

# Unprecedented, Exhaustive Review and Roadmap for Upconverting Nanoparticles Field Enhancement Mechanisms to be utilized in Biomedical Applications

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*Abstract-Upconverting nanoparticles (UCNPs) have been of crucial significance in multiple applications involving photochemical, biomedical and optical ones. For the biomedical applications, one main problem that always stands as a challenge, hindering the upconversion scheme from being deployed inside human cells, is the challenging trade-offs among biomedical and field enhancement requirements imposed by the biomedical design constraints that deprive the UCNPs from field enhancement. Another challenge is imposed due to the constraint on the material choice that should achieve the required targeting, treatment/imaging, and electromagnetic design objective without any harm threatening the human body, which involves the dose limited by biodegradability and biocompatibility of the material. Although multiple field enhancement and manipulation techniques have been applied to UCNPs, there has never been an exhaustive review on applicability of all possible field enhancement or tuning mechanisms in biomedical applications. In this work, an exhaustive review over all possible upconverting nanoparticles field enhancement and emission wavelength manipulation mechanisms is provided, organized, suggesting the potential of new techniques and discussing the applicability of each in biomedical applications.*

**Keywords:** UVC, NIR, UCNPs, biomedical, field enhancement, resonance, synthesis parameters, photon dynamics, lattice structure, crystal field, photon transfer, QM efficiency

## I. INTRODUCTION

Near Infrared (NIR) -UVC Lanthanide doped upconverting nanoparticles have been heavily needed in biomedical, military and photochemical applications. Most studies have been concerned with exploring the influence of different chemical and physical parameters on the increase in photoluminescence intensity and wavelength tuning. In general, field enhancement approaches, cited in literature so far, involve changing dopants, dopant concentration, host material, size of the upconverter, dispersibility of the upconverting nanoparticles, cavity, refractive index of the UCNPs, making periodic structures

(arrays), Fano-Feshbach modes, localized/surface plasmon resonance, Bloch modes, whispering gallery modes, Fabry-

Perot structures, suppressing quenching factors, defect tuning, crystal structure, core-shell structures, impurities, calcination and operation temperatures, and source parameter optimization. These mechanisms have been scattered in different research papers that might have or have not been applied specifically to upconverters. Thus, there is a crucial need for exhaustively listing the possible approaches, organizing them, clarifying their applicability in biomedical applications and setting up a roadmap for field enhancement according to the application of concern; biomedical. Biomedical applications are distinguished with arduous challenges because of the multiple design constraints imposed on the coating thickness, coating material, size of the nanoparticles, morphology, concentration/dose limit of the UCNPs and multiple other constraints. Broadly-speaking, they can be categorized into pre- or post-synthesis methods. This is, indeed, helpful for researchers to know since the pre-synthesis methods are resource exhaustive in terms of the operational cost of the devices used, whereas the post-synthesis ones can be applied after a single sample preparation. Because of the financial support limitation, research plans could be optimized based on this categorization. Second, a further categorization could be whether these methods are theoretically or practically driven. Knowing the theories developed related to each field enhancement approach could save extensive resources wasted on long chains of experimental trials, which is helpful for chemistry related applications that usually cling to the experimental aspect alone, ignoring the guiding physical principles.

Another important design objective for UCNPs has been wavelength tuning to suit multiple targets such as viruses or other organisms. Some of these approaches include Forester/Luminescence Resonant Energy Transfer (FRET/LRET), antenna effect, ligand effects, the influence of Lanthanide (Ln) dopants, morphology, and cross relaxation, which are detailed in the second section.

## II. EXHAUSTIVE REVIEW

1. Review on applicability of Field Enhancement Mechanisms for UCNPs in Biomedical Applications:

### 1.1) First Approach: Partially Material Independent Methods (size, refractive index, morphology source dependent)

Although there could be a partial dependence on the material choice of these approaches, they are theoretically driven and based on the size and refractive index or the dielectric constant in general, which let us think broadly about the phenomena themselves rather than about a material dependent approach.

- For Fano-Feshbach modes competition:
  - They do not apply to our case since they depend on the resultant destructive interference among several radiative poles so that the far field is of destructive interference pattern [1].
  - Bound states in continuum: requiring inversion symmetry of the crystal, but it should be broken in our case so that the upconversion process is possible [2].

