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Visible transparent white light emitting ink from Ce^{3+} sensitized monodispersed Tb, Sm co-doped LaF_3@C-dots nanocomposite

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Experimental Section

Materials:

Lanthanum Nitrate hexahydrate [$La(NO_3)_3$. $6H_2O$, 99.99%], , Samarium Nitrate hexahydrate [$Sm(NO_3)_3$. $6H_2O$, 99.9%], cerium nitrate hexahydrate [$Ce(NO_3)_3$, $6H_2O$], Terbium chloride [$TbCl_3$, anhydrous, 99.9%], Oleic acid [OLAH, 99%], Sodium oleate [Na-OL, 99%], Ammonium fluoride [NH_4F], Ethanol Amine [98%], Tetraethyl ortho silicate [TEOS], (3-Aminopropyl)triethoxysilane [APTES], IGEPAL CO-520, Poly(methyl methacrylate) (PMMA) were purchased from Sigma-Aldrich. Sodium Hydroxide, Methanol, Ethanol, , hexane and other solvents were purchased from Merck India.

Synthesis of doped LaF_3 Nanocrystals:

Monodispersed doped LaF_3 NCs were synthesized by thermal decomposition of mixed metal oleate in presence of fluoride source. For mixed metal oleate synthesis, x mmole $Sm(NO_3)_3.6H_2O$, y mmole $TbCl_3$, z mmole $Ce(NO_3)_3.6H_2O$ and {1-(x+y+z)} mmole $La(NO_3)_3.6H_2O$ were mixed with 3.5 mmole of NaOL in mixed solvent of 3 ml EtOH, 3 ml H_2O and 8 ml hexane and heated to 75 °C for 5 hrs in refluxed condition. The mixed oleate was washed with DI H_2O to remove $NaNO_3$ and NaCl.

The mixed oleate was dissolved in 14 ml of octadecene, 5 ml of OLAH and stirred vigorously at 80°C for 30 min to remove hexane and to obtain a transparent clear homogenous solution. The solution was cooled down to room temperature. 3 mmol NH_4F, 1 mmol NaOH dissolved in 5 ml MeOH was added drop wise (slowly) to mixed oleate solution. The overall mixture was stirred at

RT for 1 hr. Again the solution was heated to 80°C for 30 min to remove dissolved MeOH to obtain a bright transparent yellow colour solution. The solution was again heated to 110°C under dynamic evacuation to remove trace amount of water. The mixture was further heated to 305 °C for 80 min in presence of N_2 atmosphere. The nanocrystals were precipitated with addition of acetone as nonsolvent. The washing process was carried out for 3-4 times to remove excess oleic acid. Finally the product was dissolved in hexane and stored for further use.

LaF_3@d-SiO_2 synthesis: dense silica (SiO_2) layer has been deposited over the surface of LaF_3 NCs by modified stober process to make the NC water soluble and C-dot decoration. Doped LaF_3 NCs was dissolved in 12 ml of hexane to get a solution of 5000 mg/L. The solution was sonicated and 100 µl of IGEPAL CO-520 was added dropwise. Again 400 µl of IGEPAL CO-520 was added slowly under vigorous stirring. 100 µl of NH_3 (25% V/V) was added into the solution and sonicated for 30 min. Afterthat 100 µl of TEOS was added and stirred for overnight. LaF_3@d-SiO_2 NCs was precipitated by addition of 2 ml acetone. The product was washed with 80% ethanol 3-4 times. The as-obtained NCs were stored in ethanol for further use.

APTES modification of d-SiO_2@LaF_3: The surface of NC was further functionalised with APTES to obtain positive charge on NC surface. 1000 mg/L of d-SiO_2@LaF_3 was dissolved in 10 ml of EtOH and sonicated for 1 min. Desired amount of APTES was added to the solution and further sonicated for 10 min. The mixture was stirred for 15 hr. The product was washed with EtOH and kept in EtOH for further use.

C-dots synthesis:

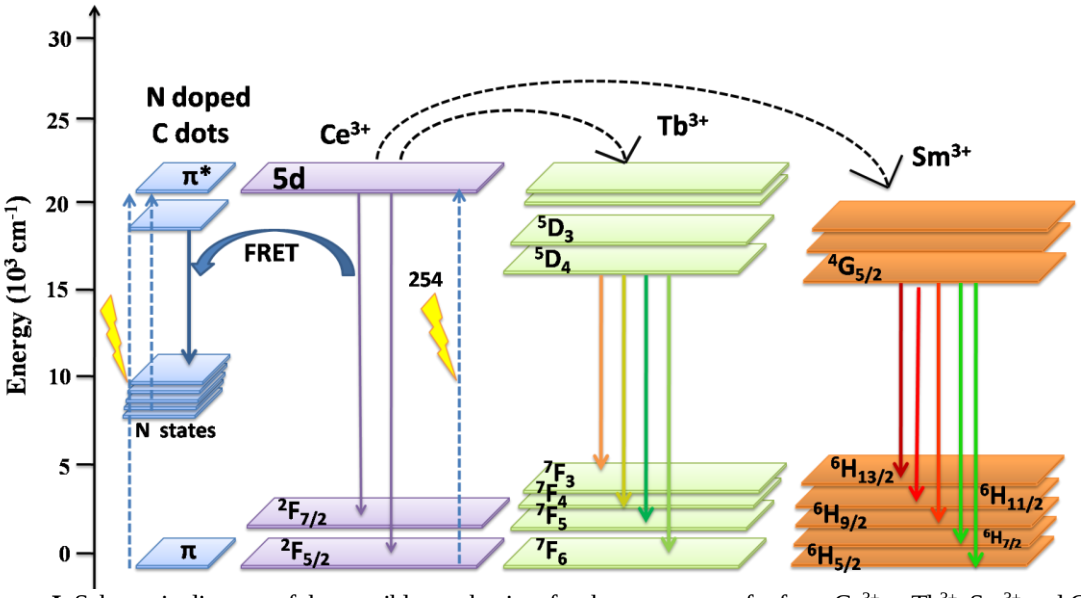
N doped C-dot was synthesized by thermal decomposition of amine in presence of oxidising agent. 3 ml of ethanolamine and 4.5 ml of H_2O_2 were taken in a round bottom flask fitted with condenser. The temperature of solution was raised to 200° C with a ramp rate of 2°C/min. The solution was kept at this temperature for 1 hr in N_2 atmosphere. The product was dissolved in 100 ml ethanol/H_2O for further use.

Synthesis of C-dots decorated d-SiO_2@LaF_3 nanocomposite:

White light emitting nanocomposites was synthesized by decorating N doped C-dots onto the d-SiO_2 coated LaF_3 NCs surface. In a typical synthesis, 5000 mg/ L of APTES modified d-SiO_2@ doped LaF_3 NCs was dissolved in 5 ml of DI water. Then 500 µl of N doped C-dots solution in DI H_2O (Crude C-dots solution was diluted with 100 ml of H_2O) was added and stirred over night. The final product was washed with Ethanol and H_2O to remove free C-dots form nanocomposite. The product was stored in DI H_2O/EtOH for further use and LED fabrication.

