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# Dual Mode Emission of Core-Shell Rare Earth Nanoparticles for Fluorescent Encoding

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## Supporting Information

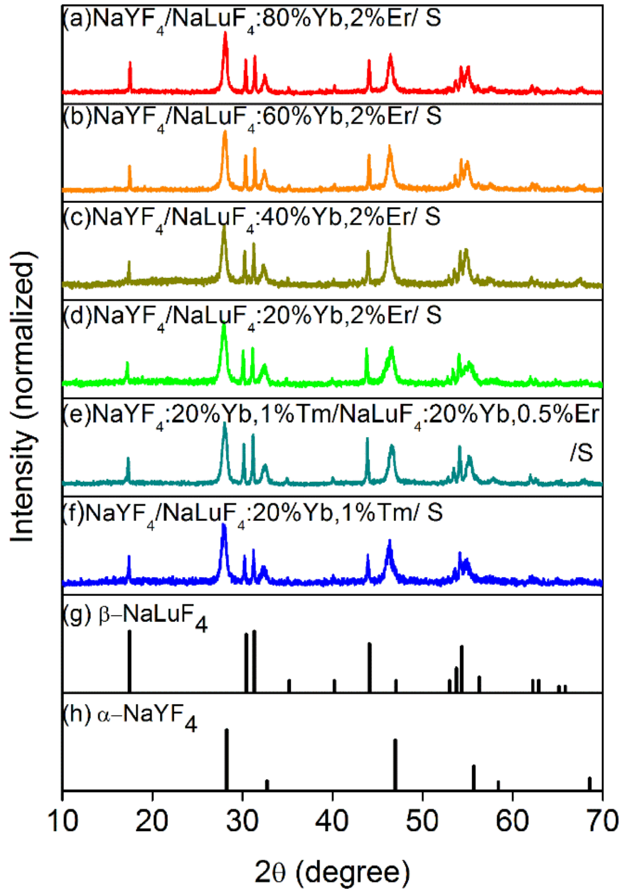


Fig. S1. XRD patterns of various dual mode emission core-shell hybrid NPs, "S" in the figure means $SiO_2$:Eu(DBM)$_3$phen shell. (a) $NaYF_4$:$NaLuF_4$:80%Yb,2%Er/$SiO_2$:Eu(DBM)$_3$phen NPs, (b) $NaYF_4$:$NaLuF_4$:60%Yb,2%Er/$SiO_2$:Eu(DBM)$_3$phen NPs, (c) $NaYF_4$:$NaLuF_4$:40%Yb,2%Er/$SiO_2$:Eu(DBM)$_3$phen NPs, (d) $NaYF_4$:$NaLuF_4$:20%Yb,2%Er/$SiO_2$:Eu(DBM)$_3$phen NPs, (e) $NaYF_4$:20%Yb,1%Tm/$NaLuF_4$:20%Yb,0.5%Er/$SiO_2$:Eu(DBM)$_3$phen NPs, (f) $NaYF_4$:$NaLuF_4$:20%Yb, 1%Tm/$SiO_2$:Eu(DBM)$_3$phen NPs, (g) standard β-$NaLuF_4$ (JCPDS 27-726) and (d) standard α-$NaYF_4$ (JCPDS 77-2042).

