Structure design and applications of upconversion nanoparticles

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Chapter 1

Introduction
1.1 Background

Usually, nanomaterials are defined as materials whose size is at least in one dimension limited to 1-100 nm. Among these nanomaterials, the lanthanide (Ln) ions doped upconversion (UC) nanomaterials, capable of converting several photons to one higher energy photon, are very attractive for a broad range of applications (e.g. display, biology, anti-counterfeiting, solar cells, etc).\textsuperscript{1-7} For example, for the biomedical field, UC nanomaterials allow the excitation wavelength to fall in the so-called “bio-window” (~650-1300 nm), \textit{i.e.}, the optimal spectral range for minimal absorption of human tissue and negligible auto-fluorescence of the biological background (Figure 1.1).\textsuperscript{4,8} Therefore, this type of material is expected to significantly improve the quality of bio-imaging, labelling and therapy.

![Absorption spectra of main components in human tissues.](image1)

\textbf{Figure 1.1} Absorption spectra of main components in human tissues.

Lanthanides refer to a series of elements in the periodic table. They consist of the 15 Ln elements from Lanthanum to Lutetium (with atomic numbers from 57 to 71), as shown in Figure 1.2.

![Lanthanides in the periodic table of chemical elements.](image2)

\textbf{Figure 1.2} Lanthanides in the periodic table of chemical elements.
Lanthanides have special electronic configurations. The electronic configurations of Ln atoms are given by:

\[ 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^n 5s^2 5p^6 5d^m 6s^2, \ n=0-14, \ m=0, 1 \]

On the other hand, lanthanides are mostly stable in the trivalent form (Ln\(^{3+}\)), whose relevant electronic configurations are given by:

\[ 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^n 5s^2 5p^6, \ n=0-14 \]

It should be noted that for the electron filling 5s\(^2\)5p\(^6\) states have priority over 4f\(^n\) states, which means that the 4f\(^n\) electrons are shielded by the outer 5s\(^2\)5p\(^6\) electrons. This is the reason that the Ln\(^{3+}\) are usually characterized by sharp absorption and emission peaks, relatively weak absorption and relatively long lifetimes of the excited states. Furthermore, because of the shielding of 5s\(^2\)5p\(^6\) electrons, these spectral characteristics are only weakly affected by the environment (such as surrounding crystal field).\(^9\)

Theoretically, dipole-dipole transitions within the 4f shell (f-f transition) are parity forbidden. Actually, this rule is strictly followed for isolated atoms. If the ions experience interactions with their surroundings, these transitions are often observed. Pioneering work of Judd, Ofelt, Blasse, Henderson, Imbusch and others has demonstrated that this partial relaxation of the parity rule comes primarily from the uneven components of the crystal field when the lanthanide ions are embedded in a crystal without inversion symmetry.\(^10-13\) Specifically, due to the crystal field the energy levels of ions will split due to the electrostatic interaction in the crystal environment - also known as “Stark splitting” - and the 5d configuration is “mixed” with the 4f\(^n\) configurations. The overlapping 4f5d configurations lead to a kind of “partially allowed” dipole-dipole transition, making it possible to observe luminescence from the 4f-4f transition.\(^14, 15\) Notably, this “partially allowed” transition is also strongly affected by the selection rules, resulting in relatively weak transition probabilities and long lifetimes of energy levels (reaching up to tens to hundreds of milliseconds). Besides, due to the complex electronic configurations, the energy levels of Ln\(^{3+}\) are mostly rich and usually exhibit a ladder-like feature (Figure 1.3). The ladder-like energy levels and relatively long lifetimes enable a relatively effective UC luminescence.
1.2 Mechanisms of upconversion luminescence

Upconversion luminescence is a sort of incoherent Anti Stokes emission where absorption of several low energy photons results in emission of a higher energy photon. It was firstly proposed by Bloembergen in 1959 and later reported independently by Auzel and Ovsyakin & Feoflov. After that UC mechanisms have been intensively studied and so far three major mechanisms are widely accepted, i.e. (a) excited state absorption (ESA); (b) energy transfer upconversion (ETU); and (c) photon avalanche (PA).

(a) Excited state absorption (ESA)

ESA is the simplest UC process. In this process, UC is induced by the sequential absorption of photons within the levels of a given ion. As shown in Figure 1.4, because of the rich ladder-like energy levels and long lifetime of intermediate energy levels, excited Ln ions are capable of absorbing another photon to be excited to higher energy levels (E1→E2). The Ln ions in excited state E2 may relax radiatively to the ground state resulting in UC luminescence. In principle, ESA process could occur in all the lanthanide ions with matched energy schemes.
(b) **Energy transfer upconversion (ETU)**

The ETU process usually takes place between two types of Ln ions, indicated as activator and sensitizer, respectively. As shown in Figure 1.5, upon absorption of one photon the sensitizer in its ground state G is excited to the excited state E1. Different from the ESA process, the E2 state of the activator is populated via energy transfer from two or more of its neighboring excited sensitizing ions. UC luminescence is generated when the activators in E2 decay back to the ground state. Usually the sensitizer, *e.g.* Yb$^{3+}$, has an absorption cross section larger than that of the activator, *e.g.* Er$^{3+}$. ETU has been proven to be the most effective upconversion process and most of the UC systems employed in applications are based on the ETU mechanism.

