Structure design and applications of upconversion nanoparticles

Zuo, J.

Link to publication

Creative Commons License (see https://creativecommons.org/use-remix/cc-licenses):
Other

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: https://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (http://dare.uva.nl)
Chapter 2
Precisely Tailoring Upconversion Dynamics via Energy Migration in Core-Shell Nanostructures*

Upconversion emission dynamics was thought to be determined mainly by the activator and its interaction with neighboring sensitizers. Although this vision is challenged from time to time, direct evidence is hard to obtain from bulk materials where spatially separated doping is difficult. With the aid of precise architecture of nanostructures, we have acquired here quantitatively the relationship between the energy migration path and the upconversion luminescence dynamics. We demonstrate that excitation energy migration affects greatly upconversion emission dynamics. “Dopant ions spatially separated” nanostructures are designed as model systems and the intimate link between the random nature of energy migration and upconversion emission time behavior is unraveled by theoretical modelling and confirmed spectroscopically. Based on this progress, we have successfully realized fine control of upconversion emission time behavior (either rise or decay process) by tuning the energy migration paths in various specifically designed nanostructures. This result is significant for applications of this type of materials in super-resolution spectroscopy, high density data storage, anti-counterfeiting and biological imaging.

*The content of this chapter has been published in Angew. Chem. Int. Ed., 2018, 57, 3054-3058 (highlighted as cover story) by Jing Zuo, Dapeng Sun, Langping Tu, Yanni Wu, Yinghui Cao, Bin Xue, Youlin Zhang, Yulei Chang, Xiaomin Liu, Xianggui Kong, Wybren Jan Buma, Evert Jan Meijer, and Hong Zhang.
2.1 Introduction

Lanthanide (Ln) ions doped upconversion (UC) materials have attracted extensive attention due to their potential applications in a large variety of fields, e.g. display,\textsuperscript{1-3} biology,\textsuperscript{4-14} anti-counterfeiting,\textsuperscript{15-19} and solar cell,\textsuperscript{20-22} etc. Recent advances in upconversion emission applications rely more and more on precisely engineering the material structure on nanometer scale, in which energy migration behavior plays a key role. So far, most of the related investigations have focused on steady-state effects of energy migration.\textsuperscript{23-33} That is, excited states could randomly “walk”, thus a long range energy transport (more than several nanometers) between Ln$^{3+}$ ions is possible. However, the lack of a detailed microscopic picture of UC mechanism in such structures, especially the ambiguous recognition of the energy migration dynamics and its effect on the time behavior of UC emission, remains a major bottleneck for further development of these structures.

In most cases, energy migration among sensitizers is neglected in UC dynamics treatment partly due to the difficulty of quantitative analysis the energy migration dynamics in bulk materials. In that case, despite that UC emission involves complex interactions between multiple Ln$^{3+}$ ions, its dynamics is solely determined by the energy transfer processes within one activator-sensitizer pair (Figure 2.1a).\textsuperscript{34-36} Despite suspicions on this assumption from time to time,\textsuperscript{37-41} there is no quantitative evidence of the role of the excitation energy migration in UC dynamics.

Figure 2.1 Schematic diagram of (a) the traditional UC mechanism which relies on the monomer (sensitizer) to monomer (activator) sequential energy transfer interactions, and (b) the UC process in the “dopant ions spatial separated” nanostructure, in which the three basic processes: photon absorption, energy migration and UC emission are spatially separated.

This awkward scenario is primarily due to the lack of appropriate material system. Indeed, even in the traditional sensitizer-activator co-doping materials, energy migration still plays an important role in their UC process.\textsuperscript{37} However, its effect is difficult to be evaluated as energy migration process is indistinguishable from energy transfer between sensitizers and activators. In our opinion, this dilemma can be solved by introducing a smart nanosystem named as “dopant ions spatial separated” (DISS) nanostructure.\textsuperscript{33} By locating sensitizers and activators into different regions of a single nanoparticle, the three basic processes of UC (i.e. light absorption, energy migration and UC emission) can be well separated (Figure 2.1b). Therefore, the role of energy migration in UC luminescence dynamics could be quantitatively depicted by 1) tuning the migration layer thickness or 2) varying the dopant concentration of the ions as energy carriers in the migration layer. On top of that, traditional treatment of UC mechanism based on simultaneous
rate equations is not able to describe properly the actual energy migration processes, because it provides only an averaged macroscopic statistical result. Therefore, we set up a time-correlated Monte Carlo simulation model to fill the gap. Compared with previous simulation approaches, our model is capable to monitor UC luminescence dynamics from the level of multiple ion-to-ion interactions, yielding a more comprehensive vision without restriction of Ln\(^{3+}\) ions distribution in the nanostructure.

Combining the experimental and simulation results, we find that despite each step of energy migration (e.g. \(\text{Yb}^{3+} \rightarrow \text{Yb}^{3+}\)) only costs a relatively short time (around microseconds), its randomly walking nature significantly prolongs the migration time up to several hundred microseconds for a distance of several nanometers. This result tells us that the conventional understanding of UC mechanisms is incomplete and in some nanostructures it might be misleading by ignoring the actual energy migration process. More importantly, by precisely tuning energy migration paths in DISS nanostructure, either rise or decay of UC emission dynamic traces can be quantitatively tailored in a wide range. Our study thus not only offers a new distinct microscopic picture on how energy migration affects UC and the temporal characteristics of UC emission, but is also an excellent starting point for rational design of novel functional and efficient UC nanostructures.

2.2 Simulation section

2.2.1 Construction of the Monte Carlo simulation model.

The basic picture of Monte Carlo simulation model of UC was set up according to a three-dimensional random walk of excited states in the sublattice (consisted by sensitizer and activator ions), and the UC is induced by a “collision” of two or more excited states (Figure 2.2). In contrast to previously reported models of UC phenomena related to Monte Carlo simulation or DFT (density functional theory) calculation, our model includes three significant features: 1) It not only simulates the energy migration process, but also contains the light absorption and UC emission processes. Thus it offers a clear microscopic vision of entire UC process from light absorption to UC emission. 2) It is particularly advantageous in dealing with the situation of complicated nanosystems, such as studying the energy migration on the core-shell interface of heterogeneous structures. 3) By taking time evolution process into the system, it not only can be applied for the steady-state simulation, but also enables us to analyze the UC dynamic processes.