Various dual mode emission core-shell hybrid NPs were synthesized by a facile mothed. In these NPs, $Yb^{3+}$, $Er^{3+}$(and/or $Tm^{3+}$) codoped heterogeneous $NaYF_4$/$NaLuF_4$ nanocrystals served as cores and amorphous $SiO_2$ embedded with Eu(DBM)$_3$phen were coated as shells. The UC crystals varied by tuning the $Ln^{3+}$ doping. Firstly, we synthesized water soluble $Ln^{3+}$ doped $NaYF_4$/$NaLuF_4$ nanocrystals by a heterogeneous-core-mediated method. We used cubic $NaYF_4$ nanocrystals as cores to induce the growth of hexagonal phase $NaLuF_4$ crystal shells. Secondly, through improved Stöber method, silica shells embedded with Eu(DBM)$_3$phen complex were coated on the $NaYF_4$/$NaLuF_4$ nanocrystals, forming the core-shell hybrid NPs. The structures of these core-shell hybrid NPs were characterized by XRD. Fig. S1 shows all the XRD patterns of corresponding NPs. The curve (a)-(f) is the XRD pattern of $NaYF_4$:$NaLuF_4$:80%Yb,2%Er/$SiO_2$:Eu(DBM)$_3$phen, $NaYF_4$:$NaLuF_4$:60%Yb,2%Er/$SiO_2$:Eu(DBM)$_3$phen, $NaYF_4$:$NaLuF_4$:40%Yb,2%Er/$SiO_2$:Eu(DBM)$_3$phen, $NaYF_4$:$NaLuF_4$:20%Yb,2%Er/$SiO_2$:Eu(DBM)$_3$phen, $NaYF_4$:20%Yb,1%Tm/$NaLuF_4$:20%Yb,0.5%Er/$SiO_2$:Eu(DBM)$_3$phen, and $NaYF_4$:$NaLuF_4$:20%Yb, 1%Tm/$SiO_2$:Eu(DBM)$_3$phen NPs, respectively. The diffraction peaks of both the cubic phase $NaYF_4$ and the hexagonal $NaLuF_4$ crystals in all core-shell hybrid NPs XRD patterns were well in accord with the standard data (Fig. S1h: α-$NaYF_4$ (JCPDS 77-2042), Fig. S1g: β-$NaLuF_4$ (JCPDS 27-726)). It is worth to point that no obvious peak from the $SiO_2$ shell is observed in these patterns Because of amorphous nature of $SiO_2$ and organic Eu(DBM)$_3$phen complex. The XRD results give the fact that the dual emission core-shell hybrid NPs can be well reproduced.

