Supporting Information

Ultrasmall monodisperse $NaYF_4:Yb^{3+}/Tm^{3+}$ nanocrystals with enhanced near-infrared to near-infrared upconversion photoluminescence

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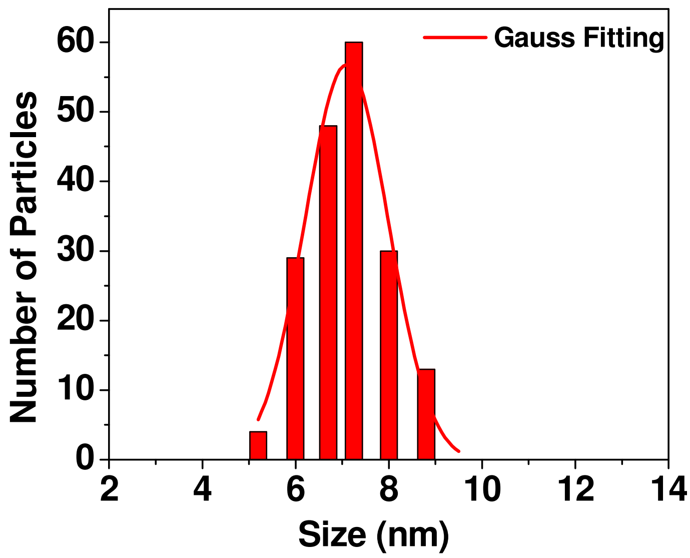

Figure S1. Histogram of the particle sizes obtained from TEM images of more than 200 $NaYF_4$:2% Tm^{3+}, 20% Yb^{3+} nanocrystals. The average size of synthesized nanocrystals was calculated to be about 7.1 nm with a standard deviation of about 0.9 nm.

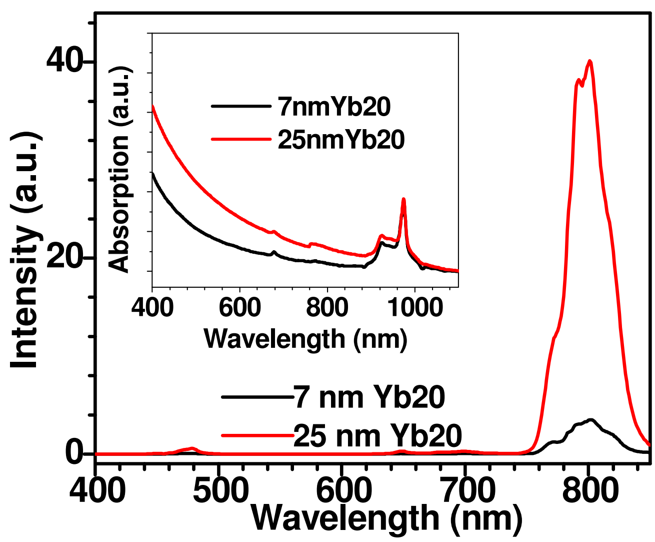

Figure S2. UC photoluminescence spectra of the synthesized ~7 nm nanocrystals of $NaYF_4$: 2%Tm^{3+}, 20% Yb^{3+} as well as 25-30 nm nanocrystals of $NaYF_4$:2% Tm^{3+}, 20% Yb^{3+} under diode laser excitation at 975 nm. The absorption of the two nanocrystal suspensions was matched at 975 nm for the $^{2}F_{7/2} \rightarrow ^{2}F_{5/2}$ transition of Yb^{3+} ions, as displayed in the inset.

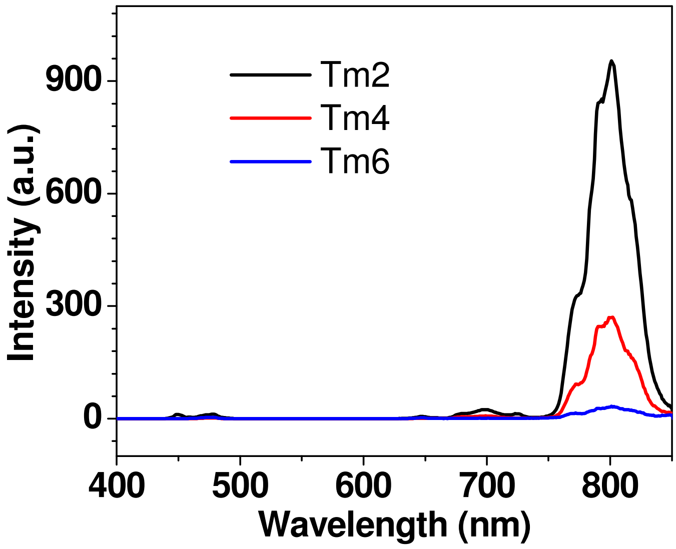

Figure S3. UC photoluminescence of ultrasmall nanocrystals $NaYF_4$ doped with 100% Yb^{3+} and co-doped with 2%, 4%, and 6% of Tm^{3+} ions under excitation with 975 nm diode laser. The intensity of the UC PL decreases with the increase in concentration of Tm^{3+} ions, suggesting that the optimal concentration of Tm^{3+} ions is around 2%.

