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## Remote manipulation of upconversion luminescence

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The precise control over the luminescence profile of lanthanide-doped upconversion nanomaterials is of fundamental importance for their applications in wide-ranging fields of research. Conventional chemical approaches can lead to color-tunable emissions, but they generally require stringent modification either on dopant composition or doping concentration. In this Tutorial Review, we highlight a number of complementary methods that offer remote dynamic modulation of upconversion luminescence across the visible spectrum. This review serves to provide a summary of existing guidelines for controlling the emission spectrum of upconversion nanocrystals with fixed materials composition. The review will also discuss the major approaches to manipulating excitation energies and consider likely research challenges for further development of the field at the interface between nanotechnology and biological science.

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### Key learning points

- (1) Understand the basic principle of photon upconversion in lanthanide-doped nanocrystals.
- (2) Recognize the key advantages of upconversion among various spectral conversion processes.
- (3) Achieve tunable upconversion emission through spatial and temporal control.
- (4) Identify major scientific challenges for manipulating upconversion emission.

## 1. Introduction

Lanthanide-doped upconversion nanoparticles (UCNPs) have gained tremendous attention over the past few years due to their remarkable and unique optical properties, such as sharp emission peak, low auto-fluorescence background signal, long luminescence decay time and high resistance to photo-bleaching and photo-blinking, as well as the anomalous capability of merging two or more photons into a higher energy photon.<sup>1</sup> Such attributes make these nanoparticles ideal for use

in a rich assortment of emerging applications, including high-resolution bio-imaging, quantitative analysis of biological samples, photodynamic therapy, lasing, remote photo-activation, anti-counterfeiting, volumetric full-color display, and photonic quantum logic gates.<sup>2</sup> Robust synthesis of high quality UCNPs with precisely controlled size, shape, and composition has laid the foundation for unravelling fundamental upconversion luminescence mechanisms. By taking advantages of versatile surface-coating strategies, it has proven feasible that UCNPs can be made water dispersible and biocompatible, thereby significantly boosting their prospect for utilities in biological settings.<sup>3</sup>

The realization of upconversion luminescence from different types of lanthanide ions is not a trivial process. Thus far, the underlying physical origins of various upconversion processes, such as excited-state absorption (ESA), energy transfer upconversion (ETU), cooperative sensitization upconversion (CSU), energy migration-mediated upconversion (EMU), have been extensively investigated both theoretically and experimentally (Fig. 1). The knowledge that we gained over the course of investigations is immensely valuable. For instance, by properly selecting the type of lanthanide dopants in a nanocrystal, one can precisely modulate the upconversion emission of the nanocrystal over

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the entire visible spectrum (Fig. 2). The mechanistic investigation of UCNPs also opens new opportunities for designing multifunctional particle architectures that exploit the fundamental optical properties of both lanthanide and transition-metal ions.<sup>4</sup>

The requirement of a specific emission band is hinged upon the situation in which the nanoparticle is used. Due to their abundant levels of energy state, most lanthanide ions exhibit multi-peak emissions. For bio-related applications, both the excitation and emission wavelengths are in principle expected to be located within the near-infrared (NIR) window which penetrates deeper into biological tissues. When used for illuminating living cells NIR light is much less harmful than blue and ultraviolet light, which can induce strong phototoxicity due to DNA damage and the associated disruption of cellular processes. However, there are some exceptions for which blue-ultraviolet light emission can turn into an advantageous resource to therapeutic uses. Indeed, numerous studies have

demonstrated the beneficial effect of upconverted blue-ultraviolet light under a diverse array of conditions for targeted, localized drug delivery or phototherapy. For high-sensitivity biological imaging and molecular detection requiring the use of UCNPs as energy donor, the precise tuning of emission profiles is crucial as the efficiency of such an energy transfer largely depends upon the nature of the particle's emission. When considering the prospect of UCNPs for color display, the monochromaticity of the emission must be carefully regulated. To obtain high-purity emission, a doping strategy that can efficiently suppress unwanted emission peaks needs to be developed.

In essence, spectral management in UCNPs involves selectively enhancing or quenching a particular emission peak by redistribution of the excitation energies over the lanthanide ions. This raises the interesting question of what is the most effective strategy to control the emission properties of UCNPs? Clearly, that is a challenging question to answer since many factors, such as particle size, shape, crystal structure, the type of



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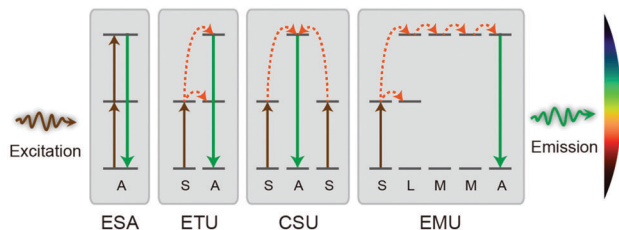
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**Fig. 1** Schematic illustration of simplified energy level diagrams depicting four major anti-Stokes processes involving lanthanide-doped nanoparticles. A: energy activator; S: energy sensitizer; L: energy ladder; M: energy migratory ion. ESA: excited-state absorption involving promotion of higher-lying energy levels through sequential absorption of pump photons by a single ion; ETU: energy transfer upconversion realized through energy delivery between two neighboring ions; CSU: cooperative sensitization upconversion featuring cooperative interaction in the framework of a sensitizer-activator exchange-coupled dimer; EMU: energy migration upconversion characterized by the migration (or hopping) of excitation energy via the migratory ion sublattice.

solvent molecules, the choice of surface ligands, and the effects of temperature and pressure, may influence the luminescence behaviors of UCNPs. Indeed, to access different color emissions, one has to perform a new set of reactions which require stringent controls over a number of parameters. This is clearly time consuming and resource intensive, and sometimes requires a degree of serendipity. Nonetheless, progress is being made in developing color tunable nanocrystals without the need for repeated synthesis. Recently, Han *et al.*<sup>5</sup> have introduced a simple post-synthetic cation exchange reaction at nanoscale to modulate the emission color of UCNPs at room temperature, while preserving the size and morphology of the original template.

Despite significant progress made, the tuning of upconversion luminescence by way of chemical modification is virtually an irreversible process. Moreover, it is almost impossible to distinct the effect of crystal field on luminescence from other extrinsic effects at work for the samples under investigation. Apart from *de novo* chemical modification of UCNPs, many other strategies have recently emerged to provide a remote control over the particle's emission without the need for reconstruction of the nanoparticles. In this Tutorial Review, we attempt to provide a concise survey of several approaches that can be implemented to control upconversion luminescence through external stimuli. These include excitation condition, temperature, and the near-field effects arising from plasmon, magnetic, and electric field enhancement. We believe that the ability to remotely fine-tune the emission color of UCNPs is likely to provide new directions for future research, and should have profound implications on many different disciplines, ranging from advanced bioimaging and chemical sensing to anti-counterfeiting and optoelectronics.

## 2. Strategies for remote-control upconversion

### 2.1 Expanding excitation range

One of the major hurdles in upconversion research is the stringent constraint over the laser output wavelength that needs to match well with the absorption wavelength of lanthanide ions. Trivalent Yb<sup>3+</sup> ion is the most extensively used sensitizer in UCNPs activatable by a 980 nm diode laser, thanks to its large cross-section absorption around this NIR wavelength



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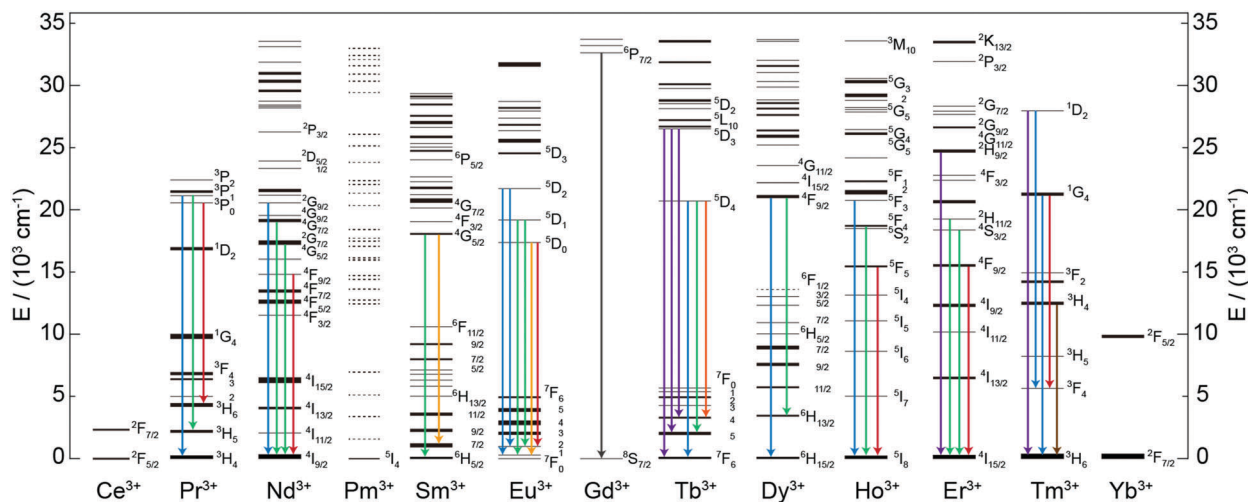


Fig. 2 Partial energy level diagram of lanthanide ions commonly used for achieving upconversion emission. The radiative transitions corresponding to typical emissions are highlighted.

