Research article

Xiaoru Dai, Ke Wang, Lei Lei*, Shiqing Xu, Yao Cheng* and Yuansheng Wang

Pumping-controlled multicolor modulation of upconversion emission for dual-mode dynamic anti-counterfeiting

<https://doi.org/10.1515/nanoph-2020-0150>

Received February 28, 2020; accepted March 28, 2020

Abstract: Lanthanide up-conversion features stepwise multi-photon processes, where the difference in photon number that is required for specific up-conversion process usually leads to significant variance in pumping-related processes/properties. In this work, a pumping-controlled dual-mode anti-counterfeiting strategy is conceived by taking advantage of the combination of up-conversion processes with different photon numbers. The combination of Er^{3+} and Tm^{3+} , which are spatially separated within a designed core/triple-shell nano-architecture, is taken as an example to illustrate such idea. Upon infrared excitation, the emission color of a designed pattern can be switched from red to purple by increasing the excitation power density from 5 to 11 W/cm^2 , while a bright luminescent trajectory including red, white and blue-green color with different length is observed when rotating the pattern above 600 rpm. In addition, the relative up-conversion emission intensities of the Er^{3+} and Tm^{3+} ions can be manipulated through tailoring interfacial or inner defects in the core/triple-shell nano-crystals, which enable an ultrahigh sensitivity for the pumping-controlled emission

color variation to be observed under excitation power well below 11 W/cm^2 .

Keywords: anti-counterfeiting; dual-mode; power dependent; up-conversion.

1 Introduction

Lanthanide-activated phosphors are famous as powerful multicolor-emitting materials due to the fact that the abundant ladder-like energy levels enable even single trivalent lanthanide ion to provide multiple emissions with various wavelengths in the visible region [1]. Such ability can be further developed to find applications in specific areas concerning anti-counterfeiting by means of controlled emission color change upon certain stimulation. Up to now, several methods, including manipulating near-field effects (i. e., electronic, magnetic, and plasmon field) [2–7], environmental temperature or excitation conditions (i. e., excitation wavelength/pulse width/power density) [8–11], have been applied to realize the control of emission color change. These offer a powerful platform for the design of multi-mode anti-counterfeiting techniques, where two or more various stimulation-induced emission color change effects can be judiciously integrated into single luminescence material so as to greatly outperform the single-mode techniques in terms of security capability [12, 13].

Lanthanide up-conversion features stepwise multi-photon processes, where the difference in photon number that is required for specific up-conversion process usually leads to significant variance in pumping-related processes/properties. These important characteristics have been recently utilized for the color tuning of up-conversion emission, represented either by excitation power density dependent multi-color emission or pulse-width modulated control over the emission color [14–17]. Inspired by this, it is therefore feasible to construct pumping-based multi-mode anti-counterfeiting techniques by simply taking full advantage of the combination of up-conversion processes with

***Corresponding authors: Dr. Lei Lei**, Institute of Optoelectronic Materials and Devices, China Jiliang University, Hangzhou, 310018, PR China, E-mail: leilei@cjl.u.edu.cn; and **Yao Cheng**, CAS Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, PR China, chengyao@fjirsm.ac.cn. <https://orcid.org/0000-0002-2131-0222> (L. Lei)

Xiaoru Dai and Shiqing Xu: Institute of Optoelectronic Materials and Devices, China Jiliang University, Hangzhou, 310018, PR China, E-mail: shiqingxu@cjl.u.edu.cn (S. Xu)

Ke Wang: School of Pharmacy, Health Science Center, Xi'an Jiaotong University, Xi'an, 710061, PR China

Yuansheng Wang: CAS Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, PR China

different photon numbers. In the present work, the combination of Er^{3+} and Tm^{3+} is taken as an example to illustrate such idea. These two lanthanide ions are spatially separated within a designed core/triple-shell nano-architecture. Upon 980 nm excitation, the green and red emissions of the Er^{3+} ions are attributed to a two-photon UC [18–21], while the blue ones from the Tm^{3+} ions are ascribed to three and four-photon UC [22–24]. On one hand, the excitation power density dependent emission color variation can be expected. We show that how the sensitivity can be influenced by specific nano-architecture parameters (e. g., core size and interfacial defect concentration). On the other hand, the life-time decay curves for the correspond emissions of both the Er^{3+} and Tm^{3+} ions in the core/triple-shell nano-crystals (NCs) exhibited distinctly diverse rising edge, which leads to a bright multicolor trajectory when a designed pattern made of such core/triple-shell NCs is rotated. These two pumping-related phenomena can then be integrated for a dual-mode anti-counterfeiting design.

