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Enhanced luminescent efficiency of aqueous dispersible NaYF₄:Yb/Er nanoparticles and effect of surface coating Anees A. Ansari¹*, Ranvijay Yadav², S.B. Rai²

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Abstract

In a general approach, we designed and synthesized monodispersed, well defined, highly emissive and aqueous dispersible NaYF4:Yb/Er upconversion nanoparticles and thereafter their surface were coated with an inert $NaYF_4$ and silica layers, respectively. The crystalline phase, morphology, composition and optical properties of the as-synthesized samples were well characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), UV-Vis absorption (UV-Vis), optical band gap energy, Fouriertransform infrared spectroscopy (FT-IR) and upconversion luminescence spectra, respectively. It is found that the synthesized hexagonal phase nanoparticles consist of highly crystalline spherical shaped, monodisperse with narrow size distribution, which can easily disperse in nonpolar cyclohexane solvent to form transparent colloid solutions. Optical band gap energy clearly shows the effect of surface coating of an inert inorganic and porous silica layers surrounding the surface of seed core-nanoparticles due to increase the crystalline size. The upconversion luminescence intensity was remarkably improved after formation of passive NaYF₄ layer due to the decrease of non-radiative rate arising from surface/defect of particles in the form of surface dangling bonds and capping agent. The growth of silica shell after inert shell formation, the emission intensity of Er^{3+} transitions were little affected in respect to inert shell coated core/shell nanoparticles, indicating that silica has been effectively grafted surrounding the core/shell nanoparticles. Our results indicate that surface coating of inactive and silica shell is a key step in producing highly upconversion nanocrystals with increased brightness for a variety of upconversion luminescent bioimaging and biosensing applications.

Keyword: NaYF₄:Yb/Er@NaYF₄@SiO₂ core/shell/shell nanoparticles, absorption spectra, band gap energy, upconversion properties,

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Introduction

Upconversion nanoparticles has been the subject of much interest over the past decade owing to the possibility of developing visible super fluorescent fiber sources and visible fiber lasers excited in the near infrared¹⁻⁶. Among various upconversion host matrixes, lanthanide ions-doped hexagonal-phase sodium yttrium fluoride (NaYF₄) has been turned out to be the most excellent host matrix for Yb^{3+}/Er^{3+} co-doped infrared-to-visible photoconversion¹⁴. Due to their inherent low phonon energies (~350 cm⁻¹), large anti-stokes shift, long lifetimes, narrow emission bandwidth, high chemical stability, deep tissue penetration, low background interference, good biocompatibility and weak toxicity, which provoked them great research interest in biological sciences³⁻⁵. These upconversion nanoparticles absorb in near-infrared (NIR) spectral region (~ 980 nm), which is a biologically transparent window, and emit high energy visible photons through an upconversion process¹⁻⁶. Additionally, upconversion materials convert low energy, near infrared photons into high energy ultraviolet-visible (UV-Vis) photons with stable fluorescence and require very low excitation power densities $(5-10 \text{ W/cm}^2)$ to emit photons³⁻⁵. Until now, several approaches including microemulsion method, hydrothermal/solvothermal method, co-precipitation, microwave irradiation procedure and polyol method have been developed for the synthesis of different controlled size and shape upconversion nanoparticles^{7,8}. However, most of these controlled size upconversion nanoparticles are synthesized in organic solvents or at high temperature and obtained nanoparticles are hydrophobic and show poor dispersibility in water. The direct use of these nanoparticles for biological applications is limited owing to the low solubility in water and unsuitable surface property, which do not have functional chemical groups or appropriate sites for attachment of biomolecules^{7,8}. Besides, the used toxic organo-metallic precursors and hazardous coordinating solvents have become matters of substantial environmental concern. Therefore, developing an effective and user-friendly procedure to synthesize upconversion nanoparticles with well-defined crystal sizes and good dispersibility is still a challenge. Although, the luminescence efficiency of the upconversion nanoparticles is low (<1%) and this aspect remains a concern. Thus, designing a protective layer on the upconversion nanoparticles should be an effective strategy to improve the luminescent efficiency. Surface modification of upconversion nanoparticles offers a promising way to enhance the luminescence of these nanoparticles⁷⁻⁹.