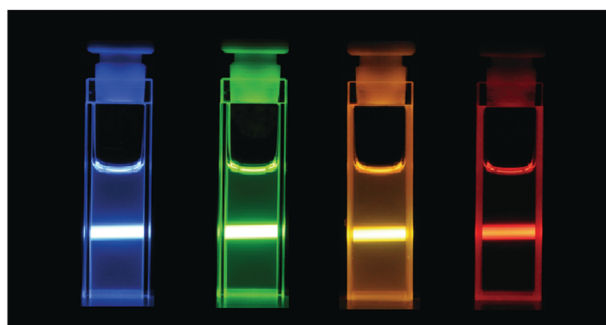


Fig. 3 Digital photographs of UCNP colloidal dispersions upon 980 nm laser excitation. Samples from left to right are NaYF<sub>4</sub>:Yb/Tm(30/1 mol%), NaYF<sub>4</sub>:Yb/Ho(10/1 mol%), NaYF<sub>4</sub>:Yb/Er(60/10 mol%) and NaYF<sub>4</sub>:Er/Tm(20/2 mol%) nanoparticles, respectively. Note that all samples are coated with an inert NaYF<sub>4</sub> shell.

relative to that of other lanthanides (Fig. 3). For an upconversion process to proceed, trivalent lanthanide ions such as Er<sup>3+</sup>, Tm<sup>3+</sup> and Ho<sup>3+</sup> that feature ladder-like arranged energy levels are in most stances co-doped as activators. When irradiated with the 980 nm laser, the Yb<sup>3+</sup> ion can absorb pump photons and then transfer the excitation energy to an adjacent activator ion. The cascade transfer of the excitation energy gives rise to upconverted luminescence that is typically observed in UCNPs.

However, one has to bear in mind that the 980 nm excitation can be significantly absorbed by water molecules and thus cause an overheating problem, which hinders the practical applications of UCNPs in biological settings. The overheating effect induced by 980 nm excitation could be principally diminished upon 800 nm laser excitation because of low absorption coefficients displayed by water molecules or biological tissues at this particular wavelength. Trivalent Nd<sup>3+</sup> ion is well suited for such purpose, as it features a sharp absorption band centered around 800 nm. Indeed, many research groups have confirmed that the use of Nd<sup>3+</sup> ion as sensitizer, in

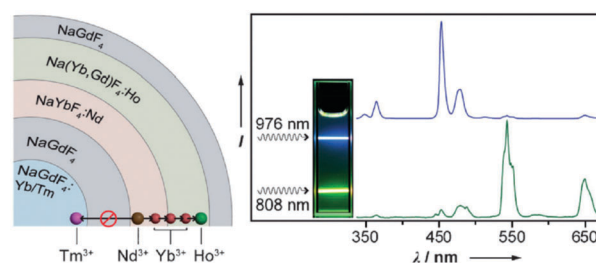


Fig. 4 Left: Schematic design of UCNPs for dual-color tuning through core-shell engineering. Right: Emission spectra of the UCNPs under excitation at 808 and 976 nm, respectively. Reproduced from ref. 9 with permission from the John Wiley and Sons, copyright 2013.

combination with Yb<sup>3+</sup>, facilitates the energy transfer and the process of photon upconversion upon 800 nm excitation.<sup>6–8</sup>

It should be noted that the Nd<sup>3+</sup>–Yb<sup>3+</sup> sensitizer pair is responsive to both 980 and 800 nm excitations. Wang and co-workers<sup>9</sup> have demonstrated dual-color emission from core-shell structured UCNPs when excited at two different wavelengths (Fig. 4). To realize the color tuning, Ho<sup>3+</sup> and Tm<sup>3+</sup> ions need to be embedded into separate layers. An inter-layer made of NaGdF<sub>4</sub> separates Tm<sup>3+</sup> and Nd<sup>3+</sup> ions to suppress cross-relaxation that typically depopulates an excited state due to interaction of dopant ions. Upon 976 nm excitation, the blue emission resulting from Tm<sup>3+</sup> activation is much stronger than the green emission of Ho<sup>3+</sup>. Notably, an array of Yb<sup>3+</sup> ions was used as energy mediator to direct the energy transfer from Nd<sup>3+</sup> to Ho<sup>3+</sup> ions. As a result, under 808 nm excitation the core-shell nanoparticles give rise to green emission.

Lee and co-workers<sup>10</sup> have recently designed multi-shell structured UCNPs which are capable of yielding orthogonal UV and visible emissions in response to 808 and 980 nm excitations. These nanoparticles offer a convenient method to spatially and temporally regulate photochemical reactions. As proof of principle, the researchers have demonstrated

reversible two-way photoswitching of spiropyran molecule between its two unique optical, electronic, and structural states. In 2016, Liu and co-workers<sup>11</sup> reported the design of hexagonal-phase  $\text{NaYF}_4\text{:Nd/Yb@NaYF}_4\text{:Yb/Tm}$  nanocrystals with the ability to emit light at 803 nm when illuminated at 745 nm. This task was accomplished by taking advantages of the large absorption cross-section of  $\text{Nd}^{3+}$  in the spectral range of 720 to 760 nm plus efficient energy migration through  $\text{Nd}^{3+} \rightarrow \text{Yb}^{3+} \rightarrow \text{Yb}^{3+} \rightarrow \text{Tm}^{3+}$ . This strategy enables the researchers to achieve deep-tissue imaging, while mitigating the attenuation effect typically associated with the visible emission or the overheating constraint imposed by conventional 980 nm excitation. It is also possible to obtain dual-color emissions through both upconversion and downshifting processes, as exemplified by Chen and co-workers,<sup>12</sup> who have utilized a 980 nm laser and a UV lamp (273 nm) to illuminate  $\text{NaGdF}_4\text{:Yb/Tm@NaGdF}_4\text{:Eu}$  nanoparticles. This advance is of potential interest for the development of anti-counterfeiting inks, providing positive, instant identification and verification of materials with the naked eye.

Inspired by the fundamental working principle of laser, the groups of Wrachtrup, He, Jin and Xi have investigated lanthanide-doped UCNPs as luminescent probes for stimulated emission depletion (STED) super-resolution imaging.<sup>13–16</sup> For example, Jin and colleagues<sup>16</sup> have successfully demonstrated that the visible upconversion emission of  $\text{Tm}^{3+}$ , arising from laser excitation at 980 nm, could be visibly counteracted by applying another beam of de-excitation at 808 nm (Fig. 5a). Interestingly, the 808 nm doughnut-shaped STED beam instantly depletes upconversion emission and dims the overlapping area, which results in a luminescence spot size far below the diffraction limit. This smart design enables the researchers to achieve super-resolution imaging with a lateral resolution of 28 nm, under a relatively low power density of  $9.75 \text{ MW cm}^{-2}$  (Fig. 5b and c).

Another promising field of application of UCNPs is their utility for solar energy harvesting, as these nanomaterials have the ability to minimize non-absorption energy losses in photovoltaic devices by converting two or more sub-bandgap NIR photons into one usable above-bandgap photon. When an UCNP-based upconverter is placed at the rear side of a solar cell, the transmitted sub-bandgap photons through the solar cell can be absorbed by the upconverter and further convert into light that could be reused by the solar cell. This design, in combination with a reflector layer, potentially enables the breaking of the Shockley–Queisser efficiency limit for a single junction cell. Nevertheless, most lanthanide ions have very narrowband absorption in the NIR spectral region. Therefore, solar energy harvesting through the use of UCNPs remains enormously difficult and fairly inefficient. The use of multi-wavelength-sensitizable UCNPs is likely to boost energy conversion efficiency. As an illustration, Qiu *et al.*<sup>17</sup> reported the observation of enhanced visible emission from  $\text{LaF}_3\text{:Ho}^{3+}$  phosphors upon excitation with a dual-laser configuration (970 and 1150 nm).

