## DISSERTATION

## Synthesis and characterization of gold nanoparticles obtained using plant extracts.

Mgr inż. Magdalena Klekotko Supervisor: Prof. dr hab. inż. Marek Samoć

## ABSTRACT

This dissertation presents the interdisciplinary studies in the field of physics, chemistry and biology, concerning the synthesis of gold nanoparticles using plant extracts and the characterization of the obtained structures.

The first part of the thesis is devoted to the theoretical background, which includes a general introduction to nanotechnology and the classification of nanomaterials, a description of the main properties of gold nanoparticles, a presentation of the fabrication methods and the applications of such structures. Nanotechnology deals with the production of materials in the nanometer scale, their characterization and the possible ways of their usage. Nanostructures are a wide and diverse group of materials, which can be classified according to the various parameters, including dimensions (zero-, one-, two- and three-dimensional structures), composition (organic, inorganic and carbon-based structures) or their origin (natural and artificial structures). Concerning these factors, gold nanoparticles can be classified as inorganic, metallic, plasmonic nanostructures, with the variety of sizes and shapes, produced mostly in an artificial way. The main feature of the gold nanoparticles is the so called localized surface plasmon resonance – the collective oscillations of electrons at the surface of the nanostructure induced by the incident electromagnetic wave with specific parameters. This phenomenon leads to another important property of gold nanoparticles, which is the light-to-heat conversion. The oscillating electrons cause the rise of the temperature at the surface of the nanostructure and then the heat is transferred to the environment. Additionally, gold nanoparticles exhibit one- and multiphoton excited luminescence, which makes them useful markers for bioimaging. Moreover, despite the inert nature of macroscopic gold, nanoparticles made of this metal reveal catalytic activity towards various types of reactions. The growing interest in gold nanostructures, caused by their unique features, resulted in the development of the numerous methods of their fabrication. Some of them were described in detail, including lithographic techniques, chemical synthesis and biological synthesis employing bacteria, fungi and plants. The last section of the theoretical part concerns the biomedical applications of gold nanoparticles, such as bioimaging, diagnostics, drug delivery systems, photothermal and photodynamic therapy. The toxicity of such structures was also discussed within this section.

The experimental part is dedicated to the synthesis of gold nanoparticles using various plant extracts and the optimization of each process to provide maximal reaction yield and decrease polydispersity of the obtained structures. It additionally includes a description of chemical syntheses of some kinds of gold nanoparticles, which were used as reference samples in certain experiments. The obtained gold nanostructures were characterized using UV-Vis spectroscopy, transmission electron microscopy, atomic force microscopy and two-photon microscopy. The first section of the experimental part focuses on the biological synthesis of spherical, triangular and hexagonal gold nanoparticles, with the sizes ranging from 5 nm to 300 nm. The synthesis was performed using three different plant extracts (mint, ginger and aloe). After the optimization of each reaction and the characterization of the obtained structures, gold nanoparticles synthesized using mint extract were selected for further studies. In the next step, the influence of the pH conditions on the synthesis was examined. Then the kinetics of the reaction was determined for the process of the formation of spherical and anisotropic structures. In order to decrease the polydispersity of the obtained mixture of gold nanoparticles the separation using centrifugation in sucrose density gradient was performed. Subsequently, the MTT assay was applied to evaluate the toxicity of gold nanoparticles synthesized using mint extract, in comparison to the gold nanorods synthesized chemically, which revealed lower toxicity of the biologically synthesized gold nanostructures. Finally, in order to identify the molecules responsible for the reduction and the stabilization of the formed gold nanoparticles,

different fractions of the mint extract were separated according to the molecular weight of its components and each fraction was used for the synthesis of nanostructures. According to the obtained results and after performing additional experiments, including NMR measurements and electrophoresis, it was assumed that macromolecules with the molecular weight higher than 3 kDa, such as proteins, are involved in the synthesis of gold nanoparticles using mint extract. In the next section, the photothermal stability of biologically synthesized gold nanoparticles was examined. In this experiment gold nanotriangles synthesized chemically were used as a reference sample. The morphology of both types of the nanoparticles changed during the irradiation, but the final effects were different. Biologically synthesized nanostructures were more susceptible to the structural deformation, however, they exhibited higher colloidal stability than their chemical counterparts. The last section of the experimental part deals with the synthesis of the gold nanoparticles using cistus extract, which leads to the production of anisotropic, popcorn-shaped nanostructures with highly folded surface. The photoluminescent properties of the obtained nanoparticles were examined. Chemically synthesized gold nanostars, exhibiting efficient two-photon excited luminescence, were used as a reference sample. The results showed that the gold nanoparticles synthesized using cistus extract may be applied as markers for bioimaging using multiphoton microscopy.

The presented literature data reveal unique properties of gold nanoparticles and various possible applications of such structures, which provides a stimulus for exploration of the new and improved methods of their fabrication. Experimental results confirm that employment of the plant extracts for the synthesis of gold nanoparticles allows to produce these structures in a simple, low-cost and eco-friendly manner. Moreover, the obtained nanoparticles exhibit low toxicity and may be useful for biological and medical applications.