Up to now much effort have been expanded to enhanced overall photoluminescence efficiency of upconversion nanoparticles⁸⁻¹¹. Recently, we and some other research groups have been effectively grown a shell of inert inorganic crystalline materials surrounding the

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lanthanide ions-doped core-nanoparticles to improve the photoluminescence efficiency by enhancing the energy transfer from sensitizer to the activator⁸⁻¹³. These upconversion core/shell nanostructure shows luminescence enhancement because the shell can shield dopant ions and inhibit defect sites on the particle surface from luminescence quenching^{8,13}. However, most of the inorganic inert shell materials are hydrophobic in aqueous environment. Therefore, direct use of these hydrophobic core/shell nanoparticles in biological applications is limited on account their weak dispersibility in aqueous environment and poor biological conjugation activity. It is therefore necessary to modify the surfaces of these core/shell nanoparticles with active functional groups or hydrophilic ligands to improve their solubility in aqueous environment so that these nanoparticles can be bonded to biomolecules as required. Previously, some literature reports demonstrated that the presence of some functional groups (such as -COOH, -NH₂, or -SH)on the surface of upconversion nanoparticles could not only increase their water dispersity but also allow further conjugation with biologically active molecules $^{14-20}$. Additionally, these upconversion nanoparticles not only exhibit upconversion luminescence efficiency, but also have appropriate surface properties that can be used to conjugate with biomolecules through terminal functional groups, such as antibodies and DNA with. Among the various employed surface coating materials mesoporous silica has been paid much attention because they have several attractive features, such as a stable mesoporous structure, tunable pore sizes with a narrow distribution, high specific surface area and pore volume, nontoxic nature, good biocompatibility, and welldefined surface properties. Some reports in literature have been discussed with silica coating being a protective matrix because of its reliable chemical stability, optical transparency, chemical inertness, cheapness, biocompatibility, non-toxicity, photochemical stability even under laser photolysis, and easily transferred into a wide range of solvent¹⁷⁻²⁰.

In this report, we propose the strategy to successful synthesis of well-defined NaYF₄:Yb/Er (core)-nanoparticles with an average size of 100-115 nm, which are well monodispersed and demonstrated high aqueous dispersibility in aqueous and non-aqueous solvents. These upconversion core nanoparticles were coated with crystalline inactive NaYF₄ layer and thereafter with amorphous silica shell around the surface of core nanoparticles to improve the luminescent efficiency and aqueous dispersibility, respectively. Comparative crystalline nature, morphology and optical properties of core, core/shell and core/shell/shell nanoparticles were analyze systematically to investigate the influence of surface coating on optical and solubility on as-prepared upconversion nanomaterials. These luminescent

core/shell/shell nanoparticles are promising for use as luminescent probes in biological labelling and imaging technology.

Experimental

Materials and methods

Yttrium oxide (99.99%, Alfa Aesar, Germany), Ytterbium oxide (99.99%, Alfa Aesar, Germany), Erbium nitrate (99.99%, BDH Chemicals Ltd, England), ethylene-diamine tetraacetic acid(EDTA), sodium fluoride, Tetraethyl orthosilicate (TEOS, 99 wt% analytical reagent A.R.), C₂H₅OH, NaOH, HNO₃ and NH₄OH were used as a starting materials without any further purification. Y(NO₃)₃6H₂O, Yb(NO₃)₃6H₂O and Er(NO₃)₃6H₂O were prepared by dissolving the corresponding oxide in diluted nitric acid. Nanopure water was used for preparation of the solutions. Ultrapure de-ionized water was prepared using a Milli-Q system (Millipore, Bedford, MA, USA). All other chemicals used were of reagent grade.