2 Experimental

2.1 Chemicals and reagents

$\text{Yb}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ (99.9%), $\text{Er}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ (99.9%), $\text{Y}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ (99.9%), $\text{Tm}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ (99.9%), $\text{Yb}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ (99.9%), $\text{Lu}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ (99.9%), $\text{NaAc} \cdot 3\text{H}_2\text{O}$ (99.995%), $\text{Ca}(\text{Ac})_2$ ($\geq 99.8\%$), LiAc (99.9%), NH_4F ($\geq 98\%$), 1-Octadecene (ODE, 90%), and Oleic acid (OA, 90%) were supplied by Sigma Aldrich Company. Dimethyl sulfoxide (DMSO, 99.9%), KCl (99.5%), and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (99%) were purchased from Aladdin Chemical Reagent company. NaCl ($>99.5\%$) were purchased from Hangzhou Gaojing Fine Chemical Industry Co., Ltd. Minimum Eagle's medium (MEM), SP20 and MCF-7 cells were purchased from Procell Life Science & Technology Co., Ltd. Dulbecco's Minimum Eagle's medium (DMEM) and penicillin streptomycin solution were purchased from Hyclone Laboratories, Inc. Fetal bovine serum (FBS) origin South America was provided by CLARK Bioscience. 3-[4, 5-dimethylthiazol-2-yl]-2, 5-diphenyl tetrazolium bromide (MTT) was purchased from BioPro, Inc. Cyclohexane and absolute ethanol were purchased from Sinopharm Chemical Reagent Company. All chemicals were of analytical grade and used as received without further purification.

2.2 Synthesis of NaErF_4 : 10Yb NCs

$\text{Er}(\text{Ac})_3$ (0.72 mmol), $\text{Yb}(\text{Ac})_3$ (0.08 mmol), and NaAc (0.8 mmol) were added into a 50 mL three-necked bottle

containing 8 mL OA. The mixture was heated at 150 °C for 30 min to remove water from the solution. Then 12 mL ODE was quickly added to the above solution and the resulted mixture was heated at 150 °C for another 30 min to form a clear solution, and then cooled down to room temperature. Afterwards, 8 mL methanol solution containing NH_4F (3 mmol) was added and the solution was stirred at 60 °C for 30 min. After the methanol was evaporated, the solution was further heated at 290 °C under N_2 for 90 min and then cooled down to room temperature. The products were precipitated by addition of ethanol, collected by centrifugation, washed with ethanol for three times, and finally re-dispersed in 4 mL cyclohexane.

2.3 Synthesis of NaErF_4 @ NaYF_4 core-shell NCs

$\text{Y}(\text{Ac})_3$ (0.8 mmol) and NaAc (0.8 mmol) was added into a 50 mL three-necked bottle containing OA (8 mL). The mixture was heated at 150 °C for 30 min to remove water from the solution. A solution of ODE (12 mL) was then quickly added and the resulted mixture was heated at 150 °C for another 30 min to form a clear solution, and then cooled down to 80 °C. Thereafter, the pre-prepared NaErF_4 core NCs in 4 mL cyclohexane was added to the above solution and kept at 110 °C for 40 min. After the removal of cyclohexane, 8 mL methanol solution containing NH_4F (3 mmol) was added and the solution was stirred at 60 °C for 30 min. After the methanol was evaporated, the solution was further heated at 290 °C under N_2 for 120 min, and finally cooled down to room temperature.

2.4 Synthesis of NaErF_4 @ NaYF_4 @ NaYbF_4 : 20Ca/1Tm core/dual-shell NCs

$\text{Yb}(\text{Ac})_3$ (0.632 mmol), $\text{Ca}(\text{Ac})_2$ (0.16 mmol), $\text{Tm}(\text{Ac})_3$ (0.008 mmol) and NaAc (0.8 mmol) was added into a 50 mL three-necked bottle containing OA (8 mL). The mixture was heated at 150 °C for 30 min to remove water from the solution. A solution of ODE (12 mL) was then quickly added and the resulted mixture was heated at 150 °C for another 30 min to form a clear solution, and then cooled down to 80 °C. Thereafter, the pre-prepared NaErF_4 @ NaYF_4 core-shell NCs in 4 mL cyclohexane was added to the above solution and kept at 110 °C for 40 min. After the removal of cyclohexane, 8 mL methanol solution containing NH_4F (3 mmol) was added and the solution was stirred at 60 °C for

30 min. After the methanol was evaporated, the solution was further heated at 290 °C under N₂ for 120 min, and finally cooled down to room temperature.