(c) **Photon avalanche (PA)**

PA is a more complicated process. It usually includes the processes of ESA and ETU in populating the excited states. As shown in Figure 1.6, this process starts with a weak ESA process in ion 2, pumping electrons to energy level E2 (Ion 2) from E1 (Ion 2). The electron pumped to energy level E2 (Ion 2) will soon relax back to energy level E1 (Ion 2), transferring simultaneously its energy to the neighboring ion 1. As a result, Ion 1 is excited from its ground state G to energy level E1 (Ion 1). If the two energy levels of E1 (Ion 1 and Ion 2) match well, the energy at E1 (Ion
1) tends to be transferred back to the initial E1 of Ion 2, repopulating E1 (Ion 2). Together with the newly obtained E1 population (Ion 2) promoted by additional photons, these repopulated E1 states (Ion 2) are ready to be pumped to E2 (Ion 2) again and get involved in another round of circulation. The “pumping→transferring→pumping” loop will run continuously, causing an effective accumulation of excited states. When the accumulation reaches a critical point, a large scale of excited E2 states (Ion 2) decay back to the ground state G, producing emissions with an avalanching effect. However, the loop of PA process only works well in very limited systems. Furthermore, it usually requires a relatively high pump intensity (above a certain threshold) to make the accumulation effective. These drawbacks have limited the PA process to be widely used in practical applications.

![Scheme of PA upconversion mechanism](image)

**Figure 1.6** Scheme of PA upconversion mechanism

Apart from the three classic UC mechanisms mentioned previously, other mechanisms contribute to the UC luminescence process as well. These include (d) cross relaxation (CR), (e) cooperative sensitization upconversion (CSU), (f) energy migration upconversion (EMU), *etc.* as depicted in Figure 1.7.
**Figure 1.7** Scheme of CR, CSU and EMU upconversion mechanism

**(d) Cross relaxation (CR)**

CR results from the interactions between two ions and occurs when the distance between the ions is small enough. As shown in Figure 1.7 (upper left), the excited ion 1 can then transfer part of its energy to the neighboring ion 2 along the E2 (Ion 1) + E1 (Ion 2) → E1 (Ion 1) + E2 (Ion 2) path, provided that the energy differences of the two ions match each other.\(^{20, 21}\) The CR process is widely regarded as being mainly responsible for the well-known “concentration quenching effect” (see section 1.4.3). CR may also be used to manipulate the UC emission spectrum and UC channel.

**(e) Cooperative Sensitization Upconversion (CSU)**

CSU involves three ions as shown in Figure 1.7 (the upper right). After being excited to excited state E1, Ion 1 and Ion 3 (the same type) interact simultaneously with Ion 2. Ion 2 is pumped to a higher energy level at the expense of the energies of Ion 1 and Ion 3. The excited state relaxes back to the ground state in Ion 2 and emits an UC photon. The cooperative transitions correspond to a higher order of perturbation, which involves quasi-virtual pair levels. Therefore, its efficiency is generally about 3-4 orders of magnitude lower than that of ESA or ETU process. At present, the CSU mechanism has been observed in the UC process of Yb\(^{3+}/\)Tb\(^{3+}\), Yb\(^{3+}/\)Eu\(^{3+}\), and Yb\(^{3+}/\)Pr\(^{3+}\) ion pairs.\(^{22-24}\)

**(f) Energy Migration-mediated Upconversion (EMU)**

Liu and Wang recently demonstrated the EMU in nanomaterials.\(^{25}\) This mechanism is similar to the ETU process, but with more ions involved over a longer distance. A typical example of the EMU process is shown in Figure 1.7 (lower half). Excited Ion 1 interacts with Ion 2 in an ETU
process. Ion 2 will transfer its energy to the neighboring Ion 3, followed by a random hopping between the medium ions (Ion 3) until being extracted by Ion 4 to generate UC emissions. This multi-step energy migration mechanism allows for the possibility to produce effective UC emissions even when Ion 1 (sensitizer for harvesting excitation photons) and Ion 4 (activator for upconversion luminescence) are quite far apart (such as several nanometers). Another form of the EMU process starts with migration of excited states and ends with an ETU process. This part will be discussed in detail in section 1.6.2 and Fig 1.11.

It should be noted that factors such as ions doping concentration, host materials, and types of dopant ions will also influence the real luminescence mechanism. Therefore, when working on some specific UC materials, it is much safer to make an analysis of the mechanism based on a comprehensive consideration of all possible influencing factors.

1.3 Lanthanide-doped upconversion nanoparticles

Activator (also named as emitter) and sensitizer co-doping was proven to be an effective approach for increasing upconversion luminescence.$^{1,26}$ Most ETU dominated UC nanosystems are co-doping systems, including host, energy donor (sensitizer) and accepter (activator) as shown in Figure 1.8.

![Figure 1.8 Typical structure of lanthanide-doped upconversion nanoparticles](image)

Host materials are used to provide a proper crystal field environment for the UC processes (including absorption, energy transfer/migration and UC emission). The role of the sensitizers is to absorb energy from a light source and transfer it to emitters. Typical lanthanide sensitizers are Yb$^{3+}$ and Nd$^{3+}$. The Yb$^{3+}$ ion has a relatively large absorption cross-section around 980 nm ($\sim 9.11 \times 10^{-21}$ cm$^2$), associated with the $^{2}F_{7/2} \rightarrow ^{2}F_{5/2}$ transition.$^{27}$ The absorption cross section of Nd$^{3+}$ around 800 nm is $\sim 1.2 \times 10^{-19}$ cm$^2$ and is associated with the $^{4}I_{9/2} \rightarrow ^{4}F_{5/2}$ transition.$^{27}$ The most commonly used activators include Er$^{3+}$, Tm$^{3+}$ and Ho$^{3+}$. Their UC emission wavelengths and associated transitions are listed in Table 1.