Advances in the study of organic dyes are leading to exciting opportunities for creating hybrid UCNPs that offer improved

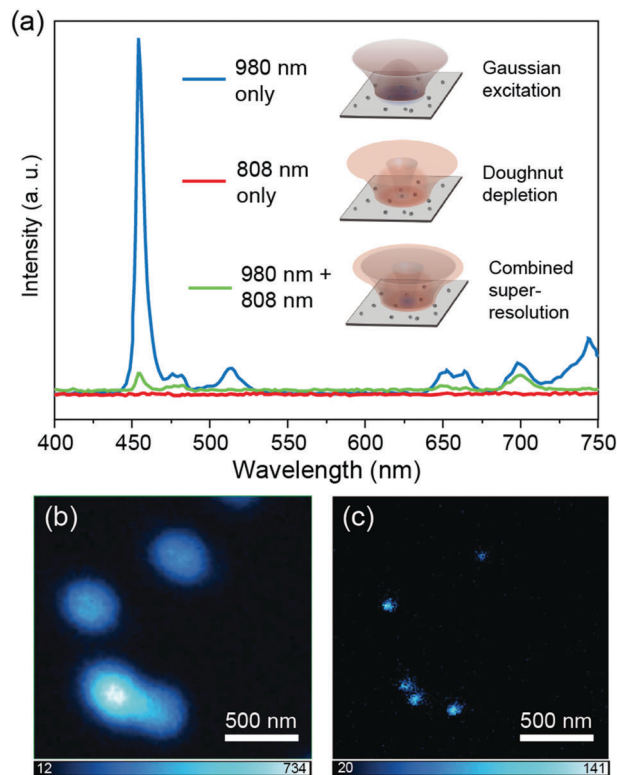


Fig. 5 (a) Upconversion emission spectra of  $\text{NaYF}_4\text{:Yb/Tm}$  (20/8%) UCNPs upon 980 nm, 808 nm and dual excitations. (b and c) Respective confocal and upconversion-STED super-resolution images. Reproduced from ref. 16 with permission from the Springer Nature, copyright 2017.

energy conversion efficiency. By coupling UCNPs with an organic NIR dye molecule, it has been possible to increase absorptivity and substantially extend the range of wavelength that the hybrid nanosystem absorbs. For example, in 2012 Hummelen and co-workers<sup>18</sup> showed that combining  $\text{NaYF}_4\text{:Yb/Er}$  nanoparticle and a cyanine dye molecule, which is structurally modified to bind to the particle's surface, permits a broadband excitation over the 740–850 nm range. Consequently, the spectral response of the dye-sensitized nanoparticle in the range of 720–1000 nm is enhanced by a whopping 3300 times when compared with the control sample without dye modification.

Three years later, Chen *et al.*<sup>19</sup> demonstrated that the upconversion quantum efficiency of  $\text{NaYbF}_4\text{:Tm@NaYF}_4\text{:Nd}$  UCNPs can be enhanced by  $\sim 100$  times by coupling a NIR-sensitive organic dye. The researchers attributed the dramatic enhancement to the broadened NIR excitation range and the enlarged absorption cross-section ( $1.47 \times 10^{-14} \text{ cm}^2$  per single dye-sensitized UCNP). Another exciting feature of this design is that the dye-sensitized UCNPs can be excited with a power density comparable to that of solar irradiation at the earth's surface ( $0.016 \text{ W cm}^{-2}$ ). The importance of dye sensitization on photon upconversion has further stimulated an effort to develop hybrid nanosystems featuring a set of wavelength selective absorptive dyes for enhanced light-harvesting process.<sup>20</sup> The dye-sensitized upconversion mechanism remains less well understood, but some trends can be discerned. For instance, the emission of

dye molecules chosen should overlap with the  $\text{Yb}^{3+}$  absorption band. Ideal dye candidates should possess rigid structures with multiple functional groups that allow them to tightly bind to particle surface. Therefore, the identification of suitable dye sensitizers remains a daunting challenge and often requires a good understanding of the mechanism that governs excited states in organic molecules.

Apart from photoluminescence, lanthanide-doped upconversion nanomaterials can also be excited by a beam of electrons to generate cathodoluminescence.<sup>21</sup> The luminescence intensity could be readily tuned by adjusting excitation voltage and current density. Helium ion beam ( $\alpha$ -beam) has also proven to be an effective form of excitation source for pumping upconversion processes.<sup>22</sup> Unlike the ETU process induced by NIR laser excitation, the interaction between the  $\alpha$ -beam and the crystal lattice generates a large number of excitons, carrying energies ranging from 0.1 eV to 1000 eV. Such high energies are able to not only excite many  $\text{Yb}^{3+}$  ions but also allow a substantial amount of  $\text{Tm}^{3+}$  ions to be populated prior to the event of energy transfer from  $\text{Yb}^{3+}$  to  $\text{Tm}^{3+}$ . More importantly, this technique allows for high-resolution luminescence beyond the diffraction limit. For good measure, the research team registered a spatial resolution of  $\sim 28$  nm, contrasting to  $\sim 253$  nm of imaging resolution obtained under conventional NIR laser excitation (Fig. 6). By combining this capability with scanning transmission ion microscopy, they further demonstrated simultaneous luminescence imaging and 3D mapping of cellular structures on a whole cellular level.

## 2.2 Varying excitation power density

For upconversion involving a single-wavelength excitation, the easiest way to alter upconversion process is to vary power density of the excitation. Indeed, in 2000, both theoretical and experimental investigations suggested that the upconversion luminescence of lanthanide ions strongly depends on the pumping power.<sup>23</sup> Due to the effects of nonlinearity, UCNPs possessing different upconversion processes usually exhibit

disparate response to the power density. Generally, high-order upconversion emission requires more excitation photons involved. Thus the emission from a high-lying level only occurs upon a relatively high excitation power. On the other hand, the increase in the power density is likely to lead to a larger rate of increase in the emission intensity from the high-lying level than that occurring at a low-lying level.<sup>24</sup> An illustration of this principle can be found in the photoluminescence study of hexagonal-phase  $\text{NaYF}_4\text{:Yb/Tm}$  nanoparticles by Zhou *et al.*,<sup>25</sup> who observed a 70-time fold enhancement in  $\text{Tm}^{3+}$  emission at 450 nm ( $^1\text{D}_2 \rightarrow ^3\text{F}_4$  transition) relative to its emission at 800 nm ( $^3\text{H}_4 \rightarrow ^3\text{H}_6$  transition) at a power density of  $1.1 \times 10^7 \text{ W cm}^{-2}$ . It is worth noting that a continuous NIR illumination over a prolonged period will inevitably deplete a sizable portion of excitation energy due to phonon coupling, and may locally heat the lattice atoms.

In 2010, Boyer *et al.*<sup>26</sup> demonstrated an interesting structural switching of photoresponsive dithienylethene molecule by simply changing the power intensity of excitation (Fig. 7). At a high power density of  $500 \text{ W cm}^{-2}$ , dominant emissions arise from  $\text{Tm}^{3+}$  activation. This gives rise to ultraviolet and blue light, which can drive a ring-closing reaction within the dithienylethene molecule. In contrast, a low power density of  $15 \text{ W cm}^{-2}$  results in a ring-opening reaction within the organic molecule, as a result of green emissions from  $\text{Er}^{3+}$ .

In a nanocrystal co-doped with  $\text{Yb}^{3+}$  and  $\text{Tm}^{3+}$  ions, the doping of  $\text{Tm}^{3+}$  at a high concentration is generally meant to maximize the transfer of the excitation energy absorbed by the  $\text{Yb}^{3+}$  sensitizer. But at high concentrations, the luminescence quenching of  $\text{Tm}^{3+}$  often takes place due to the deleterious cross-relaxation, typically observed in heavily doped nanocrystals. One solution in the past was maintaining a relatively low concentration of the activator – typically less than 2 mol%. The upconversion efficiency can be expected to follow an approximately linear

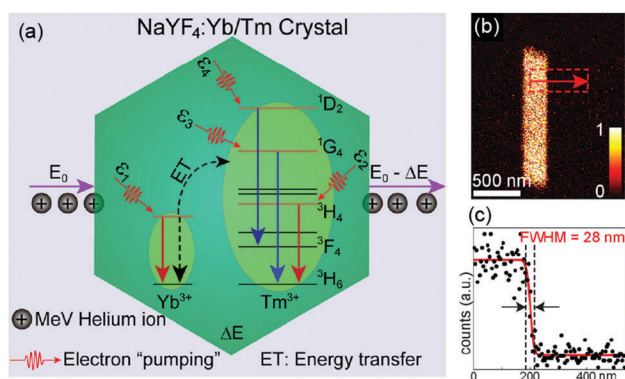


Fig. 6 (a) Proposed upconversion mechanisms of Yb–Tm codoped system under ion-beam stimulation. (b) Ionoluminescence image of a single nanorod. (c) The corresponding line-scanning profile extracted from the intensity counting at the region marked in (b) along the arrow, indicating an imaging resolution of about 28 nm. Reproduced from ref. 22 with permission from the Springer Nature, copyright 2015.

