Neodymium-doped ZnO nanoparticles for NIR II biomarkers

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Motivation

Recently, design and preparation of the nanoparticles (NPs) suitable for labeling of the living cells has become an important task of modern nanotechnology. Among the requirements to this type of nanomaterials is their biocompatibility and luminescence in the NIR region because biological tissues have a maximum light transmission in the 850-1100 nm range. These requirements are fulfilled by trivalent lanthanides (RE^{3+})-doped transition metal oxide materials which can exhibit high photostability, high luminescence quantum yield, narrow bandwidth, long-lived emission and large Stokes shifts. Among the transition metal oxides, ZnO is known to be a wide-gap semiconductor and environmentally friendly material, which can be used as a suitable matrix. To date, a preparation of doped ZnO nanoparticles has received much attention, but most of works are aimed on fabrication of NPs exhibiting luminescence in the visible spectral region.

It can be expected that ZnO nanocrystals doped with lanthanide ions will become photoluminescent materials in the near infrared region of 860-1600 nm (NIR). In particular, ZnO nanocrystals doped with neodymium ions, which have several important luminescent bands in the NIR region, including the transition $^4F_{3/2} \rightarrow {}^4I_{9/2}$ (at ~ 900 nm), $^4F_{3/2} \rightarrow {}^4I_{11/2}$ (1060 nm) and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ (1350nm) are of interest for applications as luminescent biomarkers. Nevertheless, the preparation of nanosized lanthanide-doped particles is still challenging. Namely, because of the large mismatch between ionic radii, creation of luminescence Re^{3+} centers in host transition metals oxides nanoparticles by chemical means remains a problem. Therefore, development of new and cost-efficient technologies to produce high-quality nanosized lanthanide-doped particles with improved luminescence properties is highly anticipated.

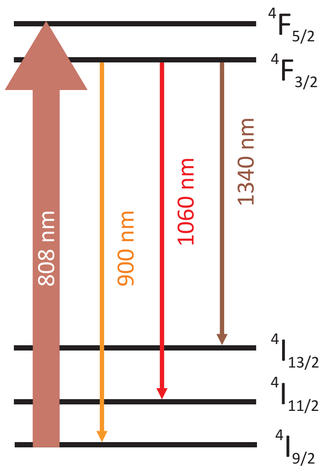

Fig. 1. Simplified energy levels scheme of Nd^{3+} ion

This work is focused on the laser-assisted method for Nd-doped ZnO NPs preparation and testing their luminescent properties. The preparation method is based on laser ablation of zinc target in neodymium nitrate solution using ns-pulsed Nd:YAG laser. Among the different synthesis methods pulsed laser ablation in liquids (PLAL) has demonstrated to be an efficient and versatile technique to produce high-quality nanoparticles (NPs). PLAL technique offer a number of advantages such as simplicity, capability of producing quickly a wide range of nanomaterials without using any surfactants or stabilizers, possibility of control over their morphology and inner structure, as well as synthesis of composite nanostructures by combination of ablation and laser-induced modification processes. In addition, laser ablation, in which NPs are formed under conditions of high temperature and pressure, may be promising for the formation of doped NPs providing an increase of the inclusion of dopant atoms under non-equilibrium conditions.

Materials and methods

The experimental setup used for NP generation is schematically shown in Fig. 1a. To prepare NPs, a nanosecond pulsed Nd^{3+}: YAG laser (LOTIS TII, LS 2134D, Belarus) operating in a double-pulse mode at fundamental wavelength (1064 nm, energy 80 mJ/pulse, repetition rate 10 Hz, and pulse duration 10 ns) was used. Pure metallic zinc plate immersed in 0.01 M neodymium nitrate solution was used as target for ablation. The laser radiation power density on the target surface was 10^8 -10^9 W/cm^2, with the ablated spot size being 200μm. To find the optimal conditions, both aqueous and ethanol solutions of neodymium nitrate of the same concentration were used as a liquid.

Laser ablation is accompanied by the formation of plasma plume (Fig. 2b) which expands and collapses resulting in the nanoparticles formation that can occur both by the condensation of target species as well as in result of the interaction with the components of the liquid.

Laser-assisted modification of generated NPs was performed immediately after their preparation via LAL (Fig.2c). For this, approximately 5 mL of the formed colloid was poured into another cuvette and irradiated with an unfocused beam of the second harmonic (wavelength of 532 nm) of the same laser for 30 min. The laser irradiation fluence was 0.3 J/cm^2. No plasma formation was observed during this stage of colloid treatment.