**Table 1 Typical lanthanide activators and UC emissions and transitions$^{28-30}$**

<table>
<thead>
<tr>
<th>Activators</th>
<th>UC emissions (nm)</th>
<th>Associated transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tm$^{3+}$</td>
<td>290, 345, 362, 450, 475</td>
<td>$^{1}I_{6} \rightarrow ^{3}H_{6}$, $^{1}I_{6} \rightarrow ^{3}F_{4}$, $^{1}D_{2} \rightarrow ^{3}H_{6}$, $^{1}D_{2} \rightarrow ^{3}F_{4}$, $^{1}G_{4} \rightarrow ^{3}H_{6}$, $^{1}G_{4} \rightarrow ^{3}F_{4}$, $^{3}F_{3} \rightarrow ^{3}H_{6}$</td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>415, 525, 542, 655</td>
<td>$^{2}H_{9/2} \rightarrow ^{4}I_{15/2}$, $^{2}H_{11/2} \rightarrow ^{4}I_{15/2}$, $^{4}S_{3/2} \rightarrow ^{4}I_{15/2}$, $^{4}F_{9/2} \rightarrow ^{4}I_{15/2}$</td>
</tr>
<tr>
<td>Ho$^{3+}$</td>
<td>542, 655</td>
<td>$^{5}F_{4}$, $^{5}S_{2} \rightarrow ^{5}I_{8}$, $^{5}F_{3} \rightarrow ^{5}I_{8}$</td>
</tr>
</tbody>
</table>
1.4 Construction of UCNPs with high UC luminescence efficiency

The UC efficiency is one of the most important parameters of UC materials. It is quantified by the UC quantum yield (QY) parameter defined as the ratio of the number of emitted UC photons to the number of absorbed photons. The UC luminescence intensity is usually described by formula (1-1):\(^{31}\)

\[ I_{UCL} = kp^n \] (1-1)

where \( I_{UCL} \) is the UC luminescence intensity, \( k \) a material-related coefficient, \( P \) the power density of pump laser and \( n \) the number of the photons required to induce one upconverted photon. In practice, the obtained “\( n \)” values are usually not integers -which can be attributed to the saturation effect of the intermediate states and involvement of various UC processes-and larger than 1.\(^{31}\) It was reported that the UC QY is only 3±0.3% under 150 W/cm\(^2\) excitation power density for NaYF\(_4\): 20%Yb, 2%Er bulk material.\(^{32}\) Furthermore, this value decreases by more than one order of magnitude when the material is nanometers in size. Such values often do not match the requirements for practical applications.

In recent years, numerous efforts have been devoted to increase the UC luminescence efficiency, especially for the nanosized materials with potential biomedical and other applications. As we look back on these efforts, five general approaches have been demonstrated to be effective in QY enhancement, i.e.
1) Host material manipulation
2) Plasmonic enhancement
3) Doping concentration optimization
4) Surface passivation
5) Dye sensitization

1.4.1 Host material manipulation

A proper host material plays an important role in constructing efficient UCNPs, the lattice phonon energy associated with vibrations of the lattice being a key parameter. The excited ions can relax to a lower energy state via two ways, either by emission of a photon (radiative relaxation) or by transferring the energy to the lattice surrounding (nonradiative relaxation). An ideal host material for upconversion luminescence should thus be characterized by a low lattice phonon energy. Theoretically, any material that satisfies such conditions can be regarded as a potential host material candidate for UCNPs. Fluoride host materials -especially sodium rare-earth fluoride (NaREF\(_4\))- are till now the most effective host materials for UC. Apart from their chemical stability, their lattice photon energy is low (~350 cm\(^{-1}\)).\(^{33}\) So far, the most efficient NaREF\(_4\) host materials are hexagonal NaYF\(_4\), NaGaF\(_4\) and NaLuF\(_4\).

The crystal phase is also important for an effective UC luminescence. The local site symmetry and crystal field strength around Ln\(^{3+}\) dopants determine their intrinsic electronic transition rates. Taking NaREF\(_4\) as example, it is confirmed that hexagonal phase UCNPs are able to produce over 10-fold higher UC emissions than their cubic counterparts. In the cubic phase structure, the ion sites are highly symmetric, whereas in hexagonal phase structure there are two types of low-symmetry cation sites where Na\(^+\) and RE\(^{3+}\) distribute randomly. The low crystal structure symmetry is favorable for increasing the radiative transition rate of excited states, which leads to
a more efficient UC emission.

Another promising approach is to tailor the local crystal field around the activators by intentionally doping extra non-luminescent cationic ions such as Li\(^+\), Sc\(^{3+}\), and so on.\(^{34-36}\) The introduced cationic ions are able to partially replace the initial cationic ions in the crystal lattice or occupy the interstitial sites around the activators. This strategy is in favor of further lowering the local symmetry around the activators.

### 1.4.2 Plasmonic enhancement

In the case of the electromagnetic interaction between metal and incident light of a specific wavelength, oscillating electrons at the interface of metallic structures are able to generate so-called localized surface plasmon resonances (LSPR). As proved by many previous studies, LSPR is able to positively influence the QY of fluorescent phosphors such as dyes, QDs and UCNPs if the interaction distance is appropriate.\(^{37,38}\) In details, there are usually three working strategies:

a) Depositing UCNPs onto a layer of gold islands, dense metal nanoparticles (Au or Ag), or 3D plasmonic antennas.

b) Attaching or self-assembling metallic nanoparticles on the surface of UCNPs.

c) Utilizing multilayer nanostructures such as UCNPs@silica@metal.