Figure 2.2 Schematic diagram of the microscopic picture of UC emission which is induced by the “collision” of the randomly walking excited states.
As a proof of concept simulation, four reasonable simplifications are taken in this model:

1: The construction of nanoparticles: the crystal structure of nanoparticle was simplified to a simple cubic structure which only contains sensitizers and activators. According to the Ln\(^{3+}\) doping concentration (e.g. 20% sensitizer and 2% activator) and the lattice parameters of hexagonal phase NaYF\(_4\) (or NaLuF\(_4\)) matrix, the calculated distance between the nearest neighboring ions is about 0.8 nm. Therefore, a 20 nm diameter nanoparticle is modeled as a 25×25×25 cube sublattice, which consists 15625 grid points, and each grid point is randomly set as one sensitizer or activator ion with the ratio of 10 to 1.

2: The energy states of ions: as shown in Figure 2.3, sensitizer ions have two energy levels (labeled as \(S_1\) and \(S_0\), respectively) and activator ions have three energy levels (labeled as \(A_2\), \(A_1\) and \(A_0\), respectively).

![Figure 2.3](image)

**Figure 2.3** The Monte Carlo simulation model of UC processes in the \(\beta\)-NaYF\(_4\): 20%Yb, 2% Er nanostructure. \(S_0, 1\) and \(A_{0,1,2}\) are the simplified energy levels of sensitizer (Yb\(^{3+}\)) and activator (Er\(^{3+}\)), respectively. The number labeled in the picture are the interaction rates between energy levels (unit: s\(^{-1}\)).

3: The simulation parameters: the advantage of this model is that almost all the simulation parameters can be quantitatively obtained from the experimental results or quantum mechanics calculations, as labeled in Figure 2.3 and Table 2.1.
Table 2.1 The simulation parameters used in this work

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulation time period (s)</td>
<td>3</td>
</tr>
<tr>
<td>Time step (s)</td>
<td>10^{-6}</td>
</tr>
<tr>
<td>Recombination rate of S_1 (s^{-1})*</td>
<td>10^3</td>
</tr>
<tr>
<td>Recombination rate of A_1 (s^{-1})*</td>
<td>10^3</td>
</tr>
<tr>
<td>Recombination rate of A_2 (s^{-1})*</td>
<td>7·10^3</td>
</tr>
<tr>
<td>Energy migration rate of S_1→S_0 (s^{-1})*</td>
<td>10^5</td>
</tr>
<tr>
<td>Energy transfer rate of S_1→A_0 (s^{-1})*</td>
<td>2.5·10^4</td>
</tr>
<tr>
<td>Energy transfer rate of S_1→A_1 (s^{-1})*</td>
<td>3.2·10^3</td>
</tr>
<tr>
<td>Energy transfer rate of A_1→S_0 (s^{-1})*</td>
<td>1.0·10^4</td>
</tr>
<tr>
<td>Energy migration rate of A_1→A_0 (s^{-1})*</td>
<td>5·10^3</td>
</tr>
<tr>
<td>Energy transfer rate of A_1→A_1 (s^{-1})*</td>
<td>600</td>
</tr>
<tr>
<td>Absorption cross section of S_0 (cm^2)*</td>
<td>1.17·10^{-20}</td>
</tr>
<tr>
<td>Absorption cross section of A_0 (cm^2)*</td>
<td>1.7·10^{-21}</td>
</tr>
<tr>
<td>Surface quenching rate (s^{-1})</td>
<td>10^5</td>
</tr>
<tr>
<td>Quantum yield of A_2 state</td>
<td>50%</td>
</tr>
</tbody>
</table>

*Calculated from crystal structure of β-NaYF₄: 20%Yb, 2% Er (JCPDS: 16-0334).

More specifically:

a) the recombination rate of S_1 and A_{1,2} states are obtained from the measured lifetime of each energy state (i.e. ~ 1 ms lifetime for S_1, A_1 states, and ~ 140 μs lifetime for A_2 state).
b) the absorption cross section of S_0 and A_0 are obtained from the previous reports.\(^{33,47}\)
c) the emission quantum yield of A_2 state (i.e. 50%) is evaluated from the luminescence efficiency of lanthanide ions doped phosphors.
d) based on the assumption that the energy transfer/migration processes only occurs between two closest neighboring ions, their energy transfer/migration probability can be considered as a sum up of three parts:\(^{34}\)

\[ P = \left( \frac{R_0}{\tau_s} \right)^s \quad (s = 6, 8, 10) \]  

(2-1)

1) s=6 for dipole-dipole interactions (P_{dd}).
2) s=8 for dipole-quadrupole interactions (P_{dq}).
3) s=10 for quadrupole-quadrupole interaction(P_{qq}).

Where \( \tau_s \) is the actual lifetime of the donor excited states, \( R_0 \) is the critical transfer distance for which excitation transfer and spontaneous deactivation of the sensitizer have equal probability. \( R \) is the real distance between the two ions. From literature,\(^{48}\) if \( R \) is fixed to 7\( a_0 \) (\( a_0 = 0.53 \) Å), the Yb\(^{3+}\)→Yb\(^{3+}\) energy migration rate (i.e. S_1→S_0) is \( \sim 1.6\times10^8 \) s\(^{-1}\), more specifically: \( P_{dd} \sim 2.8\times10^6 \) s\(^{-1}\), \( P_{dq} \sim 1.4\times10^7 \) s\(^{-1}\) and \( P_{qq} \sim 1.4\times10^8 \) s\(^{-1}\). Accordingly, for the β-NaYF₄: 20%Yb, 2% Er
nanoparticle where the ion-to-ion distance \( R' \) is fixed to \( \sim 0.8 \) nm (\( R' \) is calculated from the Ln\(^{3+} \) ions doping concentration and the lattice parameters of \( \beta\)-NaYF\(_4 \) or NaLuF\(_4 \) matrix), three interaction parameters are changed to: \( P_{dd}' \sim 2.8 \times 10^4 \) s\(^{-1} \), \( P_{dq}' \sim 3.0 \times 10^4 \) s\(^{-1} \) and \( P_{qq}' \sim 6.4 \times 10^4 \) s\(^{-1} \), and the sum up of the three parts is \( \sim 10^5 \) s\(^{-1} \), as placed in the Figure 2.3 and Table 2.1.

e) the surface quenching rate is discussed in the following sections (Table 2.3 and Figure 2.7).

4: Because of the relatively small effects, some secondary processes are reasonably ignored without affecting the basic understanding of the model, including: stimulated emission, cross relaxation (\( A_2 + S_0 \rightarrow A_1 + S_1 \)) and excited states absorption (\( A_1 + h\nu \rightarrow A_2 \)) processes, etc.