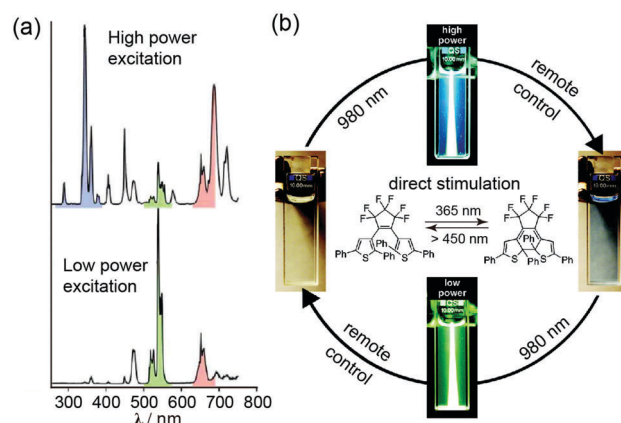


Fig. 7 (a) Upconversion luminescence spectra of  $\text{NaYF}_4\text{:Yb/Tm@NaYF}_4\text{:Yb/Er@NaYF}_4$  nanoparticles under 980 nm excitation at high ( $500 \text{ W cm}^{-2}$ ) and low ( $15 \text{ W cm}^{-2}$ ) power densities. (b) Demonstration of reversible photoswitching of dithienylethene molecule in its open and closed forms using UCNPs. The switching was enabled by varying the excitation intensity. Reproduced from ref. 26 with permission from the American Chemical Society, copyright 2010.



relationship with increasing power density, but a plateau is quickly observed to occur. By examining the dependence of saturation power on  $\text{Tm}^{3+}$  concentration through use of a specially designed fiber, Zhao *et al.*<sup>27</sup> have found no sign of reaching the saturation point for nanoparticles doped with 8 mol% of  $\text{Tm}^{3+}$  under a high pump power of  $2.5 \times 10^6 \text{ W cm}^{-2}$ , meaning that the luminescence saturation threshold could be appreciably increased with high power excitation.

For energy migration-mediated processes, the effective population in the  $^1\text{I}_6$  energy level of  $\text{Tm}^{3+}$  is critical for pumping the  $^6\text{P}_{7/2}$  energy level of  $\text{Gd}^{3+}$  and the energy transfer from  $\text{Gd}^{3+}$  to a given  $\text{X}^{3+}$  activator in succession (Fig. 8a). The emission of the activator is hardly observable upon excitation with a relatively low power (Fig. 8b). This observation was best illustrated in the investigation of  $\text{NaGdF}_4\text{:Yb/Tm@NaGdF}_4\text{:Mn}$  nanoparticles in which  $\text{Mn}^{2+}$  emission can only be efficiently observed under a high-power 980 nm excitation.<sup>4</sup> On a separate note, Zhang *et al.*<sup>28</sup> achieved emission switching using  $\text{NaGdF}_4\text{:Yb/Tm/Er@NaGdF}_4\text{:Eu@NaYF}_4$  nanoparticles by changing the power density of the laser in use. On low power density irradiation, only  $\text{Er}^{3+}$  ions doped in the core region could be effectively excited, giving rise to green emission through a two-photon upconversion process. With increasing power density, the generation of three-, four-, and five-photon upconverted emission from  $\text{Tm}^{3+}$  was successful, in addition to the two-photon upconverted  $\text{Er}^{3+}$  emission. Notably, the 5-photon ETU process through  $\text{Tm}^{3+}$  also enabled  $\text{Eu}^{3+}$  emission *via*

$\text{Gd}$ -mediate energy migration. As a result of the multiphoton upconversion processes in effect, a bright white emission was observed under excitation at 980 nm with a power density of  $15 \text{ W cm}^{-2}$ , while a red emission from  $\text{Eu}^{3+}$  dominated the whole visible spectrum when the power density was increased to about  $30 \text{ W cm}^{-2}$ .

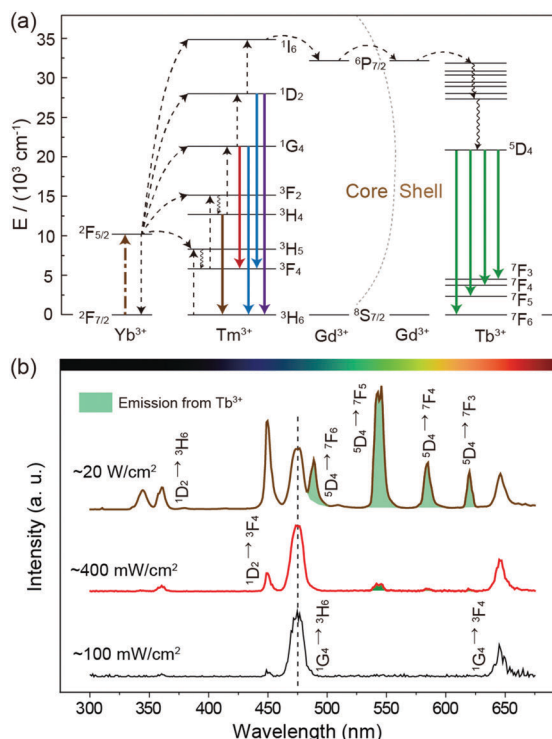
### 2.3 Altering excitation pulse width

Almost all upconversion emissions involving continuous-wave (CW) laser excitation are governed by steady-state processes, in which the deactivation of the excitation energy and the energy transfer process occur at the same rates. Non-steady-state upconversion emission, characterized by different rates between the decay of the excited state and the energy transfer upconversion process, can only be achieved by a very short laser pulse. It has long been known that the pumping of a lanthanide ion to a particular energy level often contains many steps, including energy transfer process, nonradiative relaxation process, and cross-relaxation. As the temporal dynamics of each excited state at the non-steady state involve a nonlinearly coupled differential system, it is feasible to bring about emission color manipulation through temporal modulation of the pulsed excitation.<sup>29</sup>

Deng *et al.*<sup>30</sup> have now achieved this goal by exploiting the non-steady-state upconversion, based on the design and synthesis of a new class of Yb/Ho/Ce-doped core-shell nanocrystals (Fig. 9a). In their work, the emission color of the nanocrystals was turned by adjusting the pulse width and intensity of a 980 nm pulsed laser. With a rational designed multi-layered core-shell structure, the nanocrystals can emit three primary colors (red, green, blue; RGB) with tunable ratios and intensities (Fig. 9b). This phenomenon can be explained by considering the effect of relaxation and energy transfer probabilities of variously excited states on the dynamics of energy level pumping. If the pulse width is short, the system does not have enough time to reach the equilibrium condition, which only obtained under CW or long-pulsed excitation. Only energy levels accessible through fast processes can be populated. Combined with an 808 nm CW laser excitation, the dual-laser system enabled to extend the color gamut beyond the three primaries (Fig. 9c). The ability of emitting variable emission colors on demand allows the researchers to demonstrate full-color volumetric 3D displays with wide-color gamut and high spatial resolution. This work presents a tantalizing opportunity on the precise control of color emission in a wide range of applications such as optical memory, multiplexed optical chemical sensing, anti-counterfeiting<sup>31</sup> and so on.

### 2.4 Excitation by sequential pulse pumping

The demonstration of lasing from UCNPs offers interesting possibilities for the verification of the upconversion efficiency, but the realization of such stimulated emission is far from straightforward. To begin with, one must overcome the difficulty in assembling ultra-small particles as optical gain media. In addition, it would be necessary to achieve sufficient population inversion and minimize the associated optical damage to the nanoparticles. These hurdles proved very difficult to address,



**Fig. 8** (a) Proposed mechanism of energy migration upconversion in  $\text{NaGdF}_4\text{:Yb/Tm(20/0.5)\%@NaGdF}_4\text{:Tb(15\%)}$  nanoparticles. (b) Upconversion emission spectra of the nanoparticles upon 980 nm laser excitation at different power densities ( $0.1$ ,  $0.4$  and  $20 \text{ W cm}^{-2}$ ).