All these strategies are highly dependent on a precise tuning of the distance between nanoparticles and metallic structures. In this thesis, we do not discuss this aspect in more detail and interested readers are referred to previously published reviews.\(^{39,40}\)

### 1.4.3 Doping concentration optimization

Potentially, the easiest way to improve the UC QY is to raise the dopant concentrations of Ln ions within the nanoparticle. However, the optimized doping concentration of Ln ions is usually restricted to a relatively low level, i.e., in the range of 0.2-2% for activators (e.g. Er\(^{3+}\), Tm\(^{3+}\) or Ho\(^{3+}\)) with 20-40% for sensitizer (Yb\(^{3+}\)).\(^2\) Further increase of the doping concentration of Ln\(^{3+}\) could make the cascade energy transfer/migration processes more effective, leading to the trapping of energy in the quenching sites and quenching of the UC emission.\(^{33, 41}\) This phenomenon is the so-called “concentration quenching” effect. Over the years, various efforts have been made to increase the optimal doping concentration of Ln\(^{3+}\) ions in nanoparticles. Recently, it was reported that concentration quenching may be improved in some specially designed nanostructures. For example, in the ultra-small (diameter 7-10 nm) NaYF\(_4\): x\% Yb\(^{3+}\), 2% Tm\(^{3+}\) nanoparticles, it was demonstrated that the near-infrared UC emission of Tm\(^{3+}\) at 808 nm was increased by 43 times with the increase of the relative content of Yb\(^{3+}\) ions from 20% to 98%.\(^{42}\) On the other hand, a monotonous increase of the Yb\(^{3+}\) concentration up to 98% resulted in about one order of magnitude enhancement of UC intensity in KLu\(_2\)F\(_7\): x\% Yb\(^{3+}\), 2% Er\(^{3+}\) nanoparticles.\(^{43}\) The particularity of the KLu\(_2\)F\(_7\) crystal structure is that the doped Yb\(^{3+}\) ions were distributed as numerous discrete clusters within the nanocrystal, and the intra-cluster Yb\(^{3+}\) ions interact with each other stronger than inter-cluster Yb\(^{3+}\) ions since the distance of the former is shorter than the latter. Consequently the excited Yb\(^{3+}\) ions tend to localized within their own clusters, instead of migrating to other clusters. With this approach, the suppression effect towards concentration quenching effect can be notably enhanced under the condition that the interior space of these clusters is free from quenching centers.
Very recently, several groups including ours have reported independently a new strategy to overcome the “concentration quenching” effect. Simply by an inert shell coating, the doping concentration of Er\(^ {3+}\) in a NaYF\(_4\) nanohost can reach 100% without UC emission quenching. Further details will be discussed in Chapter 3.

### 1.4.4 Surface passivation

The surface properties of UC nanomaterials are closely related to the UC emission efficiency of Ln\(^ {3+}\), as there exist on the surface various quenching sites (e.g., surface defects, lattice strains, surface ligands and solvent molecules) that possess high-frequency vibrational modes.\(^ {44,45}\) It has been demonstrated that a notable increase (over 10 times) in UC emission was accomplished by giving UCNPs a protective shell. At present, the commonly applied shells can be categorized into two main forms according to their response to incident light: inert shells and active shells.

Inert shells like NaYF\(_4\), NaGaF\(_4\) and NaLuF\(_4\) do not contain any “active” Ln\(^ {3+}\) ions such as sensitzizers or activators. This strategy is simple but effective in spatially separating the sensitzizers/activators in the core and the surface quenching sites.\(^ {46,47}\) An active shell refers to a shell which contains activators or sensitzizers. The active shell usually plays two simultaneous roles: (i) deactivating the surface-related quenching sites, similar to the inert shell, and (ii) introducing additional core-shell energy transfer processes.\(^ {48}\) The idea of localizing UC-related Ln\(^ {3+}\) ions within different layers in the active core/active shell structure provides considerable control for UCNP-related function designs.\(^ {8}\)

### 1.4.5 Dye sensitization

Although Nd\(^ {3+}\) and Yb\(^ {3+}\) ions have been used to increase the absorption cross section of UC systems, the nature of 4f-4f forbidden transition remains an essential restriction for the Ln\(^ {3+}\) ions. Starting from 2012, infrared organic dyes have become a popular candidate as antenna ligands to improve the absorption ability of UC nanoparticles.\(^ {49-51}\) According to the report of Zou et al., the organic infrared dye (IR-806) sensitized NaYF\(_4\):Yb\(^ {3+}\), Er\(^ {3+}\) nanoparticle has a much larger extinction coefficient (~5 × 10\(^ 6\) times) than the UC nanoparticle itself. It was demonstrated that the entire UC emission output of dye-sensitized nanoparticles was vastly improved to about 3300 times.\(^ {49}\) Nevertheless, most organic molecules that are suitable for sensitizing UCNPs suffer harmful photobleaching phenomenon. Photostability concerns thus generally lead to hesitance to employ organic dye related nanomaterials.

### 1.5 Emission and excitation spectral manipulations of UCNPs

Depending on the specific application requirements, manipulations of UCNPs emission and excitation spectral characteristics have also been attached a lot of interest.

#### 1.5.1 Emission spectral manipulation

The feature of UCNPs emissions comes from the rich ladder-like energy levels of Ln\(^ {3+}\) activators. Contributions have been made to manipulate UC emissions in order to meet the requirements of diverse applications. For in vivo bioimaging applications, near-infrared or red emissions are pursued since they have a relatively deep tissue penetration. When it comes to photosensitizing theranostics, ultraviolet or blue emissions have a high priority owing to the high photon energy they possess, which is able to trigger related photochemical reactions. Another example is that
although multi-band emissions have advantages in multicolor labeling and multiplexed biodetection, single band emissions are still highly desired as an ideal solution to avoid different channel signals performing fluorescence cross talk in multiplexed biosensing. All these considerations explain the surge in recent research activities on UC emission manipulation.