2.2.2 Algorithm of Monte Carlo simulation

Based on the fixed parameters, the UC in a nanoparticle could be simulated as follows:

(1) For steady-state scenario: at the start of the simulation, all the ions are numbered and placed in the ground states. The macroscopic UC phenomena are rebuilt by the statistics of microscopic event probabilities for each ion (including: pump absorption, energy transfer/migration, excited states recombination and upconversion emission). The time evolution of the system is divided into a series of events successively with step time (\( \Delta t \)) of 1\( \mu \)s, and each step is accompanied by the possible excited state generation or depletion for every ion following the order of numbers. After each step, the microscopic distribution of excited states is updated to reflect the new energy configuration in the nanoparticle.

1: For each ground state ion, at each time step, we calculate the microscopic probabilities for the pump absorption:

\[
P_{abs} = \rho \frac{\sigma \Delta t}{E_{hv}}
\]  

(2-2)

where \( \rho \) the excitation power density, \( \sigma \) the absorption cross section of the ion, \( E_{hv} \) the photon energy and \( \Delta t \) the time step (\( i.e. 1 \) \( \mu \)s in this work). Then we generate a random number \( q \) in the interval [0,1], if \( q \) is located into the interval [0, \( P_{abs} \)], the ion is excited in this time step, otherwise it remains at the ground state.

For example, if we assume \( \rho \) is 100 W/cm\(^2 \), \( \sigma \) is 1.17\( \times \)10\(^{-20} \) cm\(^2 \) (referred as the Yb\(^{3+} \) ions), and the excitation wavelength is 980 nm, the \( P_{abs} \), the possibility of sensitizer ions being excited within one time step (1 \( \mu \)s), is then calculated as low as 5.76\( \times \)10\(^{-6} \). Therefore, under the steady state condition, even taking the long lifetime of Yb\(^{3+} \) excited state (\( i.e. 1 \) ms) into account, only dozens of (~ 85) Yb\(^{3+} \) ions could be excited simultaneously although the number of Yb\(^{3+} \) ions in one single nanoparticle is \( \sim 1.4 \times 10^4 \). The very limited number of excited states is beneficial to tracking the time evolution of the system.

2: For each excited ion, we calculated its microscopic probabilities at each time step for the following processes: a) energy transfer, b) energy migration, c) recombination to the ground state without upconversion emission, d) upconversion emission and e) surface quenching (only if the excited states are located on the particle surface). The probability of each event is:

\[
P_i = R_i \Delta t
\]

(2-3)

where \( R_i \) the rate of each event (as labeled in Table 2.1) and \( \Delta t \) the time step (\( i.e. 1 \) \( \mu \)s in this work).
Figure 2.4 The typical microscopic ions distribution in the sublattice.

Let us turn to the example shown in Figure 2.4. At step $k$, if the excitation starts at one sensitizer ion located at the lattice point $A_{x,y,z}=(0,0,0)$, and we assume that the six nearest neighboring positions around it are (i) one ground state activator ion at the lattice point $A_{1,0,0}$, (ii) four ground state sensitizer ions at the lattice points $A_{0,±1,±1}$ respectively, and (iii) one surface quenching site at the lattice point $A_{-1,0,0}$, then the probability of each event $m_i$ at step $k+1$ can be obtained as:

\[
p_{i}^{k}=egin{cases} 
  m_1: & \text{recombine to the ground state at (0,0,0), with 0.001 probability} \\
  m_2: & \text{energy transfer to (1,0,0), with 0.025 probability} \\
  m_3: & \text{energy migration to (0,-1,0), with 0.1 probability} \\
  m_4: & \text{energy migration to (0,1,0), with 0.1 probability} \\
  m_5: & \text{energy migration to (0,0,-1), with 0.1 probability} \\
  m_6: & \text{energy migration to (0,0,1), with 0.1 probability} \\
  m_7: & \text{surface quenching to (-1,0,0), with 0.1 probability} \\
  m_8: & \text{remains the excited state at (0,0,0), with 0.474 probability}
\end{cases}
\]

In this case, in order to choose which event occurs at step $k+1$, we generate a random number $q$ in the interval $[0,1]$ and choose an event $m_i$ for which

\[
q \in \left[\sum_{i=0}^{m_{i}-1} p_{i}^{k}, \sum_{i=0}^{m_{i}} p_{i}^{k}\right] \tag{2-4}
\]

and recording the time of the event $m_i$ as: $(k+1)\Delta t$.

By circularly running the simulation program over $10^6$ time steps (i.e. over 1 second in the real time), stable statistics output results for one single nanoparticle can be obtained (error less than 15%).

(2) For the time-resolved simulation: it differs from the steady-state scenario only in the pump absorption process. Typically, we assume $5 \sim 10\%$ sensitizer ions have already been excited at the
beginning of the first time step, and a long enough time evolution interval (such as 0 ~ 5 ms) is chosen to make sure all the dynamic processes are finished. After that we circulate the running of the simulation program over $10^3$ times to obtain the stable statistics output results.

In summary, the algorithm flowchart of Monte Carlo simulation is shown in Figure 2.5.

![Algorithm flowchart of UC Monte Carlo simulation](image)

**Figure 2.5** The algorithm flowchart of UC Monte Carlo simulation.

### 2.2.3 Verification of the simulation

To testify the rationality of our model, we simulate some macroscopic UC phenomena and compare them with the experimental results.

(i): The simulation of UC emission efficiency. As an example, the UC efficiency of the NaYF$_4$: 20% Yb 2%Er@NaYF$_4$ nanostructure (core diameter is 20 nm) is simulated under the excitation power density of 100 W/cm$^2$ (Table 2.2).
Table 2.2 The simulation results for NaYF<sub>4</sub>: 20% Yb 2%Er@NaYF<sub>4</sub> nanostructure (simulation time period: 3 seconds)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorbed photons</td>
<td>249758</td>
<td>100</td>
</tr>
<tr>
<td>Recombined on the S&lt;sub&gt;1&lt;/sub&gt; state</td>
<td>195585</td>
<td>78.3</td>
</tr>
<tr>
<td>Recombined on the A&lt;sub&gt;1&lt;/sub&gt; state</td>
<td>46829</td>
<td>18.7</td>
</tr>
<tr>
<td>Recombined on the A&lt;sub&gt;2&lt;/sub&gt; state</td>
<td>3627</td>
<td>1.45</td>
</tr>
<tr>
<td>UC emission photons</td>
<td>1882</td>
<td>0.75</td>
</tr>
<tr>
<td>Excited states number</td>
<td>~ 85</td>
<td>-</td>
</tr>
</tbody>
</table>

As shown in Table 2.2, the simulated UC efficiency (UC emission photons/Absorbed photons) is 0.75 ± 0.1%, which is in line with the reports. The unique advantage of the Monte Carlo simulation is its relatively clearer microscopic vision. Herein, the simulation reveals that, due to the small absorption cross section of lanthanide ions, only 85 ± 10 ions (including both sensitizers and activators) are kept excited among the overall 15625 grid points under the general excitation density of 100 W/cm<sup>2</sup>. Thus the “collision” of the excited states is relatively scarce. In that case, most of the absorbed energy (~ 97%) will be consumed through the sensitizer/activator recombination process (either radiative or nonradiative process) during the random walk period of excited states.

