PRACA DOKTORSKA

"Optical properties of chiral heterostructures with gold nanoparticles"

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Abstract in English

Despite the enormous progress of science and medicine over the last century, there is still a lack of efficient tools for detecting and imaging biomolecules important to human health. Since many of them are chiral, this issue could be resolved by exploring their selective interaction with sensor materials like gold nanoparticles. These selective interactions can often be observed as changes in the chiral optical properties of nanoparticle-biomolecule assemblies. Thus, studying these properties can lead to the invention of new methods for the selective detection of chiral molecules, such as proteins or their aggregates, and the creation of new advanced materials exhibiting unique chiral optical properties.

The aim of this doctoral thesis is to explore how assembling plasmonic gold nanoparticles or gold nanoclusters with various chiral molecules influences their optical properties and discover new chiroptical properties emerging upon the assembly. The thesisstarts with the literature review introducing the topic of chiral heterostructures with plasmonic gold nanoparticles and gold nanoclusters, which shows that there are still many open questions concerning the heterostructure assembly and their chiroptical properties. Some of these questions are addressed within the framework of this thesis using various spectroscopy and microscopy methods. The first part of the presented research focuses on the chiroptical properties of chiral biomolecule-coated gold nanoclusters. I explored the circular dichroism and circularly polarized luminescence spectra of ATT (6-aza-2-thiothymine) stabilized chiral gold nanocluster and its two enantiomers, functionalized with L- and D-arginine. Although the enantiomers were characterized by mirror-like circular dichroism (CD) spectra, their circularly polarized luminescence (CPL) was of one handedness. Further studies have shown that one of the possible explanations is the kernel-structure relaxation since arginine-free ATT nanoclusters exhibited CPL of the same sign and order of magnitude. Moreover, I analyzed their two-photon excited CPL using the home-built system I developed during my doctoral research. The obtained signal was two orders of magnitude stronger than one-photon excited CPL, which was explained by the different radiative relaxation pathways of one-photon and two-photon luminescence of studied nanoclusters. The results presented in this topic not only proved the broken symmetry between chiral light absorption (CD) and chiral photoluminescence (CPL) of ATT-stabilized gold nanoclusters but also showed that their nonlinear chiroptical effects can be stronger than their linear counterparts.

The second issue addressed in this work concerned the still poorly understood template-assisted assembly of gold nanoclusters. I checked if the helical assembly method using a liquid-crystal template creating helical nanofilaments would be applicable to atomically precise achiral gold nanoclusters $Au_{25}(PET)_{18}$. As confirmed by the resulting microscopy image, surface functionalization of $Au_{25}(PET)_{18}$ with two ligands, dodecanethiol and liquid-crystalline ligand derived from the template, allowed efficient mixing with the template material and lead to the helical assembly of nanoclusters. Moreover, the helical assembly influenced the optical properties of gold nanoclusters: red-shifted the luminescence of studied nanoclusters, but also

generated new chiroptical properties. Using the CPL microscope I constructed, I discovered that helically-assembled gold nanoclusters generate strong circularly polarized luminescence of the handedness depending on the helical twist of the nanofilaments hosting them. This confirmed that achiral gold nanoclusters could obtain chiral optical properties upon binding to helical nanofilaments.

The last part of this dissertation focused on finding the origin and application of chiral optical properties emerging upon assembling the plasmonic gold nanoparticles with chiral biomolecules. For this purpose, I studied the optical properties of chiral heterostructures assembled using the achiral anisotropic gold nanoparticles, like nanobipyramids and nanorods, and chiral bovine insulin protein aggregates. Not only did I discover that such assembly is possible by controlling the parameters such as solution pH or NaCl concentration but also that a new chiroptical property – induced circular dichroism, emerges upon the assembly. The observed signal did not result from the helical arrangement of gold nanoparticles but, as confirmed by the heterostructures morphology and optical properties, coulombic interactions between the gold nanoparticles and chiral protein molecules. Thus, I explored if the induced optical chirality could be used for selective biosensing of insulin protein aggregates. By studying the optical properties of chiral heterostructures with insulin protein aggregates characterized by different structures I observed that the location and strength of induced circular dichroism is connected with the aggregate internal structure and the exposure of the chiral tyrosine residues. Finally, I studied the chiral heterostructures made from gold nanorods and insulin amyloid fibrils. The experiments showed that it is possible to induce circular dichroism under such conditions. Although, as confirmed by polarization-resolved single-molecule microscopy, at the single-particle level, single gold nanorods bound to insulin fibrils did not show any induced chirality.

The results presented in this doctoral thesis proved that the optical properties of chiral heterostructures with gold nanoparticles can be used to understand the interactions of chiral organic molecules with their inorganic environment and to selectively detect some of them, which in the future can be used to develop new methods for selective detecting and imaging of chiral molecules like proteins or DNA.