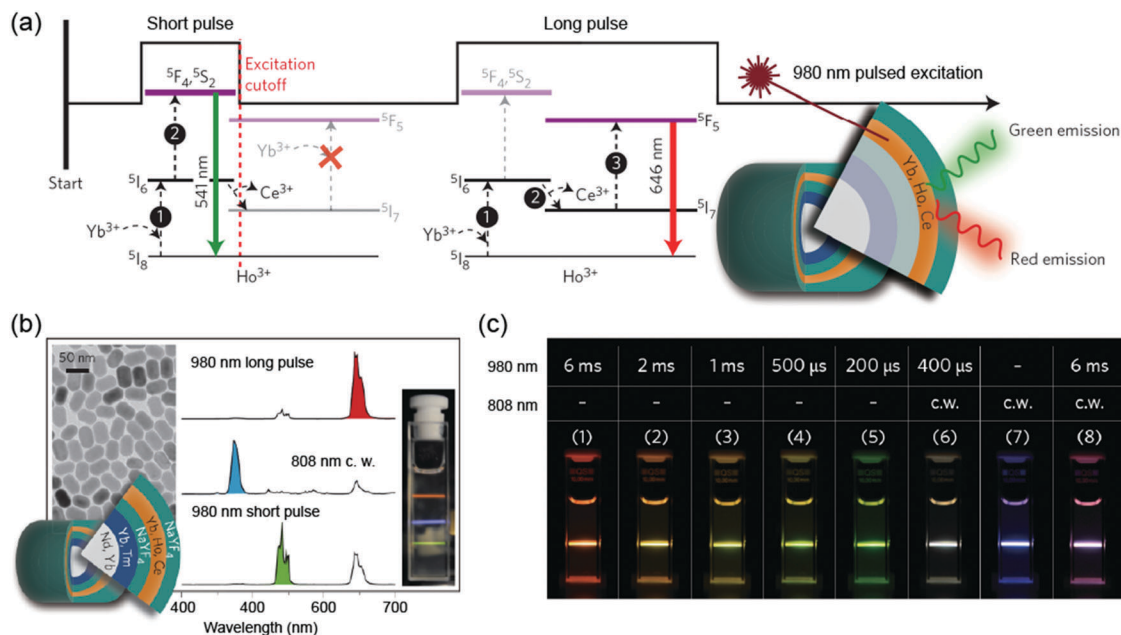


Fig. 9 (a) Proposed upconversion mechanisms for green/red emissions from a  $\text{Yb}^{3+}$ - $\text{Ho}^{3+}$ - $\text{Ce}^{3+}$  triply doped system under 980 nm pulsed laser excitation. (b) Rational design of pulse-duration-sensitive UCNPs capable of emitting tunable colors. Left inset: Representative TEM image of the as-synthesized nanoparticles and schematic drawing showing the layout of multilayer structures. Main panel: Upconversion emission spectra of the colloidal nanoparticles under different excitation conditions. Right inset: Corresponding photograph of the colloidal sample showing multicolor tuning under different excitation conditions. (c) Luminescence photographs of the same colloidal sample shown in (b), recorded under various excitation conditions. Reproduced from ref. 30 with permission from the Springer Nature, copyright 2015.

but there are now precedents as exemplified by the work of Yu and co-workers.<sup>32</sup> These researchers obtained amplified spontaneous emission from a Fabry–Perot cavity containing UCNPs. They dispersed  $\text{NaYF}_4:\text{Yb}/\text{Er}$  core-shell nanoparticles in optically transparent cyclohexane and fabricated the microcavity by coating a drop of silica resin containing the as-synthesized nanoparticles onto an optical fiber. To accomplish enough optical gain, Yu and co-workers constructed a 3-pulse excitation system that is able to generate three 980 nm pulses with a relatively short pulse width (6 ns) and time delay (10 ns) between adjacent pulses. The results indicate that the sequential nanosecond-pulsed excitation is necessary to generate a larger population inversion of  $\text{Er}^{3+}$  ions that are embedded in the core-shell nanoparticles. In 2016, the same research team took one step further and demonstrated deep ultraviolet lasing, through 5-photon upconverted emission at 311 nm, by confining energy migration to manipulate multiphoton upconversion.<sup>33</sup>

## 2.5 Polarization anisotropic modulation

In 2013, Qiu and co-workers<sup>34</sup> demonstrated micro-polarized optical detection of upconversion emission of hexagonal-phase  $\text{NaYF}_4:\text{Yb}/\text{Tm}$  microrods at a single particle level, from which unique luminescent phenomena have been discovered upon excitation with a 980 nm linearly polarized laser. By rotating a half-wave-plate located close to the polarizer, polarized upconversion emission was recorded as a function of the polarization angle (Fig. 10). To study the interplay between the azimuth of laser polarization and the crystallographic axis, the same research team focused the linearly polarized laser beam onto

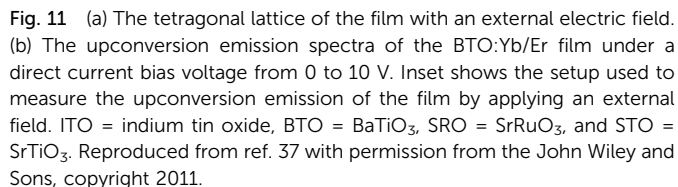
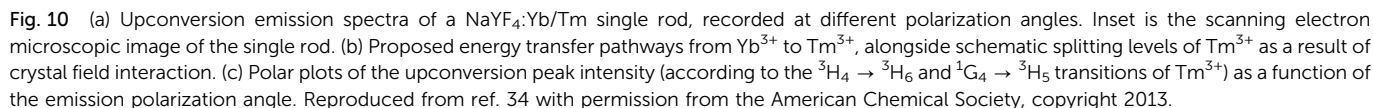
two nanodisks with face-up and side-up configurations.<sup>35</sup> It was found that for the side-up form, the upconversion luminescence intensity changes periodically when the polarization angle of the excitation light varies from 0 to 360°. By comparison, the upconversion luminescence intensity was independent of the polarization angle in the case of the face-up form. Despite its usefulness, this polarization-dependent approach has limited emission tunability due to random orientation of the anisotropic particles in dispersion.

Jaquie and co-workers<sup>36</sup> demonstrated that polarized spectroscopy can be used to determine the orientation dynamics of a single UCNP when entering into a single beam optical trap. Analysis of real time experiments in combination with numerical calculations allowed for the determination of dynamic viscosity of the medium in which the UCNP is suspended. As proof of concept, this technique was successfully implemented for measuring intracellular dynamic viscosity.

## 2.6 Electric field fine-tuning

Similar to the pulse pumping method, the application of electric fields perhaps presents another convenient approach for *in situ* and real-time manipulation of upconversion emission in lanthanide-doped nanoparticles. This rationale is built upon the fact that the variation of an electric field applied to the nanoparticles can alter the local site symmetry of lanthanide dopants and in turn their optical properties. In 2011, Hao and co-workers<sup>37</sup> came up an idea to control the upconversion luminescence of  $\text{BaTiO}_3:\text{Yb}/\text{Er}$  film by tuning an electric field (Fig. 11). Under a bias voltage of 10 V applied to





the ferroelectric BaTiO<sub>3</sub> host material, which results in an increased distortion of Er<sup>3+</sup> site symmetry. These results show that the spatially modulated electric-field effect is fundamental to the external control of upconversion emission.

Although electric field fine-tuning is a convenient approach for enhancing upconversion luminescence, it is usually limited to ferroelectric materials. Conventional fluoride-based host materials do not exhibit electric-field-dependent emission. In 2015, Smalyukh and co-workers<sup>38</sup> designed mesostructured composite materials comprising ordered dispersion of rod-like UCNPs in a nematic liquid-crystal medium. They demonstrated tunable upconversion and polarized luminescence when the composite was electrically switched at low voltages ( $\sim 1$  V). The combination of complex, pre-engineered soft matter materials with the electric-field-responsive polarization of upconversion luminescence may enable a wide range of nanophotonic applications, such as distributed-feedback mirror-free cholesteric lasers.

## 2.7 Magnetic field manipulation

Another area that has seen growth is the modulation of luminescence in lanthanide-doped systems through external magnetic field manipulation (Fig. 12). The high luminescence sensitivity of lanthanide-doped glass-ceramics or  $\text{NaYF}_4$  nanoparticles to magnetic field can be harnessed for developing an optical sensor for magnetic field without using magnetic fluids.<sup>39</sup> For example, Li and co-workers<sup>40</sup> prepared optical-magnetic bifunctional  $\text{NaGdF}_4\text{:Nd/Yb/Er}$  nanocrystals and found that the nanocrystal's luminescence could be tuned by varying the applied magnetic field both at room temperature and ultralow temperatures. However, available data indicate that applying a magnetic field to upconversion nanoparticles tends to suppress luminescence intensity.<sup>39,40</sup> A more likely explanation is the enhanced cross-relaxation process, reduced absorption capability, and improved local site symmetry in consequence of the magnetic field effect.