(ii): The simulation of non-linear relationship between laser power (P) and UC intensity (I). We simulate the non-linear \( P-I \) relationship \( (I=p^n, n>1) \), which is also regarded as a feature of UC process. As shown in Figure 2.6 (inset), it is easy to find out that in a fixed space, the “collision” possibility of the excited states will increase nonlinearly with the number of the excited states. Notably, for a two-photon process (induced by two excited states “collision”), the simulated \( n \) value is 1.97 (Figure 2.6), which agrees well with the theoretical value \( (n=2) \).  

![Figure 2.6](image_url)  

**Figure 2.6** The simulated UC emission intensity as a function of pump power. Inset: the schematic diagram of excited states “collision” induced UC emission.

(iii): The simulation of surface quenching effect. We also simulate the surface quenching effect of the nanosized UC material. It is known that, due to the existence of surface defects, organic groups,
solvent molecules etc., the energy of excited states could be trapped by the surface quenching sites of the nanoparticle. In our model, we assume that an ion located on the particle surface has a possibility to transfer its energy to the surface quenching sites, and once the energy is trapped by the surface quenching sites, it will be consumed immediately and never come back to the lanthanide ions. So the key point is to determine the surface quenching rate, which could be authenticated by (a) the UC efficiency of bare core nanoparticle and (b) particle size dependent UC emission.

(a) Obviously, the UC efficiency of bare core nanoparticle is directly related to the surface quenching rate. As shown in the Table 2.3, in our model, if the surface quenching rate is set as $10^5 \text{s}^{-1}$, then for a bare core nanoparticle with a 20 nm diameter, as high as $84.9\%$ excited states will be quenched by the surface quenching sites. Therefore, its UC emission efficiency is significantly decreased to $0.026\%$, which is well consistent with experimental observation.  

Table 2.3 The simulation results for 20 nm NaYF$_4$: 20% Yb 2%Er bare core nanostructure (simulation time period: 3 seconds).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorbed photons</td>
<td>249758</td>
<td>100</td>
</tr>
<tr>
<td>Quenched by surface</td>
<td>211956</td>
<td>84.9</td>
</tr>
<tr>
<td>Recombined on the $S_1$ state</td>
<td>30410</td>
<td>12.2</td>
</tr>
<tr>
<td>Recombined on the $A_1$ state</td>
<td>7107</td>
<td>2.85</td>
</tr>
<tr>
<td>Recombined on the $A_2$ state</td>
<td>135</td>
<td>0.054</td>
</tr>
<tr>
<td>UC emission photons</td>
<td>64</td>
<td>0.026</td>
</tr>
<tr>
<td>excited states number</td>
<td>8-15</td>
<td>-</td>
</tr>
</tbody>
</table>

(b) The other way to verify the surface quenching rate is to analyze the size dependent UC emission of nanoparticle. The smaller the particle size, the stronger the surface quenching effect. As shown in Figure 2.7, taking the same surface quenching rate ($10^5 \text{s}^{-1}$) into account, the simulated results of the particle size dependent UC emission intensity do well agree with the experimental results (integration from 500 nm to 700 nm), which confirms the rationality of the surface quenching rate we set up.

![Figure 2.7](image.png)
2.2.4 The microscopic picture of energy migration dynamics

Utilizing the time-resolved simulation, we can understand the Yb\(^{3+}\)→Yb\(^{3+}\) energy migration dynamics from a unique angle:

![Diagram showing energy migration dynamics](image)

**Figure 2.8** The microscopic manifestation of the decay lifetime for a) isolated Yb\(^{3+}\), and b) energy migrated Yb\(^{3+}\) in the NaYF\(_4\): 20% Yb sublattice.

1) For an isolated Yb\(^{3+}\) ion, the lifetime (e.g. 1 ms) is the average time of excited state of the ion (Figure 2.8a), which can be calculated by:

\[
\tau = \frac{1}{I_0} \int_0^\infty I(t)dt
\]  

where \(I(t)\) and \(I_0\) are the luminescence intensity as a function of time \(t\) and the maximum emission intensity, respectively.

2) For a sublattice consisting of many Yb\(^{3+}\) ions (each ion plays as one grid point), the excited state lifetime will not be affected by the energy migration process. However, its microscopic manifestation has changed: due to the efficient energy migration, the excited states of Yb\(^{3+}\) tend to migrate among a large number of grid points before relaxing to ground state, but the time spent on each migrated grid point is correspondingly reduced. For example, we calculate the Yb\(^{3+}\)→Yb\(^{3+}\) energy migration dynamics in an infinite NaYF\(_4\): 20% Yb sublattice (Yb\(^{3+}\)-Yb\(^{3+}\) distance is fixed to 0.8 nm). As shown in the Figure 2.8b, the expectation value of each step of Yb\(^{3+}\)→Yb\(^{3+}\) energy migration is only \(~1.7\ \mu s\) (calculated from the simulation parameters labeled in the Table 2.1), and the average number of migrated grid point is \(~600\). Therefore, the average “lifetime” of each excited state is still 1 ms.