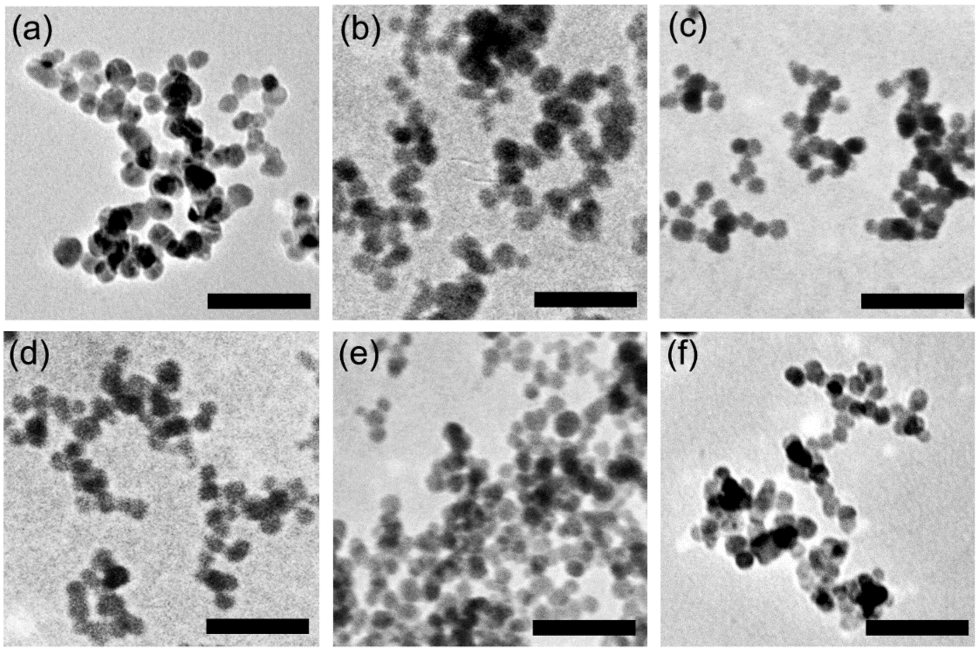


Fig. S2 TEM images of UC crystals. (a) $NaYF_4$:$NaLuF_4$:80%Yb,2%Er, (b) $NaYF_4$:$NaLuF_4$:60%Yb,2%Er, (c) $NaYF_4$:$NaLuF_4$:40%Yb,2%Er/$SiO_2$:Eu(DBM)$_3$phen NPs, (d) $NaYF_4$:$NaLuF_4$:20%Yb,2%Er, (e) $NaYF_4$:20%Yb,1%Tm/$NaLuF_4$:20%Yb,0.5%Er, (f) $NaYF_4$:$NaLuF_4$:20%Yb, 1%Tm. Scale bar: 100 nm.

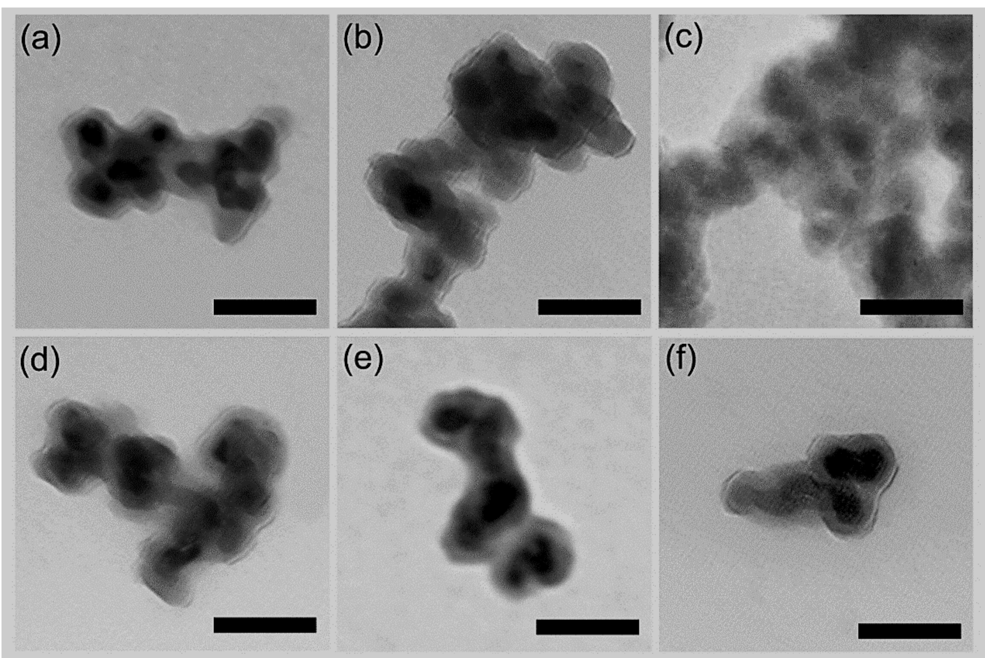


Fig. S3 TEM images of dual mode emission core-shell hybrid NPs. (a) $NaYF_4$:$NaLuF_4$:80%Yb,2%Er/$SiO_2$:Eu(DBM)$_3$phen NPs, (b) $NaYF_4$:$NaLuF_4$:60%Yb,2%Er/$SiO_2$:Eu(DBM)$_3$phen NPs, (c) $NaYF_4$:$NaLuF_4$:40%Yb,2%Er/$SiO_2$:Eu(DBM)$_3$phen NPs, (d) $NaYF_4$:$NaLuF_4$:20%Yb,2%Er/$SiO_2$:Eu(DBM)$_3$phen NPs, (e) $NaYF_4$:20%Yb,1%Tm/$NaLuF_4$:20%Yb,0.5%Er/$SiO_2$:Eu(DBM)$_3$phen NPs, (f) $NaYF_4$:$NaLuF_4$:20%Yb, 1%Tm/$SiO_2$:Eu(DBM)$_3$phen NPs. Scale bar: 100 nm.

