

Streszczenie w języku angielskim: Magda Antoniak „Synthesis and optical properties of luminescent nanomaterials with extended functionalities”

This doctoral thesis presents the results of research on the synthesis, modification, and characterisation of physicochemical properties of multifunctional luminescent nanomaterials mainly based on lanthanide doped nanoparticles (NPs) and semiconductor quantum dots (QDs). In the course of conducted research, five novel luminescent nanostructures with enhanced functionalities were obtained by the use of strategies including synthesis of hybrid NPs composed of two distinct nanocrystals, co-encapsulation of NPs within core-shell polymeric nanocapsules (NCs), covering nanocrystals by biocompatible molecules such as long peptide chains, and intentional doping of NPs with simultaneous investigation of their optical properties under high temperature and pressure. The morphology, structure and phase composition of designed materials were comprehensively determined using various techniques such as transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), as well as X-ray diffraction (XRD).

Firstly, colloidal hybrid nanostructures (HNSs) were synthesized consisting of rareearth ions co-doped NaYF_4 NPs as a core decorated by CdSe QDs of different sizes, ranging from 6.6 to 7.0 nm. Comprehensive linear and nonlinear optical (NLO) properties have been measured and discussed considering both types of fluorescent nanocomponents and their possible interaction as well as influence on each other. The possibility of dualwavelength excitation of the samples was examined using a 980 nm CW laser diode and/or a NIR 800 nm femtosecond laser. The combination of three distinct excitation sources triggers their intensive one- and two-photon excited emission (TPEE) of semiconductor QDs as well as visible upconversion (UC) and NIR f-f emissions of lanthanide doped nanocrystals. Possible application of HNSs as a complex anti-forgery luminescent ink has been demonstrated.

Followingly, using nanoemulsification/solvent-evaporation methods, colloidal coreshell NCs loaded with $\text{NaYF}_4:\text{Yb},\text{Er}$ upconverting NPs and semiconductor CdSe QDs were synthesized. Simultaneous co-encapsulation of two different kinds of fluorophores/nanocomponents into multimodal NCs allows of combining their mechanistically distinct linear and NLO properties. Cytotoxicity studies has revealed the potential of using the $\text{NaYF}_4:\text{Yb},\text{Er}/\text{CdSe}$ co-loaded NCs for fluorescence imaging in biological samples.

Then, CdSe QDs and Fe_3O_4 NPs were co-encapsulated in order to obtain multimodal nanoplatform with dual optical and magnetic properties. Upon ultraviolet excitation or nearinfrared fs laser $\text{CdSe}/\text{Fe}_3\text{O}_4$ co-loaded NCs exhibit intense one- or two-photon induced visible emission. Applying an alternating magnetic field (AMF) and/or 808 nm laser excitation leads to heat generation by NCs. Entrapping more than one type of nanocomponents within the core of polymeric NCs has turned out to be beneficial owing to the spatial confinement resulting in no dissolution of optically active components.

Next, the as-synthesized trioctylphosphine oxide-capped CdSe QDs were covered by Pumilio homology domain based proteins enabling the transfer of hydrophobic QDs into an aqueous solution. Linear optical features of CdSe QDs before and after functionalization were compared, indicating their excellent absorption and emission properties in water environment. Moreover, their NLO properties were examined with the TPEE method by means of a tunable femtosecond laser system. The results indicate that hydrophilic colloidal QDs covered by only single peptide coats can provide new HNSs possessing well-defined optical properties and might be potentially useful for NLO bioimaging applications.

Finally, due to the rapid synthesis at room temperature, $\text{NaBiF}_4:\text{Yb},\text{Er}$ upconverting NPs based on novel non-rare earth inorganic matrix were obtained using ‘green chemistry’ method. Their intense anti-Stokes UC luminescence allows of temperature sensing with the maximum relative sensing sensitivity equal to 1.07%/K at 303 K, which is comparable value with those estimated for other similar optical nanothermometers based on lanthanide ions. Visible upconverted emission of these NPs has been investigated upon high pressure in a diamond anvil cell (DAC). Furthermore, the pressure dependence of Stokes emission at ~ 1550 nm has been studied for the first time in the case of NPs doped with Yb^{3+} and Er^{3+} and has been proposed as an alternative to ruby crystal commonly used as a non-contact pressure sensor. These results confirm that using NPs composed of non-rare earth

matrix doped with Yb^{3+} and Er^{3+} ions it is possible to design sensitive and reliable non-contact temperature and pressure nanosensor.