2.5 Synthesis of

NaErF₄@NaYF₄@NaYbF₄:20Ca/ 1Tm@NaYF₄ core/triple-shell NCs

It is similar with that of NaErF₄@NaYF₄ NCs except replacing NaErF₄ core by NaErF₄@NaYF₄@NaYbF₄:20Ca/1Tm core/dual-shell NCs.

2.6 Preparation of designed patterns

Stamps were prepared by carving designed patterns on round oaks with a diameter of 2 cm. The surfaces of stamps were dipped in the corresponding NCs-contained cyclohexane suspension and then stamped on normal A4 paper.

2.7 Characterizations

X-ray diffraction (XRD) analysis was carried out with a powder diffractometer (Bruker D8 Advance) with a Cu-K_α (λ = 1.5405 Å) radiation. The morphology and scanning transmission electron microscopy (STEM) of the products were characterized by a field emission transmission electron microscopy (TEM, FEI Tecnai G² F20) equipped with an energy dispersive X-ray spectroscopy (EDS, Aztec X-Max 80T). UC emission spectra and life-time were carried out on an Edinburgh Instruments FLS920 spectrofluorimeter equipped with an adjustable laser diode (980 nm). The 980 nm laser for illuminating photographs is connected with a beam expander to obtain a big beam size of about 2.5 cm in diameter. Zeta potential was detected by Malvern Instruments Ltd Zetasizer Nano ZS 90. Fourier Transform Infrared (FTIR) spectra of the NCs were measured on a Nicolet FTIR spectrometer using the KBr method. Thermo Gravimetric Analysis (TGA) was carried out by TA Instruments SDT Q600.

The lifetime is fitted by:

$$I = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} \quad (1)$$

where I is the PL intensity, A_1 and A_2 are fitted constants, and τ_1 and τ_2 are the corresponding PL lifetimes. The mean lifetimes are calculated by the following equation:

$$\tau = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \quad (2)$$

3 Results and discussion

A general co-precipitation procedure was used to synthesize the core and core/multi-shell NCs (Figure S1). The size of the NaErF₄: 10Yb core NC can be facilely controlled by reaction time. With prolonging the reaction time from 90 min, 120 to 180 min, the particle size of the NaErF₄: 10Yb core NCs increases from 14 nm, 27 to 50 nm (Figure 1e, i, m and Figure S2). NaYF₄, NaYbF₄: 20Ca/1Tm, and NaYF₄ layers were sequentially coated on the surface of those NaErF₄: 10Yb core NCs, and then three types of NaErF₄: 10Yb@NaYF₄@NaYbF₄: 20Ca/1Tm@NaYF₄ core/triple-shell NCs with different particle size (24, 57, and 124 nm) were achieved (Figure 1a–p). XRD (Figure S3), high-resolution transmission electron microscopy (HRTEM, Figure S4) images, and EDS (Figure S5) spectra manifested the as-prepared products possessed hexagonal structure, single crystalline nature and nominal elements, respectively. The atomic number sensitive high-angle annular dark-field (HAADF) TEM characterization was adopted to study the core/multi-shell structure [25]. Owing to the much larger atomic number of Er (Z = 68) and Yb (Z = 70) than that of Y (Z = 39), a distinct contrast between different layers was clearly observed, confirming the successful growth of core/multi-shell NCs (Figure 1r–t and Figure S6). In contrast, the core NaErF₄: 10Yb NCs exhibited uniform brightness (Figure 1q). With coating the NaYF₄@NaYbF₄: 20Ca/1Tm@NaYF₄ shells out of the NaErF₄: 10Yb core, the absorption intensity ratio of the Yb³⁺ to Er³⁺ ions increased evidently owing to the greatly increased Yb³⁺ ions concentration (Figure S7).

The calculated mean particle size corresponding to Figure 1e–p manifests that the core NC's with a bigger size possess thicker shells (Figure 2a). FTIR reveals that the NC surface OA ligand is not influenced by the particle size (Figure 2b), while TGA curve indicated that the coated OA content is reduced from ~22 to ~7% with the increase of the particle size from 15 to 50 nm (Figure 2c). Furthermore, Zeta potential analysis manifests the NCs with bigger particle size showed less negative Zeta potential (Figure 2d). Based on the above analysis, it is reasonable to speculate that the OA-coated core NCs with negative zeta potential probably inhibit the adsorption of F⁻ ions on the surface of the core NCs followed by the suppression of shell growth. As a result, the core NCs with bigger particle size possessed thicker shell under the same shell growth procedure.

