Supplementary Material (ESI) for Nanoscale

Electronic Supplementary Information

Intracellular imaging of HeLa cells by non-functionalized $NaYF_4:Er^{3+}$, Yb^{3+} upconverting nanoparticles

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1. Description of the Upconversion Process

The luminescent trivalent lanthanide (Ln^{3+}) ions, in particular erbium (Er^{3+}) and thulium (Tm^{3+}), have the ability to convert low energy excitation light (typically NIR) into higher energies, such as visible or UV, via a multiphoton process known as upconversion [1]. In contrast to typical two-photon absorption (TPA) materials, which are excited via virtual states, the Ln^{3+} ions have "real" electronic excited states (see Figure S1) thus cumbersome and expensive ultrafast lasers are not required and the process can be observed with small hand-held NIR laser diodes. Upconversion may occur via three known mechanisms namely excited state absorption (ESA), energy transfer upconversion (ETU) and photon avalanche (PA) [2]. The energy transfer upconversion mechanism is usually the most prominent in Ln^{3+}-doped nanoparticles where either Er^{3+} or Tm^{3+} is co-doped with the ytterbium ion (Yb^{3+}). The Yb^{3+} ion is added as a sensitizer since its only excited state is resonant with the NIR pump wavelength and has the highest absorption coefficient (at 980 nm) among the other Ln^{3+} ions. Therefore, it acts as an efficient sensitizer to transfer the absorbed energy to neighboring Er^{3+} or Tm^{3+} ions in close proximity.

Figure S1 shows the typical upconversion processes in Er^{3+}/Yb^{3+} co-doped nanoparticles, which occurs via successive energy transfers from excited Yb^{3+} ions to neighboring Er^{3+} ions. The first step in the upconversion process is the absorption of an NIR photon from a Yb^{3+} ion exciting it from the $^2F_{7/2}$ ground state to the $^2F_{5/2}$ excited state. This is followed by an energy transfer from the excited Yb^{3+} ion to a neighboring Er^{3+} in close proximity exciting it from the $^4I_{15/2}$ ground state to the intermediate $^4I_{11/2}$ state (denoted as 1 in Figure S1). A second energy transfer from another Yb^{3+} ion then promotes the Er^{3+} ion to the higher $^4F_{7/2}$ excited state (denoted as 2). The $^4F_{7/2}$ excited state then non-radiatively decays to the lower lying green $^2H_{11/2}$, $^4S_{3/2}$ and red $^4F_{9/2}$ excited states resulting in the observed green and red emissions. Alternatively, the $^4F_{9/2}$ excited state can be directly populated from the $^4I_{13/2}$ excited state. Following the promotion of the Er^{3+} ion to the $^4I_{11/2}$ intermediate state, the ion can decay non-radiatively to the $^4I_{13/2}$ excited state and following energy transfer from an excited Yb^{3+} will directly populate the $^4F_{9/2}$ excited state (denoted as 3).