- Resonances [wave-guide resonance] :since it only depends on the size and dielectric constant of the material, it is constrained by the biodegradable size of the nanoparticles. Second, it is also constrained by the nature of the shell material, which is required to be a metal to achieve an appropriate efficiency that meets the requirement of the biomedical application. Similarly, the problem of surface plasmon resonance and localized surface plasmon resonance require the use of non-biodegradable shell materials. Surface One can think then of plasmon resonance in semiconductors for multilayered structure, it is important to introduce a spacer between the metal and the UC to avoid surface quenching. Surface Quenching and cross relaxation happens when the finally emitted frequency is downconverted in the same type/ different types of ions, respectively. Despite its low QM efficiency, it is still one approach of field enhancement.

- Bloch modes:

However, they require periodicity (array structures) and thus are not applicable to our case.

- Fabry Perot:

Nonetheless, it requires the external layer to be highly reflective to NIR so that the incident emission remains confined. The problem is that if it is reflective to NIR, it would be reflective to the incident radiation as well and will minimize the coupling, which is a paramount design requirement. It is also inapplicable in our case due to RI similarity between the coating and the core layer and the inability to make a thick coating due to its high loss.

- Source parameters optimization with respect to Application constraints; namely virus and exposure limit in our case:

The following source parameters could be optimized: (pulse width, repetition rate, power, intensity, polarization, angle). However, our resource limitations remove them from the available options.

- Whispering Gallery Modes (WGM) [3], [4], [5]:

They are inapplicable in our case for the following reasons:

1) A wavelength of .4 nm can only interact with our structure given the dimensions obtained in the TEM results in the design section [6].

The way to go about this is either increasing the diameter and thus sacrificing biodegradability, which is unacceptable as this is a fundamental design requirement, or making the height  $\ll$  diameter, sacrificing upconversion.

2) Its very low radiative coupling efficiency [the only coupling possible in our case] [7].

And thus we can't achieve the 2 important required coupling conditions (1) phase synchronization and (2) significant overlap of the WGM and the coupler mode [8].

3) Theoretically, it's based on total internal reflection inside the structure, which means that it reached the absorber inside the resonator and then got reflected to the boundary, which is impossible to happen before they reach the activator as they must pass by it. Thus, it is also inapplicable in our case.

- In-depth Review of the Best Surface Texturing Methods (Manipulating the external morphology irrespective of the material):

Various studies have turned attention to moth eye structures as promising antireflective coatings for a broad range of applications. Many studies have been dedicated to the fabrication process [9], [10], [11], [12], [13], [14], [15], [16], [17] fitting it into solar cell or other applications, or optimizing the geometric parameters of the structure [18], [19], [20], [21], [22], [23], [24]. Other works have explained the general antireflection principles derived from previously published work in this field [25]. However, there is still no profound explanation for the theoretical basis of the anti-reflectivity of surface texturing structures,

which led most of the studies to turn into mere optimization of the geometric parameters of the overall structures. This imposes a constraint on the maximum anti-reflectivity attained to the conventional optimization limits given the shallow conceptual look at moth eye structures as miraculous gift from nature. Thus, the need for finding the underlying theory that would give a broader and deeper insight into the conceptual basis controlling antireflection which will pave the way for other novel antireflection routes. Setting more profound design criteria that enhance antireflectivity will also add new and complement existing dimensions of thinking about moth eye antireflectivity such as the effect of self-similarity on anti-reflectivity [26], [27], [28].

- Source Parameters Optimization:

Increasing intensity to  $\text{GW}/\text{cm}^2$  has been found to be significant for increasing the UC emitted intensity. This could be supported by fs laser, which is not currently available but can be theoretically studied. Despite the inapplicability of this case in our application inside the human body, this could have other potential applicability in in-vitro bioassays for example. One practical study has suggested the potential of a pulsed laser source to enhance the UC PL over the continuous-wave (CW) one [29]. However, most of the attention has been dedicated to the source intensity rather than the pulsed source parameters.

Besides, fs laser can be used to introduce lattice site defects that can reduce the crystal field symmetry, enhancing the resulting UC.