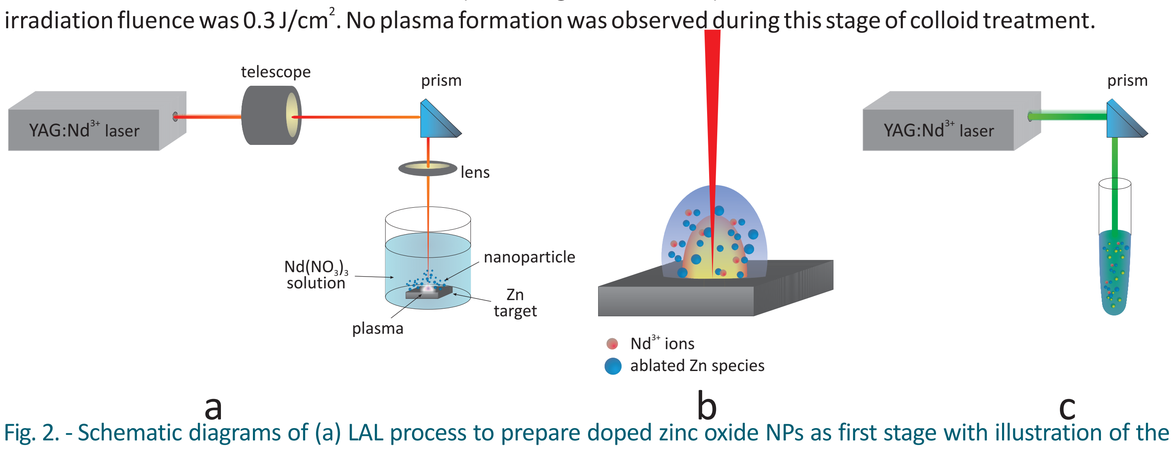

Fig. 2. - Schematic diagrams of (a) LAL process to prepare doped zinc oxide NPs as first stage with illustration of the plasma formation (b) and (c) laser-assisted modification of as-prepared NPs as second stage.

NPs morphology

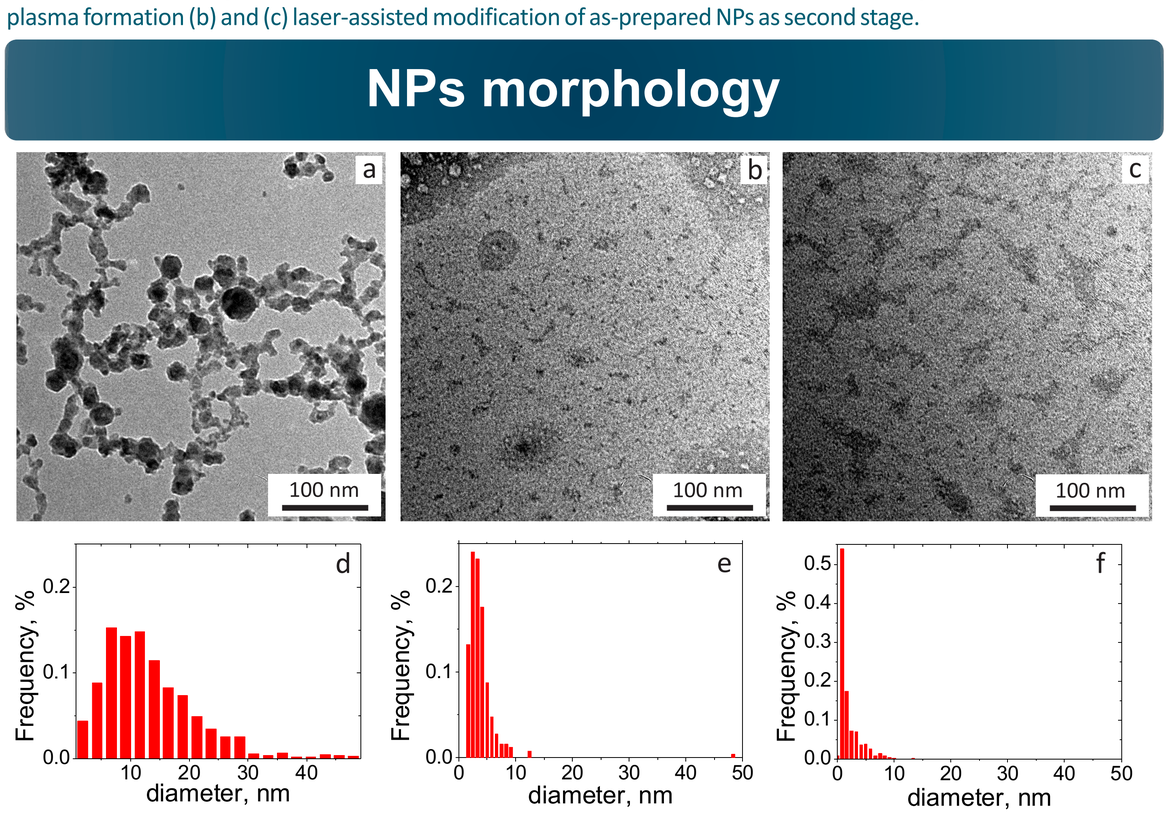

Fig. 3. - (a) - TEM images of the ZnO nanoparticles prepared by laser ablation in water, and ZnO:Nd nanoparticles prepared by laser ablation in $Nd(NO_3)_3$ solution as prepared (b) and after laser-induced modification (c). Figures (d), (e) and (f) show size distributions of the ZnO nanoparticles prepared in water, and $Nd(NO_3)_3$ solution before and after laser irradiation, respectively.

