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Precisely Tailoring Upconversion Dynamics via Energy Migration in Core–Shell Nanostructures

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Abstract: Upconversion emission dynamics have long been believed to be determined by the activator and its interaction with neighboring sensitizers. Herein this assumption is, however, shown to be invalid for nanostructures. We demonstrate that excitation energy migration greatly affects upconversion emission dynamics. “Dopant ions’ spatial separation” 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 new fundamental insight, 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.

Yttrium (Y) and lanthanide (Ln) ions doped upconversion (UC) materials have attracted extensive attention owing to their potential applications in a large variety of fields, for example, display,[1] biology,[2] anti-counterfeiting,[3] and solar cells.[4] 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.[5] That is, excited states could randomly “walk”, thus making the long-range energy transport (more than several nanometers) between Ln3+ ions 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.

Based on traditional understanding, energy migration among sensitizers is always neglected in UC dynamics treatment. In that case, although UC emission involves complex interactions between multiple Ln3+ ions, its dynamics are solely determined by the energy transfer processes within one activator–sensitizer pair (Figure 1a).[6] Despite some discussion of this assumption,[7] there is no direct evidence of the effect of the sensitizer-to-sensitizer energy migration on UC dynamics.

This unsatisfactory situation is primarily due to the lack of appropriate material systems. Indeed, even in the traditional sensitizer–activator co-doping materials, energy migration still plays an important role in their UC process.[8] However, its effect is difficult to evaluate as the 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 termed “dopant ions’ spatial separation” (DISS) nanostructure.[9] 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 1b). Therefore, the role of energy migration in UC dynamics could be quantitatively determined by 1) tuning the migration layer thickness or 2) varying the dopant concentration of the ions as energy carriers in the migration layer. Secondly, traditional treatment of the 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 (Figure S1–S7, Table S1–S3, in the Supporting Information). Compared with previous approaches,[5c,7,9] our model is capable of monitoring UC dynamics from the level of multiple ion-to-ion interactions,
yielding a more comprehensive vision without restriction of the distribution of Ln$^{3+}$ ions in the nanostructure.

Combining the experimental and simulation results, we find that despite each step of the energy migration (e.g. Yb$^{3+}$$\rightarrow$Yb$^{3+}$) only costs a relatively short time (around microseconds), its randomly walking nature significantly prolongs the migration time up to several hundred microseconds. This result tells us that the conventional understanding of the 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 a DISS nanostructure, either the 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 the rational design of novel functional and efficient UC nanostructures.

We prepared a DISS nanostructure: YbEr@Yb@YbNd (short for NaYF$_4$: 20% Yb, 2% Er @NaYF$_4$: 20% Yb @NaYF$_4$: 10% Nd, 20% Yb) to explore the temporal effect of energy migration. The pure hexagonal phase of the nanoparticle was confirmed by the X-ray powder diffraction (Figure S8). The uniformed sizes (or thickness) of the core and each shell were verified to be approximately 25.0 nm, 2.8 nm, 3.0 nm, respectively (Figure S9). To perform spectroscopic studies, a binary pulse excitation setup was designed, in which the interval ($\Delta t$) between a 800 nm and a 980 nm nanosecond pulse is tunable from ~200 µs to 1000 µs (Figure 2a).

Typically, 980 nm laser excites Yb$^{3+}$ ions all over the whole nanoparticle, whereas 800 nm only excites Nd$^{3+}$ ions located in the outer layer (Figure 2b). The UC emission comes from 1) 980 nm excitation, 2) 800 nm excitation, and 3) 980 nm and 800 nm co-excitation. Clearly, the first two parts (1 and 2) are $\Delta t$ independent, and part (3) depends on $\Delta t$. Strikingly, the strongest UC emission occurs not at $\Delta t=0$, but at the point when the 980 nm pulse is approximately 200 µs behind the 800 nm pulse (Figure 2c). Furthermore, since the time constant of Nd$^{3+}$$\rightarrow$Yb$^{3+}$ energy transfer is very short (ca. 20 µs, Figure S10), the approximately 200 µs time delay should be mainly attributed to the additional Yb$^{3+}$$\rightarrow$Yb$^{3+}$ energy migration time 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 NaYF$_4$:20% Yb sublattice, despite each step of Yb$^{3+}$$\rightarrow$Yb$^{3+}$ energy migration only takes about 1.7 µs (Figure S5), and even if the migration distance is just a few nanometers, the time delay for UC will still be several hundred microseconds because 1) the random walk nature of energy migration, and 2) the non-linear nature of UC emission.