Characterisation:

The crystalline phases of the products were determined by X-ray powder diffraction (XRD) using a Bruker AXS D8SWAX diffractometer, with Cu Kα radiation (λ = 1.54 Å), employing a scanning rate of 0.5° S^{-1} in the 2θ range from 10° to 80°. Transmission electron microscopy (TEM) images and high angle annular dark field scanning TEM (HAADF-STEM) images were taken using an ultrahigh resolution field emission gun transmission electron microscope (UHR-FEG TEM, JEM-2100F, Jeol, Japan) operating at 200 kV. For the TEM observations, the sample was dissolved in hexane/EtOH and was drop cast on a carbon-coated copper grid. Room-temperature photoluminescence (PL) measurements were carried out with a fluorescence spectrometer (Hitachi, F-2500). Fourier transform infrared (FT-IR) spectra of the samples were taken by using a Perkin Elmer Spectrochem 100 FT-IR Spectrometer.



Scheme-I: Schematic diagram of the possible mechanism for the energy transfer from Ce^{3+} to Tb^{3+}, Sm^{3+} and C-dots in nanocomposite.

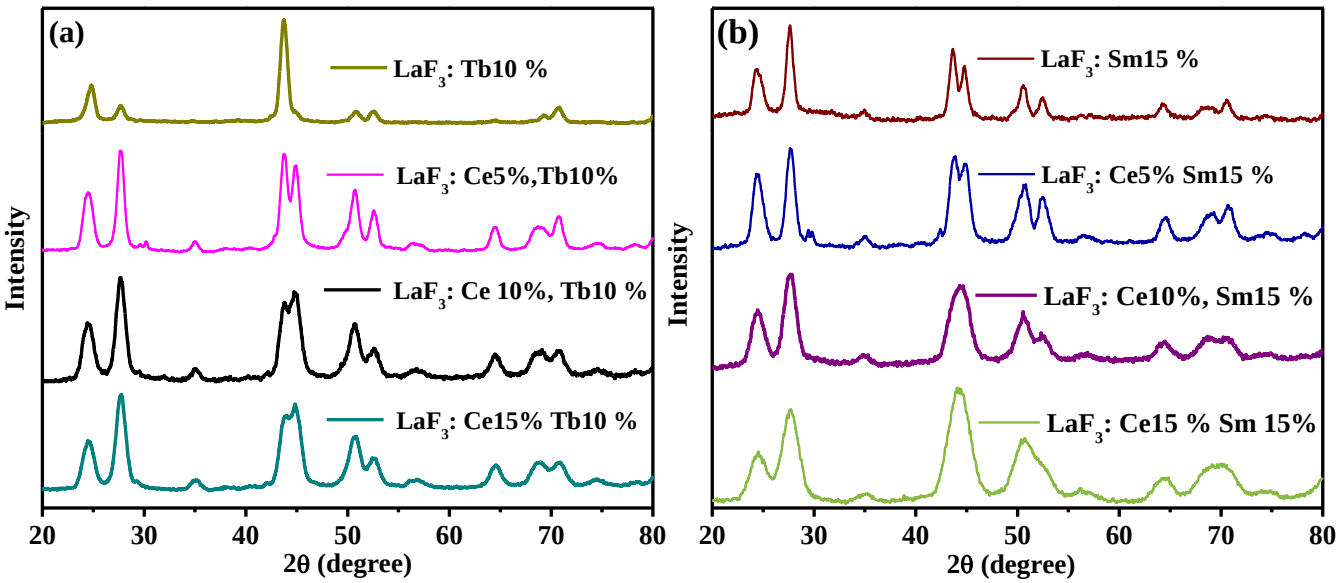


Fig. S1: (a) XRD pattern of Tb doped and Ce, Tb co-doped LaF_3 nanocrystals. (b) XRD pattern of Sm and Ce, Sm doped LaF_3 nanocrystals. All of the nanoparticles were found to be in pure hexagonal phase and matched well with COD: 9009994.