Reviews on the chemical structure of Wavelength Upconversion Materials and Coatings that are appropriate for our application as well as synthesis methods of our material, coating methods (achieving the required chemical bonding and morphology), viral cell intra and extracellular interactions, body systems responses to each stage of the virus life cycle, are not mentioned in this work.

## 1.2- Review on Material Dependent Luminescence Enhancement Approaches for all Upconverting Materials of Concern:

In this review, all possible material optimization approaches are exhausted for the locally available lanthanide ions; Er, Yb, Gd so as to optimize the quantum efficiency of the upconverters of concern.

In this approach, one or multiple of the independent variables are varied to obtain a new value for any of the dependent variables. These Independent variables include: Doping Concentration, the choice of Multiple dopants, Synthesis Process Conditions, and Multi-Layering whereas the dependent variables include manipulating band gap, ion migration, refractive index, magnetic permeability, host material crystal field symmetry, phonon energy, the ion transfer process, shielding activators from quenching, hybridization and plasmonic enhancement. Plasmonic

Enhancement includes surface plasmon resonance (SPR), localized surface plasmon resonance (LSPR) which is usually applied to metals. An analogous one is applied to semiconductors where the electron density is sufficient to produce the required effect. Cavity and Fano-Feshbach modes competition are two more field enhancement mechanisms and bound states in the continuum.

1.2.1) Doping Concentration: the dopants are what effectively take part in the upconversion process, where the absorber (which is alternatively called the sensitizer or the activator) absorbs the low energy incident excitation and transfers it non-radiatively to the activator/sensitizer. The nature of dopants affect the UC process in a sense that the donor has a certain absorption efficiency, the spectral overlap between both ions, transition probability to higher states in the activator, metastate lifetime and number of available sites whether for absorption or emission and their distance, which is translated into concentration, influence the overall quantum efficiency of the upconverting nanoparticles. Doping concentration is an immensely affecting factor yet it is limited by the dose limit a human body can tolerate or a cell culture, on the small scale, can survive within.

### 1.2.1.1) Changing the Identity of Ln Dopants:

The need for doping emanates from the fact that maximum transition probability between E1 and E2 happens when the difference in the two eigenstates is maximum. Maximum transition probability from E1 to E2 means also maximum emission probability from E2 to E1. This is resolved by having an atom of a min of three levels in which a higher probability in time is given to second level and thus another photon can raise it to E3 which then emits to E1 without passing by E2. However, long lifetime of E2 means lower absorption rate required for UC. The solution of this is doping the luminescent sites into solid lattices with many Ln ions. A transition from an energy state to another by a photon happens when the photon energy interacts with the dipole of the atom (e.r); where r is the position of the electron, e, from the reference taken at the nucleus. These dipole transitions are the more allowed and desirable transitions required for UC than electronic ones.

Best combinations found are  $\text{Yb}^{3+}/\text{Tm}^{3+}$ , and  $\text{Yb}^{3+}/\text{Ho}^{3+}$ . The biodegradability of  $\text{Ho}^{3+}$  is unclear so far in literature.  $\text{Tm}^{3+}$  is not available at a commercial scale. Thus, the combination we choose should remain as it is.

### 1.2.1.2) Changing Ln concentrations:

This includes changing the concentration of either the sensitizer or the activator. Either of that is found to be

experimentally dependent on the host and the concentration of the other ion taking part in the energy exchange process.

For the sensitizer, a theoretical monotonic increase in the efficiency is predicted. This is supported experimentally by some hosts such as CaF<sub>2</sub>, till 100% of Yb concentration. However, other hosts, such as fluorides hosts, do not confirm this theoretical prediction for surface quenching is limiting the efficiency at a Yb concentration of 20% or above in Er/Yb matrix.

1.2.2) Choice of the Host Material :host material found so far, NaYF<sub>4</sub>, based on practical measurements of the upconversion. It should not take part in the upconversion process yet the sort of nonradiative energy transfer from a lower level in one donor to another activator requires breaking the crystal field symmetry for the transition to be allowed and this is where the host matrix influences the overall efficiency. Besides, the lattice phonon energy affects the QM efficiency in multiple other aspects explained. Like the dopants, the choice of the host matrix is also constrained by the cytotoxicity, biocompatibility, biodegradability and long-term health effects including the effect of on macrophages.