For a non-linear UC process, n value of the pump photon number obeys the power law $I \propto P^n$ under non-saturation excitation, where I , P , and n are the UC emission intensity, excitation power and number of required

Figure 1: (a–d) are schematic illustration of the core (C), core/shell (CS), core/dual-shell (CSS) and core/triple-shell (CSSS) via successive layer-by-layer growth strategy. (e, i, m), (f, j, n), (g, k, o), and (h, l, p) are the C, CS, CSS, and CSSS NCs with different sizes, respectively. (q)–(t) are the HAADF-TEM images corresponding to the products shown in (i), (h), (l), and (p), respectively.

pumping photons, respectively. As shown in Figure 3a and Figure S8, the emission peaks at 360 nm ($\text{Tm}^{3+}: {}^1\text{D}_2 \rightarrow {}^3\text{H}_6$), 454 nm ($\text{Tm}^{3+}: {}^1\text{D}_2 \rightarrow {}^3\text{F}_4$), 478 nm ($\text{Tm}^{3+}: {}^1\text{G}_4 \rightarrow {}^3\text{H}_6$), 545 nm ($\text{Er}^{3+}: {}^3\text{H}_{11/2}, {}^3\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$) and 660 nm ($\text{Er}^{3+}: {}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$) in the core/triple-shell NCs are belonged to 4-, 4-, 3-, 2-, and 2-photon processes, respectively. After coating the outer NaYF_4 shell, the Tm^{3+} emission intensity enhances greatly (~ 316 times) while that of Er^{3+} ions were slightly increases

(~ 1.8 times), indicating the outer shell is mainly introduced to inhibit the energy transfer from Tm^{3+} ions to the outer surface defects (Figure S9). It should be noted the UC emission intensity of the core/triple-shell NCs almost keeps unchanged with prolonging the irradiation time (Figure S10). The proposed UC energy transfer mechanism based on the above results was shown in Figure 3b and Figure S11. All the three types of core/triple-shell NCs

Figure 2: (a) Calculated mean particle size of the Core, CS, CSS and CSSS NCs shows in Figure 1e–p. FTIR spectra (b) and TGA curves (c) of the NCs with different particle sizes. (d) Dependence of Zeta potential versus particle size.

exhibit red color under 980 nm laser excitation at 5 W/cm² owing to the much stronger red emission intensity than that of green and blue ones (Figure 3c–d and Figure S12). Moreover, the blue to red intensity ratio increases greatly from 0.06 to 4.13% with the NC size changed from 24 to 124 nm. As a result, with the increase of the excitation power density to 11 W/cm², the output color of the core/triple-shell NCs with the smallest size changes to yellow (Figure S12), which was owing to the larger specific n value of green band than that of red one. By contrast, under the same power variation condition, the emission color of the core/triple-shell NCs with 57 and 124 nm turn to white (Figure 3c, e) and violet (Figure 3d, f), respectively, which were attributed to the larger enhancement degree of Tm³⁺ ions than that of Er³⁺ ions. Comparing with previous reported systems for excitation power density induced color tuning, the present researched core/triple-shell NCs possessed the highest sensitivity (Table S1), where below 2.2 times as much as the initial power density could switch the UC emission color.

Although core-shell architecture greatly improves the UC emission intensity via passivating the surface defects [21, 26–29], there are still a large number of interfacial

defects between the core and the shell owing to the existence of lattice stress [25]. In the present researched core/triple-shell NCs, there existed core/first-shell, first-shell/second-shell and second-shell/third-shell interfacial defects. As shown in Figure 4a–c, lots of voids between the shells were formed and became larger with the prolonging of the e-beam irradiation time, indicating the existence of physical interfacial defects [25]. With the increase of the core and core/triple-shell size, the proportion of the Tm³⁺ ions located in the double interfacial as well as the corresponding interfacial defects decrease more than that of Er³⁺ situation (Figure 4d), which results the activators in the second shell increased more than those in the core. As we go back to Figure 3a, with increasing the particle size, the emission intensity of Tm³⁺ ions enhances by ~142.6 times while that of Er³⁺ only increased by ~1.5 times, which was consistent with our anticipation.