Preparation of NaYF₄:Yb/Er nanoparticles

In a typical synthesis procedure, for preparation of $NaYF_4:Yb^{3+}/Er^{3+}$ nanoparticles EDTA was used as a chelating agent for complex formation with trivalent lanthanides. 7.8 mL of 2M Y(NO₃)₃6H₂O, 2 mL of 2M Yb(NO₃)₃6H₂O and 0.2 mL of 2M Er(NO₃)₃6H₂O were dissolved together in dist. water and heated upto 80 °C. In another solution EDTA in equivalent amount was prepared in dist. water and injected into the metal solution for complex formation. Later on, 1:3 molar ratio amount of NaF dissolved in dist. water was mixed up in this forgoing reaction and kept for constant stirring with heating (80 °C) on hot plate for 1 h ²¹. This suspension was filled in Teflone-line stainless autoclave and sealed for different time interval for hydrothermal crystallization. After autoclave cooled at room temperature the final powder product was then collected by centrifugation, washed with distilled water and absolute ethanol, and dried in oven at 80 °C for 6 h for further characterization.

Preparation of NaYF₄:Yb/Er@NaYF₄ core/shell nanoparticles

For the preparation of NaYF₄:Yb³⁺/Er³⁺@NaYF₄ core/shell nanoparticles, 0.400 g core-nanoparticles was dispersed in minimum amount of dist. water along with ethylene glycol with the help of ultrasonic bath and then constant stirring for 30 min. Typically, 0.632 g Y(NO₃)₃6H₂O dissolved in dist. water and after that a solution of NaF dissolved in dist. water was introduced into foregoing mixed system, and the suspension was refluxed at 100

°C for 3 h until the precipitation was occurred. This white precipitate was centrifuged and washed with ethanol to remove excess un-reacted reactants. The core/shell nanoparticles were collected after centrifugation and allowed to dry in ambient temperature for further characterization.

Preparation of silica coated NaYF4:Yb/Er@NaYF4@SiO2 core/shell/shell nanoparticles

The NaYF₄:Yb³⁺,Er³⁺@NaYF₄@SiO₂ core/shell/shell nanoparticles were prepared through a versatile solution Stober method as follows^{12,20}. The synthesized core/shell nanoparticles (50 mg) were well dispersed in a mixed solution of deionized water (50 mL), ethanol (70 mL) and concentrated aqueous ammonia (1.0 mL) in a three-neck round-bottom flask. Afterward, 1.0 mL of tetraethyl orthosilicate (TEOS) was added drop-wise in 2 min, and the reaction was allowed to proceed for 5-6 h under continuous mechanical stirring. After 6 h of continuous stirring at room temperature, the silica-coated core/shell/shell nanoparticles were separated by centrifugation, washed several times with ethanol and dried at room temperature.

Characterization

The crystalinity of the powder samples was examined by X-ray diffraction (XRD) at room temperature with the use of PANalytical X'Pert X-ray diffractometer equipped with a Ni filter using Cu K_a (λ =1.54056 Å) radiations as X-ray source. The size and morphology of the samples were inspected using a field emission transmission electron microscope (FE-TEM) equipped with the EDX (FETEM, JEM-2100F, JEOL, Japan) operating at an accelerating voltage of 200 kV. EDX analysis was used to confirm the presence of the elements. The samples for TEM were prepared by depositing a drop of a colloidal ethanol solution of the powder sample onto a carbon-coated copper grid. The FTIR spectra were recorded on a Perkin-Elmer 580B IR spectrometer using KBr pellet technique in the range 4000-400 cm⁻¹. The UV/Vis absorption spectra were measured in the Perkin-Elmer Lambda-40 spectrophotometer in the range 190–600 nm, with the sample contained in 1 cm³ stoppered quartz cell of 1 cm path length. The upconversion luminescence spectra were recorded using iHR320 (Horiba Jobin Yvon) spectrometer equipped with R928P photon counting photomultiplier tube and a 980 nm diode laser with 2.4 W maximum power as an excitation source. All measurements were performed at room temperature.