Typical TEM images of $Yb^{3+}$, $Er^{3+}$ (and/or $Tm^{3+}$) codoped heterogeneous $NaYF_4$/$NaLuF_4$ UC nanocrystals are shown in Fig. S2. The image (a)-(f) is $NaYF_4$:$NaLuF_4$:80%Yb,2%Er, $NaYF_4$:$NaLuF_4$:60%Yb,2%Er, $NaYF_4$:$NaLuF_4$:40%Yb,2%Er/$SiO_2$:Eu(DBM)$_3$phen NPs, $NaYF_4$:$NaLuF_4$:20%Yb,2%Er, $NaYF_4$:20%Yb,1%Tm/$NaLuF_4$:20%Yb,0.5%Er, and $NaYF_4$:$NaLuF_4$:20%Yb, 1%Tm nanocrystals, respectively. The scale in the figure is 100 nm. We can see that all the UC core nanocrystals are almost spherical which have uniform size of about 21.6 nm on average. After coating, the morphology and structure of the hybrid NPs have also been determined using TEM. Fig. S3(a)-(f) are TEM images of the core-shell hybrid NPs using UC crystals of (a)-(f) in Fig. S2 as cores, respectively. The $SiO_2$ shell embedded with $Eu(DBM)_3phen$ were coated on above UC core crystals. As can be seen, the hybrid NPs have a core-shell structure and the obvious diffraction contrast can be identified between the central particles and the outer shell. The thickness of the $SiO_2$ shells is about 9.2 nm for all types of hybrid NPs. The high uniformity of all types of NPs we prepared give the fact that the NPs in our work are well reproduced.

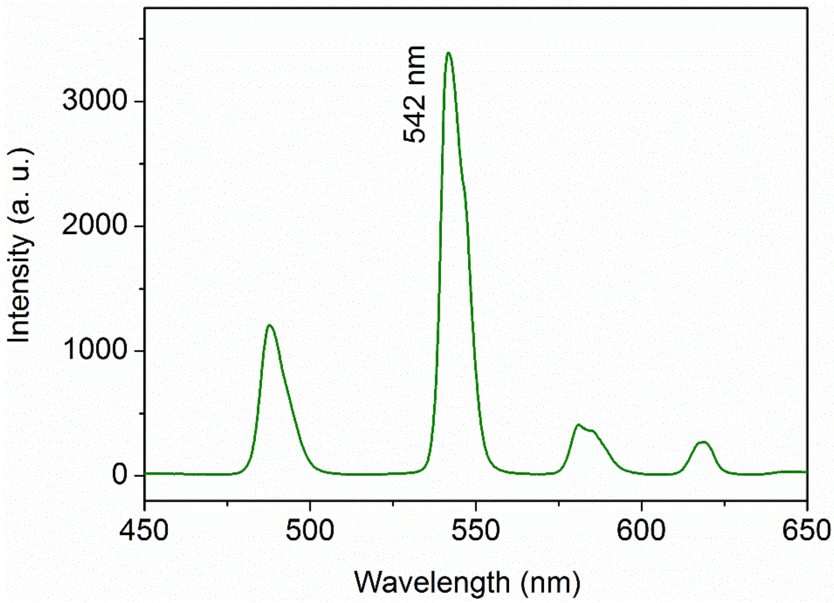


Fig. S4 The luminescence spectrum of $NaYF_4/NaLuF_4$:20%Yb,1%Tm@$SiO_2$:$Tb(SA)_3$ dual emission core-shell hybrid NPs under excitation of 354 nm.

Pumped by a 354 nm light from a xenon lamp source, the luminescence spectrum of $NaYF_4/NaLuF_4$:20%Yb,1%Tm@$SiO_2$:$Tb(SA)_3$ dual emission core-shell hybrid NPs water solution was recorded. As shown in Fig. S4, there are characteristic peaks of $Tb^{3+}$ ions, among which the strongest peak center at 542 nm which in green light region.