ABSTRACT OF DISSERTATION

The dissertation discusses the linear and nonlinear optical properties of noble metal nanoclusters (NCs), as probes with unique optical properties. These very small nanostructures (with diameters below 2 nm) have attracted strong interest among researchers in recent years due to their attractive optical properties: strong Vis-NIR photoluminescence, improved photostability, distinctive chirality and others properties, such as catalytic or magnetic. This thesis focuses on optical properties of nanoclusters.

The dissertation is sectioned into two main parts: literature overview and experimental section. The introduction addresses the research motivation and main goals of this study, which are: synthesis of atomically precise gold nanoclusters, characterization of their linear optical properties: luminescent and chiroptical ones and then nonlinear optical properties (absorption, fluorescent and chirality), determined exclusively through fluorescence of nanoclusters. Each subsection present current state of knowledge and recall examples solely from recent reports.

The second part of this thesis consists of three articles, supplemented with short description of research work which I performed in terms of these manuscripts. Here I present a short introduction, which highlights the aim of the study, address current research problems and propose modern solutions. Then, I demonstrate methodology applied to proposed solution and major results, which I obtained through the study. Then, I shortly discuss obtained results. The detailed description of my research work is presented in followed articles and supplementary materials.

Studies presented in Chapter 3 demonstrate strategies to enhance one- and two-photon properties of nanoclusters via luminescent techniques: gold doping of silver nanoclusters, rigidification of an outer layer of nanoclusters and plasmonic enhancement in the vicinity of plasmonic nanoparticles. The aim of this dissertation is to develop functional nanomaterials with unique and strong optical properties that can potentially be used in the imaging and detection of biological materials, with the particular emphasis on applications in multiphoton microscopy. For this purpose atomically precise gold and silver nanoclusters have been proposed, presenting relevant stability and improved optical properties. Thesis provide the detailed description of synthesis methods, including the purification and separation of mixtures of nanoclusters. Due to the unique, fluorescent and chiral optical properties of nanoclusters, main part of the thesis research is devoted to a detailed analysis of one- and two-photon chiral optical response established on the basis of fluorescence techniques.

Chapter 3.1 of the experimental study includes Article 1, which describe the plasmon-enhanced luminescence of single fluorophores, atomically precise gold nanoclusters, Au_{18}, detected in the close proximity of gold nanorods. This study presents how low quantities of nanoclusters can be detected, down to individual particles. In this work I synthesized nanoclusters and performed detailed characterization of nanoclusters and nanorods: size-

purity of nanoclusters and optical properties of both materials. I have verified optimal conditions of detection of single nanoclusters through plasmonic nanoparticles, including choice of medium of detection, separation of gold nanorods, choice of concentration of nanoclusters and selection of particular excitation parameters. I have observed 25-times enhanced near-infrared emission of nanoclusters.

Article 2 presented in the chapter 3.2 discuss how optical properties of nanoclusters are strongly dependent on the structure of atomically precise nanoclusters. Here systematic study on changes of optical properties of nanoclusters were verified on the level of single-atom doping: by doping of one gold atom to the structure of Ag_{25} NCs, obtaining $Ag_{24}Au_1$ NCs, or by doping of several atoms, obtaining $Ag_{25-x}Au_x$ NCs. I have analyzed the continuous changes in absorption and luminescence, quantum yield and luminescence lifetime, and finally the nonlinear optical properties of nanoclusters: two-photon absorption and two-photon brightness. I have observed that incorporation of heteroatom into Ag_{25} nanoclusters stabilizes the structure and results in strongly enhanced quantum yield (10-times), elongated luminescence lifetime (from 1.1 to 1.8 μs) and increased two-photon brightness (from 1.5 to 20 GM) compared to undoped nanoclusters. Further doping of gold atoms deteriorate optical properties due to changed geometry and electron charge localization. Here, the nonlinear optical properties of nanoclusters are established on a wide range of wavelengths, including off-resonance region of excitation.

Article 3 included in the chapter 3.3. consider luminescence as a tool to establish two-photon circular dichroism of nanoclusters. In this work, I have synthesized arginine stabilized AuNCs in two enantiomeric forms and analyzed their chiroptical properties in linear and nonlinear range. I have determined their two-photon properties in a wide range of wavelengths, obtaining high values of two-photon absorption (1743 GM) and two-photon brightness (1102 GM). Due to remarkable fluorescent and chiral properties of these NCs I obtained strong, 245-fold enhanced two-photon circular dichroism with respect to the one-photon dissymmetry factor. Due to over two-magnitude stronger two-photon chiroptical properties, comparable with literature findings of other works on nanoclusters, I raised a question about the general rule of boosting the chiroptical properties under nonlinear excitation.

In conclusion, this thesis presents silver and gold nanoclusters as interesting probes due to their one- and two-photon properties. These properties can be significantly improved by applying a range of techniques, which influence the structure of nanoclusters. The major studies of this work show the utility of analyzed fluorescence as a mean to determine another properties of nanoclusters, such as absorption cross sections and chirality in the one- and two-photon regime. Proposed techniques: two-photon excited luminescence and two-photon fluorescence-detected circular dichroism offer a wide range of possibilities to describe the nonlinear optical properties: two-photon absorption, two-photon brightness, two-photon circular dichroism, simultaneously opening new paths of applications of NCs in the biological materials investigations, e.g. in chiral multiphoton microscopy.