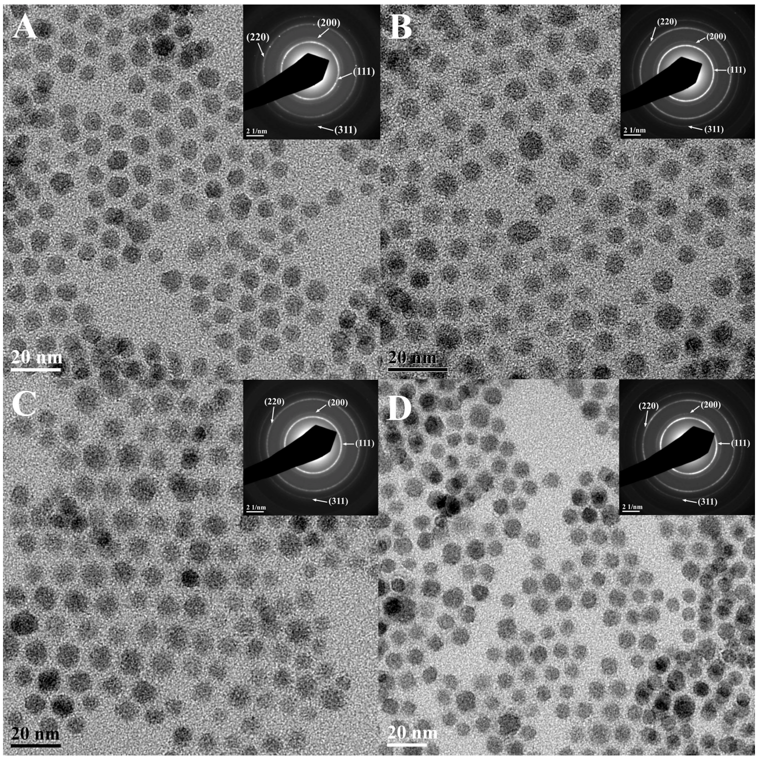

Figure S4. TEM micrographs of nanocrystals $NaYF_4$ doped with 2% Tm^{3+}, and co-doped with 20% (A), 40% (B), 60% (C), and 100% (D) Yb^{3+} ions. The insets show the selected area electron diffraction (SAED) patterns of the corresponding $NaYF_4$: Yb^{3+}/Tm^{3+} nanocrystals, indicating the same cubic crystal structure.

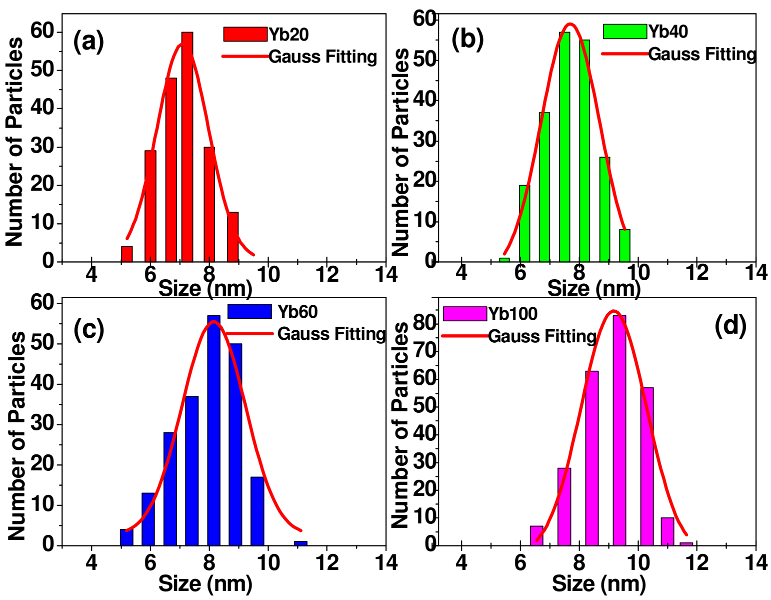

Figure S5. Histograms of the particle sizes for $NaYF_4$ nanopowders codoped with 2%

Tm^{3+} and with (a) 20% Yb^{3+}, (b) 40% Yb^{3+}, (c) 60% Yb^{3+}, and (d) 100% Yb^{3+} ions. These data were obtained from the TEM images of more than 200 $NaYF_4$:Yb^{3+}/Tm^{3+} nanocrystals and show slight increase in size of the $NaYF_4$:Yb^{3+}/Tm^{3+} nanoparticles with the increment of Yb^{3+} ions doping. The average sizes for nanoparticles with relative content of Yb^{3+} ions of 20%, 40%, 60%, and 100% were calculated to be about 7.1 (with a standard deviation of 0.9), 7.6 (with a standard deviation of 1.0), 8.4 (with a standard deviation of 1.1), 9.2 (with a standard deviation of 1.1), respectively.