1.2.2.1) For phonon dynamics, the lower the phonon energy, the lower the non-radiative losses (i.e. the lower the number of photons needed to cause a radiative transition). Accordingly, NaYF<sub>4</sub> is the best for its lowest phonon cut-off energy and maximum UC efficiency.

The low phonon energy is required for several reasons. One of them is that phonon assistant energy transfer is involved in the UC process along with the resonant transfer. The weight of the nonresonant, phonon-assisted ET is not negligible for the mismatch between the energy levels of the absorber and activator we are dealing with. Phonon-assisted ET is advantageous for it prevents back transfer.

Second, if the phonon energy is high, this will change the energy levels upon phonon production, which would lower the UC efficiency.

The parity rule only works if there is a center for inversion symmetry in the crystal, forbidding E<sub>3</sub>-> E<sub>1</sub> transition. So, it must be broken and thus the hexagonal phase crystal structure is chosen while the cubic one is completely ignored. The moral is to prevent a center of inversion symmetry for the doped impurity ions participating in UC.

On the other hand, energy can be lost from an electronic transition to phonons increasing their vibrations. Also, undesired thermal coupling of energy levels can occur due to high perturbation. Thermal coupling can modulate the energy levels and thus photon transfer

probabilities, resulting in a lower UC QM efficiency. Last, UC happens due to transitions to incompletely filled 4f subshells, but they may be filled with phonons, though they are shielded from external perturbation. That's why phonon energy needs to be kept low.

1.2.2.2) For the local crystal field of the lattice, the lower the symmetry, the more f levels interactions with the higher energy levels and thus, the more the UC emission intensity. UC happens due to transitions to incompletely filled 4f subshells, but they may be filled with phonons, though they are shielded from external perturbation. For NaYF<sub>4</sub>, the hexagonal phase is much better than the cubic phase because of its lower symmetry.

Besides, the only way to relax the parity rule [the wave function describing the transition from E<sub>2</sub> to E<sub>1</sub> is the same as the one describing the transition from E<sub>1</sub> to E<sub>2</sub> with a negative sign] is the asymmetry of the crystal. Thus, this enables the parity-forbidden intra-4f electronic transitions of the lanthanide ion to become partially allowed by intermixing the f states with higher electronic configurations.

This local crystal field can be tailored by cationic doping which is found practically to lower the symmetry of the crystal field which causes the higher f intra-transitions to be parity forbidden.

Reported dopings like Li and Sc would not be suitable since these elements are not biodegradable.

Possible ways to reduce the crystal field symmetry are:

I- increasing the UC radiative transition rate by lowering site symmetry by introducing lattice defects through damaging the crystal to break a site or bond. This is suggested to be done by fs laser.

II-Doping:

A less symmetric alternative, e.g. sulfur, would solve the problem.

III-Choosing other absorbers with different energy level spacings but practical success has not yet been documented between rare earth ions and other non rare earth ions.

1.2.2.3)Crystal Structure:

The crystal structure is limited in our case by the materials. However, there have been only two reported crystal structures for the host of concern; the hexagonal and the cubic ones. Since the hexagonal phase lattice is the only one of them breaking parity rule due to breaking the center of inversion symmetry and this is the phase adopted in this work, no extra work will be done in this area.

#### 1.2.2.4) Impurities:

Impurities at a ppm level can prevent ion transfer between the intended sensitizer and absorber or provide a wrong ion transfer and emission route if radiative transitions exist in the impurities.

1.2.3) Synthesis Process Conditions: Exhaustively reviewing all synthesis process methods and the variables affecting the UC process, we found that: precursor concentration and quantity, relative concentration of dopants, calcination temperature, EDTA concentration, and finally milling can all affect the process and need to be optimized around the practically found values in literature. Since all of these are temperature conditions during synthesis -aside from the concentration issue previously explained-, they do not affect the biomedical design objectives nor they are constrained except by the final size that should remain within the biodegradable size.

1.2.3.1) Temperature: High temperature may increase IR emission if it matches phonon bandgap. Besides, lowering the temperature too much may prevent transition to higher states. The temperature in the application of concern, inside the human body, is a constraint. However, the material used has proved experimentally to increase its UC efficiency as temperature increases.