In 2015, Qiu and co-workers<sup>41</sup> found that the broadening and shift of f-f transitions is highly dependent upon magnetic field intensity. For example, the emission intensity of NaYF<sub>4</sub>:Yb/Er(18/2%)

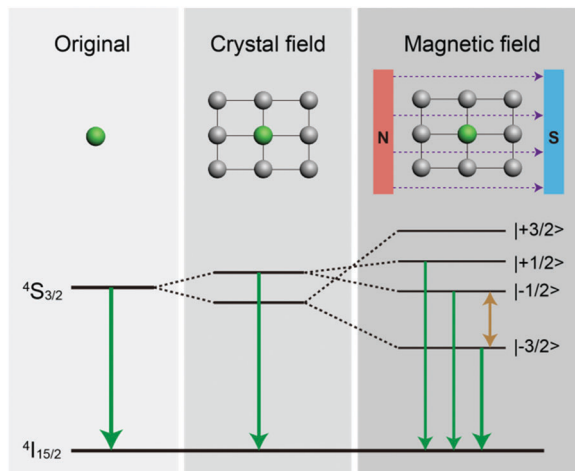


Fig. 12 A simplified energy level diagram showing the splitting of energy level  $^4S_{3/2}$  of  $\text{Er}^{3+}$  ion in which the gap between the Zeeman levels  $|-1/2\rangle$  and  $|-3/2\rangle$  increases with applied external magnetic field.

UCNPs is enhanced by a factor of 2.5 under a field intensity of 20 T, which can be ascribed to the magnetic field-induced Zeeman effect and different  $g$  factors for various Zeeman levels. Moreover, the larger red emission enhancement factor relative to the green emission has been associated with enhanced energy transfer from  $\text{Yb}^{3+}$  to  $\text{Er}^{3+}$  and increased nonradiative transitions in  $\text{Er}^{3+}$  energy levels from  $^4S_{3/2}$  to  $^4F_{9/2}$  and  $^4I_{11/2}$  to  $^4I_{13/2}$ . In the future, the method of Qiu and colleagues could reveal details of luminescence enhancement through magnetic manipulation and the nature of the coupling between optical and magnetic properties of UCNPs.

## 2.8 Temperature-dependent upconversion

UCNPs can be prepared by a variety of chemical methods. These include co-precipitation, hydrothermal treatment, and thermal decomposition at relatively high temperatures (200 to 330 °C). Low-temperature synthesis seems to make the crystal nucleation and growth processes more difficult. Furthermore, an elevated temperature is useful in accelerating the cation-exchange reaction dominated in lanthanide-based particle systems.<sup>5</sup> Temperature is a key factor that not only affects the quality of particle synthesis but also strongly dictates the ultimate luminescence performance of the phosphors. In principle, the luminescence intensity of a lanthanide-doped nanoparticle is determined by the competition between radiative and nonradiative transitions in the emitters. Because the phonon density of inorganic crystal lattices is highly sensitive to local temperature, the process of photon upconversion can be conveniently altered through the change in temperature.<sup>42</sup> The nonradiative transition rate from an emission level can be expressed as

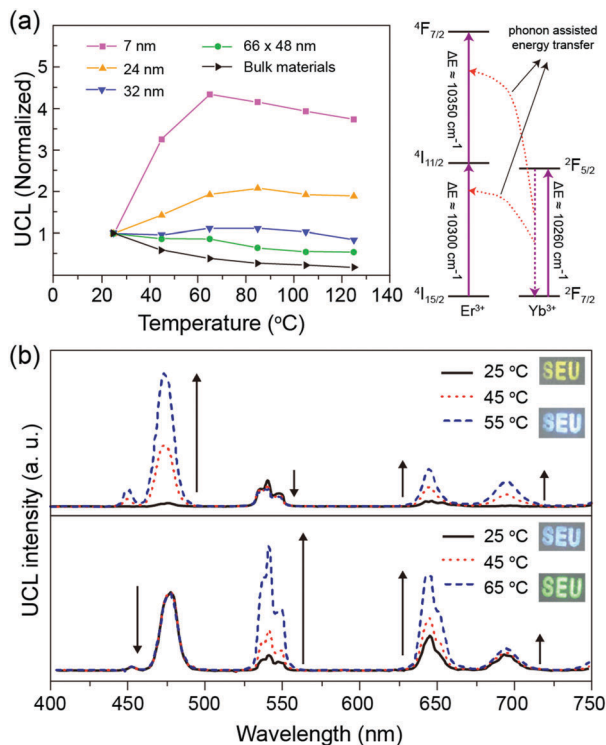
$$W_{\text{NR}} = W_{(0)} [1 - \exp(-\hbar\omega/kT)]^{-\Delta E/\hbar\omega}$$

where  $W_{(0)}$  represents the nonradiative transition rate from the emission level to the nearest lower-lying level at 0 K,  $\hbar\omega$  is the maximum phonon energy of the host material that couples to

the electronic transition of the rare-earth ion,  $\Delta E$  is the energy gap between the emission level and the nearest low-lying level, and  $T$  is the absolute temperature. It has been reported that the emission intensity of cubic-phase  $\text{NaYF}_4:\text{Yb}/\text{Er}$  UCNPs quenches monotonously with elevated temperatures from 10 to 400 K, while their hexagonal-phase counterparts display a maximal luminescence intensity at around 100 K.<sup>43</sup> The sharp temperature-dependent changes in the spectral shape, luminescence lifetime, and luminescence intensity of UCNPs make them an ideal candidate for thermal sensing. It is important to note that thermal quenching behavior is typically observed in nanophosphors, as the lattice vibration of the nanophosphors tends to intensify at an elevated temperature. On account of phonon-mediated energy transfer, the nonradiative depopulation of excited emitting states to the ground state could also be aggravated. In that regard, a substantial reduction in the emission luminance of the nanophosphor occurs.

In 2014, Shao and co-workers<sup>44</sup> reported an anomalous emission enhancement with increasing temperature (from 25 to 125 °C) for small-sized UCNPs (<30 nm). The researchers attributed the divergence to the change in phonon-assisted energy transfer processes (Fig. 13a). The lack of low-energy phonon modes in smaller nanoparticles due to the phonon confinement effect limits the energy transfer between  $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$  ions. At high temperatures, the increase in phonon density can promote the energy transfer efficiency and subsequently enhance the upconversion luminescence. One year later, the same research group developed a unique composite material comprising nanowires and small-sized nanoparticles.<sup>45</sup> Upon doping different types of emitter ions, the composite material showed a reversed trend of color modulation in response to heating (Fig. 13b). Zhou *et al.*<sup>46</sup> reported that with the assistance of surface phonons, the detrimental heat can be harnessed by coupling lanthanide ions with surface ligands to boost the photoluminescence by up to three orders of magnitude in ultra-small UCNPs.

As already discussed, high temperature conditions are often required for the synthesis of nanophosphors with high quantum yields. At the same time, in the context of large-scale temperature variation, UCNPs are expected to change irreversibly in crystal structure and phase. It is generally accepted that during higher temperature annealing process, most impurities and lattice defects of inorganic crystals can be removed in accompany with much improved crystallinity. A number of research groups have reported that a phase transition from cubic to hexagonal occurs in  $\text{NaYF}_4$  crystals at above 400 °C. However, a further increase of the temperature from 500 to 700 °C leads to a reversed phase transition back to the cubic phase.<sup>47</sup> It is worth mentioning that the local temperature of a nanocrystal can be quickly boosted through laser irradiation by means of laser-induced annealing, leading to a permanent change in crystal structure.<sup>48</sup> For instance, Xiong and co-workers<sup>49</sup> reported on a phase transition from hexagonal to cubic in  $\text{NaYF}_4$  nanocrystals by utilizing a 980 nm laser operated at a power density of 600 W cm<sup>-2</sup> and a duration time of 40 min, and they further proved that the resulting



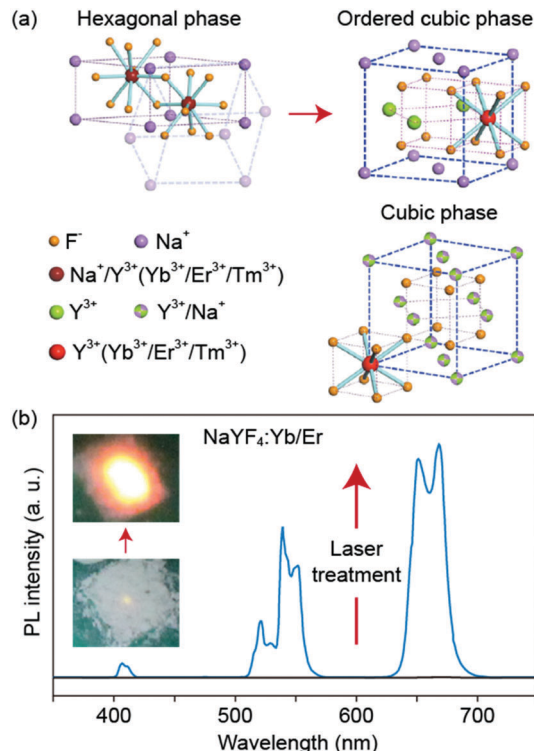
**Fig. 13** (a) Left panel: Integrated upconversion emission intensities of particles with different sizes as a function of temperature. Right panel: Proposed phonon-assisted energy transfer process from  $\text{Yb}^{3+}$  to  $\text{Er}^{3+}$  ions. (b) Upper panel: Temperature-dependent upconversion emission spectra of composite nano-powders between  $\text{NaYF}_4\text{:Yb/Ho}$  nanowires and  $\text{NaGdF}_4\text{:Yb/Tm}$  nanoparticles. Lower panel: Temperature-dependent upconversion emission spectra of composite nanopowders made of  $\text{NaYF}_4\text{:Yb/Tm}$  nanowires and  $\text{NaGdF}_4\text{:Yb/Ho}$  nanoparticles. (a) Reproduced from ref. 44 with permission from the American Chemical Society, copyright 2014, while (b) reproduced from ref. 45 with permission from the John Wiley and Sons, copyright 2015.

product features a new, well-ordered cubic lattice, responsible for the observed intense luminescence (Fig. 14).