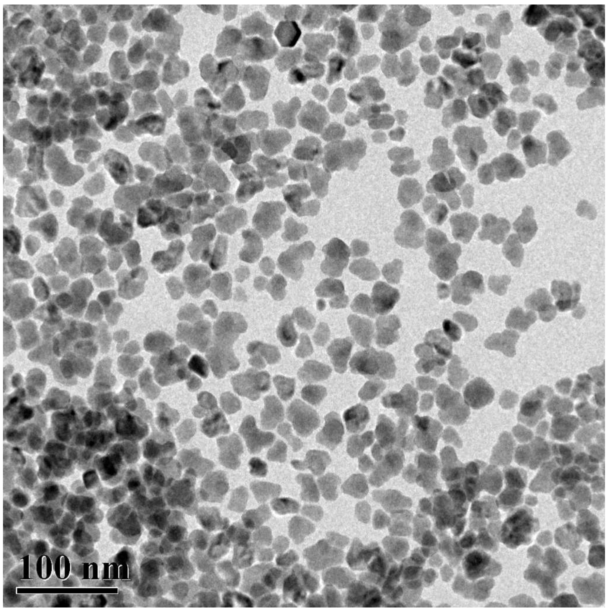

Figure S6. TEM image of 25~30 nm nanocrystals of $NaYF_4$ doped with 2% Tm^{3+}, and with 20% Yb^{3+} ions. Nanocrystals were synthesized following the protocol described in Ref. 11.

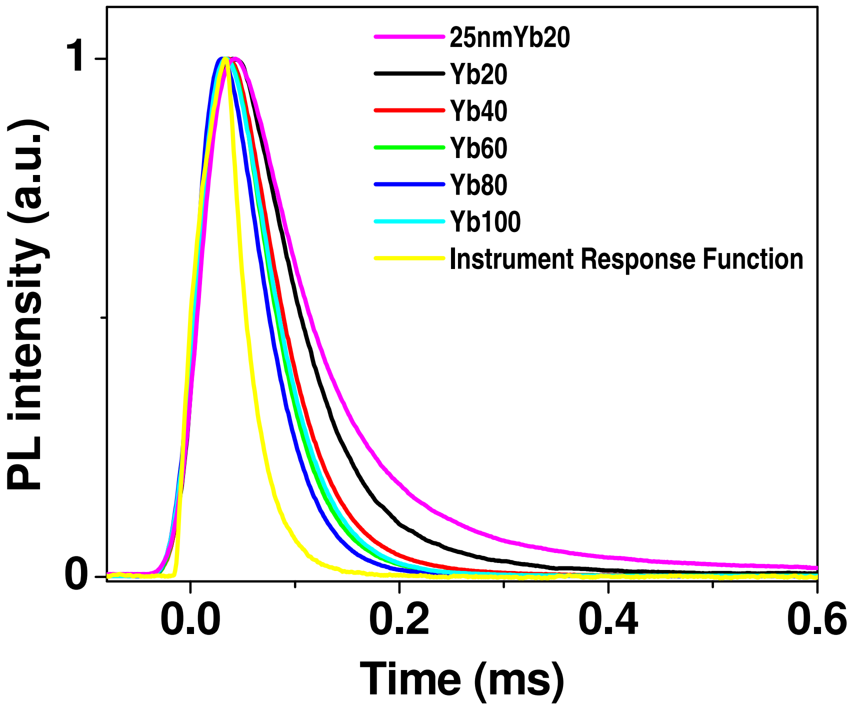

Figure S7. Decays of PL at 802 nm for 25-30 nm size nanocrystals of $NaYF_4$:2% Tm^{3+}, 20% Yb^{3+} and 7-10 nm size nanocrystals of $NaYF_4$:2% Tm^{3+}, 20-100 % Yb^{3+}.

The PL decay profiles were recorded at the Infinium oscilloscope (Hewlett-Packard) coupled to the photomultiplied tube (PMT) of the Fluorolog-3.11 Jobin Yvon spectrofluorimeter, using excitation at 975 nm from laser diode (Q-Photonics) operating in pulsed mode. The 7 nm nanocrystals of $NaYF_4$:2% Tm^{3+}, 20% Yb^{3+} have an average PL lifetime of ~60.1 μs, which is significantly shorter than the 79.3 μs of 25-30 nm nanocrystals of $NaYF_4$:2%Tm^{3+}, 20%Yb^{3+}. This is because nanocrystals with smaller size not only have higher surface/volume ratio and larger portion of doped rear-earth ions on the surface, but also have higher passivation on the surface. This surface passivation can increase rate of the nonradiative decay, correspondingly shortening the photoluminescence lifetime. The PL lifetime gradually becomes shorter (decreasing from 60.1 μs to 35.0 μs) for 7 nm $NaYF_4$ nanocrystals with the increase in relative content of Yb^{3+} ions from 20% to 80%. This might be due to that the replacement of Y^{3+} with Yb^{3+} ions caused the increased lattice defects because of slight mismatch between Y^{3+} and Yb^{3+} ions. An abrupt increase in PL lifetime time is observed when increasing the content of Yb^{3+} ions from 80% to 100%, since the mismatch between Y^{3+} and Yb^{3+} ions and corresponding lattice defects do not exist anymore in these nanocrystals.