However, if we add Er\(^{3+}\) (or other energy quenching site) into the sublattice to cut off the energy migration path, obviously, the average “lifetime” of Yb\(^{3+}\) excited states will be affected by the number and location of Er\(^{3+}\). Thus, we can effectively tailor the UC dynamics by controlling the ions distribution in “dopant ions spatial separated” nanostructure.

\[
1.7 \mu s + 1.7 \mu s + \ldots + 1.7 \mu s = 1\text{ms}
\]
2.3 Results and discussion

2.3.1 Verification of the non-neglectable energy migration time

The first example is the DISS nanostructure: YbEr@Yb@YbNd (short for NaYF$_4$: 20% Yb, 2% Er @NaYF$_4$: 20% Yb @NaYF$_4$: 10% Nd, 20%Yb), which aims to explore the temporal effect of energy migration in UC. The pure hexagonal phase of nanoparticles was confirmed by the X-ray powder diffraction (Figure 2.9). Furthermore, the uniformed sizes (or thickness) of the core and each shell were verified to ~ 25.0 nm, ~ 2.8 nm, ~ 3.0 nm, respectively (Figure 2.10).

![Figure 2.9](image_url)

**Figure 2.9** The X-ray powder diffraction of YbEr@Yb@YbNd nanostructure (short for NaYF$_4$: 20% Yb, 2% Er @NaYF$_4$: 20% Yb @NaYF$_4$: 10% Nd, 20%Yb). All the peaks well accord with the standard hexagonal structure of NaYF$_4$ nanoparticles (Joint Committee on Powder Diffraction Standards file number 16-0334).

![Figure 2.10](image_url)

**Figure 2.10** The TEM images of the as-synthesized a) NaYF$_4$: 20% Yb, 2% Er bare core, b) NaYF$_4$: 20% Yb, 2% Er @NaYF$_4$: 20% Yb core-shell and c) NaYF$_4$: 20% Yb, 2% Er @NaYF$_4$: 20% Yb @NaYF$_4$: 10% Nd, 20%Yb core-shell-shell nanostructures. From the TEM images, the size (or thickness) of the core and each shell is measured to be ~ 25.0 nm, ~ 2.8 nm, ~ 3.0 nm.
To perform spectroscopic studies, a two colour pulse excitation setup is developed, in which the interval (Δt) between a 800 nm and a 980 nm nanosecond pulse is tunable from -200 μs to 1000 μs (Figure 2.11a). Typically, a 980 nm laser pulse excites Yb³⁺ ions all over the whole nanoparticle, whereas the 800 nm pulse only excites Nd³⁺ ions located in the outer layer (Figure 2.11b). The UC emission comes from (i) 980 nm excitation, (ii) 800 nm excitation, and (iii) 980 nm and 800 nm co-excitation. Obviously, the first two parts (i and ii) are Δt independent, and part (iii) depends on Δt. Strikingly, the strongest UC emission occurs not at Δt = 0, but at the point when the 980 nm pulse is ~ 200 μs behind the 800 nm pulse (Figure 2.11c).

Since Nd³⁺→Yb³⁺ energy transfer is very fast (~ 20 μs), the ~ 200 μs time delay should be mainly attributed to the additional Yb³⁺→Yb³⁺ energy migration under the 800 nm excitation. Significance of this result is that: (1) it is the first acquisition in real time of energy migration contribution to UC emission, and (2) it confirms that the energy migration temporal effect is non-negligible. This result is consistent with the prediction of Monte Carlo simulation. In NaYF₄:20% Yb sublattice, despite each step of Yb³⁺→Yb³⁺ energy migration only consumes ~ 1.7 μs (as shown in Figure 2.8), and even if the migration distance is just a few nanometers, the time delay for UC is several hundred microseconds. As indicated in Figure 2.12, for the aiming of 80% migrated ratio (we count the time for 80% excited states reaching to the core area at least once), according to the simulation, the required migration time is 16 μs, 42 μs, 84 μs and 142 μs for 2, 4, 6, and 8 migration layer (0.8 nm thickness per layer), respectively. To further validate our comprehension of energy migration dynamics, two types of DISS nanostructure are designed to tune the rise and decay of the time trace of UC luminescence, respectively.

Figure 2.11 (a) Schematic diagram of the experimental setup for binary pulsed (800 nm and 980 nm) excitation. (b) The YbEr@Yb@YbNd UC nanostructure used in the binary pulsed excitation experiment. (c) Time gap (difference between 800 and 980 nm pulses) dependent UC emission intensity of the YbEr@Yb@YbNd nanoparticles (integrated from 500 nm to 700 nm).
Chapter 2. Precisely Tailoring Upconversion Dynamics via Energy Migration in Core-Shell Nanostructures

Figure 2.12 (a) Schematic depiction of energy migration in NaYF$_4$: 20% Yb, 2% Er@NaYF$_4$: 20% Yb@NaYF$_4$: 10% Nd, 20%Yb DISS nanostructure. (b) The energy migration dynamic process among Yb$^{3+}$ ions in the NaYF$_4$: 20% Yb middle layer, also named as “migration layer” here. (c) The simulated results of the migrated ratio evolution of Yb$^{3+}$ excited states in the middle layers with different thicknesses.

2.3.2 Tuning the rise of UC emission time trace

To quantitatively tune the rise of the time trace of UC emission, the DISS nanostructure characterized with spatially separated absorption (sensitizer) and emission (activator) regions is suggested. As an example, the 800 nm excited YbEr@Yb@Nd core/shell/shell nanostructure (short for NaYF$_4$: 20% Yb, 2% Er@NaLuF$_4$: 20% Yb@NaYF$_4$:20%Nd) is employed here. The UC emission of this structure relies fully on the Yb$^{3+}$→Yb$^{3+}$ energy transfer to transport the absorbed energy from the outer layer to the core area (Figure 2.13a). The pure hexagonal phase and narrow size distribution of the nanoparticles are confirmed by Fourier-transform diffraction pattern and TEM images (Figures 2.13b and Figure 2.14). The core/shell/shell structure is identified from the darkness variation, i.e. the lighter lanthanide element (Y, brighter parts) and the heavier one (Lu, darker parts), in the TEM image (Figures 2.13b). Obviously, because of the non-neglectable Yb$^{3+}$→Yb$^{3+}$ energy migration time (~ 1.7 µs per step) in the NaLuF$_4$: 20% Yb$^{3+}$ middle layer, the time for Er$^{3+}$ ions to receive the excitation energy can be well controlled by the layer thickness, appearing as a tunable rise of UC luminescence time trace. Specifically, increasing the thickness of the middle layer from 0 to ~ 4.5 nm results in prolongation of rise of
~ 540 nm ($^2\!H_{3/2},^4S_{3/2} \rightarrow ^{4}\!I_{5/2}$) from 195 to 390 μs (Figure 2.13c, solid traces). Similar result is observed for $^4\!F_{9/2} \rightarrow ^{4}\!I_{15/2}$ transition (~ 650 nm), varying from 383 to 607 μs (Figure 2.15). It should be noted that without the long distance energy migration, such a large time span modulation of the rise edge is hard to achieve in traditional Yb$^{3+}$/Er$^{3+}$ co-doping systems.$^{41,51}$ Importantly, such a tuning effect is well predicted from our simulation (Figure 2.13c, dotted traces). The sample without middle layer (the red solid and dotted traces in Figure 2.13c) exhibits relatively large deviation between the experimental data and simulation result. The deviation most probably comes from the model simplification, which ignores the efficient Er$^{3+}\rightarrow$Nd$^{3+}$ energy quenching process.$^{28}$ The influence of Yb$^{3+}$ dopant concentration on energy migration dynamics is also studied. As shown in Figure 2.13d, the rise of the UC emission is getting faster when the Yb$^{3+}$ dopant concentration increases. This phenomenon can be ascribed to the migration process. With the Yb$^{3+}$ dopant concentration increasing from 10% to 40%, the energy migration becomes more efficient from $2\times 10^4$ s$^{-1}$ to $1\times 10^6$ s$^{-1}$ (cf. Figure 2.16 and Table 2.4). Furthermore, to verify the universality of our approach, another DISS nanostructure, i.e. NaYF$_4$: 20% Yb, 2% Er @NaYF$_4$: 20% Yb @NaYF$_4$: 10% Nd, 20% Yb is tested, and similar results were obtained (Figure 2.17).