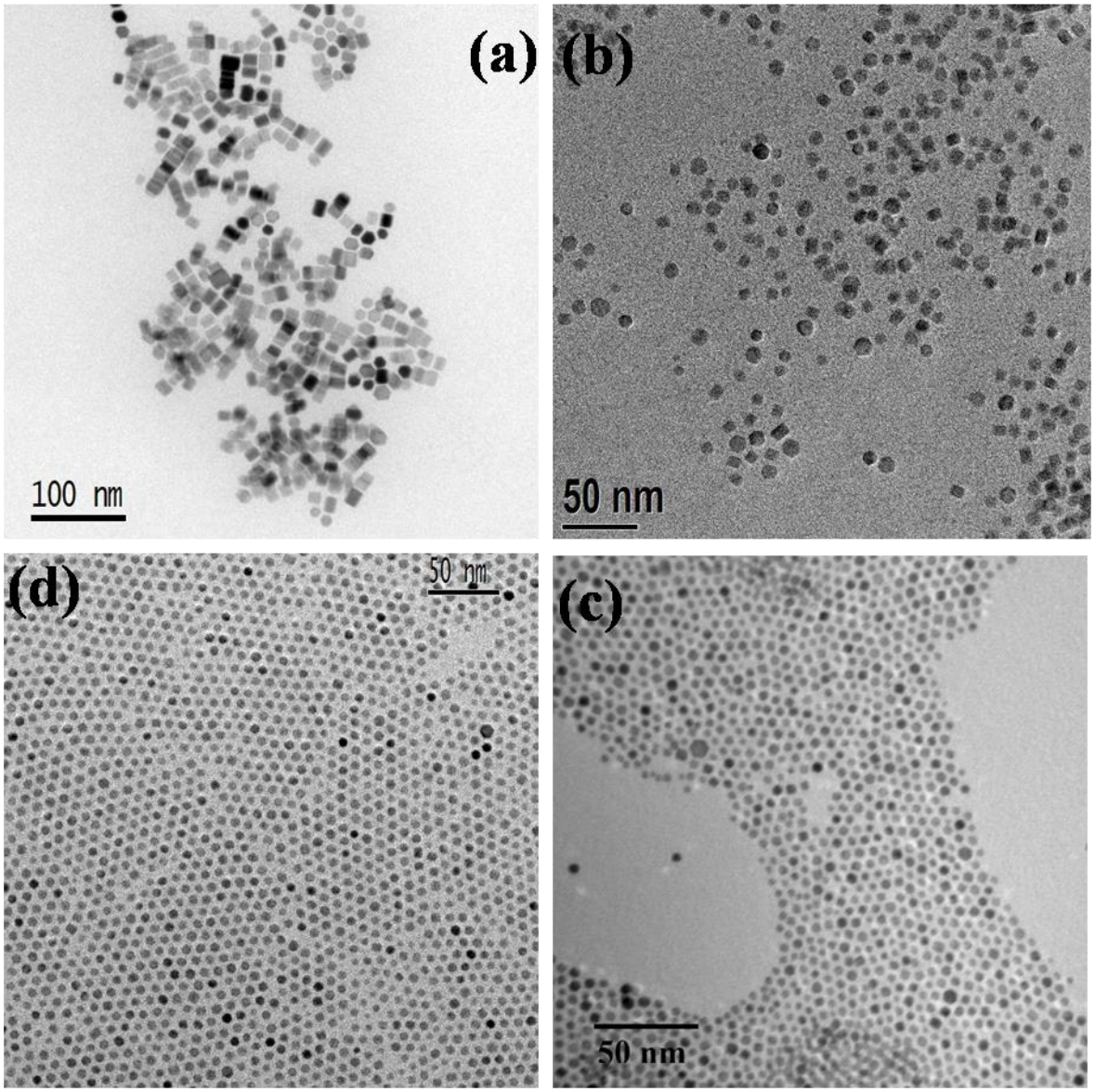


Fig. S2: TEM image of (a) 5%, (b) 10%, (c) 15% and (d) 20% Tb doped LaF_3 nanocrystals. The size of nanocrystals is found to decrease from 14 ± 3 nm to 8 ± 2 nm.

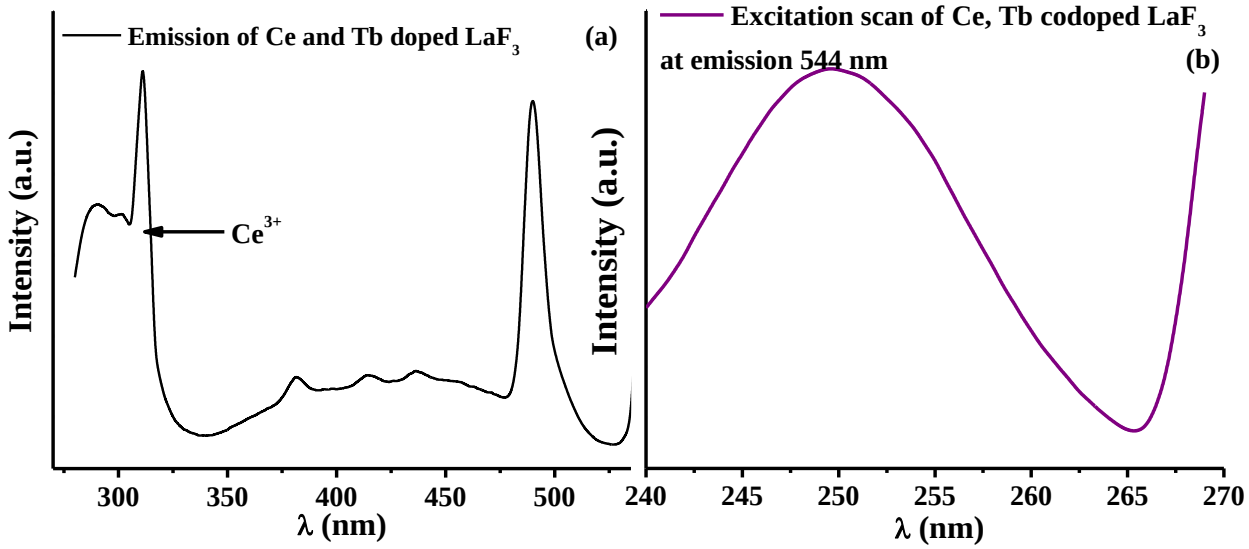


Fig. S3: (a) Emission spectra of Ce (15%) and Tb (10%) co-doped LaF_3 nanocrystals. New emission profile has been observed in 290 to 330 nm region along with characterized peaks of Tb^{3+}. (b) Excitation scan of Ce and Tb co-doped LaF_3 nanocrystals at emission of wavelength 544 nm.