Results and discussion

Crystal structure, size and morphologies of the nanoparticles

X-ray diffraction pattern was employed to examine the composition, phase purity and crystalline nature of the as-prepared nano-products. Fig. 1 illustrate the XRD pattern of the as obtained core, core/shell and core/shell/shell nanoparticles. The broad reflection peaks of XRD pattern indicate that the prepared samples are in small grain size with high crystalinity, which are in good agreement with face-centered cubic NaYF₄ (space group Fm 3m) crystal structure data(JCPDS card No. 77-2042) and small amount of hexagonal phase NaYF₄ crystal structure data(JCPDS card No. 28-1192)⁷. The diffraction peak positions and intensity are perfectly matched with the literature reports^{7,22,23}. As illustrated in Fig. 1c, the diffraction peaks of the silica surface modified core/shell/shell nanoparticles are broadened with decrease relative diffraction intensity with respect to the seed core-nanoparticles. It indicates that the structure of the seed core brings partial disorder to the ordered porous framework of the silica shell. Whereas, there is no defined characteristic peak for amorphous SiO₂ is observed after one coating process due to the thinner property of the SiO₂ layer. It suggests that the presence of the SiO₂ coating significantly influence nanoparticle crystallinity, resulting the change in reflection intensity of XRD pattern. Although, it is difficult to discern the diffraction and territory of inert NaYF₄ shell from the XRD data, since NaYF₄ shell shows similar crystal structure and lattice constants to NaYF₄.

Transmission electron microscopy images give the direct evidence to investigate the formation of shell on the surface of upconversion core-nanoparticles. It is observed from the low resolution TEM micrographs that the as prepared core-nanoparticles are in spherical shape, fairly uniform monodispersed, large surface area, highly crystalline and well define size distribution with average particle sizes of 90-115 nm (Fig.2a&b). As shown in Figure 2b&c, the typical high resolution TEM image revealed their high crystalline nature and structural uniformity with porous surface. Moreover, the surface of the nanoparticles is quite rough, highly porous as apparently observed in the TEM images (in inset Fig.2b). This porous surface of the luminescent nanoparticles are facilitating for the high dispersibility in organic solvents. The TEM image clearly shows that the obtained silica coated core/shell/shell nanoparticles still retain the uniform nanoparticle morphology, which are highly agglomerated (Fig.2d). As seen in Fig. 2d, the silica core/shell/shell nanoparticles are highly agglomerated with different particle size distribution. In this micrograph, the dark areas are related to the high concentration of luminescent core-nanoparticles with aggregate

nature and light grey color for amorphous silica surface coating. It is known that silica layer contain a large number of surface silanol groups which are highly soluble in aqueous solvents. We believe that these surface silanol groups promote to increase in aggregation process through hydrogen bonding in aqueous solvent. High-magnification TEM image shows that the thickness of the silica shell is very uniform and about 25-30 nm (in inset Fig. 2d), and the uniform ordered mesopores can be observed. No significant changes in the morphology and composition of silica coated core/shell nanoparticles are observed after the silica surface modifications, as evidenced by TEM imaging shown in Fig. 2d. The FE-TEM image in inset Fig.2b shows the crystalline fringes of the nanoparticles. The electron diffraction pattern (inset of Fig. 2a) from the FE-TEM also demonstrated unambiguously the single-crystalline nature of the sample. The selected-area electron diffraction (SAED) pattern shows spotty polycrystalline diffraction rings corresponding to the (111), (200), (222), (220), (311) and (422) planes of the β -phase NaYF₄ lattice, consistent with the XRD (JCPDS card No. 28-1192) results^{7,22,23}. These results suggest the high crystallinity of the as-prepared β -NaYF₄ nanoparticles.

Energy dispersive X-ray analysis was used to determine the compositional changes before and after growing a layer of NaYF₄ and amorphous silica around the surface of core nanoparticles. The EDX analysis demonstrated the existence of all expected basic chemical elements such as Na, Y, F, Yb, Er, O and Si, indicating that the doped elements are homogeneously distributed inside the crystal lattice of NaYF₄ nanoparticles (Fig.3). It should be noted that the origin of strong Cu peaks that appeared in the EDX spectra are from the copper micrometer-grids. The C peak also came from the carbon-coated Cu-TEM grid. No other impurities are evident in the figure implying that the resulting core and core/shell/shell nanoparticles are pure in chemical composition.