Optical properties

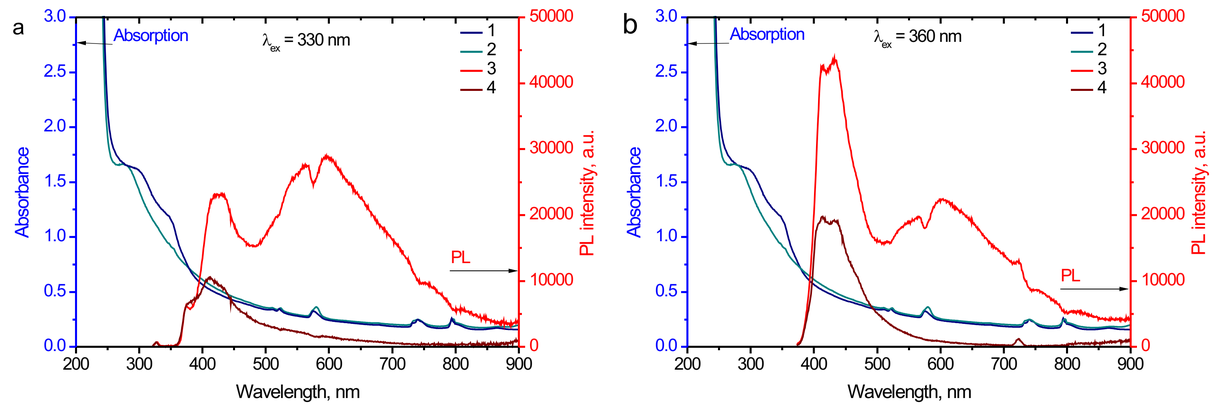

Fig. 4. - PL emission spectra of the colloids prepared by laser ablation of Zn in $Nd(NO_3)_3$ solution in water (3) and ethanol (4), registered in visible range under excitation at 330 nm (a) and 360 nm (b); (1) and (2) - UV-Vis absorption spectra of the corresponding colloids in water and ethanol, respectively.

Colloidal solutions obtained in both solvents are characterized by an intense absorption band in the region of 200-450 nm, which is associated with exciton absorption in ZnO nanostructures. The intensity of the exciton band is much higher in water than in ethanol, which indicates a more efficient ablation of zinc in water compared to ethanol.

In addition, the absorption spectra also show peaks at 521 nm, 578 nm, and 794 nm, which are characteristic absorption bands of the Nd^{3+} ion.

The PL emission spectra depend on the composition of the liquid in which the laser ablation is carried out. A colloid prepared in water exhibits luminescence in the entire visible region, which consists of two bands with maxima at about 420 and 600 nm, which is typical of defect-containing zinc oxide nanostructures. Defect formation is typical for particles produced by laser ablation in liquids. However, in the case of particles obtained in ethanol, no defective luminescence band is observed.