Figure 2.13 (a) Schematic depiction of the UC process in the YbEr@Yb@Nd DISS nanostructure under 800 nm excitation. (b) Typical TEM image (left), zoom area of TEM image (upper right) and Fourier-transform diffraction patterns (lower right) of the YbEr@Yb@Nd nanostructure. (c) The energy migration distance (i.e. middle layer thickness) dependent 540 nm UC emission traces. Solid traces are the experimental results and dotted traces are the simulation results. (d) The influence of Yb$^{3+}$ dopant concentration in the middle layer (~ 2.5 nm) on the 540 nm UC emission traces.
Chapter 2. Precisely Tailoring Upconversion Dynamics via Energy Migration in Core-Shell Nanostructures

Figure 2.14 The TEM images of (a) the NaYF₄: 20% Yb, 2% Er bare core nanoparticle (~ 25 nm), (b) the NaYF₄: 20% Yb, 2% Er @NaLuF₄: 20% Nd nanoparticle (~ 30 nm), (c) NaYF₄: 20% Yb, 2% Er @NaLuF₄: 20% Yb (~ 2.5 nm) @NaYF₄: 20% Nd nanoparticle (~ 36 nm), and (d) NaYF₄: 20% Yb, 2% Er @NaLuF₄: 20% Yb (~ 4.5 nm) @NaYF₄: 20% Nd nanoparticle (~ 43 nm). From the contrast of elements Y and Lu in the TEM images, the migration layer (NaLuF₄: 20% Yb) thicknesses in b-d are calculated to be 0 nm, ~ 2.5 nm, ~ 4.5 nm, respectively.

Figure 2.15 For the NaYF₄: 20% Yb, 2% Er @NaLuF₄: 20% Yb @NaYF₄: 20% Nd series of nanoparticles, the energy migration distance (i.e. the middle layer thickness) dependent time-resolved UC luminescence traces monitored at 650 nm. Nanoparticles were excited by 800 nm. The numbers in the picture are the corresponding middle layer (NaLuF₄: 20% Yb) thicknesses.
Figure 2.16 The TEM images of the YbEr@x%Yb@Nd nanostructure (middle layer thickness is fixed to ~ 2.5 nm) with different Yb$^{3+}$ dopant concentrations in the middle layers (a) x=10, (b) x=20, (c) x=40. For the 800 nm excited YbEr@x%Yb@Nd nanostructure: (d) the distribution of simulated migration time to go through the 3 nm thick middle layer, (e) the experimental results of time-resolved 650 nm UC luminescence traces with ~ 2.5 nm thick middle layer.

Table 2.4 The calculated parameters for the NaYF$_4$: 20% Yb, 2% Er (25 nm) @NaLuF$_4$: x% Yb (3 nm) @NaYF$_4$: 20% Nd (x=10, 20, 40) nanostructures.

<table>
<thead>
<tr>
<th>Yb$^{3+}$ doping concentration</th>
<th>Yb$^{3+}$→Yb$^{3+}$ energy migration rate</th>
<th>Yb$^{3+}$-Yb$^{3+}$ distance</th>
<th>Yb$^{3+}$-Yb$^{3+}$ layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>2×10$^4$ s$^{-1}$</td>
<td>1.0 nm</td>
<td>3</td>
</tr>
<tr>
<td>20%</td>
<td>1×10$^5$ s$^{-1}$</td>
<td>0.8 nm</td>
<td>4</td>
</tr>
<tr>
<td>40%</td>
<td>1×10$^6$ s$^{-1}$</td>
<td>0.63 nm</td>
<td>5</td>
</tr>
</tbody>
</table>
Chapter 2. Precisely Tailoring Upconversion Dynamics via Energy Migration in Core-Shell Nanostructures

Figure 2.17 (a) Schematic depiction of the UC process in the NaYF₄: 20% Yb, 2% Er @NaYF₄: 20% Yb @NaYF₄: 10% Nd, 20% Yb core/shell/shell DISS nanostructure under 800 nm excitation. (b) The time traces of UC luminescence at 540 nm and (c) 650 nm subject to the middle layer thickness. Excitation is at 800 nm and the numbers in the pictures are the corresponding middle layer thicknesses.

2.3.3 Tuning the decay of UC emission time trace

Figure 2.18 The SEM images of the NaYF₄: 20% Yb, 2% Er (20 nm) @NaYF₄: 20% Yb core/active shell nanoparticles with different active shell thicknesses: (a) 0 nm (bare core), (b) 3 nm, (c) 6 nm, (d) 10 nm and (e) 15 nm. The scale bars are 50 nm.
Next we turn to tune the decay of UC emission time trace in a wide range, which is not only required for practical applications, but also very important for an in-depth understanding of the UC mechanism. Up to now, relevant modulations are almost exclusively focused on the depopulation rate of the emitting energy level of the activator, such as surface modification, Ln	extsuperscript{3+} dopant concentration manipulation, plasmonic effect and introducing extra energy transfer channels. All these approaches, however, suffer from limitations, such as (i) a limited tuning range, and (ii) UC efficiency reduction. Here, we propose a novel strategy, i.e. utilizing the energy migration process in DISS nanostructures characterized with partly overlapped sensitizer and activator regions. As an example, a series of YbEr@Yb core/active shell DISS nanostructures (short for NaYF	extsubscript{4}: 20% Yb, 2% Er@NaYF	extsubscript{4}: 20% Yb) are prepared with the SEM images shown in Figure 2.18.