Inspired by the interfacial defects tuning route, the strategy of controlling inner defect concentration was studied as well. As shown in Figure S13a, the binding energy of the Yb 4d increases with the substitution of Ca²⁺ with Lu³⁺ ions, which was attributed to the existence of chemical inner defects (F⁻ vacancy) under the Ca²⁺-doped situation

Figure 3: UC emission spectra (a) and Schematic illustration (b) of the core/triple-shell NCs. Excitation power dependent digital photographs of the core/triple-shell NCs with 57 nm (c) and 124 nm (d), respectively. (e) and (f) are the CIE chromaticity coordinates corresponding to (c) and (d), respectively.

Figure 4: HAADF-STEM images of the core/dual-shell NCs under different e-beam irradiation time: 2 s (a), 10 s (b) and 20 s (c). (d) Schematic illustration of the inner/interfacial defects variations in the core/triple-shell NCs with different sizes.

[30, 31]. The binding energy of the Ca 2p keeps unchanged with the increase of size, indicating the amount of F⁻ vacancy was mainly related to the Ca²⁺ doping content (Figure S13b). As shown in Figure 5a–b, with replacing divalent Ca²⁺ ions with Lu³⁺ ions to reduce F⁻ vacancy or doping Li⁺ ions to improve the crystallinity in the second shell [20], the Tm³⁺ emission intensity increases evidently while that of Er³⁺ ions remain the same at low excitation power density. The schematic illustrations of the defects variations with the incorporation of Lu³⁺ or Li⁺ ions is shown in Figure 5c–e. In this case, with increasing the excitation power density from 5 to 11 W/cm², the integral emission color changes from white to blue-purple (Figure 5f–g and Figure S14). It should be noted that our results also revealed that the *n* value was mainly determined by the location of the corresponding excited energy level, and almost irrelative to the particle size and doping condition. It should be noted that Yb³⁺ and Eu³⁺ ions were used to tune

Figure 5: UC emission spectra of NaErF₄:10Yb@NaYF₄@NaYbF₄:20Ca/1Tm@NaYF₄ and NaErF₄:10Yb@NaYF₄@NaYbF₄:20Li/20Ca/1Tm@NaYF₄ (a, 124 nm); NaErF₄:10Yb@NaYF₄@NaYbF₄:20Ca/1Tm@NaYF₄ (b, 57 nm). Schematic illustrations of the defects variations in the NaErF₄:10Yb@NaYF₄@NaYbF₄:20Ca/1Tm@NaYF₄ (c), NaErF₄:10Yb@NaYF₄@NaYbF₄:20Li/20Ca/1Tm@NaYF₄ (d) and NaErF₄:10Yb@NaYF₄@NaYbF₄:20Li/20Ca/1Tm@NaYF₄ (e) NCs. Excitation power dependent digital photographs corresponding to Lu³⁺ (f) and Li⁺ (g) ions doped NCs.

the initial and final output color in our previous report [19], which was different from the present studied work.

Anti-counterfeiting technology is of great importance in protecting valuable items including banknotes, tickets, diplomas, luxury products and certificates [32–38]. Comparing with the luminescent materials with a firm emission color, lanthanide-doped UC NCs featuring with excitation power-dependent multi-color variation is much more suitable to be exploited as anti-counterfeiting labels owing to the difficulty of duplication. The patterns on the filter paper were stamped with round oaks which were pre-carved with designed patterns (Figure 6a). The emission color of the stamped patterns achieved with NaErF₄:10Yb@NaYF₄@NaYbF₄:20Ca/1Tm@NaYF₄ NCs (124 nm, Figure S15a) and NaErF₄:10Yb@NaYF₄@NaYbF₄:20Li/20Ca/1Tm@NaYF₄ core/triple-shell NCs (57 nm, Figure S15b), which were invisible under daylight, changed evidently with the increase of the excitation power density. It has been reported that Er³⁺ and Tm³⁺ ions in the Yb/Tm:NaGdF₄@NaYF₄@Yb/Er:NaGdF₄ core/dual-shell NCs showed temporal color separation owing to their different

