparticles in the 20 – 200 nm range, 2D

and 3D noble metal nanostructures and nanocomposites were defined and analyzed;

- various physical methods for fabrication of nanoparticles and nanostructures based on the interaction of laser radiation with matter were developed and studied. The experimental conditions that determine the fabrication of structures with desirable properties were found for the different methods: production of colloids by laser ablation of a solid target in a liquid; pulsed laser deposition of nanostructures with different morphology: arrays of spherical particles, nanorods, and composite structures; direct laser nanostructuring of metal thin films for fabrication of monolayers of spherical particles on a substrate. The methods developed showed high efficiency in terms of speed, cost and flexibility. It was further shown that in some cases these physical methods are competitive alternatives of the well-developed, but still expensive, electron- and ion-beam lithography and multi-step chemical methods.

Using the methods developed, noble metal nanostructures were fabricated in view of SERS applications. The enhanced Raman signal obtained in some cases was

an order of magnitude higher than the signals established as standard for this technique.

Original results on the effects that arise when gold nanoparticles are in a biological object or animals were obtained *in-vivo*. It was found that the presence of gold nanoparticles with size of 40 and 100 nm in the body of adult mice does not induce clastogenic effects. However, such an effect was observed in mice embryos, where transplacental clastogenic effect was clearly expressed when 100-nm nanoparticles were used. Such an effect was not observed in the case of 40-nm particles. A detailed analysis was also performed on the effect of modification of micro RNA expression due to the presence of gold nanoparticles in mice.

The experiments on gold-nanoparticles-assisted photothermal therapy of cancer cells showed clearly a decrease of the cell viability, especially for HeLa, Graffi, and Hep-2 cells. The optimal conditions for efficient treatment in *in-vivo* and *in-vitro* schemes were defined.

In general, the goals envisaged in the project's working program were achieved accordingly. The main results were published in 30 papers in journals and conference proceedings (16 of them with impact factor). The scientific team presented 32 works at international conferences and meetings.

2012 PUBLICATIONS

1. Dikovska A Og, Nedyalkov N N, Imamova S E, Atanasova G B and Atanasov P A 2012 Au-coated ZnO nanostructures for surface enhanced Raman spectroscopy applications *Quantum Electronics* **42** 258-61
2. Koleva M E, Dikovska A Og, Nedyalkov N N, Atanasov P A and Bliznakova I A 2012 Enhancement of ZnO photoluminescence by laser nanostructuring of a Ag underlayer *Appl. Surf. Sci.* **258** 9181
3. Nedyalkov N N, Nikov Ru, Dikovska A Og, Atanasov P A, Obara G and Obara M 2012 Laser annealing of bimetal thin films: A route to fabrication of composite nanostructures *Appl. Surf. Sci.* **258** 9162
4. Balkanski R, Ganchev G, Ilcheva M, Toshkova R, Nedyalkov N, Atanasov P, Izzooti A and De Flora C 2012 Transplacental clastogenic effect of gold nanoparticles *Oncology* **4** 35-42
5. Yossifova L, Gardeva E, Toshkova R, Nedyalkov N, Alexandrov M and Atanasov P 2013 Treatment of Graffi tumor in hamsters using plasmonically activated gold nanoparticles *Acta Morphologica et Anthropologica* (in press)
6. Dikovska A Og, Tsankov N Ts, Toshkova R, Gardeva E, Yossifova L, Nedyalkov N and Atanasov P 2012 Fabrication of ZnO nanostructures and their application in biomedicine *Proc. SPIE* 8424 84242Q-1

2012 CONFERENCE PARTICIPATION

EMRS 2012 Spring Symp. V, 14-18 May 2012, Strasburg, France:

- Dikovska A Og, Tsankov N Ts, Nedyalkov N N, Atanasov P A, Kocourek T and Jelinek M, Fabrication of ZnO nano-structures by PLD;
- Nikov Ru G, Nedyalkov N N and Atanasov P A, Tuning of the optical properties of metal nanostructures fabricated on flexible substrates;
- Nikolov A S, Nikov Ru G, Nedyalkov N N, Atanasov P A and Alexandrov M T, Modification of the Ag and Au nanoparticles size-distribution by means of laser light illumination of their water suspensions;
- Nikov Ru G, Nikolov A S, Nedyalkov N N, Atanasov P A, Alexandrov M T

and Karashanova D B,
Processing condition influence on the characteristics of gold nanoparticles produced by pulsed laser ablation in liquids;

- Dikovska A Og, Alexandrov M T, Atanasova G, Tsankov N Ts, Nedyalkov N N and Atanasov P A, Silver nanoparticles produced by PLD in vacuum: role of the laser wavelength used;
- Koleva M E, Nedyalkov N N, Dikovska A Og and Atanasov P A, Optical properties in plasmonic multilayer structures;
- Atanasov P A, Nedyalkov N N, Amoruso S, Wang X and Bruzzese R, Nanoparticles size control in ultrashort-pulse laser ablation of gold thin film.

SPIE Photonics Europe 16 - 19 April 2012, Brussels, Belgium:

- Dikovska A Og, Tsankov N Ts, Toshkova R, Gardeva E, Yossifova L, Nedyalkov N and Atanasov P, Fabrication of ZnO nanostructures and their application in biomedicine;
- Nedyalkov N N, Atanasov P A, Toshkova R A, Gardeva E G, Yossifova L S, Alexandrov M T and Karashanova D, Laser heating of gold nanoparticles: Photothermal cancer cell therapy.

17th Int. School on Quantum Electronics
23 – 28 September 2012, Nessebar, Bulgaria:

- Nikov Ru G, Nedyalkov N N, Atanasov P A, Grochowska K, Iwulska A and Sliwinski G, Laser nanostructuring of Au/Ag and Au/Ni films for application in SERS;
- Nikov Ru G, Nedyalkov N N and Atanasov P A, Near field intensity enhancement and localization in noble metal nanoparticle ensembles;
- Nikolov A S, Nedyalkov N N, Nikov Ru G, Atanasov P A, Alexandrov M T and Karashanova D B, Fabrication of gold and silver nanowires by pulsed laser ablation in double distilled water;
- Nikov Ru G, Nikolov A S, Nedyalkov N N, Atanasov P A, Alexandrov M T and Karashanova D B, Investigation of Au nanoparticles produced by pulsed laser ablation of solid targets in water;
- Dikovska A Og, Nedyalkov N N, Avdeev, G V and Atanasov P A, Fabrication of metal nanorod substrates for SERS application;
- Koleva M E, Dikovska A Og, Nedyalkov N N and Atanasov P A, Ag/ZnO multilayer nano-composites prepared by laser methods.