![Figure 2.19](image)

**Figure 2.19** (a) Schematic of UC processes in YbEr@Yb core/active shell nanostructure under the 980 nm excitation. (b) Schematic of UC emission trace of YbEr@Yb nanostructure (red line) and its equivalent emission origins (black trace from part I, green trace from part II, and blue trace from part III). Shell thickness dependent 540 nm UC emission traces of the (c) core/active shell structures and (d) core/inert shell structures. (e) 540 nm decay lifetimes (left) and ~ 540 nm UC emission intensities (right) of core/inert shell structures (black curve) and core/active shell structures (red curve).

The UC processes in the DISS nanostructure can be roughly divided into three parts, as indicated in Figure 2.19a, b. In part I, Yb	extsuperscript{3+} and Er	extsuperscript{3+} are co-doped, therefore its UC emission dynamics presents as a relatively sharp rise due to the minimal energy migration time (black curve in Figure 2.19b). On the contrary, for parts II and III, the spatially separated Yb	extsuperscript{3+} and Er	extsuperscript{3+} prolong the excitation energy migration to achieve UC emission, which leads to (i) slower rise, and (ii) relatively low UC efficiency due to the energy loss during the migration (the green and blue lines in Figure 2.19b). Notably, the UC emission time trace is a profile of contributions of all the three
parts (Figure 2.19b). As indicated in Figure 2.19c, the UC emission (~ 540 nm) decay lifetime (the required time for transient emission intensity to decay from its maximum value to its 1/e value) could be tuned over a wide range from 139 to 648 μs by varying the active shell thickness from 0 to 15 nm. In the meantime, the rise component only changes little (from 36 to 144 μs) because they are all dominated by the common part I, as shown in Figure 2.20.

![Image](image_url)

**Figure 2.20** The shell thickness dependent time traces of 540 nm UC emission from the NaYF₄: 20% Yb, 2% Er (20 nm) @NaYF₄: 20% Yb core/active shell series of DISS nanoparticles. Excitation is at 980 nm. The shell thicknesses and corresponding rise time constants are indicated in the Figure.

The significance of the results is that (i) it breaks through the UC emission time tuning limitation of the traditional co-doping system. Without the assistance of energy migration in the shell, YbEr@Y core/inert shell structures (short for NaYF₄: 20% Yb, 2% Er@NaYF₄) may offer a relatively narrow tuning range from 139 to 330 μs based on surface quenching (Figure 2.19d). (ii) It encourages us to revisit the relationship between UC efficiency and the time behavior of UC emission. Based on the empirical view developed from sensitizer-activator co-doping systems, the longer UC emission decay lifetime is often related to a higher UC efficiency due to the reduction of nonradiative relaxation rate. This view is, however, not always valid. As indicated in Figure 2.19e, compared with YbEr@Y nanostructure, the YbEr@Yb DISS nanostructure exhibits a relatively long decay lifetime but a relatively low UC efficiency when the shell thickness is over 6 nm. This “abnormal” phenomenon comes from (i) the energy migration effect of the active shell, which prolongs the decay lifetime and (ii) the efficient energy back-transfer from core to active shell (decreasing the UC efficiency). This conclusion is further confirmed by the relatively short decay lifetime of Yb³⁺ excited states in core/active shell structures (Figure 2.21 and Table 2.5).
Figure 2.21 The decay lifetime traces of Yb$^{3+}$ ($^2$F$_{5/2}$ excited state) in core/inert shell (NaYF$_4$: Yb, Er@NaYF$_4$) and core/active shell (NaYF$_4$: Yb, Er@NaYF$_4$: 20% Yb) nanostructures. The excitation wavelength is 980 nm and the emission is monitored at 1040 nm.

Table 2.5 The Yb$^{3+}$ ($^2$F$_{5/2}$ excited state) decay lifetimes in core/inert shell and core/active shell nanostructures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Decay lifetime</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Active (μs)</td>
</tr>
<tr>
<td>bare core</td>
<td>205</td>
</tr>
<tr>
<td>3 nm shell</td>
<td>307</td>
</tr>
<tr>
<td>6 nm shell</td>
<td>345</td>
</tr>
<tr>
<td>10 nm shell</td>
<td>392</td>
</tr>
</tbody>
</table>

This “abnormal” phenomenon is also well predicted by our Monte Carlo simulations. As shown in Figure 2.22 and Table 2.6, on the condition of 6 nm shell thickness, due to the harmful energy back transfer effect (from core to active shell), ~ 76% Yb$^{3+}$ excited states are quenched by the surface quenching centers in the YbEr@Yb core/active shell nanostructure. Therefore, compared with the YbEr@Y core/inert shell structure, despite the core/active shell structure owns the higher absorption ability (about 3 times higher than core/inert shell structure), its Yb$^{3+}$ ($^2$F$_{5/2}$ energy level) lifetime is much shorter and its UC intensity is much weaker, which is well in line with the experimental results (Figure 2.19e).
2.4 Conclusion

In summary, long standing puzzle of the intimate link between excitation energy migration and UC emission dynamics is unraveled quantitatively through theoretical modeling and spectroscopic experiments of specifically designed “dopant ions spatially separated” nanostructure. Contribution of excitation migration to the UC emission dynamics is demonstrated to be significant due to the accumulative effect of multiple-step random walks of the excitation energy. Based on this upgraded comprehension, we propose and demonstrate a convenient and effective approach for tailoring UC dynamics (either the rise or decay edge) through tuning the excitation energy migration paths in “dopant ions spatially separated” nanostructures. Our study paves the way for application-optimized design of novel functional UC nanostructures and even to improve the UC emission efficiency.
2.5 Experimental details

Reagents. LnCl₃·6H₂O (Ln: Y, Yb, Er >99%), Ln₂O₃ (Ln: Y, Yb, Er, Nd >99%), Oleic acid (OA, 90%), 1-Octadecene (ODE, 90%), Oleylamine (OM, 90%), sodium trifluoroacetate (98%) and trifluoroacetic acid (99%) were purchased from Sigma-Aldrich and used without further purification. NaOH (>98%), NH₄F (>98%), methanol, ethanol and cyclohexane were purchased from GFS Chemical.