rising edge in the decay life-time curves [39]. As shown in Figure S16, the rising edge among the transitions of $^1G_4 \rightarrow ^3H_6$, $^1D_2 \rightarrow ^3H_6$, Er³⁺: $^4S_{3/2} \rightarrow ^4I_{15/2}$, and $^4F_{9/2} \rightarrow ^4I_{15/2}$ as well as their corresponding life-time are distinctly different, hence, temporal multicolor is anticipated to be achieved with rotating the as-prepared patterns. In this scenario, dual-mode dynamic anti-counterfeiting could be actualized based on the excitation power-dependent color variation as well as the characteristic temporal multicolor pattern. A designed pattern prepared with NaErF₄:10Yb@NaYF₄@NaYbF₄:20Ca/1Tm@NaYF₄ NCs was employed to verify the above hypothesis. On the one hand, with increasing the excitation power density from 5 to 11 W/cm², the color of the designed pattern is switches from red to purple gradually (Figure 6b). On the other hand, when rotating the pattern at 600 or 900 rpm, a bright luminescent trajectory including red, white and blue-green color with different length was observed evidently (Figure 6c). Furthermore, the SP20 and MCF-7 cells viability were yet respectively higher than 94 and 91% even the input core/triple-shell NCs concentration up to 3.4 mg/ml (Figure S17),

Figure 6: (a) Schematic illustration of the anti-counterfeiting process. (b) Digital photographs of the designed patterns with increasing excitation power density from 5 to 11 W/cm². (c) Digital photographs of the designed patterns at different rotating speed.

which revealed the present researched NCs exhibited ultra-low cell cytotoxicity. These results manifest the present studied products were very suitable for anti-counterfeiting application with high security and safety.

4 Conclusions

In summary, uniform core/multi-shell UC NCs with different size were successfully prepared through a layer-by-layer epitaxial growth procedure. The relative emission intensities of Er³⁺ ions in the core and Tm³⁺ ions in the second shell can be manipulated through tuning their corresponding interfacial or inner defects, which is further employed to optimize the sensitivity for excitation power density dependent color variations. Thanks to the diversity in the rising edges of up-conversion emissions with different photon numbers, a bright multicolor trajectory can be observed with rotating the designed pattern. The present researched UC nano-systems,

with ability of pumping-controlled dual-mode color tuning, may find potential application for multiple dynamic anti-counterfeiting with high security.

Acknowledgments: This work was supported by the National Key Research and Development Program of China (2018YFF0215205), National Natural Science Foundation of China (No. 51702306, 11974350), Zhejiang Provincial Natural Science Foundation of China (No. LD18F050001).

Conflict of interests: The authors declare that there is no conflict of interest.

References

- [1] A. A. Kaminskii, "Achievements in the field of physics and spectroscopy of activated laser crystals." *Phys. Status Solidi*, vol. 87, pp. 11–57, 1985.
- [2] Y. X. Xue, C. J. Ding, Y. Y. Rong, et al., "Tuning plasmonic enhancement of single nanocrystal upconversion