Comparative optical properties of core, core/shell and core/shell/shell nanoparticles

FTIR spectroscopy verifies the surface modification of the as-prepared samples before and after shell formation around the surface of core nanoparticles. As illustrated in Fig.4, all samples exhibits a broad with low intensity infrared band in between 3100-3600 cm⁻¹ and two weak intensity bands at around 1600 and 1217 cm⁻¹, which ascribed to asymmetric, symmetric stretching and bending vibration modes of the surface attached hydroxyl groups, respectively^{12,19,20}. Another two weak intensity bands are also observed at around 1740 and 1430 cm⁻¹, attributed to the (C=O and (C-O) functional group of surface attached EDTA

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carboxylic acid²¹. As seen in Figure 4c, a strong doublet infrared absorption peak is observed at around 1080 cm⁻¹ and two weak intensity peaks at 800 and 460 cm⁻¹, which are arise from the asymmetric and symmetric stretching vibration modes of silica (Si-O and Si-O-Si)^{12,19,20}. These are well known silica bands which confirmed the successful silica layer formation around the surface of core/shell nanoparticles.

Optical properties and colloidal stability are examined by UV-visible absorption spectroscopy. The spectra of all three samples are recorded in dist. water over the 200-600 nm UV-Vis spectral regions. Fig. 5 displays the absorption spectra of core, core/shell and silica layer grown core/shell/shell nanoparticles. It is noticed that absorption spectra of all samples are closely similar except absorption band edge. It may be due to similar refractive index $NaYF_4$ shell is covered around the surface of core nanoparticles. Whereas, a little difference such as red shift in band edge in the absorption spectra of silica coated core/shell/shell nanoparticles is observed, resulting the formation of optically active thinner amorphous silica layer around the surface of core/shell nanoparticles. It is worth noticing that the core-nanoparticles are coated with a hydrophobic layer of an inert NaYF₄ shell on their surface and there are no appropriate functional groups (such as-COOH and -NH₂) on their surface. So that, their solubility in aqueous solvent is poor, therefore, surface modification is necessary before their use in biological detections. So that they are coated by silica shell to enhancement their colloidal stability in aqueous solvent. The resultant silica surface modified core/shell/shell nanoparticles shows excellent solubility as well as colloidal stability in water to form a colloidal solution by sonication treatment, as shown in Fig.5c. This is very important for amorphous silica coated core/shell/shell nanaoparticles to fulfill bio-related applications, especially drug delivery and fluorescence imaging, because smaller nanoparticles (~100 nm diameter) can escape from phagocytes in the reticuloendothelial(RES) system, such as the liver and spleen, and circulate through blood vessels with a long blood half-life; however, bigger nanoparticles result in rapid uptake by the RES. No obvious agglomeration or settling is found after storing the sample for a period of weeks under ambient conditions. The presence of silanol molecules on their surfaces not only results in high solubility in water, but also allows further conjugation with various biomolecules, which paves the way for further bio-applications of the core/shell/shell nanoparticles.

The electronic band structure or band gap energy is estimated from the energy difference between the highest occupied and lowest unoccupied molecular orbitals. The Tauc and Menths method is used to determine the band gap energy (E_g) of the prepared samples ²⁴.

According to these authors, the E_g is associated with absorbance and photon energy by the following equation:

 $\alpha h v = (h v - E_{gap})^{n} \qquad \dots \qquad \text{Eqn} (1)$

Where α is the absorbance, *h* is the Planck constant, *v* is the frequency, E_g is the optical band gap and n is a constant associate with the different type of electronic transitions (n= $\frac{1}{2}$, 2, 3/2 or 3 for direct, indirect allowed, direct, indirect forbidden transition, respectively). In this case, E_g value is determined by extrapolating the linear portion of the curve or tail. This observed behavior can be associated with the energy difference between the valence band and conduction band for these materials. Based on this equation, the estimated E_g values for core, core/shell and core/shell/shell nanoparticles are 1.2, 1.0 and 0.8 eV, respectively. As seen in inset of Fig 5, E_g values are decreases in core/shell/shell nanoparticles in respect to bare core-nanoparticles. The differences in band gap values can be related to the difference in crystalline size, because particle size is increase after growth a shell of inert NaYF₄ and amorphous silica around the surface of core-nanoparticles. These results are verified from XRD, FE-TEM, EDX, FTIR and absorption spectral studies, suggesting the formation of silica layer around the surface core-nanoparticles.

