Two-Photon Absorption of Bimetallic Plasmonic Nanorods - Systematic Studies

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Nanoparticles are miniature objects with sizes up to 100 nm and, due to their unique chemical and physical properties, they have been of interest to researchers for many years now. Among the most investigated types of nanostructures are plasmonic nanoparticles, i.e., those in which free electrons oscillate with respect to the fixed atomic cores. Plasmonic nanoparticles can be made of different types of metals, e.g., gold or silver. They can also have different shapes, such as spherical, rod-like, or triangular. Moreover, they can be modified in many different ways, including coating with other metals such as palladium or platinum. Finally, plasmonic nanoparticles can interact in a unique manner with light, which gives rise to useful phenomena and plethora of applications in chemistry, biology, physics, and medicine.

Irradiation of the material with ultrashort high-intensity laser pulses gives rise to the nonlinear optical (NLO) phenomena because the polarization of the material is no longer linearly dependent on the incident electric field amplitude. One possible NLO process that can find its applications in biomedical-related research is two-photon absorption (2PA). 2PA can be described as an act of instantaneous absorption of two photons resulting in a transition between two real states. The fact that each of those two photons has only half of the energy required for the transition has significant consequences, such as the possibility to cause the absorption of chemical species in a more suitable spectral range, namely at higher wavelengths. Considering that gold nanoparticles exhibit shape- and size-dependent optical properties that can be tailored during their chemical synthesis, one can induce the occurrence of the 2PA even in the near-infrared (NIR) range, which is highly beneficial for all biomedical applications. NIR irradiation, particularly in the so-called biological window, is not harmful to biological tissues and allows deeper penetration of the material. Moreover, two-photon excitation translates into other useful phenomena such as light emission, heat generation, or induction and enhancement of other valuable processes. All of those aspects enable the utilisation of gold nanoparticles as agents in theranostics, bioimaging, nanosurgery, photothermal and photodynamic therapies.

Surprisingly, although gold nanoparticles interact strongly with laser light, the literature lacks a consistent and systematic description of the influence of the morphology and size of gold nanoparticles on their 2PA properties represented by 2PA cross-sections. Furthermore, the data regarding NLO properties of gold nanostructures seem incomplete, scattered, and not systemised. There is also very limited knowledge about 2PA in bimetallic nanostructures consisting of gold core and another co-metal. Yet, such structures are of particular interest due to their extended properties that are also useful in medicine.

Hence, this scientific project aims at providing a comprehensive and qualitative picture of the 2PA properties of bimetallic AuPd and AuPt plasmonic nanoparticles of a rod-like shape, exhibiting different compositions, morphologies, and overall geometrical parameters. The rod-like shape of nanostructures was selected due to two modes of light-nanoparticle interactions, reliability and good reproducibility of the synthesis protocols. Within the frame of this project, we will assess how the size of the plasmonic Au core, Pd or Pt content in the coating, and finally, the modification of the initial rod-like shape influence the 2PA properties of the nanostructures. This aim will be accomplished in few steps. Firstly, gold nanorods of different sizes will be systematically synthesised. Then, they will be further subjected to the modification with second metal (Pd or Pt), followed by microscopic imaging and spectroscopic characterisation of the as-synthesised nanostructures in the linear regime. The central part of the research will focus on the measurements of the 2PA cross-sections utilising a unique Z-scan setup available in our laboratory. The final part will be devoted to the statistical modelling of the data in order to find the relations between the NLO properties of the nanostructures and their inherent parameters. As a result, complete 2PA spectra of the investigated samples measured in a broad spectral range will be acquired. The resulting data will constitute a detailed database presented on our website *biophotonics.pwr.edu.pl* to facilitate the preliminary selection of plasmonic nanostructures with precisely defined 2PA behaviour for bio- and nanomedical applications.

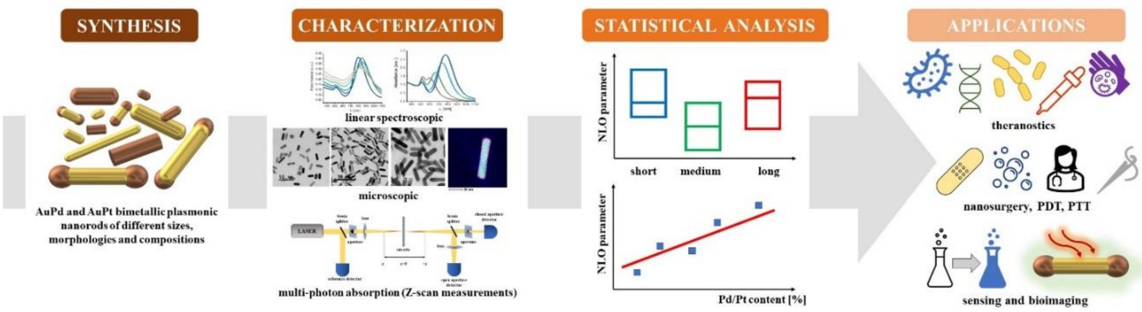

Fig. *Schematic representation of the workflow of the proposed scientific project.*