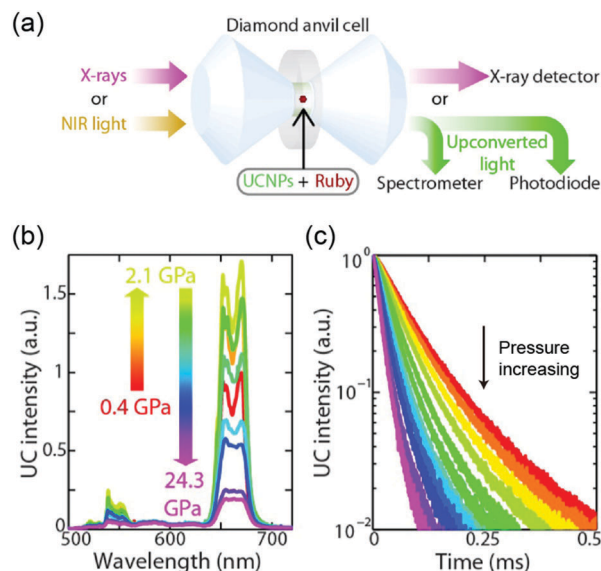
## 2.9 Applying mechanical stress

The lattice strain induced by ion doping or core-shell engineering is a universal effect in nanostructured materials. This gives opportunity for strain engineering of the optical properties. For example, the strain field in lattice-mismatched core-shell quantum dots can dramatically change the conduction and valence band energies for both core and shell components. In this manner, the optical property of such quantum dots could be significantly manipulated.<sup>50</sup> The tuning of lattice strain in UCNPs by ion doping has led to the dramatic enhancement in luminescence, as different sized dopants could induce localized lattice stress and in turn alter the crystal field splitting of activators. The complexity of this interplay has been made evident in the investigations of fluoride and oxide host lattices fused with  $\text{Li}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Sc}^{3+}$ , in combination with lanthanide activators.<sup>51,52</sup>

Apart from ion doping, researchers have uncovered that the application of pressure can be used as a means to alter the



**Fig. 14** (a) Lattice structures of hexagonal-phase  $\text{NaYF}_4$ , ordered cubic-phase  $\text{NaYF}_4$ , and directly synthesized cubic-phase  $\text{NaYF}_4$ . (b) Emission spectra of hexagonal-phase  $\text{NaYF}_4\text{:Yb/Er}$  solid powder, recorded before (black) and after (blue) exposure to a 980 nm laser for 40 min. Insets show the corresponding photographs of the samples with laser switched on and off. Reproduced from ref. 49 with permission from the John Wiley and Sons, copyright 2015.



**Fig. 15** (a) Illustration of the experimental approach used in pressure-dependent spectra measurement. (b) Pressure-dependent emission spectra of  $\alpha\text{-NaYF}_4\text{:Yb/Er}$  UCNPs on 980 nm excitation. (c) Luminescent decay curves of  $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$  transition of  $\alpha\text{-NaYF}_4\text{:Yb/Er}$  UCNPs. Reproduced from ref. 55 with permission from the American Chemical Society, copyright 2015.



luminescence of rare-earth ions. Applying external hydrostatic pressure has proven feasible in control of upconversion emission of  $\text{Tm}_2\text{O}_3$  samples.<sup>53</sup> On a separate note, hexagonal-phase  $\text{NaYF}_4\text{:Yb/Er}$  microcrystalline powder shows a decrease in emission intensity and lifetime with increasing pressure.<sup>54</sup> This observation could be attributed to the fact that high external pressure can modify electron repulsion and increase the crystal field splitting of the Stark levels in the ground and excited states. In 2015, Dionne and co-workers<sup>55</sup> found that following the increase in pressure, the hexagonal-phase  $\text{NaYF}_4\text{:Yb/Er}$  UCNPs exhibited a monotonic decrease in upconversion emission, whereas their cubic-phase equivalents experienced a nearly 2-fold increase and then a marked decrease in emission intensity (Fig. 15). *In situ* X-ray diffraction studies revealed that only 1% reduction in lattice constant is needed for realizing the 2-fold upconversion enhancement from cubic-phase nanoparticles.

### 3. Conclusion and perspective

Controlling the color of a light-responsive material has proved to be a daunting task, despite the numerous fields that contribute to the task. Conventional luminescent materials such as organic dye molecules, semiconducting quantum dots, and lanthanide-doped nanoparticles, can exhibit color-tunable emissions, but they require stringent modification on either the molecular structure or the particle size or the doping concentration of the lanthanides. The ability to remotely control luminescence of light-emitting materials with high spatiotemporal resolution presents a tantalizing opportunity on the technology development front. That is particularly true for lanthanide-doped UCNPs. These nanomaterials are much more photochemically stable than conventional contrast agents. They are capable of producing high energy light at wavelengths that can trigger critical biological reactions. Upon surface functionalization, these nanoparticles can be made biocompatible and conjugated to biomolecules for specific cell targeting, allowing cell movement and signaling to be directly monitored under *in vivo* conditions. In this review, we have described several key strategies that offer multicolor tuning capability on UCNPs without the need for structural or compositional reconstruction of the nanoparticles. Understanding the nature of luminescence tuning in response to external stimuli has enabled advances in a diverse array of disciplines. However, a looming challenge remains to construct ultra-small nanoparticles with much improved upconversion quantum efficiency. If this challenge can be met, UCNPs could become serious candidates for use as luminescent probes for large-scale biological assay.

### Conflicts of interest

There are no conflicts to declare.

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### References

- 1 F. Auzel, *Chem. Rev.*, 2004, **104**, 139–173.
- 2 M. Bettinelli, L. D. Carlos and X. G. Liu, *Phys. Today*, 2015, **68**, 38–44.
- 3 S. Chen, A. Z. Weitemier, X. Zeng, L. He, X. Wang, Y. Tao, A. J. Y. Huang, Y. Hashimoto, M. Kano, H. Iwasaki, L. K. Parajuli, S. Okabe, D. B. L. Teh, A. H. All, I. Tsutsui-Kimura, K. F. Tanaka, X. Liu and T. J. McHugh, *Science*, 2018, **359**, 679.
- 4 X. Li, X. Liu, D. M. Chevrier, X. Qin, X. Xie, S. Song, H. Zhang, P. Zhang and X. Liu, *Angew. Chem., Int. Ed.*, 2015, **54**, 13312–13317.
- 5 S. Han, X. Qin, Z. An, Y. Zhu, L. Liang, Y. Han, W. Huang and X. Liu, *Nat. Commun.*, 2016, **7**, 13059.
- 6 X. Xie, N. Gao, R. Deng, Q. Sun, Q. H. Xu and X. Liu, *J. Am. Chem. Soc.*, 2013, **135**, 12608–12611.
- 7 J. Shen, G. Y. Chen, A. M. Vu, W. Fan, O. S. Bilse, C. C. Chang and G. Han, *Adv. Opt. Mater.*, 2013, **1**, 644–650.
- 8 Y. F. Wang, G. Y. Liu, L. D. Sun, J. W. Xiao, J. C. Zhou and C. H. Yan, *ACS Nano*, 2013, **7**, 7200–7206.
- 9 H. Wen, H. Zhu, X. Chen, T. F. Hung, B. Wang, G. Zhu, S. F. Yu and F. Wang, *Angew. Chem., Int. Ed.*, 2013, **52**, 13419–13423.
- 10 J. Lai, Y. Zhang, N. Pasquale and K. B. Lee, *Angew. Chem., Int. Ed.*, 2014, **53**, 14419–14423.
- 11 L. Liang, X. Xie, D. T. Loong, A. H. All, L. Huang and X. Liu, *Chem. – Eur. J.*, 2016, **22**, 10801–10807.
- 12 Y. Liu, D. Tu, H. Zhu, R. Li, W. Luo and X. Chen, *Adv. Mater.*, 2010, **22**, 3266–3271.
- 13 R. Kolesov, R. Reuter, K. W. Xia, R. Stohr, A. Zappe and J. Wrachtrup, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **84**, 153413.
- 14 R. Wu, Q. Zhan, H. Liu, X. Wen, B. Wang and S. He, *Opt. Express*, 2015, **23**, 32401.
- 15 Q. Zhan, H. Liu, B. Wang, Q. Wu, R. Pu, C. Zhou, B. Huang, X. Peng, H. Agren and S. He, *Nat. Commun.*, 2017, **8**, 1058.
- 16 Y. Liu, Y. Lu, X. Yang, X. Zheng, S. Wen, F. Wang, X. Vidal, J. Zhao, D. Liu, Z. Zhou, C. Ma, J. Zhou, J. A. Piper, P. Xi and D. Jin, *Nature*, 2017, **543**, 229–233.
- 17 J. J. Zhou, J. Y. Deng, H. M. Zhu, X. Y. Chen, Y. Teng, H. Jia, S. Q. Xu and J. R. Qiu, *J. Mater. Chem. C*, 2013, **1**, 8023–8027.
- 18 W. Q. Zou, C. Visser, J. A. Maduro, M. S. Pshenichnikov and J. C. Hummelen, *Nat. Photonics*, 2012, **6**, 560–564.
- 19 G. Chen, J. Damasco, H. Qiu, W. Shao, T. Y. Ohulchanskyy, R. R. Valiev, X. Wu, G. Han, Y. Wang, C. Yang, H. Agren and P. N. Prasad, *Nano Lett.*, 2015, **15**, 7400–7407.