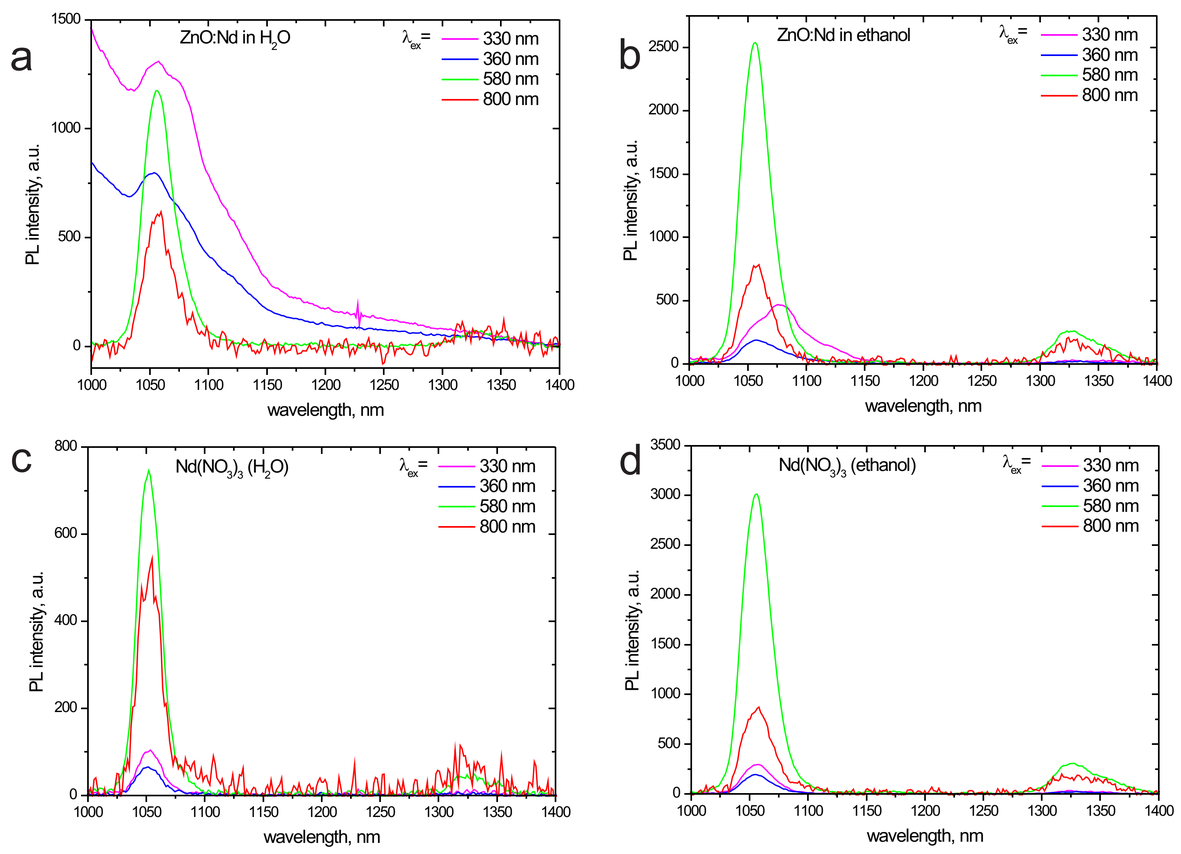

Fig. 5. - PL emission spectra of the colloids prepared by laser ablation of Zn in $Nd(NO_3)_3$ solution in water (a) and ethanol (b) registered in the near-infrared range. PL spectra of the 0.01 M $Nd(NO_3)_3$ solutions in water (c) and ethanol (d) registered in the same conditions are shown for comparison.

The excitation at wavelengths in the UV range leads to the appearance of broad asymmetric luminescence bands with a maximum in the range 1056-1079 nm associated with the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition of Nd^{3+} ions. In the spectra of ZnO:Nd colloids both in water and in alcohol this band is wide and asymmetric, which indicates the presence of several Nd^{3+} emission centers in the solution. On the contrary, in the spectra of the initial solutions of neodymium nitrate in water and ethanol, the luminescence band is symmetric and rather narrow, with a maximum at 1054 nm for both solutions. The luminescence spectra recorded at 360 nm excitation show similar patterns as at 330 nm excitation. Thus, the wide non-uniform luminescence band of colloidal solutions in comparison with the initial solutions of neodymium nitrate indicates the doping of zinc oxide with neodymium. In addition, UV excitation of the Nd^{3+} luminescence, which does not have absorption bands in this region, may indicate the transfer of excitation from the ZnO matrix to the Nd^{3+}, which additionally confirms the incorporation of Nd^{3+} into the ZnO lattice.

Conclusions

Laser ablation technique can be applied for preparation of ZnO NPs doped with Nd^{3+} ions that is confirmed by the results NPs characterization and observation of the characteristic NIR luminescence of Nd^{3+} ions in the prepared ZnO nanocrystals.

Upon excitation at 578 and 808 nm, three luminescence bands have been observed with centers at 887, 1060, and 1334 nm, attributable to the radiative transitions from the ground $^4F_{3/2}$ level of Nd^{3+} to the $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ levels, respectively. The position and shape of these peaks in the recorded luminescence spectrum differ from the peaks of Nd_2O_3 nanocrystals spectrum, which confirms the inclusion of Nd^{3+} ions in ZnO nanocrystals instead of the formation of an impurity oxide phase.The observation of the characteristic NIR luminescence of Nd^{3+} ions upon excitation both from the ground state (808 nm) and upon UV excitation indicates the formation of zinc oxide doped with neodymium, which is associated with the transfer of excitation from the zinc oxide matrix to the neodymium ion.

It has been shown that a liquid medium can serve as a tool for controlling the characteristics of ZnO:Nd^{3+} NPs obtained by laser ablation in a liquid. A higher NPs concentration and NIR PL efficiency can be achieved upon synthesis in an aqueous solution as compared to ethanol.

The research results confirm that prepared samples of zinc oxide nanocrystals doped with neodymium ions can be used as NIR-II nanoparticles for visualization of biological tissues, having suitable emission bands in biological windows.

Acknowledgements

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