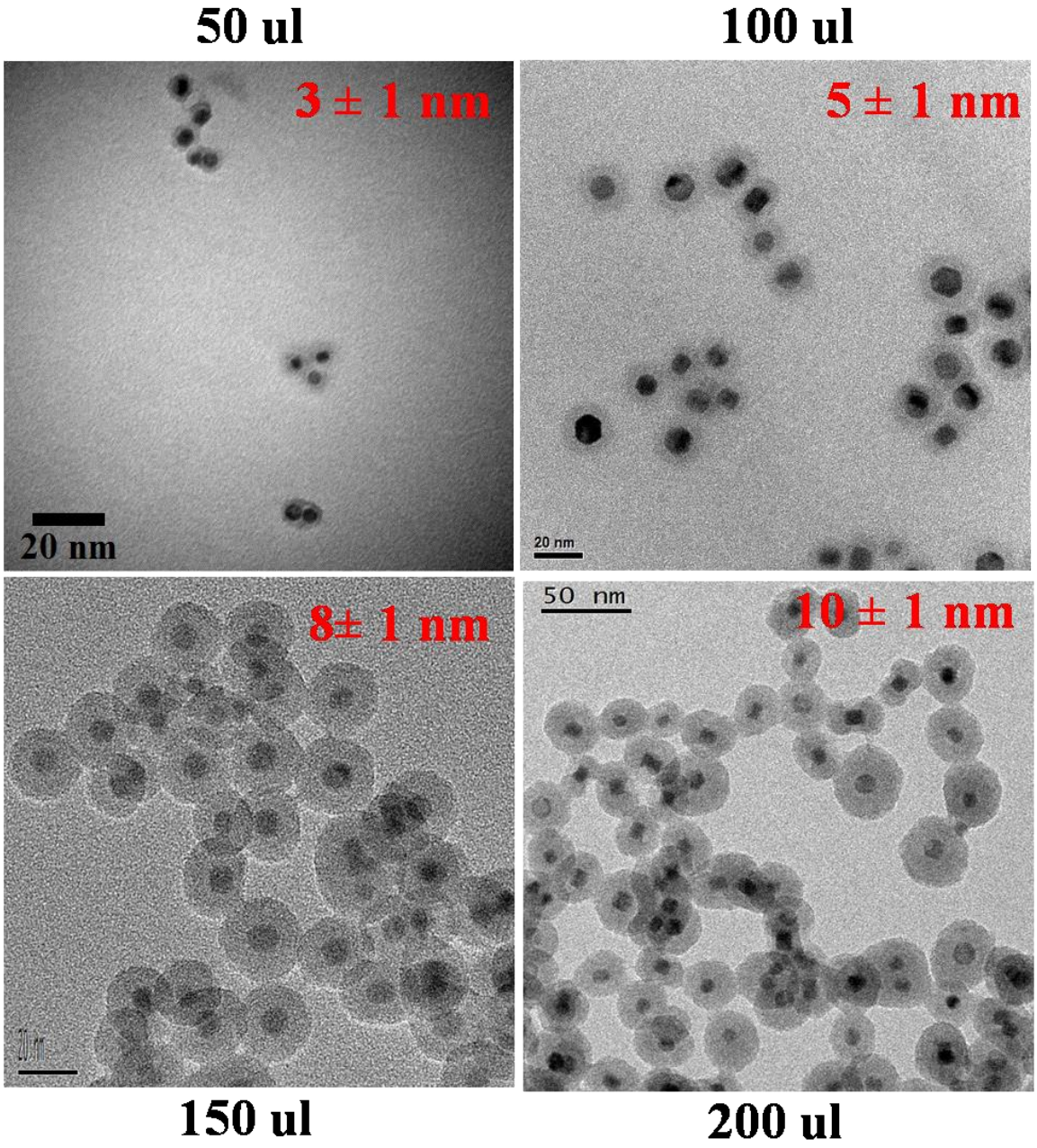


Fig. S4: TEM image of d-SiO_2 coated doped LaF_3 nanocrystals with varying thickness. Thickness was varied from 3 nm to 11 nm .

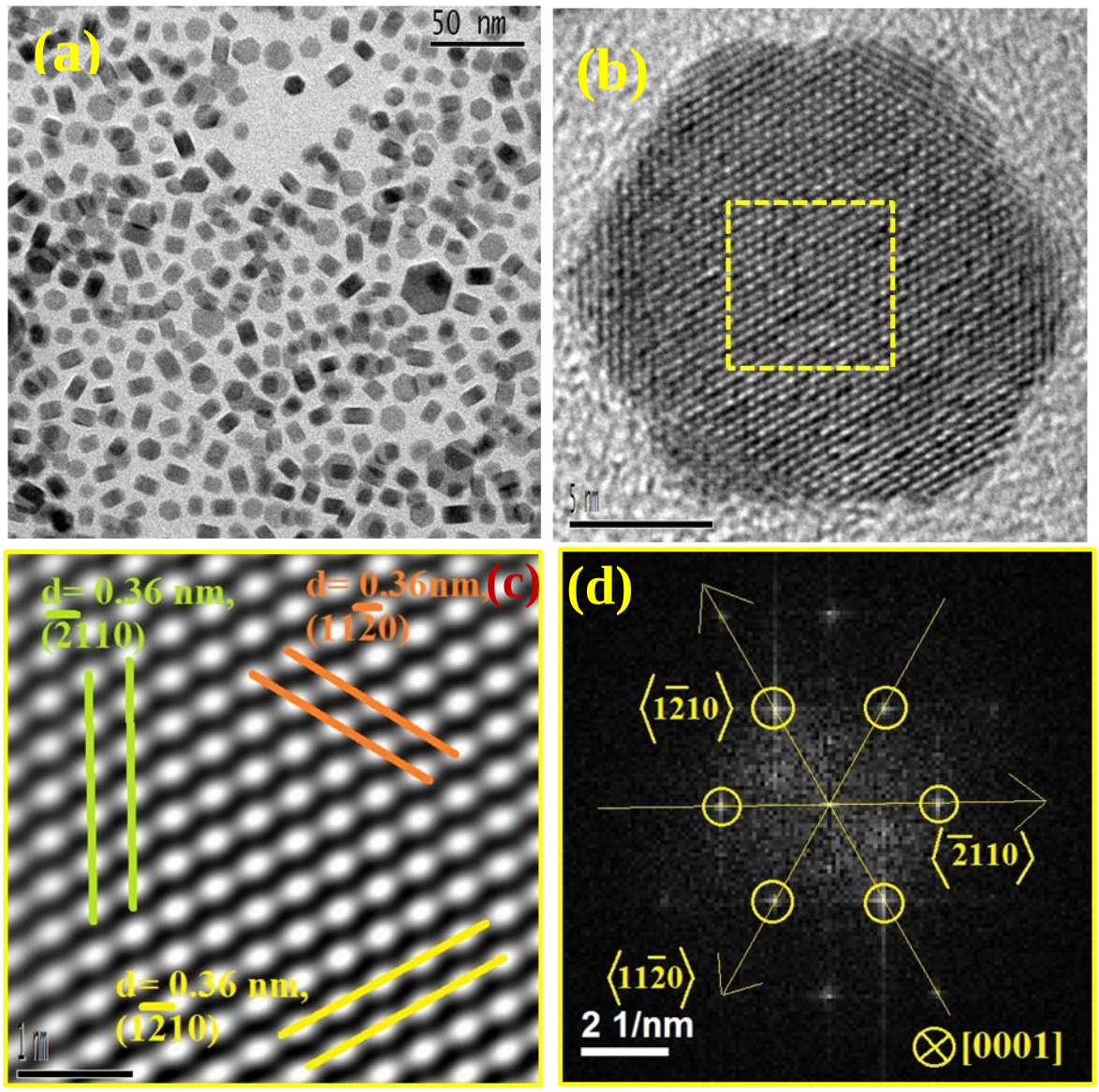


Fig. S5: (a) Large area TEM image of Ce, Tb and Sm doped LaF_3 nanocrystals. (b) HRTEM image of a single nanocrystal showing single crystalline nature of particle. (c) Reconstructed HRTEM image and (d) corresponding FFT pattern.

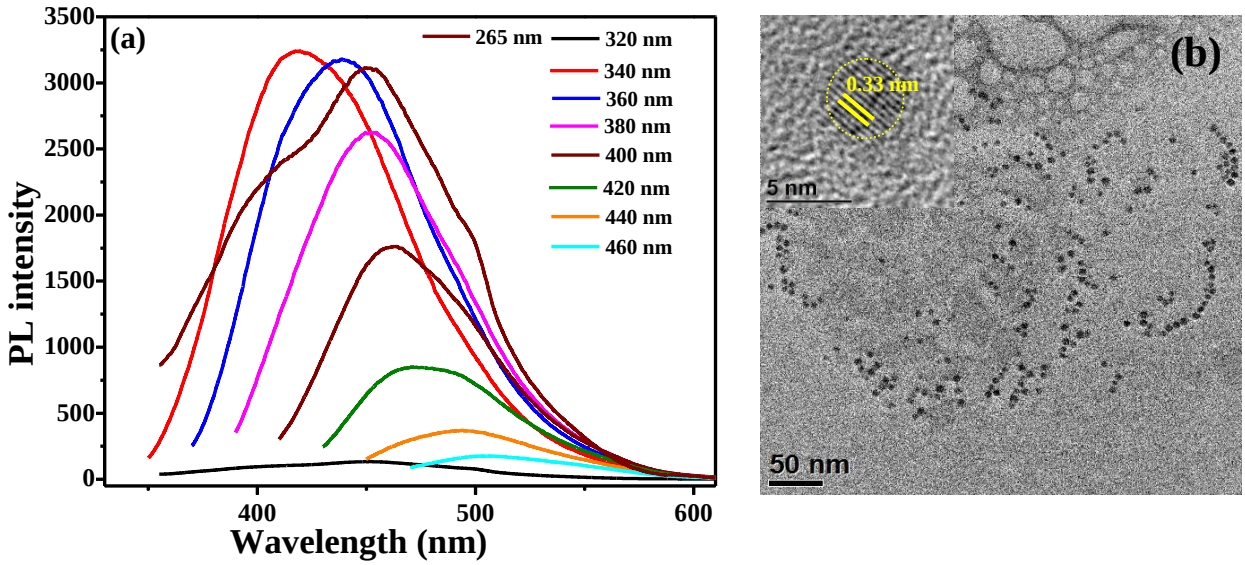


Fig. S6: (a) Excitation dependent emission profile of N doped C-dots. (b) TEM image of C-dots. Inset shows the HRTEM image of C-dot.