![Figure 1](image1.png)

**Figure 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 DISS nanostructure, in which the three basic processes: photon absorption, energy migration, and UC emission are spatially separated.

![Figure 2](image2.png)

**Figure 2.** 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).
thickness of middle layer from 0 to about 4.5 nm results in prolongation of rise of around 540 nm UC emission (\(S_{\text{f2}}\) energy state) from 195 to 390 \(\mu\)s (Figure 3c, solid traces). Similar result has also been observed for \(F_{\text{o2}}\) energy state (ca. 650 nm UC emission), which varies from 383 to 607 \(\mu\)s (Figure S13).

Note that without the long-distance energy migration, such a large time modulation of the rise is hardly achieved in traditional Yb\(^{3+}/\)Er\(^{3+}\) co-doping systems\([7c,9]\). Importantly, such a tuning effect is well predicted by our simulation model (Figure 3c, dotted traces). The only exception is the sample without a middle layer (the red solid and dotted traces in Figure 3c). The deviation most probably comes from the model simplification, which ignores the efficient Er\(^{3+}\)\(-\)Nd\(^{3+}\) energy quenching process\([5f]\). In addition, the influence of Yb\(^{3+}\) dopant concentration on energy migration dynamics has been studied. As shown in Figure 3d, the migration time will decrease as the Yb\(^{3+}\) dopant concentration increases. The reason is discussed in details in Supporting Information (Figure S14 and Table S4). Furthermore, to verify the universality of our approach, another DISS nanostructure, that is, NaYF\(_4\) : 20\% Yb, 2\% Er@NaYF\(_4\) : 20\% Yb@NaYF\(_4\) : 10\% Nd, 20\% Yb has been tested, and similar results were obtained (Figure S15).

Next we turn to tune the decay of time-resolved UC emission in a wide range, which is not only required for practical applications\([8,9]\) but also very important for an in-depth understanding of the UC mechanism.\[10\] Up to now, modulation approach was almost exclusively addressed by changing the depopulation rate of the activator emitting energy level, such as surface modification, Ln\(^{3+}\) dopant concentration manipulation, plasmonic effect and introduc-
Without the assistance of energy migration in the shell, YbEr@Y core/inert shell structures (short for NaYF4; 20% Yb, 2% Er@NaYF4), as a control, offer a relatively narrow tuning range (from 139 to 330 μs) via eliminating the surface quenching effect (Figure 4d). 2) It guides us to reconsider the relationship between UC efficiency and decay lifetime. Based on the empirical views 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 to DISS nanostructures. As indicated in Figure 4e, 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 can be explained by 1) the energy migration effect of the active shell (prolonging the decay lifetime) and 2) the efficient energy back-transfer from core to active shell (decreasing the UC efficiency) (Figure S18,19 and Table S5). It is quite gratifying to notice that the “abnormal” phenomenon is well predicted by our Monte Carlo simulations (Figure S20 and Table S6).

In summary, long-standing puzzle of the intimate link between excitation energy migration and UC emission dynamics is unraveled through theoretical modeling and spectroscopic experiments of specifically designed “dopant ions’ spatial separation” nanostructure. The contribution of excitation migration to the UC emission dynamics is demonstrated to be significant as a result of the accumulative effect of multiple-step random walks of the excitation energy. Based on this improved understanding, we propose and demonstrate a convenient and effective approach for tailoring UC dynamics (either the rise or decay) through tuning the excitation energy migration paths in “dopant ions’ spatial separation” nanostructures. Our study paves the way for application-optimized design of novel functional UC nanostructures and even to improve the UC emission efficiency.

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Conflict of interest

The authors declare no conflict of interest.

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