1.2.4) Multi-Layering whereas the dependent variables include manipulating band gap, ion migration, refractive index, magnetic permeability, host material crystal field symmetry, phono energy, the ion transfer process, shielding activators from quenching, hybridization and plasmonic enhancement. Plasmonic Enhancement includes surface plasmon resonance (SPR), localized surface plasmon resonance (LSPR) which is usually applied to metals. An analogous one is applied to semiconductors where the electron density is sufficient to produce the required effect. Cavity and Fano-Feshbach modes competition are two more field enhancement mechanisms and bound states in the continuum.

1.2.4.1) Suppression of Surface Deactivation Cites:

Surface deactivation sites include surface defects, lattice strains, as well as ligands and solvents that possess high phonon energy. They lower UC by trapping phonons or making them travel a long distance among these quenching sites rather than being utilized in the UC process, specially when a high concentration of Yb is used while Yb does not have a higher energy radiative state.

The solution for this problem could be any of the following mechanisms:

#### I) Homogeneous Core-Shell Structure:

This structure has both the core and the shell possessing the same host, which guarantees the epitaxial growth and creates a homogeneous interface between the core and the outer shell. For example, great enhancement was reported of  $\text{NaYF}_4@x/\text{NaYF}@Y$  OR  $\text{NaYF}_4@X,Y/\text{naYF}_4$ . The same case has been with  $\text{NaGdF}_4$ . However, one practical limitation of this approach is that it is difficult to prove core-shell formation for equal TEM contrast. Thus, size increase or PL change is what can be used to prove that.

#### II) Heterogeneous Core-Shell Structure:

The core and the shell possess hosts that have low lattice mismatch.  $\text{CaF}_2$  or  $\text{NaGdF}_4$  have low matrix mismatch to  $\text{NaYF}_4$  and have been implemented, yielding promising results. In contrast to the previous approach, this approach can be more easily proved by TEM through the contrast of both the core and the coating.  $\text{CaF}_2$  provides more effective quenching resistance than  $\text{NaYF}_4$  (through the homogeneous structure mentioned before). Incorporating silica in such core-shell structure has been very common, but it slightly improves UC intensity. Furthermore, biodegradability of silica is debatable.

#### III) Active Core-Shell Structure:

It either implements one of the previous two core-shell structures besides doping the shell with a Ln ion so that the shell now both prevents quenching and participates in the UC. ET between the two layers is assumed to occur as well due to the little lattice mismatch between the two hosts.

#### IV) Defect Tuning:

This is based on discovering the sites of defects causing photon trapping and then filling it through charge transport, for example. This has a significantly good effect on the duration of the luminescence. It has been proved that UC NPs can be long lasting up to several hours, called long lasting phosphors [30]. However, in this application, long lasting could harm the cells by the UVC irradiation despite its important to minimize the irradiation to which the body is exposed to. Most importantly, having these defects so as to maximize the luminescence duration sacrifices the most probable chance of having photon traps and thus sacrificing PL intensity.

#### 1.2.5) Suppressing of Quenching Factors:

Several explanations have been suggested for surface quenching. One of them is the back transfer from the activator to the sensitizer. This would lead the sensitizer to finally emit from a radiative state of a lower energy than

the absorbed, leading to down conversion. Another reason is the energy diffusion across the same type of ions, usually when the concentration of that ion is highly increased so that the distance among the ions becomes small. Within 5nm, these interactions become excessive and favored, leading to a significant influence on the UC efficiency. The problem is that activators lower levels become filled, from which there would be no forward transfer to the upper radiative states.

The reason for back transfer in Er/Yb is that their energy levels match so well, causing mid IR emission.

This quenching can be suppressed by suppressing the quenching sites to which phonons transfer in the lattice e.g by optimizing the Ln(s) concentration. Another way to think about this problem is introducing energy mismatch like if the receiver has E2 that is slightly lower than E2 of the absorber. Last, for emission from the lower levels of Er can occur, this requires choosing elements with longer lifetime at E2.

Quenching could be also suppressed by two other experimental mechanisms. First, introducing a shell which confines the energy in the core layer containing the activator so as to protect it from the surface defects existing now in the upper shell that would otherwise have acted as traps for the photons causing long distance migration and thus losing the UC path. This led to a field enhancement up to 45 fold using sandwich structure. Furthermore, manipulating the lattice structure and the inter-dopants distance so that the lattice separation is much more than the inter-ionic separation has proved an effective doping method to alleviate quenching for the excitation would be now confined in the sublattice scale [31].