(a) Multi-band emission

The strategies to tune the output color of UCNPs mainly involve two aspects: 1) host lattice manipulation and 2) control of dopant combination and concentration. The first strategy (host lattice manipulation) is closely related to the synthetic processes. For example, the UC multicolor output of NaYF₄: Yb, Er nanoparticles primarily comes from the influence of particle crystallinity and can be simply adjusted by variation of reaction time and temperature.⁵², ⁵³ Changing the host from NaYF₄ to NaScF₄, the UC emission color from Yb⁴⁺/Er³⁺ doped UCNPs varies from green to red.⁵⁴

The other strategy, i.e., manipulation of dopant combinations and concentrations, is found to be more effective and systematic in regulating UC emission. Series of studies on two typical co-doping systems, Yb⁴⁺/Er³⁺ and Yb⁴⁺/Tm³⁺ pairs, have shown the feasibility to produce multicolor output ranging from visible to near-infrared regions. For example, a general approach was reported by Wang and Liu to fine-tune the UC emission color in a broad spectral range by varying the concentration of Yb³⁺.⁵⁵ Various multi-shell structures have been developed to fully utilize features of different emitters to produce the desired multicolor output. For example, sandwich-structured UCNPs featured with a NaYbF₄ layer sandwiched in the middle of two NaYF₄ matrix layers have been able to fine-tune UC emissions by (i) varying the dopant combinations and concentrations in each of the shells and (ii) adjusting their thicknesses.⁵⁶

Apart from the two main strategies mentioned above, other approaches have been introduced to realize multi-color output such as encapsulation to integrate different optical materials (UCNPs, QDs, organic dyes, etc.) into one composite particle. For example, by tuning the molar ratio between NaYF₄: Yb, Er and NaYF₄: Yb, Tm nanoparticles encapsulated within polystyrene beads, the emission changes from green to blue.⁵⁷ However, the introduction of molecular fluorophores and QDs will evoke additional drawbacks that cannot be ignored like low photostability, worrisome toxicity, or a compromising sacrifice of UC emission intensity.

(b) Single band emission

As mentioned above, single-band emission with chromatic purity is desired to avoid interference of signals in bio-detection. Especially in the visible spectral region (~ 400-700 nm), red light has advantages such as minimal scattering and less absorption of the background. Single-band red emission of UCNPs thus has also attracted considerable research interests. However, it is not easy since the nature of UCNPs, i.e., abundant ⁴fⁿ electronic states, generally leads to multi-wavelength under single wavelength excitation conditions.

Generally, the basic strategies to achieve single-band emissions in UCNPs are (i) controlling the population of excited states or (ii) filtering the superfluous emission bands. At present, the former strategy mainly depends on the control of energy transfer in the UC process via the dopant combination or concentration. A typical example of single-band red UC emission of KMnF₃: Yb, Er nanostructure was reported by Liu and co-workers, where the Er³⁺→Mn²⁺ energy transfer depopulates the green-emitting energy levels (²H₁₁/₂ and ⁴S₃/₂) efficiently, and the energy back
transfer of Mn$^{2+}$→Er$^{3+}$ populates the red-emitting energy level ($^4F_{9/2}$).\textsuperscript{58} Another similar example is introducing Ce$^{3+}$ into NaYF$_4$: Yb, Ho nanoparticles. The Ce$^{3+}$ co-doped UCNPs produce emissions with a high red-to-green ratio by means of Ce$^{3+}$→Ho$^{3+}$ and Ho$^{3+}$→Ce$^{3+}$ energy transfer.\textsuperscript{59} It was also reported that the Er$^{3+}$/Tm$^{3+}$ combination is able to generate a pure red emission resulting from the energy transfer between Er$^{3+}$ and Tm$^{3+}$\textsuperscript{60}

The latter strategy is usually achieved by introducing extra absorbers, quenchers and other donors/acceptors for energy transfer as spectra filters. Photonic crystals and other fluorophores (organic dyes, QDs, and Au nanoparticles) have been demonstrated to interact with Ln$^{3+}$ emitters to produce highly purified red emission, a selective “screen off” effect on the UC emission spectra.\textsuperscript{61} In Chapter 3, we will discuss a new strategy to produce quasi-chromatic red emission.

1.5.2 Excitation spectral manipulation

Traditionally, excitation wavelength of UCNPs are often limited to 980 nm, which is mainly due to the absorption of the sensitizer ion, Yb$^{3+}$. Compared with Ln$^{3+}$, dye molecules exhibit much broader absorption spectra and larger absorption cross sections. They were thus introduced as “antenna molecules” to increase the excitation range of UCNPs. With the assistance of energy transfer between near-infrared dyes and UCNPs, a broad excitation band of UC (ranging from 700 to 1000 nm) has been achieved.\textsuperscript{49} However, it is hard to ignore the drawbacks like photobleaching and instability that organic dyes may bring, which limits their applications.