In order to evaluate the up-conversion quality of the as-prepared upconversion nanoparticles, we demonstrated a comparative spectral study with surface coated core/shell/shell nanoparticles and other well-known upconversion phosphors. The upconversion emission spectra of core, core/shell and silica modified core/shell/shell nanoparticles under excitation of a 980 nm NIR diode laser measured at room temperature. The upconversion spectrum shows five emission peaks located at 378, 406, 512-533, 536-558 and 643-675 nm, which correspond to ${}^{4}G_{11/2} \rightarrow {}^{4}I_{15/2}$, ${}^{4}H_{9/2} \rightarrow {}^{4}I_{15/2}$, ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$, ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$, and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transitions of Er^{3+} ions, respectively. The green emission between 512-533 nm and 536-558 nm originates from the ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$, transitions of $\mathrm{Er}^{3+7,25,26}$. A dominant red emission assigned to the ${}^{4}\mathrm{F}_{9/2} \rightarrow {}^{4}\mathrm{I}_{15/2}$ transition of Er^{3+} is observed at 643-675 nm. As seen in Fig.6, all three samples exhibit similar up-conversion spectral profile except a change in luminescence intensity is observed after assembly of shell around seed core-nanoparticles, which may be attributed to the alteration of crystallinity as well as influence of shell. The observed similar transition positions confirming that the local crystalline environments are identical before and after growth of shell. It is revealed in the spectrum that the luminescence efficiency of core-nanoparticles is generally lower than that of the reported bulk material^{27,28}. Yan and co-workers pointed out that this may result from

the energy transfer processes to the surface through adjacent dopant ions or because luminescence of surface dopant ions is quenched ²⁷. Yi and Chow also suggested that the organic surfactant with high vibrational energy on the nanoparticle surface (such as –COOH, -OH anions in this work) quenched the fluorescence ²⁸. However, both of them demonstrated that this problem can be improved by coating an inert NaYF₄ layer around the corenanoparticles.

Interestingly, we observed remarkable enhancement in luminescence intensity after epitaxial growth of inert NaYF₄ shell compared to their counter seed core-nanoparticles. Since pure NaYF₄ do not exhibit upconversion luminescence, the increased upconversion emission observed undoubtedly originated from the core-nanoparticles that became enhanced after being covered by a shell. This phenomenon can be interpreted by the fact that formation of a shell could greatly decrease the surface defects and ligand influence of the core nanoparticles, which makes the luminescent ions located on the surface capable of functioning just as well as those within the crystal matrix itself²⁷. The emission intensity for the core/shell nanoparticles is 50 times higher as compared to the core-nanoparticles. The comparison of core and core/shell nanoparticles is done for the same weight percent of nanoparticles. This results in the fact that the number of core/shell particles is larger than the number of core nanoparticles. Because of this, the increase in luminescence intensity of core/shell nanoparticles is thus an under estimation. Based on the upconversion pump efficiency formula $I \propto P^n$ $(n \ge 2)^{29}$, where I stands for the upconversion intensity, P stands for the excitation pump power, and n is the number of absorbed photons. From the power dependence curve for green and red emission, both the 536-558 and 643-675 nm emissions are two-photon processes. The increase in the luminescence intensity for core/shell nanoparticles compared to core-nanoparticles is attributed to the presence of a shell, which protects the dopants in the core, especially those near the surface, from quenching arising from surface anchored surfactant hydroxyl groups. The reduction in quenching improves the overall upconversion quantum yield of the core-nanoparticles^{12,13,28,30}. Furthermore, our group has shown strong evidence for the formation of core/shell lanthanide nanoparticles using the aforementioned synthesis procedure^{12,13} and we conclude the same is true for these core/shell nanoparticles. Nevertheless, this is not the only observed effect of the Er³⁺/Yb³⁺doped shell. According to the previously literature reports, the growth of this shell has triggered a general enhancement of the Tm^{3+} emission intensities from the Tm^{3+}/Yb^{3+} -doped core^{13-17,31}. This effect can be explained considering that the high-energy vibrational modes of the adsorbed species on the surface of the nanoparticles including the EDTA, sodium

citrate, ethylene glycol, oleic acid and oleylamine capping ligands are known to induce quenching of the luminescence of lanthanide ions¹³⁻¹⁷. To avoid this reduction in the luminescence intensity, this is a common option to passivate the surface of the nanoparticles by growing a protecting shell of undoped host material^{12,13}. In the present situation, grown an inert shell around the active Er^{3+}/Yb^{3+} -doped NaYF₄ core-nanoparticles can have this effect and, thus, trigger the enhancement observed in Figure 6b. Since this enhancement is linked to a core/shell nano-architecture, its presence can be considered as additional proof of the success in growing this kind of structure.