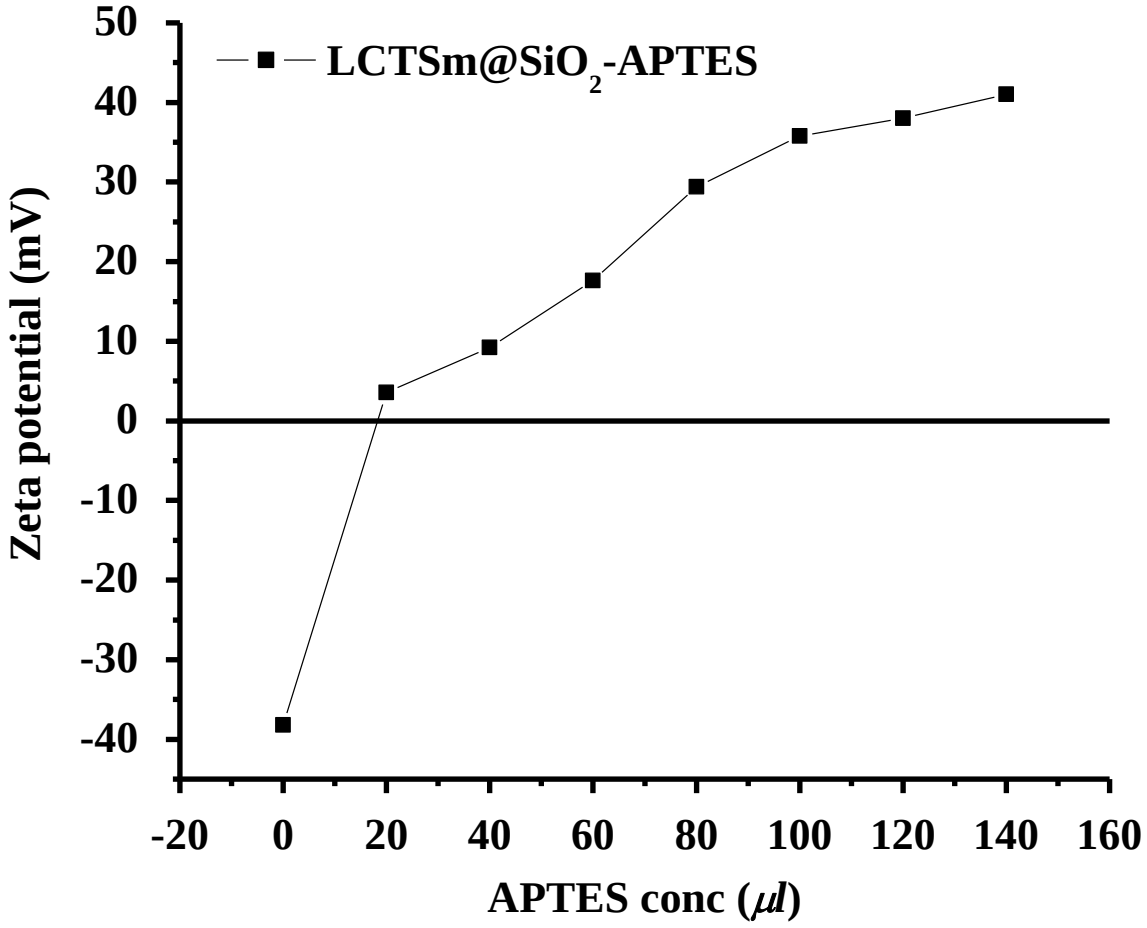


Fig. S7: Change of zeta potential of d-SiO_2 coated nanoparticles with APTES anchoring.

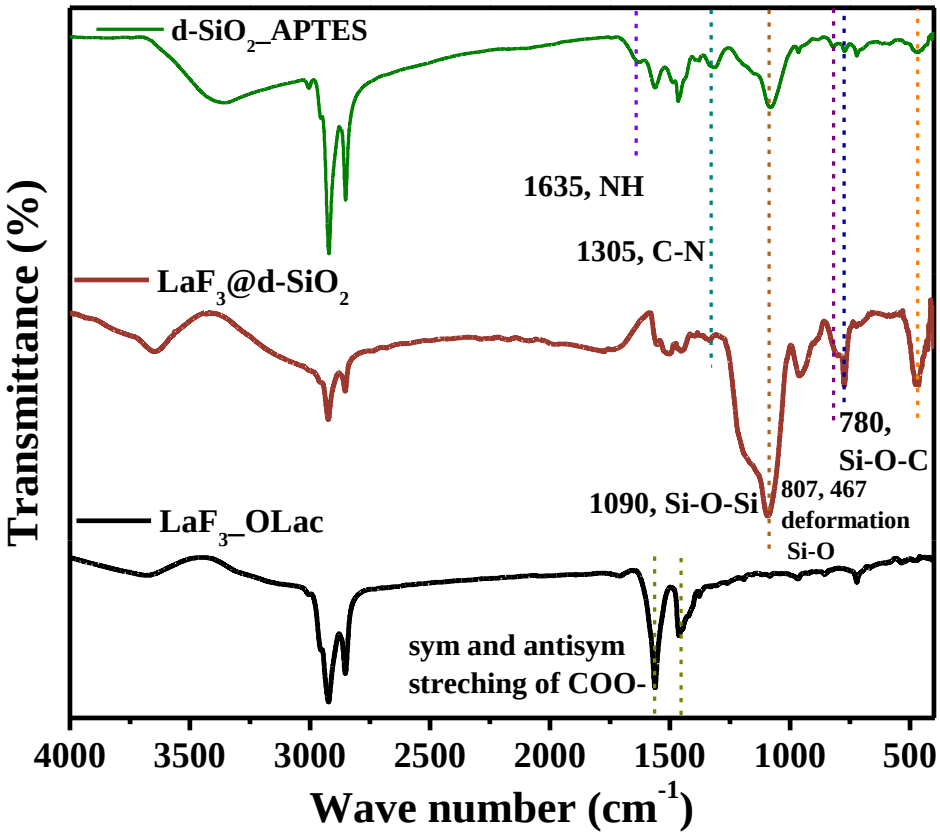


Fig. S8: FTIR spectra of as synthesized oleic acid capped LaF_3 nanoparticles. Symmetric and antisymmetric stretching modes of COO- were observed for oleate capping agent. d-SiO_2 coated nanoparticles shows characteristic Si-O-C and Si-O-Si stretching. APTES modified SiO_2 shows the appearance of stretching frequencies related to C-N and N-H of amine functional group along with the characteristics feature of SiO_2.