The quest for alternatives is thus still continuing. An early attempt was to use a 915 nm laser (instead of 980 nm) to excite the Yb$^{3+}$-sensitized UCNPs.\textsuperscript{62} Despite that this excitation approach suppressed overheating effects to a certain extent due to the relatively weak water absorption around 915 nm,\textsuperscript{63} the UC emission intensity was attenuated. On the other hand, Prasad and co-workers reported a method to shift the excitation wavelength to ~1500 nm utilizing the $^4I_{15/2}$→$^4I_{13/2}$ transition of Er$^{3+}$.\textsuperscript{64} However, this spectral region is not ideal for bioimaging and biodetection in vivo due to the relatively strong absorption of water. In 2013, a new strategy was introduced to shift the excitation band of UCNPs to ~800 nm. The construction of the energy transfer route as Nd$^{3+}$→Yb$^{3+}$→Er$^{3+}$ in NaGdF$_4$:Yb, Er@NaGdF$_4$:Nd, Yb core-shell structures made full use of the large cross section of Nd$^{3+}$ around 800 nm, and led to a relatively high UC emission intensity.\textsuperscript{65} Because of the reduced water absorption at 808 nm (only about one twentieth compared with that of 980 nm), this different route also minimized laser-induced overheating effects. As a result, the Nd$^{3+}$-sensitized UCNPs are better for in vivo applications requiring longer excitation durations or higher excitation power densities.\textsuperscript{66, 67}

1.6 Luminescence dynamics of lanthanide doped upconversion materials

The time behavior of the emission is very important for understanding the excited state properties of luminescent materials. Usually upconversion luminescence decay curves exhibit rise and decay components as shown in Figure 1.9, reflecting the populating and depopulating processes of the emissive state.
1.6.1 Rate equations for the analysis of UC dynamics

To analyse the UC dynamic process, the most widespread treatment is to simplify the complex UC processes to a one-ion (sensitizer) to one-ion (activator) interaction. For example, if a two-level sensitizer and a three-level activator are employed (as shown in Figure 1.10), the UC dynamic process can be described by the rate equations below:\[^8\]

\[
\begin{align*}
\frac{dn_{S1}}{dt} &= \rho_{exc}\sigma n_{S0} - W_0 n_{S1} n_{A0} - W_1 n_{S1} n_{A1} - A_{S1} n_{S1} \\
\frac{dn_{A1}}{dt} &= W_0 n_{S1} n_{A0} - W_1 n_{S1} n_{A1} - A_{A1} n_{A1} \\
\frac{dn_{A2}}{dt} &= W_1 n_{S1} n_{A1} - A_{A2} n_{A2}
\end{align*}
\]

where \( n_{Sx} (x = 0, 1) \) and \( n_{Ax} (x = 0,1,2) \) represent the populations of energy levels of the sensitizer (\( n_{Sx} \)) and activator (\( n_{Ax} \)), respectively; \( \rho_{exc} \) the excitation laser power density; \( \sigma \) the absorption-integrated cross section of the sensitizer; \( W_0 \) and \( W_1 \) the corresponding parameters of energy transfer from levels of the sensitizer (\( n_{S1} \)) to adjacent levels of the activator (\( n_{A1} \) and \( n_{A2} \)); and \( A_{S1} \), \( A_{A1} \) and \( A_{A2} \) the depopulation rates of the corresponding energy levels.

Notably, the energy transfer parameters (\( W_0 \) and \( W_1 \)) for the rate equations can be obtained from macroscopic measurements. However, the result is an average over the interactions of sensitizers and activators at all possible distances. Therefore, the rate equations hold relatively well for the situation that sensitizers and activators are homogenously co-doped such as bare core UCNPs. In the cases of heterogeneous structures, \( \text{e.g.} \) sensitizers and activators are distributed separately, the “fast migration” approximation is often made in employing rate equations to describe the UC process. This approximation, intensively discussed in the Inokuti-Hirayama model,\[^68\] refers to the assumption that in the cases with high sensitizer concentration- the energy migration among sensitizers before it is transferred to an activator is very fast. Therefore, in conventional treatments of UC dynamic processes, the role of energy migration among sensitizers could be neglected.
Improvement of rate equations

However, if we take a closer look at this issue from a different perspective, we may think differently. Is it true that sensitizer-sensitizer energy migration has no influence on the UC process? Usually, the sensitizer concentration is much higher than the activator concentration in sensitizer-activator co-doping systems. We can rationally assume that the absorbed energy has a high probability to hop among the sensitizers before being transferred to an activator since statistically every sensitizer has more sensitizers in its neighbourhood than activators. Therefore, the practical UC process is much closer to the situation shown in Figure 1.1. Even though energy migration between two sensitizers can be regarded as very fast, the accumulative effects of a multi-step energy transfer still have possibilities to affect the luminescence process. This assumption was supported by the work of Burshteîn and Zusman. When dealing with down-shift luminescence, they considered that the sensitizer-sensitizer energy migration process should be taken into account and added an extra parameter to describe it. Since this model was not suitable for the more complicated UC process, Zubenko later modified this model for the UC process by replacing the energy transfer coefficient \( W \) with a time-dependent energy transfer function \( F(t) \), referred as a nonlinear quenching rate. Accordingly, the dynamics of excited states concentration \( n(t) \) under short-pulsed light excitation conditions can be described by the equation below (assuming a dipole-dipole approximation):\(^{70}\)

\[
n(t) = \frac{n(0) \exp(-t/\tau_D)}{1+n(0)\tau_D(\frac{2\pi^2}{3})^{1/2}C_{DA}/\tau_0(\tau_0/\tau_D)^{1/2}\text{erf}(\sqrt{t(1/\tau_0+1/\tau_D)})-\exp(-t/\tau_D)\text{erf}(\sqrt{t/\tau_0})} \tag{1-3}
\]

where \( n(0) \) is the initial excited states concentration; \( C_{DA} \) the microparameter of donor-acceptor interaction; \( \tau_0 \) the time of excitation hopping to non-excited donors; \( \tau_D \) the excitation lifetime; and \( \text{erf}(x) = 2/\sqrt{\pi} \int_0^x \exp(-t^2) dt \) the error function. However, the application of this model should be done carefully since its solution is very complicated with parameters that are hard to be obtained.
1.6.3 Monte Carlo simulation of UC dynamics