Second, through high energy excitation to overcome the rate of depopulation of upper levels (cross relaxation or quenching) from the activator ions [32]. Thus, this means that lowering quenching would also lower the excitation power.

So, all of the above methods require multiple iterations of the material synthesis.

## 2- Review on Wavelength Tunability Mechanisms

### 2.1) Forester/Luminescence Resonant Energy Transfer (FRET/LRET):

These are the main mechanisms leading to wavelength tunability at the end. (FRET) is a mechanism describing energy transfer from a donor fluorophore to an acceptor fluorophore through nonradiative dipole–dipole coupling, which is sometimes called exciton migration. LRET is the same as FRET but with a radiative transition.

### 2.2) Core-Shell Structure:

This would be important for it protects from quenching of certain wavelengths.

### 2.3) The identity of Ln incorporated:

Obviously, this is the main reason for tailoring the emission for the different energy levels supported.

Examples of other processes they affect:

#### I) Cross relaxation:

introducing a dopant having lower radiative states emphasizes down conversion over upconversion

#### II) Introducing multiple Ln(s) leading to involving Energy Migration UC besides ETU:

reported that efficient upconversion emission is also possible for lanthanide activators (Eu<sup>3+</sup>, Tb<sup>3+</sup>, Dy<sup>3+</sup>, and Sm<sup>3+</sup>) without long-lived intermediate energy states via energy migration mediated upconversion processes.

#### III) Interparticle Energy Transfer:

It is usually implemented in a liquid medium in which some nanoparticles constitute the host doped with the absorbers NPs and other nanoparticles constituting the host doped with the activators.

### 2.4) Ligand Effects:

The use of the ligand is essential for controlling the size and the shape of resulting UC NPs using chemical reaction in a solution phase. They are basically the chemicals used for functionalization and/or surface treatment. They result in changing the phonon energy as well as providing energy levels (active sites) that take part in the photon transfer process.

### 2.5) Antenna Effect:

One utilization of this has been observed in the energy transfer between die as an antenna, for example, and NaYF<sub>4</sub>:Yb,Er. However, QY remained low around 0.1% as compared to the QY of .3% obtained without the die. Moreover, the dye does not tune the color.

### 2.6) Shape Induced Surface Effects:

Two important effects of the nanoparticles surface have to be considered; the first is on the size and the other is on the morphology. A decrease in size is associated with a decrease in QM efficiency but a blue shift of the emission in some materials. However, this is material dependent and cannot be generalized. Besides, different morphologies of the same material affect the emission wavelength, but no explanation has been provided for these experimental results so far. However, we have a limitation on the morphology by the currently available precursors.

## III. CONCLUSION AND ROADMAP FOR LUMINESCENCE ENHANCEMENT MECHANISMS:

First, the core layer that achieves the required electromagnetic interactions should be decided, abiding by the design constraints on the size, nature of the material and predictably achieving the required interactions. There will be a trade-off between the size and the required electromagnetic interaction.

Second, the coating material should be chosen so as to target a specific cell receptor and minimize the non-specific cell interactions. The coating thickness should be optimized so as to guarantee the lack of influence on the electromagnetic interactions between the excitation source and the core layer, which contains the upconverting material. The coating should also enhance the biocompatibility and reduce the cytotoxicity, increasing the lifetime of the particles to the required extent. It also should be chosen such that it can chemically bind to the core layer.

Third, for the field enhancement mechanism, it should not resort to using any non-biodegradable or cytotoxic material, and it should also maximize the intake from the incident excitation and not just respect the dose exposure limit of the irradiation. Furthermore, it should maximize the predictable required response to the incident excitation to the point that the overall QM efficiency meets the treatment dose required for the receptor.

Thus, the material -dependent and surface texturing are the only two approaches that fulfill these design objectives, based on the applicability problems for the remaining approaches. However, the material dependent approach should be guided, when possible, by the verified theories or experimental studies done in this area.

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#### V. CONFLICT OF INTERESTS

The authors declare no conflict of interests

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