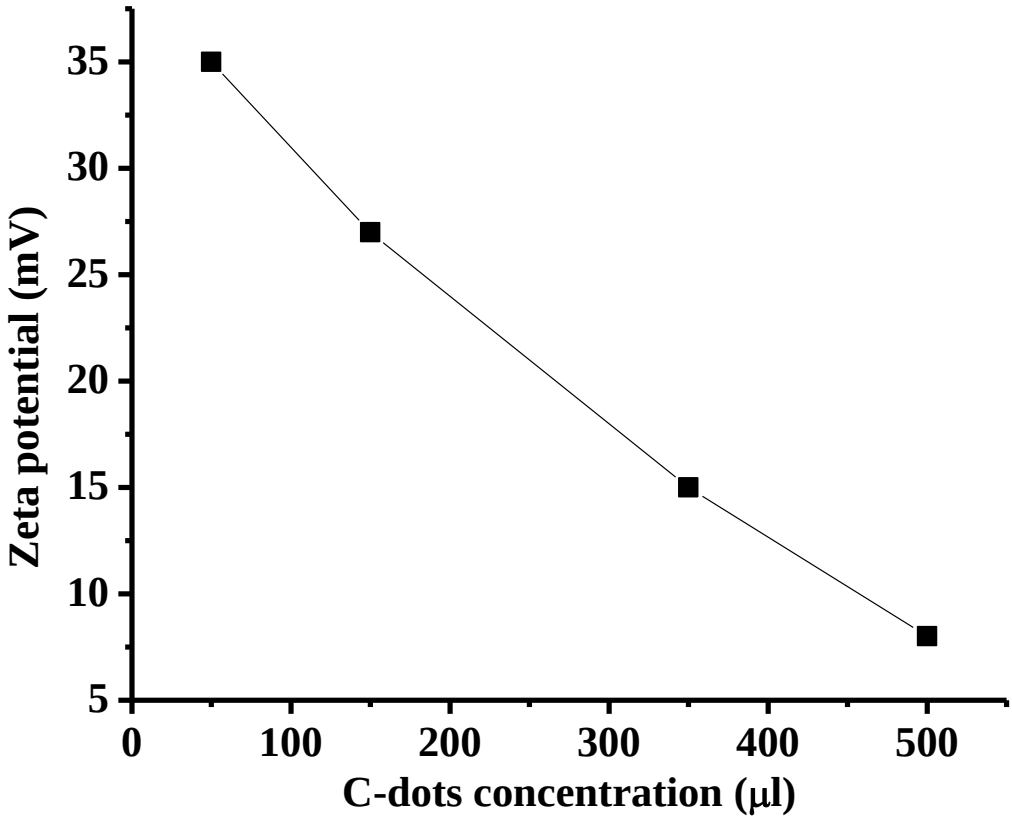
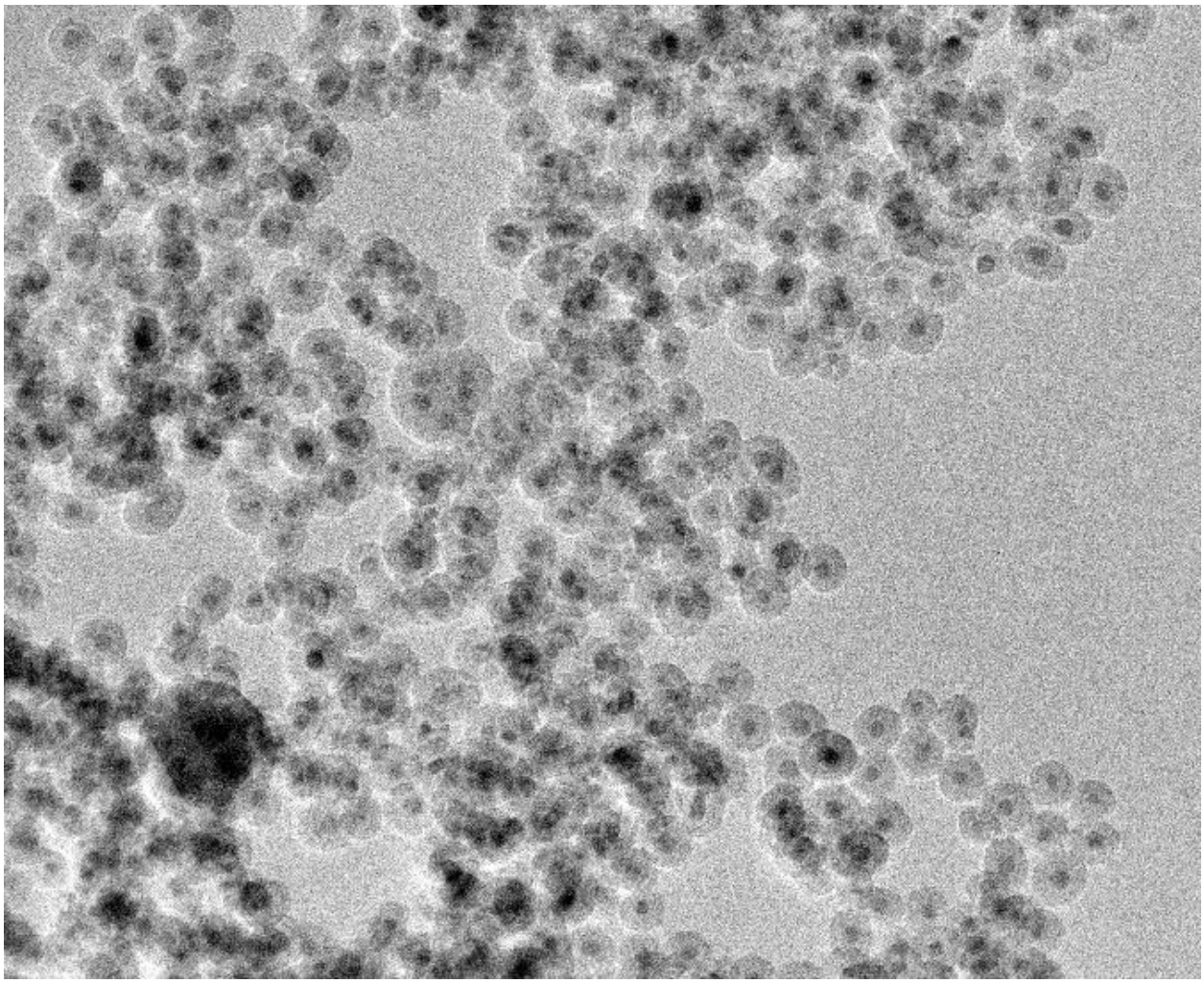


Fig. S9: Change of zeta potential of white light emitting nanocomposite with C-dots variation.