After the core/shell nanoparticles are coated with a silica layer their luminescence decreased to some extent because of the light-scattering effect on both emission and incident light by the silica layer. It is well recognized that the emission of luminescent lanthanide nanoparticles will be quenched to some extent in the environments that have a high phonon frequency^{12,17}. This phenomenon can be attributed to the involvement of large vibrational modes, such as -OH and -COOH in nanoparticles, which leads to the increase of nonradiative transition from ${}^{4}S_{3/2}$ to ${}^{4}F_{9/2}$ transitions ${}^{13-17,31,32}$. It is suggested that in amorphous silica modified core/shell nanoparticles, the non-radiative transition rate of Yb³⁺ increased greatly because of the large involvement of Si-OH bonds, leading to the obvious quenching of the Er³⁺ emission transitions. Moreover, the surface silanol (Si-OH) groups have tremendous vibration frequencies from 1000 to 3600 cm^{-1} will quench the emission of Er^{3+} to a great extent in silica modified core/shell nanoparticles. Despite the decrease in luminescence, the silica coated core/shell/shell nanoparticles still show naked-eye emissions under a NIR laser, which remains strong enough for various biomedical applications such as imaging, detection, and sensing. The presence of the silica layer is confirmed by TEM images and FTIR spectroscopy.

Conclusions

In conclusion, the fabricated highly emissive and aqueous dispersible NaYF₄:Yb/Er, NaYF₄:Yb/Er@NaYF₄ and NaYF₄:Yb/Er@NaYF₄@SiO₂ core/shell/shell nanoparticles with upconversion luminescent properties were prepared via general hydrothermal approach. The decrease band gap energy from core to core/shell/shell nanoparticles, which attributed to the quantum-size effect due to the growth of the inactive NaYF₄ and amorphous silica shell, which decrease the crystallinity of the nanomaterials, respectively. In case of an passive layer deposited surrounding the core sample the emission intensity is significantly enhanced (~ 10

times) in respect to the seed core-nanoparticles, which may be due to inert shell protect the luminescent core from the incident and emission light from the surface defects and suppress the non-radiative rate arising from surface/defect of particles. A slight decrease in upconversion efficiency of core/shell/shell nanoparticles was observed because of amorphous silica surface modification. However, silica surface modified core/shell/shell nanoparticles still possess strong upconversion luminescence property, similar to their parent core-nanoparticles. Comparative optical analysis of the core, core/shell and core/shell/shell nanoparticles indicate that the surface property of the upconversion core-nanoparticles can be changed after being coated with inert shell and porous silica. Our work has demonstrated a successful approach to prepare innovative very bright porous upconversion core, core/shell nanoparticles for broad photonic based biotechnological applications by using surface defect reduction strategies.

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Figure Captions

- Fig.1. X-ray diffraction pattern of core, core/shell and core/shell/shell nanoparticles.
- **Fig.2.** FE-TEM micrographs of (a,b&c) NaYF₄:Yb/Er (core), inset shows the SAED patterns, and (d) NaYF₄:Yb/Er@NaYF₄@SiO₂ core/shell/shell nanoparticles.
- Fig.3. Energy dispersive X-ray spectrograph core and core/shell/shell nanoparticles.
- Fig.4. FTIR spectra of the as-prepared core, core/shell and core/shell/shell nanoparticles.
- **Fig.5.** UV-vis absorption spectra of core, core/shell and core/shell/shell nanoparticles suspended in dist. water and inset shows the plot of $(\alpha h v)^2$ vs. photon energy(hv) of the core, core/shell and core/shell/shell nanoparticles.
- Fig.6. Upconversion spectra of the as-prepared core, core/shell and core/shell/shell nanoparticles.

Figure 1



Figure 2







Figure 4



Figure 5



Figure 6