Synthesis of 20 nm β-NaYF₄: 20% Yb, 2% Er bare core nanoparticles. The 20 nm β-NaYF₄: Yb, Er nanoparticles were synthesized following reported approach. Typically, 0.78 mmol YCl₃·6H₂O, 0.2 mmol YbCl₃·6H₂O, 0.02 mmol ErCl₃·6H₂O were added into a mixture of 6 mL OA, 15 mL ODE in a three-necked flask. The solution was heated to 160 ℃ for 20 min under argon atmosphere to form a transparent solution and then cooled down to room temperature. Subsequently, 10 mL methanol solution contains 100 mg NaOH and 148 mg NH₄F was added into the solution dropwise. The mixed solution was heated slowly to 70 ℃ and kept stirring for 30 minutes to remove the methanol solvent completely. After evaporation of methanol, the solution was heated to 300 ℃ and maintained for 1.5 hours under argon atmosphere. After cooled down to room temperature, the resultant mixture was washed with ethanol and purified by centrifuge 3 times at the speed of 7000 rpm (each time for 6 minutes). The as-synthesized product of 20 nm β-NaYF₄: 20% Yb, 2% Er core nanoparticles were dispersed in 4 mL cyclohexane.

Synthesis of the β-core/shell nanoparticles. The NaYF₄: 20% Yb, 2% Er@NaYF₄ (YbEr@Y), NaYF₄: 20% Yb, 2% Er@NaYF₄: 20% Yb (YbEr@Yb) nanoparticles were synthesized following a reported approach. Take the structure of 1:1 (core: shell) in mol ratio as an example, 1 mmol LnCl₃·6H₂O was added into the mixture of 6 ml OA and 15 ml ODE in a three-necked flask. The solution was heated to 160 ℃ and remained for 20 minutes under argon atmosphere to form a transparent solution and then cooled down to room temperature. Subsequently, 10 mL methanol solution containing 100 mg NaOH and 148 mg NH₄F was added into the solution dropwise. The mixed solution was heated slowly to 70 ℃ and kept stirring for 30 minutes to remove the methanol solvent completely. After evaporation of methanol, the cyclohexane solution containing 1 mmol bare core nanoparticles was added into the stirring solution. Then the mixture was heated slowly to 85 ℃ and kept stirring for another 30 minutes to remove the cyclohexane solvent completely. After the evaporation of cyclohexane, the solution was heated up to 300 ℃ and maintained for 1h under argon atmosphere. After cooled down to room temperature, the resultant mixture was washed with ethanol and purified by centrifuge 3 times at the speed of 7000 rpm (each time for 6 minutes). The obtained core-shell nanoparticles (1:1, mol ratio) were dispersed in 8 ml cyclohexane. The shell thickness was controlled by the added mol amount of the shell reactant.

Synthesis of the shell precursors. The cubic sacrificial nanocrystals of 1) NaYF₄: 20% Yb, 2) NaLuF₄: x%Yb (x=10, 20 and 40), 3) NaYF₄: 20%Yb, 10% Nd and 4) NaYF₄: 20% Nd were synthesized as shell precursors following the reported method. Taking 1mmol NaYF₄ shell precursor as an example, 1 mmol CF₃COONa and 1 mmol (CF₃COO)₃Y were added into a three-necked flask with 3 ml OA, 3ml OM and 5ml ODE. The solution was heated to 120 ℃ with robust
stirring under argon atmosphere for 30 minutes. After the solid reagents were dissolved, the as-obtained clear solution was heated to 290°C and remained for 45 minutes under argon atmosphere. Then the solution was cooled down to room temperature and washed by ethanol once with centrifugation of 7000 rpm for 6 minutes. The product is dispersed in 4 ml ODE for later use.

Synthesis of the β-core/shell/shell nanoparticles. The NaYF₄: 20% Yb, 2% Er@NaYF₄: 20%Yb@NaYF₄: 20%Yb, 10% Nd (YbEr@Yb@YbNd) and NaYF₄: 20% Yb, 2% Er@NaLuF₄: x%Yb (x=10/20/40) @NaYF₄: 20% Nd (YbEr@Yb@Nd) core/shell/shell nanoparticles were prepared following the reported approach. After the reaction for bare core structure, instead of being cooled down, the as-obtained solution was kept at 300°C. Then the cubic sacrificial nanocrystals prepared as shell precursor was injected into the bare core reaction solution in one shot within ~1 sec by a syringe with a stainless steel cannula. The mixture was ripened with stirring at 300°C under argon atmosphere to form the core/shell structure. The multi-layer shells were realized by multi-injections. For each injection, the ripening time was 30 minutes for one layer. The shell thickness of each layer is controlled by the amount of cubic sacrificial nanocrystals in each injection. After the ripening, the solution was cooled down to room temperature and washed by ethanol with centrifugation at 7000 rpm 3 times, each for 6 minutes. The as-obtained nanoparticles were dispersed in 4 mL cyclohexane. The total shell thicknesses were controlled by the total amount of shell precursors.

Characterization. The transmission electron microscopy (TEM) was performed on a Tecnai G2 F20 S-TWIN D573 electron microscope operated at 300 kV TEM. The scanning electron microscopy (SEM) was performed on a Hitachi, S-4800. Power X-ray diffraction (XRD) characterization was performed on an X-ray powder diffractometer with Cu Kα radiation (λ = 1.542Å). The upconversion steady-state emission spectra were collected at room temperature by a Maya 2000 visible spectrometer (Ocean optics). All the luminescence dynamics were recorded with a 500 MHz Tektronix digital oscilloscope and the excitation was realized by a nanosecond pulse train at 800 nm or 980 nm from an optical parametric oscillator. During the spectroscopic measurements all the samples were dispersed in cyclohexane with the same concentration of nanoparticles.

Two color pulse excitation experimental. The setup consists of two Q-switched Nd-YAG optical parametric oscillator lasers (8 ns, 10 Hz, 1mJ). The wavelengths of laser pulses were set at 800 nm and 980 nm, respectively. The time gap between the two pulses was adjusted by a digital delay generator (Model 588 - 1U Rack Mount 8 Channel DDG). The NaYF₄: 20% Yb, 2% Er @NaYF₄: 20% Yb @NaYF₄: 10% Nd, 20%Yb (YbEr@Yb@YbNd) upconversion nanoparticles were dispersed in cyclohexane with the concentration of 10 mg/ml.
References