- 20 X. Wu, H. Lee, O. Bilsel, Y. Zhang, Z. Li, T. Chen, Y. Liu, C. Duan, J. Shen, A. Punjabi and G. Han, *Nanoscale*, 2015, **7**, 18424–18428.
- 21 Z.-L. Wang, J. H. Hao and H. L. W. Chan, *J. Mater. Chem.*, 2010, **20**, 3178–3185.
- 22 Z. Mi, Y. Zhang, S. K. Vanga, C. B. Chen, H. Q. Tan, F. Watt, X. Liu and A. A. Bettiol, *Nat. Commun.*, 2015, **6**, 8832.
- 23 M. Pollnau, D. R. Gamelin, S. R. Lüthi, H. U. Güdel and M. P. Hehlen, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2000, **61**, 3337–3346.
- 24 Y. Wang, R. Deng, X. Xie, L. Huang and X. Liu, *Nanoscale*, 2016, **8**, 6666–6673.
- 25 J. Zhou, G. Chen, Y. Zhu, L. Huo, W. Mao, D. Zou, X. Sun, E. Wu, H. Zeng, J. Zhang, L. Zhang, J. Qiu and S. Xu, *J. Mater. Chem. C*, 2015, **3**, 364–369.
- 26 J. C. Boyer, C. J. Carling, B. D. Gates and N. R. Branda, *J. Am. Chem. Soc.*, 2010, **132**, 15766–15772.
- 27 J. Zhao, D. Jin, E. P. Schartner, Y. Lu, Y. Liu, A. V. Zvyagin, L. Zhang, J. M. Dawes, P. Xi, J. A. Piper, E. M. Goldys and T. M. Monro, *Nat. Nanotechnol.*, 2013, **8**, 729–734.
- 28 C. Zhang, L. Yang, J. Zhao, B. Liu, M. Y. Han and Z. Zhang, *Angew. Chem., Int. Ed.*, 2015, **54**, 11531–11535.
- 29 C. F. Gainer, G. S. Joshua, C. R. De Silva and M. Romanowski, *J. Mater. Chem.*, 2011, **21**, 18530–18533.
- 30 R. Deng, F. Qin, R. Chen, W. Huang, M. Hong and X. Liu, *Nat. Nanotechnol.*, 2015, **10**, 237–242.
- 31 Y. Han, H. Li, Y. Wang, Y. Pan, L. Huang, F. Song and W. Huang, *Sci. Rep.*, 2017, **7**, 1320.
- 32 H. Zhu, X. Chen, L. M. Jin, Q. J. Wang, F. Wang and S. F. Yu, *ACS Nano*, 2013, **7**, 11420–11426.
- 33 X. Chen, L. Jin, W. Kong, T. Sun, W. Zhang, X. Liu, J. Fan, S. F. Yu and F. Wang, *Nat. Commun.*, 2016, **7**, 10304.
- 34 J. Zhou, G. Chen, E. Wu, G. Bi, B. Wu, Y. Teng, S. Zhou and J. Qiu, *Nano Lett.*, 2013, **13**, 2241–2246.
- 35 P. Chen, M. Song, E. Wu, B. Wu, J. Zhou, H. Zeng, X. Liu and J. Qiu, *Nanoscale*, 2015, **7**, 6462–6466.
- 36 P. Rodríguez-Sevilla, Y. Zhang, N. de Sousa, M. I. Marqués, F. Sanz-Rodríguez, D. Jaque, X. Liu and P. Haro-González, *Nano Lett.*, 2016, **16**, 8005–8014.
- 37 J. Hao, Y. Zhang and X. Wei, *Angew. Chem., Int. Ed.*, 2011, **50**, 6876–6880.
- 38 H. Mundoor and I. I. Smalyukh, *Small*, 2015, **11**, 5572–5580.
- 39 V. K. Tikhomirov, L. F. Chibotaru, D. Saurel, P. Gredin, M. Mortier and V. V. Moshchalkov, *Nano Lett.*, 2009, **9**, 721–724.
- 40 Y. Liu, D. Wang, J. Shi, Q. Peng and Y. Li, *Angew. Chem., Int. Ed.*, 2013, **52**, 4366–4369.
- 41 P. Chen, H. Jia, Z. Zhong, J. Han, Q. Guo, J. Zhou, X. Liu and J. Qiu, *J. Mater. Chem. C*, 2015, **3**, 8794–8798.
- 42 D. Jaque and F. Vetrone, *Nanoscale*, 2012, **4**, 4301–4326.
- 43 W. Yu, W. Xu, H. Song and S. Zhang, *Dalton Trans.*, 2014, **43**, 6139–6147.
- 44 D. D. Li, Q. Y. Shao, Y. Dong and J. Q. Jiang, *J. Phys. Chem. C*, 2014, **118**, 22807–22813.
- 45 D. D. Li, Q. Y. Shao, Y. Dong, F. Fang and J. Q. Jiang, *Part. Part. Syst. Charact.*, 2015, **32**, 728–733.
- 46 J. Zhou, S. Wen, J. Liao, C. Clarke, S. A. Tawfik, W. Ren, C. Mi, F. Wang and D. Jin, *Nat. Photonics*, 2018, **12**, 154–158.
- 47 G. Yi, H. Lu, S. Zhao, Y. Ge, W. Yang, D. Chen and L.-H. Guo, *Nano Lett.*, 2004, **4**, 2191–2196.
- 48 Y. Wang, L. Tu, J. Zhao, Y. Sun, X. Kong and H. Zhang, *J. Phys. Chem. C*, 2009, **113**, 7164–7169.
- 49 L. Wang, X. Li, Z. Li, W. Chu, R. Li, K. Lin, H. Qian, Y. Wang, C. Wu, J. Li, D. Tu, Q. Zhang, L. Song, J. Jiang, X. Chen, Y. Luo, Y. Xie and Y. Xiong, *Adv. Mater.*, 2015, **27**, 5528–5533.
- 50 A. M. Smith, A. M. Mohs and S. Nie, *Nat. Nanotechnol.*, 2009, **4**, 56–63.
- 51 S. Han, R. Deng, X. Xie and X. Liu, *Angew. Chem., Int. Ed.*, 2014, **53**, 11702–11715.
- 52 X. Qin, X. Liu, W. Huang, M. Bettinelli and X. Liu, *Chem. Rev.*, 2017, **117**, 4488–4527.
- 53 J. Wang and P. A. Tanner, *J. Am. Chem. Soc.*, 2009, **132**, 947–949.
- 54 C. Rennero-Lecuna, R. Martín-Rodríguez, R. Valiente, J. González, F. Rodríguez, K. W. Krämer and H. U. Güdel, *Chem. Mater.*, 2011, **23**, 3442–3448.
- 55 M. D. Wisser, M. Chea, Y. Lin, D. M. Wu, W. L. Mao, A. Salleo and J. A. Dionne, *Nano Lett.*, 2015, **15**, 1891–1897.