



Editorial

ENERGY TRANSFER PROBING AS THE METHOD FOR TESTING RARE-EARTH IONS DOPED "GREEN" NANOPARTICLES AS FLUORESCENT AGENT FOR BIOIMAGING

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In spite of tremendous number of papers concerning rare-earth (RE) doped fluorescent nanoparticles (NP) and methods of their synthesis (see, for example, paper in Nature Photonics [1]) the problem of fluorescent quenching caused by –OH molecular vibrations is still not raised properly. The reason might be that most of the papers are devoted to the up-conversion fluorescent nanoparticles with the energy of emitted photons in the visible or even in UV spectral ranges. In this case the contribution of the quenching caused by the –OH groups to the overall relaxation rate is not so significant due to very high energy of optical transitions. However, in the near IR spectral range the input of the –OH groups to fluorescence quenching is significant, but until recently there were only few papers, which are raising this issue [2, 3]. This obstacle is a fundamental one, as most of the "green" methods of synthesis of water dispersible nanoparticles are carried out either in water or in other –OH containing media. Such synthetic procedures inevitably result in high concentration of –OH groups, e.g. in mesopores filled by mother solution [4] or on the surface of the NPs. Formation of pores inside a nanoparticle occurs on the stage of aggregation of primary nuclei of crystalline phase. Unlike the –OH positioned on the NPs surface, which can be removed by annealing at temperatures between 100 and 200°C, the –OH groups in the mesopores can be removed only by high temperature treatment accompanied by agglomeration of the NPs with expected loss of dispersability. Besides, the Forster radius of Nd - OH quenching in the Nd³⁺ doped phosphate laser glasses, for example, is of the order of $R_0 = 0.75$ nm [5]. This may lead to direct quenching of the Nd³⁺ donors arranged in the volume of nanoparticles with the sizes higher than 10 – 20 nm within the thin surface layer only and cannot influence significantly on the quenching of donor fluorescence when Nd³⁺ concentration is low (energy migration between donors is negligible). Thus, the main source of near IR fluorescence quenching in the rare-earth doped NPs are –OH acceptors positioned in their volume. Usually the concentration of nanoparticles in colloidal solution during in vivo experiments should be as low as possible to avoid or at least minimize intoxication. All of the above limits the use of the rare-earth doped nanoparticles for fluorescent diagnostics and laser treatment in medicine and requires the development of methods to improve and secure control of their luminescent properties.

During the last five years we have developed the energy transfer probing of the –OH acceptors positions in the RE doped NPs [6 - 10] analyzing their kinetics of fluorescence quenching. This method was originally used by us to define the dimension of acceptors in porous opal-like matrices [11]. Knowing the acceptor positions and their concentration it is possible to find the ways to develop the synthesis methods to reduce the quantity of the –OH groups in the RE doped NPs. We found that in oxide and phosphate nanocrystals the –OH acceptors can be a part of crystal lattice [10, 8]. Further studies demonstrated that fluoride crystal matrices are more promising for the synthesis of nanoparticles doped with Nd³⁺, suitable as fluorescent agent for imaging in the first biological window (750 – 950 nm), because of less quantity of crystal lattice defects causing fluorescence quenching [6]. Also, we found that first observed the fluctuation asymptotics at the late stage of fluorescence hopping quenching kinetics in the RE doped NPs [12] can be a measure of the high concentration of –OH acceptors in comparison with the concentration of the main fluorescent donors [6 - 10]. The –OH concentration can be calculated directly from the fluctuation kinetics analysis [6]. This method is much more sensitive than the traditional methods.

To conclude, the quenching of the fluorescence of active dopant (Nd³⁺) by randomly distributed

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quenchers (–OH) positioned in the volume of the NPs is a major dissipative channel that directly impacts the quality of the nanoparticles as fluorescent agent in the near IR spectral range. First, a basic understanding of the quenching mechanism has direct practical value for optimization of their efficiency. Second, the fluorescence kinetic studies provide information on the structure of a system and the types of physical interactions that are realized in the process of energy migration and dissipation of optical excitation. In view of the foregoing, the reliable and very sensitive method for the quality control of the fluorescent nanoparticles based on the analysis of the kinetics of impurity quenching, “an energy transfer probing”, is very perspective.

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