Nanoparticles and nanotechnology are rapidly growing fields of studies. Conventional fluorescent materials (e.g. organic dyes, fluorescent proteins, quantum dots) utilize short wavelength excitation and Stokes emission detection at longer wavelengths. This approach has a number of shortcomings, which limit their applications in biology. Lanthanide-doped upconverting nanoparticles (UCNPs) are emerging as a new promising optical material with promising feature of overcoming the drawbacks associated with conventional fluorescent materials. Upconversion (UC) is process in which the energy of emitted photons is larger than the energy of photons being absorbed. UC efficiency is still much weaker than Stokes emission occurring in organic dyes or quantum dots. This originates from low absorption cross section in lanthanide ions. UCNPs have to potential to become great solution for many fields of science and technology, thus it is highly desirable to solve this fundamental issue.

New methods to enhance the UC efficiency are the first major scientific goal of this project. It will be achieved by increasing the absorption cross-section in upconverting lanthanide doped nanoparticles. Increase of absorption will be accomplished by utilization of “antenna” effect. Primary sensitizers – organic dye molecules or quantum dots (QDs) attached to the surface of UCNPs, will absorb the near-infrared (NIR) radiation and efficiently transfer this energy to the secondary Yb^{3+} or Nd^{3+} sensitizers in order to achieve more efficient upconversion emission. The nanoparticles will be synthesized by thermal decomposition method. Two types of colloidal $NaYF_4$ core/shell nanoparticles doped with lanthanide ions are planned to be produced: (I) excited by NIR light and emitting in the NIR range and (II) excited by NIR light and emitting in the visible range, via an anti-Stokes luminescence mechanism. For assessing the influence of core/shell composition and particle architecture on UC luminescence, various core/shell UCNPs will be prepared. The spatial distribution of active co-dopants ions will be varied within the core or the shell.

While some initial work has been done and significant (~1000 times) enhancements of UC intensity has been demonstrated, this phenomenon is far from being well understood. Despite lanthanides being perfectly photostable (i.e. optically active electrons do not participate in forming chemical bonds) the organic primary sensitizers undergo fast photobleaching, which leads to rapid degradation of such systems, thus limiting the long-term experiments. The problem of dye/QDs-conjugated UCNPs degradation, requires finding adequate solution. Therefore, the second scientific goal of the project is development of methods to protect the primary sensitizer from degradation. This will be achieved by embedding the primary sensitizer inside polymeric or silica shell around UCNPs. Additionally, the surface of nanoparticles will be coated with proteins and conjugated with folic acid. Such biofunctionalized nanoparticles will be used for cell bioimaging. Obtained dye/QDs-sensitized UCNPs will be compared to nanoparticles without primary sensitizer.

Structure and morphology of nanoparticles will be studied. X-ray powder diffraction measurements will identify the crystal structure of nanoparticles. Transmission electron microscopy will be used to study the morphology and size of the nanoparticles and to evaluate thickness and uniformity of the shell. The emission spectra, power dependence of luminescence intensity on excitation power and measurement decay time will be performed. Photostability will be evaluated by studying UC luminescence intensity under exposing the constructs to controlled and continuous irradiation. This will be compared to photobleaching rate of dye alone. Luminescence enhancement will be also evaluated, based on integrating sphere measurements under standardized conditions (the same NPs concentration, the photoexcitation intensity and wavelength).

As a result of the project, we expect to advance the upconverting nanomaterials by enhancing their UC intensity as well as improve their photostability. These fundamental studies of energy transfer and UC enhancement by antenna, will contribute to deeper understanding of previously mentioned mechanisms, and allow for better understanding of luminescence properties of studied nanomaterials. Obtaining a relatively high emission intensity of active ions may provide solutions or technological advances for potential applications as anti-Stokes bioimaging tools, as well as improving solar cell performance.

The results will be published in international journals and will be presented on international conference in or outside the country.