- luminescence by varying gold nanorod diameter.” *Small*, vol. 13, p. 1701155, 2017.
- [3] G. X. Bai, M. K. Tsang, and J. H. Hao, “Tuning the luminescence of phosphors: Beyond conventional chemical method.” *Adv. Opt. Mater.*, vol. 3, pp. 431–462, 2015.
 - [4] C. S. Gong, W. Liu, N. He, H. G. Dong, Y. Jin, and S. L. He, “Upconversion enhancement by a dual-resonance all-dielectric metasurface.” *Nanoscale*, vol. 11, pp. 1856–1862, 2019.
 - [5] H. L. Wen, H. Zhu, X. Chen, et al., “Upconverting near-infrared light through energy management in core-shell-shell nanoparticles.” *Angew. Chem. Int. Ed.*, vol. 52, pp. 13419–13423, 2013.
 - [6] T. Y. Sun, B. Z. Xu, B. Chen, et al., “Anti-counterfeiting patterns encrypted with multi-mode luminescent nanotagants.” *Nanoscale*, vol. 9, pp. 2701–2705, 2017.
 - [7] B. Chen, Y. Liu, Y. Xiao, et al., “Amplifying excitation-power sensitivity of photon upconversion in a NaYF₄: HO nanostructure for direct visualization of electromagnetic hotspots.” *J. Phys. Chem. Lett.*, vol. 7, pp. 4916–4921, 2016.
 - [8] Z. P. Meng, S. L. Wu, and S. F. Zhang, “External current-controlled dynamic display by integrating upconversion micro-disks with power density-dependent color into NIR luminescent diodes.” *J. Mater. Chem. C*, vol. 6, pp. 13101–13107, 2018.
 - [9] D. Li, W.-Y. Lai, X. Shen, Q. Shao, and W. Huang, “Real-time naked-eye recognizable temperature monitoring based on Ho³⁺ (or Tm³⁺)-activated NaYF₄ upconversion nanowires via visual multicolor alteration.” *Mater. Chem. Front.*, vol. 3, pp. 791–795, 2019.
 - [10] R. R. Deng, F. Qin, R. F. Chen, W. Huang, M. H. Hong, and X. G. Liu, “Temporal full-colour tuning through non-steady-state upconversion.” *Nat. Nanotechnol.*, vol. 10, pp. 237–242, 2015.
 - [11] H. Zou, X. Q. Yang, B. Chen, et al., “Thermal enhancement of upconversion by negative lattice expansion in orthorhombic Yb₂W₃O₁₂.” *Angew. Chem. Int. Ed.*, vol. 58, pp. 17255–17259, 2019.
 - [12] X. M. Yin, H. Wang, Y. Tian, M. M. Xing, Y. Fu, and X. X. Luo, “Three primary color emissions from single multilayered nanocrystals.” *Nanoscale*, vol. 10, pp. 9673–9678, 2018.
 - [13] W. J. Yao, Q. Y. Tian, and W. Wu, “Tunable emissions of upconversion fluorescence for security applications.” *Adv. Opt. Mater.*, vol. 7, p. 1801171, 2019.
 - [14] H. Dong, L. D. Sun, and C. H. Yan, “Energy transfer in lanthanide upconversion studies for extended optical applications.” *Chem. Soc. Rev.*, vol. 44, pp. 1608–1634, 2015.
 - [15] A. Nadort, J. B. Zhao, and E. M. Goldys, “Lanthanide upconversion luminescence at the nanoscale: fundamentals and optical properties.” *Nanoscale*, vol. 8, pp. 13099–13130, 2016.
 - [16] M. Wu, L. Yan, T. Wang, B. Zhou, and Q. Y. Zhang, “Controlling red color-based multicolor upconversion through selective photon blocking.” *Adv. Funct. Mater.*, vol. 29, p. 180416, 2019.
 - [17] C. Zhang, L. Yang, J. Zhao, B. H. Liu, M. Y. Han, and Z. P. Zhang, “White-light emission from an integrated upconversion nanostructure: toward multicolor displays modulated by laser power.” *Angew. Chem. Int. Edit.*, vol. 54, pp. 11531–11535, 2015.
 - [18] L. P. Tu, X. M. Liu, F. Wu, and H. Zhang, “Excitation energy migration dynamics in upconversion nanomaterials.” *Chem. Soc. Rev.*, vol. 44, pp. 1331–1345, 2015.
 - [19] L. Lei, X. R. Dai, Y. Cheng, Y. S. Wang, Z. Xiao, S. Q. Xu, “Dual-mode color tuning based on upconversion core/triple-shell nanostructure.” *J. Mater. Chem. C*, vol. 7, pp. 3342–3350, 2019.
 - [20] B. S. Cao, Y. Y. He, Z. Q. Feng, Y. S. Li, and B. Dong, “Optical temperature sensing behavior of enhanced green upconversion emissions from Er-Mo: Yb₂Ti₂O₇ nanophosphor.” *Sens. Actuator B-Chem.*, vol. 159, pp. 8–11, 2011.
 - [21] G. Tian, Z. J. Gu, L. J. Zhou, et al., “Mn²⁺ dopant-controlled synthesis of NaYF₄: Yb/Er upconversion nanoparticles for in vivo imaging and drug delivery.” *Adv. Mater.*, vol. 24, pp. 1226–1231, 2012.
 - [22] F. Vetrone, V. Mahalingam, and J. A. Capobianco, “Near-infrared-to-blue upconversion in colloidal BaYF₅: Tm³⁺, Yb³⁺ nanocrystals.” *Chem. Mat.*, vol. 21, pp. 1847–1851, 2009.
 - [23] V. Mahalingam, R. Naccache, F. Vetrone, and J. A. Capobianco, “Preferential suppression of high-energy upconverted emissions of Tm³⁺ by Dy³⁺ ions in Tm³⁺/Dy³⁺/Yb³⁺-doped LiYF₄ colloidal nanocrystals.” *Chem. Commun.*, vol. 47, pp. 3481–3483, 2011.
 - [24] C. Z. Zhao, X. G. Kong, X. M. Liu, et al., “Li⁺ ion doping: an approach for improving the crystallinity and upconversion emissions of NaYF₄: Yb³⁺, Tm³⁺ nanoparticles.” *Nanoscale*, vol. 5, pp. 8084–8089, 2013.
 - [25] J. Xu, D. T. Tu, W. Zheng, et al., “Interfacial defects dictated in situ fabrication of yolk-shell upconversion nanoparticles by electron-beam irradiation.” *Adv. Sci.*, vol. 5, p. 1800766, 2018.
 - [26] K. A. Abel, J. C. Boyer, C. M. Andrei, and F. van Veggel, “Analysis of the shell thickness distribution on NaYF₄/NaGdF₄ Core/Shell nanocrystals by EELS and EDS.” *J. Phys. Chem. Lett.*, vol. 2, pp. 185–189, 2011.
 - [27] J. X. Zhao, X. Chen, B. Chen, et al., “Accurate control of core-shell upconversion nanoparticles through anisotropic strain engineering.” *Adv. Funct. Mater.*, vol. 29, p. 1903295, 2019.
 - [28] X. Chen, D. F. Peng, Q. Ju, and F. Wang, “Photon upconversion in core-shell nanoparticles.” *Chem. Soc. Rev.*, vol. 44, pp. 1318–1330, 2015.
 - [29] F. Wang, R. R. Deng, J. Wang, et al., “Tuning upconversion through energy migration in core-shell nanoparticles.” *Nat. Mater.*, vol. 10, pp. 968–973, 2011.
 - [30] L. Lei, D. Q. Chen, P. Huang, J. Xu, R. Zhang, and Y. S. Wang, “Modifying the size and uniformity of upconversion Yb/Er: NaGdF₄ nanocrystals through alkaline-earth doping.” *Nanoscale*, vol. 5, pp. 11298–11305, 2013.
 - [31] J. X. Zhao, Y. Zhang, X. X. Zhao, et al., “Direct ink writing of adjustable electrochemical energy storage device with high gravimetric energy densities.” *Adv. Funct. Mater.*, vol. 29, p. 1900809, 2019.
 - [32] Q. Q. Ma, J. Wang, Z. H. Li, et al., “Near-infrared-light-mediated high-throughput information encryption based on the inkjet printing of upconversion nanoparticles.” *Inorg. Chem. Front.*, vol. 4, pp. 1166–1172, 2017.
 - [33] M. L. You, J. J. Zhong, Y. Hong, Z. F. Duan, M. Lin, and F. Xu, “Inkjet printing of upconversion nanoparticles for anti-counterfeit applications.” *Nanoscale*, vol. 7, pp. 4423–4431, 2015.
 - [34] M. L. You, M. Lin, S. R. Wang, et al., “Three-dimensional quick response code based on inkjet printing of upconversion fluorescent nanoparticles for drug anti-counterfeiting.” *Nanoscale*, vol. 8, pp. 10096–10104, 2016.

