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Controlled synthesis of luminescent $Gd_2O_3:Eu^{3+}$ nanoparticles by alkali ions doping

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Synthesis of Gd_2O_3:1%Eu^{3+} nanoparticles

All chemicals for synthesis of Gd_2O_3:1%Eu^{3+} nanoparticles were purchased from Sigma Aldrich or Avantor Performance Materials S.A. (Poland), and used without further purification. We have modified the synthesis protocol reported by Paik et al. (Paik et al., Acs Nano, 2013, 7, 2850-2859). For synthesis of reference sample without addition of mono-positive alkali ions gadolinium acetate (3 mM) and europium acetate (3 mM) were dissolved and degassed in a mixture of 12 mL of oleic acid, 18 mL of oleylamine, and 30 mL of 1-octadecene at ~100 °C. The yellowish, transparent solution was then heated to ~300 °C under N_2 flow. Identical amounts of the reaction solution were picked up with a syringe after 45 min, 1.5 h and 3.5 h, cooled to room temperature, precipitated with a mixture of methanol and acetone (2:1 v/v), and washed several times with methanol. Finally, the nanoparticles were dissolved in 4 mL of $CHCl_3$. In order to investigate the influence of Li^+, Na^+ and K^+ ions on the morphology, crystal structure and spectroscopic properties of Gd_2O_3:1%Eu^{3+} nanoparticles we have introduced the following changes to the reaction procedure. In a typical synthesis, different amounts (6 mM, 3 mM or 1.5 mM) of either lithium hydroxide, sodium hydroxide or potassium hydroxide were dissolved and degassed in a mixture of 12 mL of oleic acid, 18 mL of oleylamine, and 30 mL of 1-octadecene at ~100 °C. Next, gadolinium acetate (3 mM) and europium acetate (3 mM) were added into the solution, followed by the evaporation at ~100 °C. The yellowish, transparent solution was then heated to ~300 °C under N_2 flow. Identical amounts of the reaction solution were picked up with a syringe after 45 min, 1.5 h and 3.5 h, cooled to room temperature, precipitated with a mixture of methanol and acetone (2:1 v/v), and washed several times with methanol. Finally, the NPs were dissolved in 4 mL of $CHCl_3$.

Fig.S1. XRD patterns of Gd_2O_3:1%Eu^{3+} NPs obtained after 1.5h of synthesis, with addition of different amounts of KOH to the reaction mixture (black lines) compared with standard (JCPDS 12-797) pattern of cubic Gd_2O_3. The crystal phase impurities are marked with the *.

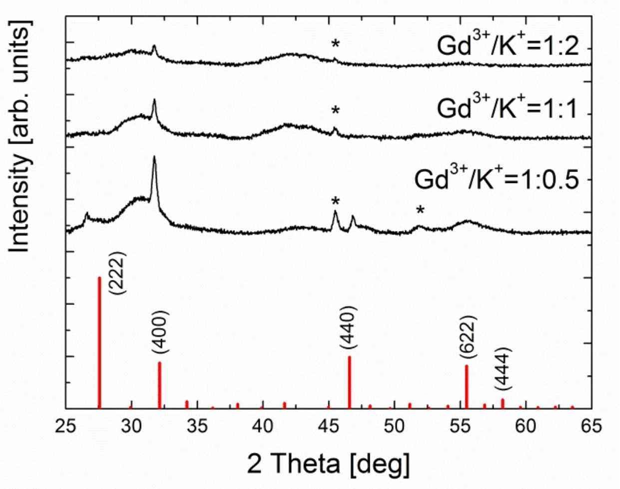

Fig.S2. Emission spectra of Gd_2O_3:1%Eu^{3+} NPs obtained without addition of any alkali ions after 45 min (a), 1.5h (b) and 3.5h (c) of synthesis. The spectra were obtained upon 266 nm excitation.

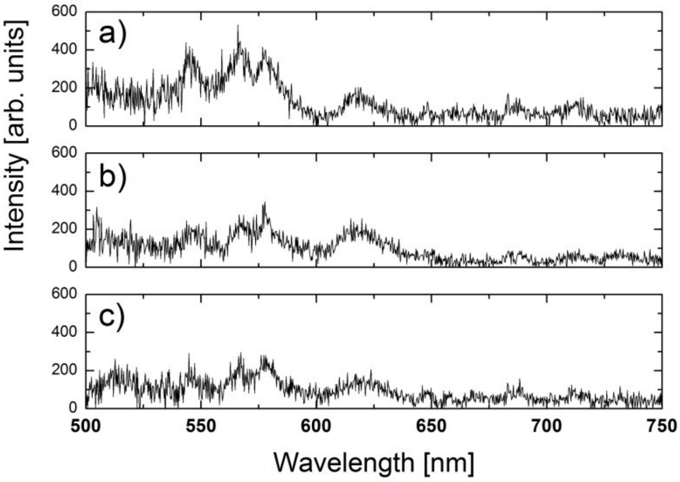

Fig.S3. Excitation spectra, recorded at λ_{em}=613 nm, of Gd_2O_3:1%Eu^{3+} NPs obtained with different relative amounts of Gd^{3+}/Na^{+} (a-c), Gd^{3+}/Li^{+} (d-f) and Gd^{3+}/K^{+} (g-i) after 1.5h of synthesis.

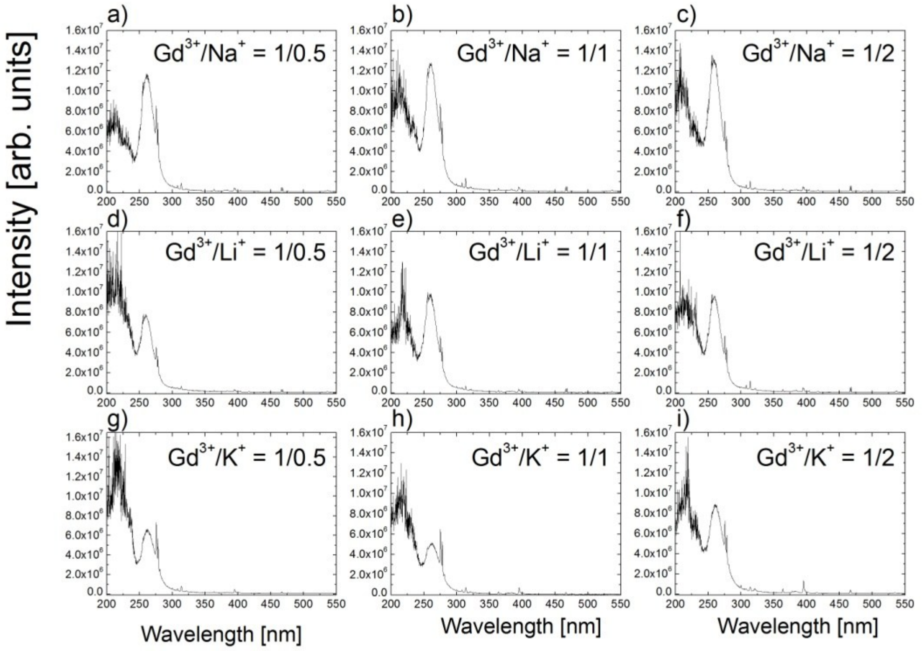

Fig.S4. Representative excitation spectra, recorded at λ_{em}=613 nm, of Gd_2O_3:1%Eu^{3+} NPs obtained with relative amount of Gd^{3+}/Na^{+} equal to 1/1 after 45 min of synthesis.