Fig. S10: Large area TEM image of d-SiO_2@Ce,Tb,Sm:LaF_3 nanocrystals before C-dots decoration.



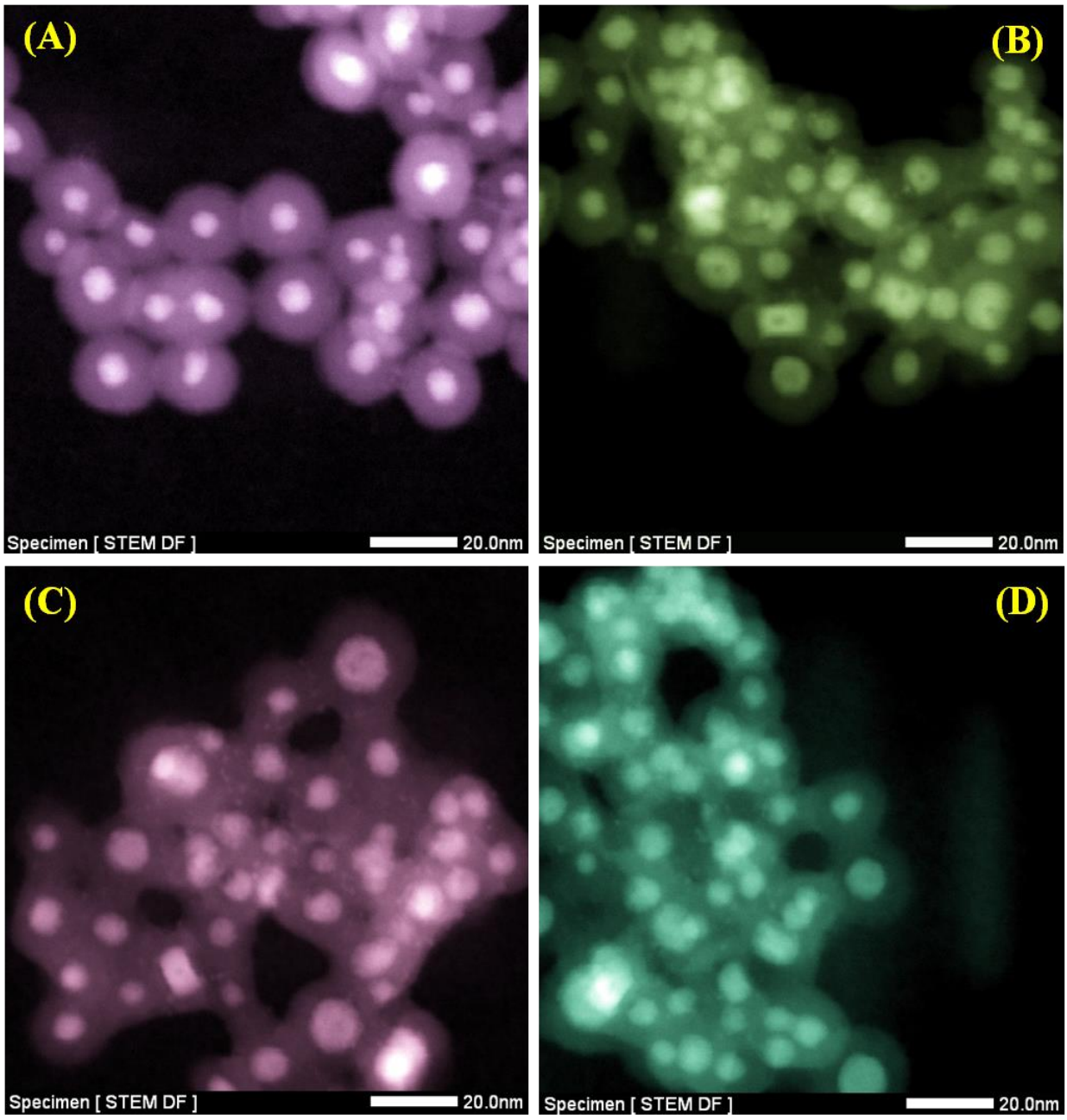


Fig. S11: STEM-DARK Field image of C-dots decorated d-SiO_2 coated doped LaF_3 nanocomposites with varying C-dots concentration.

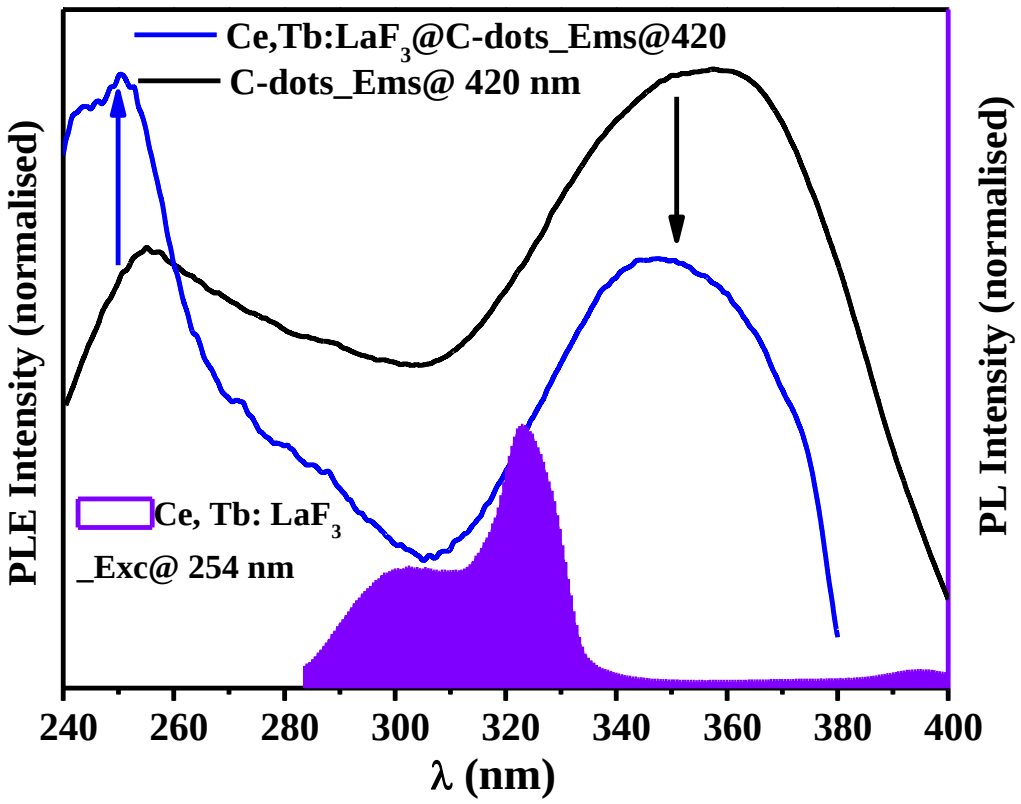


Fig. S12: Excitation profile of N doped C-dots and C dots decorated doped (Ce, Tb, Sm) LaF_3 nanocrystals at emission wavelength 420 nm. Filled graph area is the emission profile for Ce^{3+} ions with 254 nm excitation.

