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Chiral nanostructures – synthesis and investigation of their nonlinear optical properties

Streszczenie w języku angielskim

This PhD Thesis presents research on the linear and nonlinear optical properties of chiral nanomaterials with the main focus on gold nanoclusters. These very small nanostructures (with diameters of around 1-2 nm) have attracted growing attention among scientists in recent years due to their photoluminescence, chirality (depending on the nanocluster, originating from the core or induced by ligands), catalytic properties and low toxicity. For this Thesis, the optical properties of nanoclusters have been the most important.

The dissertation is divided into two main parts: theoretical and experimental. The first part begins with the presentation of research motivation and main goals of work, which are: 1) synthesis of chiral gold nanoclusters, 2) characterization of their linear optical properties, 3) examination of the structures stability in different conditions, and 4) description of the nonlinear optical properties of chiral gold nanoclusters. In the further part of the first Chapter, the recent state of art on the material is described, including methods of nanocluster synthesis, their linear optical properties (absorption, photoluminescence and chirality) as well as their structure. The chapter concludes with the analysis of nonlinear optical properties of nanoclusters (gold and silver ones), especially their multiphoton absorption.

The second Chapter presents the experimental results obtained during the doctoral studies, divided into five parts. The first of them describes synthesis methods of the materials fabricated during the doctoral thesis, including purification and separation of nanoclusters mixtures. The second part introduces an innovative method of size transformation of $Au_{25}(SR)_{18}$ nanoclusters (where SR - thiol ligand) into $Au_{23}(SR)_{16}$ ones, caused by low pH = 2 obtained with hydrochloric acid. The method development was possible because of the nanocluster stability studies carried out in a wide range of pH = 2 – 10. The mechanism of size transformation based on the kinetic studies of changes, product identification, theoretical calculations and comparison of chloride and nitrate ions is proposed. In Chapter 2.3, the main focus is put on the influence of doping gold nanoclusters with silver atoms and aggregation

of nanoclusters. Systematic studies are presented, showing the relationship between the amount of silver used in synthesis and linear optical properties, especially photoluminescence. During the research, spontaneous formation of spherical aggregates was also observed. Their optical properties are compared with aggregates stabilized with polyelectrolytes (both cationic and anionic). In the presence of poly(allylamine hydrochloride), the photoluminescence increased by an order of magnitude. All types of aggregates (spontaneously formed and stabilized with polymers) were additionally exposed to low (pH = 2) and high (pH = 10) pH.

Chapter 2.4 of the experimental part, directly related to the nonlinear optical properties of the gold nanoclusters, is the key to the whole dissertation. Here, two important areas are addressed: 1) determination of the nonlinear optical parameters in a wide range of wavelengths using the standard Z-scan technique and 2) determination of these parameters depending on the polarization of the excitation beam. In these studies, glutathione and captopril-protected nanoclusters were used, but $Au_{25}(Capt)_{18}$ gave the most interesting results. The determination of nonlinear optical parameters with linearly polarized light was carried out in the range of 550 – 1100 nm, in open and closed aperture modes, which enabled us to calculate the multiphoton absorption cross sections and the nonlinear refractive index, respectively. A two-photon absorption band presenting a maximum at 900 nm was observed, as well as a great increase in the two-photon absorption cross-section values in the range of 550 – 650 nm, up to 24,000 GM for 550 nm. In the range of 650 – 750 nm, the absorption saturation was also observed. The nonlinear refractive index in the whole range was negative. At the 875 nm wavelength, polarization-dependent measurements were additionally carried out and the values of two-photon circular dichroism and two-photon linear-circular dichroism were determined.

The work ends with a short chapter showing the two-photon excited photoluminescence of nanoclusters and the examples of applications these nanoparticles in fluorescence one- and two-photon imaging of biological materials, including neuronal cells, HeLa cells and DNA.

In conclusion, gold nanoclusters are an interesting material due to their one- and multiphoton optical properties. These properties can be modulated with size, ligand or aggregation of nanoclusters. In many cases, changes are possible thanks to simple changes of the nanoparticle environment (pH, solvent, addition of polymer). On the example of nanoclusters, the utility of the modified Z-scan method (with circularly polarized light) is also presented. The techniques offers a wide range of possibilities to describe the nonlinear optical properties of materials, and applications in the biological materials investigations (for example in chiral multiphoton microscopy).