Abstract in English

The thesis entitled "Application of nonlinear optics methods in sensing" was prepared under supervision of Prof. Katarzyna Matczyszyn from Institute of Advanced Materials, Wroclaw University of Science and Technology, Poland, and Prof. Pierre-François Brevet from Institut Lumière Matière, Université Claude Bernard Lyon 1, Villeurbanne/Lyon, France. It was a part of the "BioTechNan - the programme of interdisciplinary cross-institutional post gradual studies KNOW in the field of Biotechnology and Nanotechnology" programme, co-financed by the European Union from the European Social Fund. The original work language of this thesis is English.

The thesis is divided into 7 chapters, the first one including a list of abbreviations used in the work. Further, an abstract in English and Polish language is presented. Chapter 4 includes theory crucial to understand the study. With a brief introduction to the fabrication methods of gold nanoparticles, focusing on the *Turkevich* method, the author follows with characterization methods, used in this study: UV-Visible spectroscopy, Transmission Electron Microscopy, Zeta potential measurements and Dynamic Light Scattering. Chapter 4.3 is dedicated to nanoplasmonics, including Maxwell-Garnett theory, Drude model and Localised Surface Plasmon Resonance description. Afterwards, the most crucial terms of nonlinear optics are introduced. A general problem includes a comparison of linear and nonlinear optical processes, with a theoretical explanation on the origin of each. The specificity of various nonlinear optical processes is mentioned, as well as the corresponding Jablonski diagrams. This leads to the meaning of a symmetry centre for nanoparticles, described in Chapter 4.4.1, followed by the method of Hyper Rayleigh Scattering (HRS) section number 4.4.2 with a description of the Hyper-Rayleigh Scattering phenomenon itself and a depiction of a typical HRS measurement setup. A subsection 4.4.2.1 includes polarization-resolved measurements. The definition, origin and meaning of retardation parameters ζ^{V} and ζ^{H}, as well as depolarization ratio D^{V} are discussed. A short review on HRS of metallic nanoparticles is included in 4.4.3. The reader is guided through HRS studies of silver and gold nanoparticles of various sizes and centrosymmetrical shapes. The last subchapter of the theoretical introduction, namely 4.5, focuses on the applications with gold nanoparticles: starting with the older publications and moving to the recent use published in the scientific literature. This subchapter includes a subsection 4.5.1, dedicated to sensing, explaining crucial attributes of a good sensor.

Chapter 5, called *Results and discussion* is divided in four parts. 5.1 is dedicated to a PhD candidate statement about the substantive contribution to the presented publications, meanwhile sections

5.2-5.4 include the synopsis of each publication and the publication itself.

Section 5.2 considers gold nanotriangles as an example of non centrosymmetrically-shaped nanoparticles. Centrosymmetric nanoparticles, such as nanospheres, nanorods or nanocubes are well described in the literature. The behaviour of the latters is driven by volume-dependent phenomena although experimentally the consequences of the imperfect geometrical shapes are observed as well. In our current work, nanotriangles of mean edge length ranging from 26 to 87 nm were synthesised and characterised. Noteworthy, the samples contained significant amount of nanospheres, i.e. from 26 to 58%, thus it is a novel approach to study a mixture of various shapes. The first hyperpolarizability is significantly lower compared to centrosymmetric nanoparticles, however the influence of stabilizing agent is unsure: in fact, the values for triangles and spheres from this synthesis are close. Furthermore, it is revealed that the HRS signal exhibits a surface-dependent behaviour also for big nanoparticles, which is contradictory to centrosymmetrical nanoparticles, for which the electric dipole approximation is not sufficient above 50 nm diameter. Indeed, it is further confirmed by polarization-resolved studies that the retardation parameters, whose growth is associated with size increase in the case of centrosymmetrical nanoparticles, remain low. The depolarization ratio demonstrates a value of around 0.45, far from 0.2 expected for a point-like one-fold structure, in line with a dominant three-fold symmetry.

The HRS response of gold nanotriangles is rather driven by their non centrosymmetrical shape, than the size growth. They are an excellent fit for applications where a low retardation level is desired.

Section 5.3 describes the influence of surrounding medium on the HRS response of gold nanospheres. The surrounding medium refractive index was modified by introduction of different amounts of glycerol into 40 and 100 nm nanospheres' suspensions. The HRS signal exhibits an abrupt drop for low glycerol additions, followed by an increase. This cannot be explained in terms of Localized Surface Plasmon Resonance (LSPR) peak shift, thus it is addressed to surface-specific processes. The change is more significant for smaller nanoparticles, however shift of the irradiation wavelength from 820 to 790 nm does not impact the outcome essentially. All polarization-resolved parameters, i.e. the depolarization ratio and retardation parameters present a non monotonous behaviour with the increase of the refractive index. A the lowest glycerol contents, which is desired for sensing purposes, a drop in intensity is observed. Thus, the relative HRS signal change per Refractive Index Unit (RIU) is considered as a Figure of Merit of choice and equals about 4000. It is observed from UV-Vis spectra that the colorimetry is not suitable for detection of such low changes.