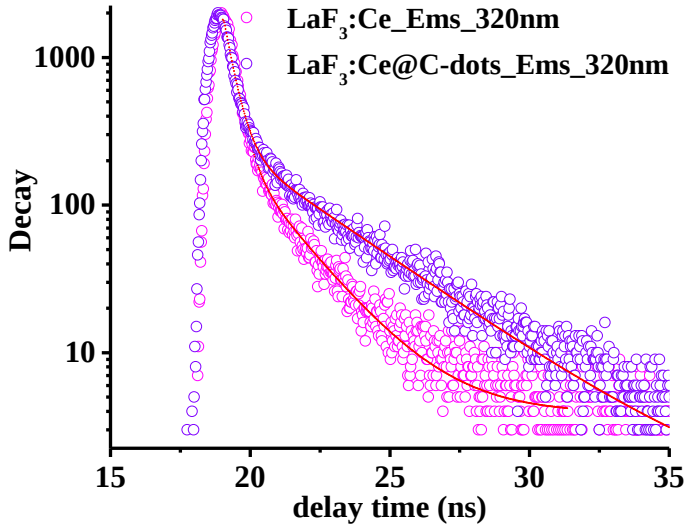


Fig. S13: PL decays of LaF_3: Ce and LaF_3:Ce@C-dots nanoparticles.

Table S1 PL decay components of LaF_3:Ce and LaF_3:Ce@C-dots nanoparticles:

Samples	**Emission wavelength (nm)**	**Decay life times (ns)**	**Contributions (%)**	**Average decay time (ns)**
LaF_3:Ce	320	$t_1 = 0.32$ $t_2 = 1.84$	$f_1 = 0.74$ $f_2 = 0.25$	$t_{av} = 0.70$
LaF_3:Ce@ C-dots	320	$t_1 = 0.36$ $t_2 = 3.35$	$f_1 = 0.92$ $f_2 = 0.0759$	$t_{av} = 0.587$

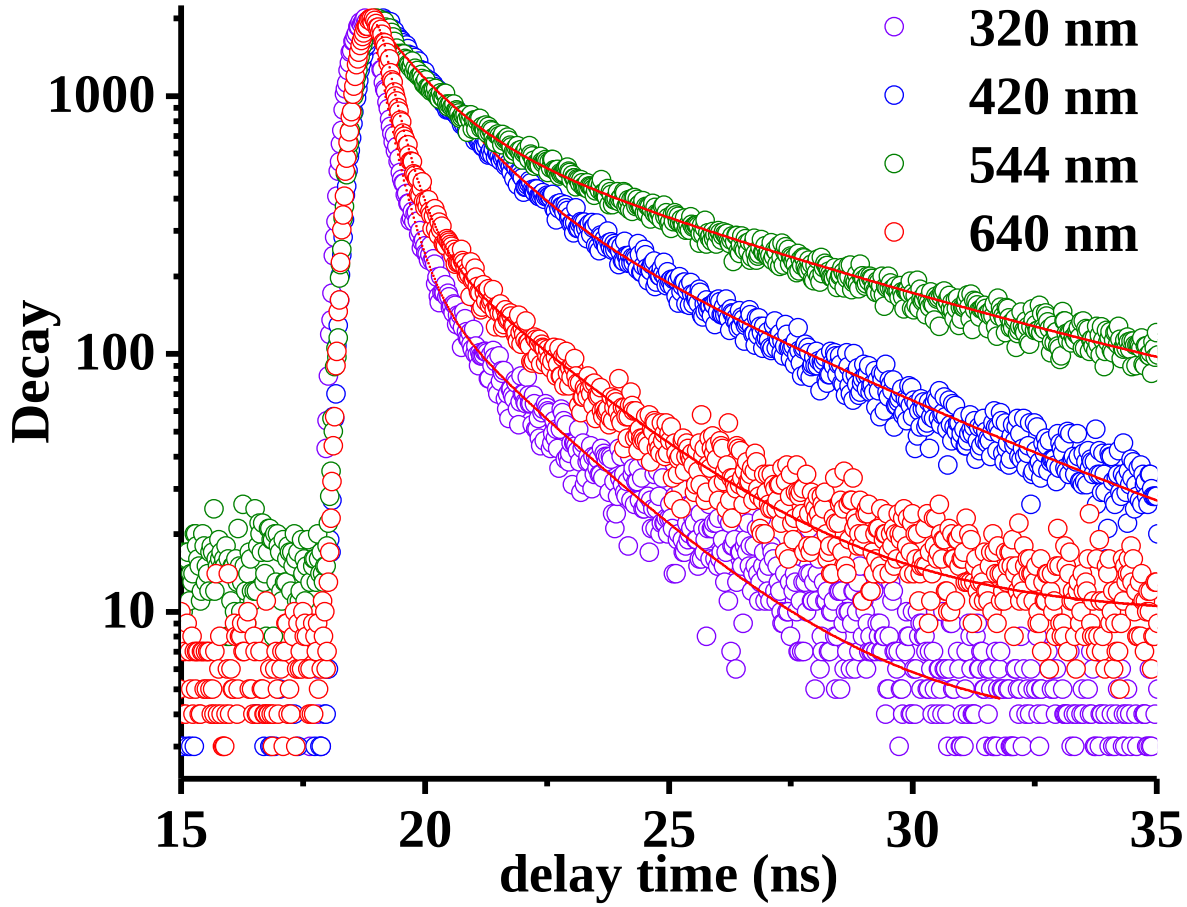


Fig. S14: PL decays of LaF_3: Ce and LaF_3:Ce, Tb, Sm@C-dots white light emitting nanocomposite.

Table S2 PL decay components of LaF_3:Ce,Tb, Sm@C-dots nanoparticles:

Samples	**Emission wavelength (nm)**	**Decay life times (ns)**	**Contributions (%)**	**Average decay time (ns)**
LaF_3:Ce,Tb,Sm@ C-dots	420	$t_1 = 1.3$ $t_2 = 4.92$	$f_1 = 0.47$ $f_2 = 0.529$	3.21
	544	$t_1 = 1.12$ $t_2 = 6.57$	$f_1 = 0.29$ $f_2 = 0.701$	4.94
	640	$t_1 = 0.38$ $t_2 = 2.63$	$f_1 = 0.57$ $f_2 = 0.427$	1.34