First employed during the Manhattan Project to solve neutron diffusion problems for atomic bombs, Monte Carlo simulations have become a powerful analysis tool for uncertainty propagation problems.\textsuperscript{71} Aided by the rapid progress in computer technology, it has been extended to a wide range fields from physics to economics.\textsuperscript{72} Generally, it involves simulations for mathematically depicted uncertainty problems where random variables are employed to find a solution that can in principle be conclusive.\textsuperscript{73} Compared with physical experiments, Monte Carlo simulations are able to perform random sampling and test large amounts of trials on a computer. Basically, there are three basic steps involved as shown in Figure 1.12. Firstly, based on the distributions of input variables, the system will randomly generate possible values as samples of the input variables $\mathbf{X}$. Secondly, for these individual samples, their values will be used in a numerical experimentation to describe their possible performance by the analysis model function $\mathbf{Y} = f(\mathbf{X})$. Thirdly, after a large amount of attempts in this manner, values of the output variables $\mathbf{Y}$ are collected for further statistical analysis. The accumulation of the large amount of resultant data enables us to extract the probabilistic characteristics and to establish a comprehensive picture of the targeted issue.

For UCNPs, UC luminescence can be seen as the end result of multiple interactions occurring among an ensemble of sensitizers and activators. Understanding the dynamics of this process is still hampered by many uncertainty problems. Monte Carlo simulation may help in solving these problems, \textit{e.g.} the relationship between excitation energy migration and UC luminescence dynamics. In \textbf{Chapter 2}, we will introduce a Monte Carlo model to quantitatively depict the influence of energy migration on the UC process and demonstrate both computationally and experimentally that this influence cannot be ignored. By applying Monte Carlo simulation on “dopant ions’ spatial separation” nanostructures, we will show that it is possible to elucidate the time evolution of the excited states in UCNPs.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure11.png}
\caption{Schematic illustration of UC process depicting the energy migration among sensitizers.}
\end{figure}
1.7 Applications of upconversion nanoparticles

Nanoscale UC materials have some unique properties, which make them applicable in various fields, including biology, RGB printing, security, display and optical storage etc. Here, we briefly introduce three applications of UCNPs.

1.7.1 Bio-imaging applications

In both clinical and fundamental bio-medical fields, imaging of protein molecules, cells, tissues or organs is an important approach to trace various biological events. Among the various imaging approaches, such as magnetic resonance imaging (MRI), ultrasonic, and X-ray computed tomography (CT), photoluminescence (PL) imaging offers significant advantages due to its wide application range, high precision, convenience and high safety.

PL imaging techniques often use luminescent probes as contrast agents to visualize and quantify biological progress at molecular and cellular levels. Early attempts to visualize cells with light-related techniques by Antoni van Leeuwenhoek and Robert Hooke could be traced back to 17th century. Traditionally, the probes are mainly organic dyes. Other materials like quantum dots, carbon dots, fluorescent proteins, etc. are used as well. However, their emission is Stokes-shifted, and excitation in the UV or short-wavelength visible region is usually required. The relatively large absorption and scattering effects of the biological materials prevent clear imaging at deeper sites in tissue. Apart from the toxicity of materials (quantum dots), short wavelengths also bring concerns on photobleaching (organic dyes) and photostability (proteins). In contrast, UCNPs are new promising contrast agents circumventing to a large extent these limitations due to their unique properties which have described in the previous sections. An example of high quality imaging of a tumor site in a mouse with UCNPs is shown in Figure 1.13. It is currently also a hotspot in exploring the multimode approaches in combining UC PL imaging with other imaging modalities.6, 75-78
1.7.2 Photodynamic therapy (PDT)

PDT, as a representative non-invasive treatment to kill cytopathic cells, has been recognized as a regulatory approved modality in the clinic for the treatment of many malignant carcinomas.\textsuperscript{79} It mainly involves three key components. One is introducing a photosensitive molecule responding specifically to certain wavelengths as a photosensitizer, another one is the targeting entity, and the third one is the administration of light-triggering.\textsuperscript{80} The mechanism is shown in Figure 1.14. In this way, when the photosensitizer is localized to target cells or tissues, proper wavelength light irradiation is able to activate the photosensitizer to interact with the surrounding molecular oxygen ($O_2$), resulting in the generation of so-called “reactive oxygen species” (ROS) that cause cell apoptosis. In PDT, the biological responses are restricted to specific areas of tissues exposed to light. PDT is a methodology known for its non-invasive, highly selective, and localized characteristics. In Chapter 4, we utilize PDT to evaluate the performance of our newly designed UC nanostructures.

Most photosensitizers used in PDT are UV or visible sensitive, which restrict current PDT treatments to low dosages of photosensitizers and superficial dermatopathy. By introducing UCNPs, PDT can be more competitive, because (i) excitation is shifted to the near-infrared which...
increases the penetration depth in human tissue and also suppress the photodamage; (ii) emission of UCNPs at longer wavelengths can be utilized for simultaneous bio-imaging. Besides, UCNPs can act as a nanoplatform to load not only photosensitizers, but also other bio-functional groups like targeting entities or drugs. For example, visible light emission from UCNPs can be applied to photodynamic therapy (PDT), whereas the prognosis of the lesion can be estimated using other imaging modalities such as MRI or CT.81-83