- [35] X. Liu, Y. Wang, X. Li, et al., "Binary temporal upconversion codes of Mn^{2+} -activated nanoparticles for multilevel anti-counterfeiting." *Nat. Commun.*, vol. 8, p. 899, 2017.
- [36] G. Gong, Y. Song, H. H. Tan, et al., "Design of core/active-shell $NaYF_4: Ln^{3+}@NaYF_4: Yb^{3+}$ nanophosphors with enhanced red-green-blue upconversion luminescence for anti-counterfeiting printing." *Compos. Pt. B Eng.*, vol. 179, p. 107504, 2019.
- [37] J. Liu, H. Rijckaert, M. Zeng, et al., "Simultaneously excited downshifting/upconversion luminescence from lanthanide-doped core/shell fluoride nanoparticles for multimode anticounterfeiting." *Adv. Funct. Mater.*, vol. 28, p. 1707365, 2018.
- [38] Y. J. Zhang, H. Y. Yang, H. L. Ma, et al., "Excitation wavelength dependent fluorescence of an esipt triazole derivative for amine sensing and anti-counterfeiting applications." *Angew. Chem. Int. Ed.*, vol. 58, pp. 8773–8778, 2019.
- [39] H. Huang, F. Huang, L. Lin, et al., "Perceiving linear-velocity by multiphoton upconversion." *ACS Appl. Mater. Interfaces*, vol. 11, pp. 46379–46385, 2019.

Supplementary material: The online version of this article offers supplementary material (<https://doi.org/10.1515/nanoph-2020-0150>).