1. R. Scheps, *Prog. Quantum Electron.*, 1996, **20**, 271-358.
2. F. Auzel, *Chem. Rev.*, 2004, **104**, 139-173.

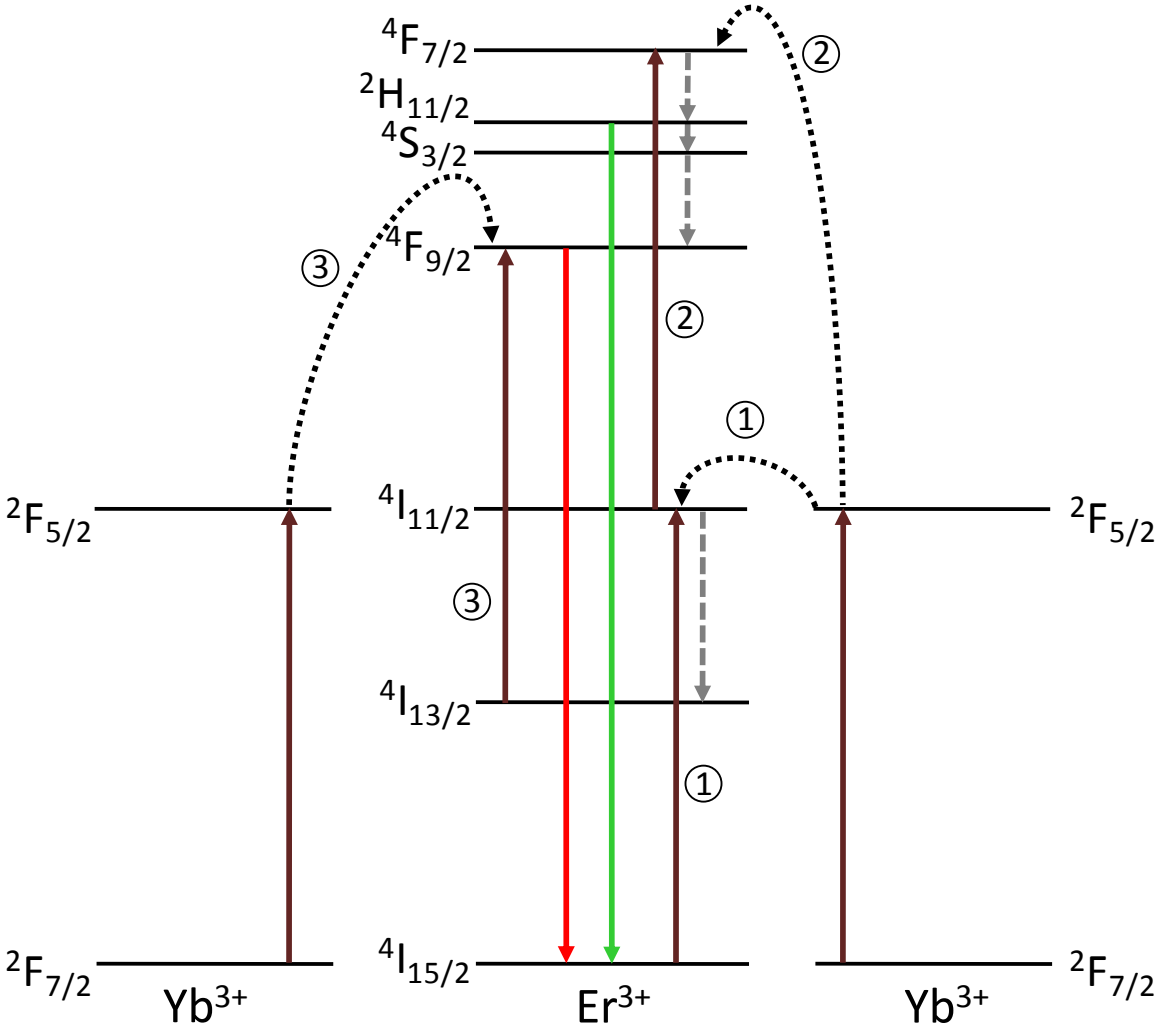

Figure S1: Schematic representation of the possible energy transfer processes involved in the upconversion of Er^{3+}/Yb^{3+} co-doped nanoparticles.

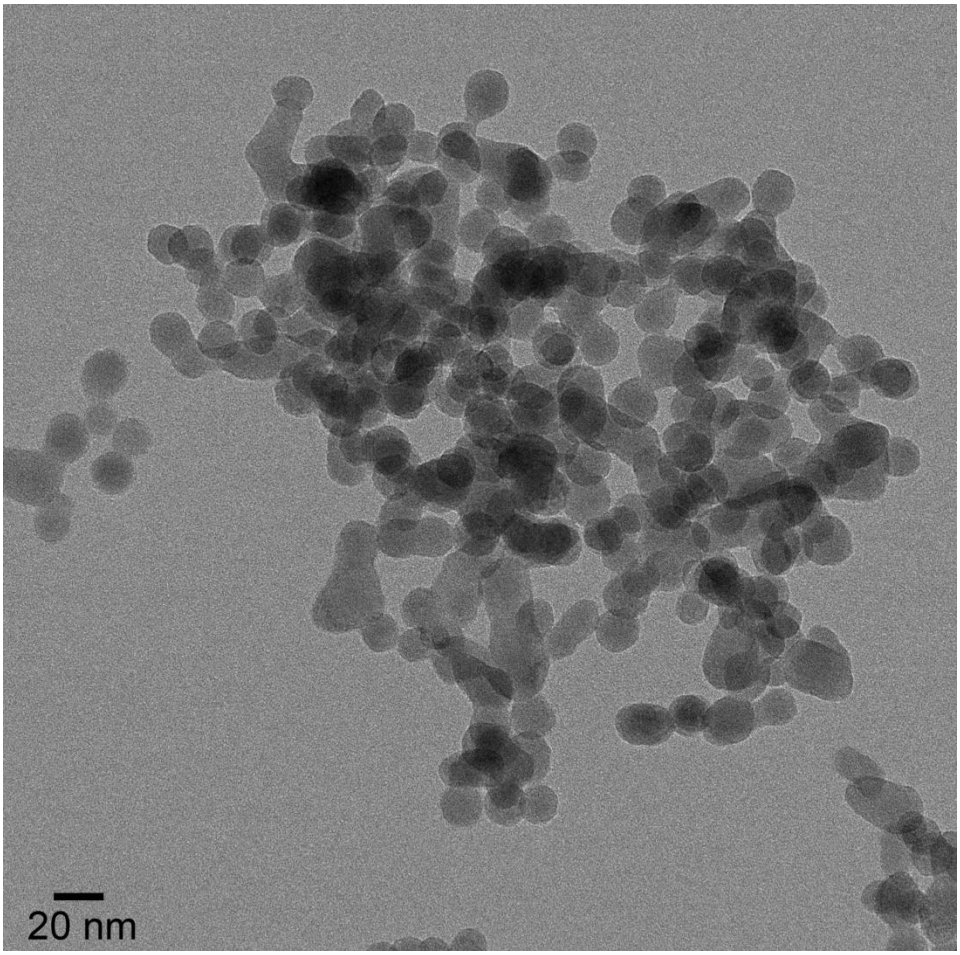

Figure S2: TEM image of the polyethyleneimine (PEI)-capped $NaYF_4:Er^{3+}$, Yb^{3+} nanoparticles.