1.7.3 Photovoltaic (PV) cells

PV cells are devices able to convert solar energy to electric energy. Significant efforts have been invested in increasing the conversion efficiency of PV cells. After years of efforts, laboratory silicon solar cells are getting closer and closer to the Shockley-Queisser limit of conversion efficiency (31% for single junction silicon cells).84 To utilize the full solar spectrum is one of the directions in PV cells research. For conventional materials applied in solar cells, photons with energy $E_{\text{ph}}$ less than the material bandgap $E_g$ cannot be absorbed. When $E_{\text{ph}}$ is larger than $E_g$, photons can be absorbed, but the excess energy $\Delta E = E_{\text{ph}} - E_g$ is consumed because of the thermalization during relaxation of the electrons to the conduction band edge. The spectral distribution of sunlight at Air Mass 1.5 global (AM 1.5G) consists of photons with wavelengths ranging from ultraviolet to infrared (280–2500 nm, 0.5–4.4 eV). This insensitivity to the full solar spectrum leads to an approximate “wasted” fraction of up to 50%.7,85

Introducing nanomaterials with certain optical advantages such as adding extra spectral conversion materials like UCNPs is an effective approach to compensate the loss to some extent. For instance, the functional region of the commonly applied crystalline-silicon (c-Si) solar cells is in the spectral region from ultraviolet to 1100 nm, which basically requires UCNPs of (i) longer excitation wavelengths (>1100 nm), (ii) shorter emission wavelength (<1100 nm) and (iii) higher conversion efficiency and transparency to the upconverted light. Although $\text{Er}^{3+}$ doped UCNPs have absorption ~1480–1580 nm ($^{4}I_{15/2} \rightarrow ^{4}I_{13/2}$ transition) and are able to emit photons at ~980 nm ($^{4}I_{11/2} \rightarrow ^{4}I_{13/2}$), ~800 nm ($^{4}I_{9/2} \rightarrow ^{4}I_{15/2}$), ~660 nm ($^{4}F_{9/2} \rightarrow ^{4}I_{15/2}$) and ~550 nm ($^{4}S_{3/2} \rightarrow ^{4}I_{15/2}$), the actual efficiency of these UCNPs is rather low because of concentration quenching effect (details will be discussed in Chapter 3). Given by this, compared to conventional c-Si solar cells wide bandgap solar cells (GaAs, amorphous Si, dye-sensitized and organic solar cells) would benefit more from the incorporation of UCNPs since the working zone of these solar cells is mainly located within the visible region and can only extend to a maximum wavelength of ~900 nm. Therefore, $\text{Yb}^{3+}$-sensitized co-doping UCNPs ($\text{Yb}^{3+}$-$\text{Er}^{3+}$ codoping, etc.) can be favorably applied in these wide bandgap solar cells due to the large absorption cross-section of $\text{Yb}^{3+}$ at ~980 nm (~900 nm) and their efficient visible (~550 nm and ~660 nm) and NIR (~800 nm) UC emissions. Presently, UCNPs are mainly used as spectral converters, which are readily applicable to existing solar cells so that the two parts can be tuned independently.86-89
1.8 Outline and scope of this thesis

This thesis describes the exploration of UC dynamic processes by quantitatively including the influence of energy migration (sensitizer-sensitizer). This improved understanding will be demonstrated to enable not only the fine tuning of the UC dynamics but also the design of novel structures (such as NaErF₄@NaYF₄ nanostructures and their derivatives) with more advanced properties. The thesis is structured as follows:

Chapter 2: In this chapter, we unravel the intimate link between the random nature of energy migration and UC emission time behavior. A Monte Carlo model is established to quantitatively analyse UC dynamics. The simulation not only clarifies the energy loss channels in UC process, but also guides us to develop a novel strategy in fine tuning the UC emission dynamics. Tailoring the energy migration paths in specifically designed “dopant ions’ spatial separation” nanostructures, we show that it is possible to obtain detailed control of the UC emission dynamics (either the rise or decay process) over a broad time range.

Chapter 3: In this chapter, we designed a new kind of UC nanostructure, core-shelled NaErF₄@NaYF₄ and its derivative (NaErF₄:0.5% Tm@NaYF₄), featured with efficient quasi-monochromic red emission (~ 660 nm) under different wavelength excitations (~ 800 nm, ~ 980 nm and ~ 1530 nm). The intensive emissions from this structure (100% Er) relaxed completely the limit of activator doping concentration resulting from the concentration quenching effect (typically <3%). Proof-of-concept experiments are presented for the potential benefit of this structure in solar cells and anti-counterfeiting.

Chapter 4: This chapter describes studies to apply the newly developed structure in Chapter 3 into imaging-guided photodynamic therapy (PDT) of cancer. On the basis of NaErF₄@NaYF₄ nanostructure, a new type of photoswitchable UC nanoparticles (PUCNPs), NaErF₄@NaYF₄@NaYbF₄:0.5%Tm@NaYF₄ is constructed. By combining multi-band excitable NaErF₄@NaYF₄ (inner part) and 980 nm excitable NaYbF₄:0.5%Tm@NaYF₄ (outer part), we are able to realize a quasi-monochromatic red emission (~660 nm, from Er³⁺) upon ~800 nm excitation, whereas strong UV-blue emissions (from Tm³⁺) together with the red emission appear upon ~980 nm excitation. In this way, the “always ON” red emission can be employed for real-time imaging while the UV-blue emissions induced PDT can only be triggered to be “ON” by 980 nm. As a proof of concept, we demonstrate that the PUCNPs are effective for in vitro and in vivo imaging-guided PDT.

Chapter 5: This chapter is an extension of the applications of NaErF₄@NaYF₄ nanostructures and focuses on the detection of traces of water. It is shown that NaErF₄@NaYF₄ enables a more sensitive detection with a detection limit of ~5 ppm, one order of magnitude lower than the current UC probers.
References

23. Salley, G. M.; Valiente, R.; Gudel, H. U., Cooperative Yb³⁺-Tb³⁺ Dimer Excitations and Upconversion in...


