Research article

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Thermal-responsive multicolor emission of single NaGdF₄:Yb/Ce/Ho upconversion nanocrystals for anticounterfeiting application

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Abstract: This study presents a novel and high-level anticounterfeiting strategy based on Ce/Yb/Ho triply-doped NaGdF₄ nanocrystals with temperature-responsive multicolor emission. A critical factor leading to the multicolor emission is confirmed by comparing the luminescence thermal behaviors of nanocrystals in various atmospheres. Through analyzing the temperature-dependent lifetimes of Yb³⁺ ions in air, we demonstrate that thermally-induced multicolor emission mainly originates from the gradually-attenuated H₂O quenching effect. Because the cross-relaxations between Ce³⁺ and Ho³⁺ ions and the nonradiative transitions of Yb³⁺ ions create plenty of phonon heat, the multicolor emission of nanocrystals can be achieved under 975 nm excitation at a relatively low power density. This recognition method is efficient and convenient for security authentication. The as-synthesized core nanocrystals can be directly used to fabricate anticounterfeiting ink without further processing (e.g. core/shell or hybrid). Therefore, the small-sized β-NaGdF₄:Yb/Ce/Ho nanocrystals are promising candidate for security application.

Keywords: anticounterfeiting; luminescence; nanocrystals; quenching; upconversion.

Globally, the business of counterfeit goods causes the economic losses of more than \$USD 1.7 trillion annually [1]. Product counterfeiting acts in the fields of drug, valuable commodity, and currency etc. have seriously threaten the health of consumer, the interest of enterprise, and the financial security of society. Anticounterfeiting strategies can make the genuine product difficult to be replicated and effectively impede fraudulent goods from being traded in a market [2, 3]. As one of security strategies, lanthanide-doped upconversion nanocrystals (UCNCs) have advantages of a low background fluorescence and a strong resistance to photobleaching. Upconversion (UC) bulk materials applied in currencies and high-value documents are Yb/Er co-doped crystals with the green emission [4, 5]. These anticounterfeiting materials only can exhibit nearly unchanged color under excitation. The constructed security pattern with them is still likely to be imitated by using other substitutes with the similar emission.

The security level of the UC materials for anticounterfeiting applications can be further improved by achieving a color-tunable emission. Recently, considerable efforts have been devoted to the studies of multicolor emissions. For example, various activators and sensitizers doped core/shell nanocrystals (NCs) were designed to produce multicolor emission by utilizing upconversion and downshifting excitations [6–9], adjusting laser power [10–12], or using pulsed laser [13–15]. These strategies greatly raise the security level of anticounterfeiting technology. However, a relatively complex identification equipment would be needed to trigger the multicolor emissions of these novel upconversion materials. First, the collaborative effects of upconversion and downshifting emissions need multi-mode excitation sources [4, 6–9]. In addition, power-dependent multicolor emissions need to adjust the laser power, which often requires an ultra-high power laser [10]. Finally, tunable lifetime multiplexing would require a time-gated decoding instrument [13, 14]. The complicate structure designs of materials and the special recognition methods limit their commercial applications. Thus, developing a convenient recognition method is quite

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important and urgent for anticounterfeiting UCNCs with the high level security.

It is well known that luminescent materials generally show low luminescent efficiency at higher temperature due to thermal quenching. However, Li et al. firstly found that $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped UCNCs with a size smaller than 30 nm exhibit an anomalous temperature-dependent upconversion luminescence (UCL) enhancement [16]. Since then, the luminescence thermal behavior of upconversion materials has been a research hotspot recently [17–19]. For the thermal-induced UCL enhancement of small-sized UCNCs, a lattice thermal expansion effect and a surface phonon-assisted energy transfer upconversion have been sequentially proposed to explain the anomalous UCL thermal behavior [20, 21]. For the former viewpoint, in a constant case of a surface quenching effect at elevated temperature, the enhanced UCL of small-sized NCs seems to be attributed to the reduced Yb^{3+} - Yb^{3+} energy migration efficiency to surface quenchers, caused by the lattice thermal expansion of the nanoparticles. However, Wang et al. hold that the thermally-induced UCL enhancement originates from a negative thermal lattice expansion effect, leading to the increase of Yb^{3+} - Er^{3+} energy migration efficiency [22]. For the latter one, the surface phonon-assisted energy transfer upconversion elucidates well the enhanced UCL of small-sized NCs in air, yet it cannot explain why the same NCs exhibit temperature-dependent UCL decline in dry atmosphere [23]. Our substantial evidences suggest that the anomalous UCL thermal behavior is related to H_2O molecules on the surface of Yb/Ln double-doped UCNCs ($\text{Ln} = \text{Ho}^{3+}$, Er^{3+} , or Tm^{3+}) [23]. For triply-doped UCNCs, we need more evidences to reveal the underlying mechanism of their enhanced UCL at elevated temperature.

In previous studies, utilizing the anomalous UCL thermal behavior, we have successfully achieved multicolor emissions by doping various activators into core/shell NCs [24], hybridizing both active- and inert-shell NCs [25], or mixing both large- and small-sized NCs [26]. So far single core nanocrystals with multicolor emission have not been reported yet. In this work, we report Ce/Yb/Ho triply-doped NaGdF_4 core nanocrystals with a thermal-responsive multicolor emission. The color-changing mechanism is revealed through investigating the UCL thermal behaviors in various atmospheres and analyzing the Yb^{3+} lifetimes at elevated temperature. Particularly, the multicolor emission of the core nanocrystals can be achieved by prolonging irradiation time at a low power density. Finally, the $\beta\text{-NaGdF}_4\text{:Yb/Ce/Ho}$ core-only nanocrystals are experimentally substantiated for used as security ink to print anticounterfeiting patterns with more secure merits and convenient recognition methods.

The $\beta\text{-NaGdF}_4\text{:20%Yb/30%Ce/2%Ho}$ nanocrystals were synthesized by a conventional co-precipitation protocol [27], the detailed procedures of which were described in the Supporting Information (Section A). In our system, Yb^{3+} ions act as sensitizers for Ho^{3+} ions. 30 mol% of Ce^{3+} ions are doped along with Ho^{3+} ions to obtain a strong red emission [28]. Transmission electron microscopy (TEM) image shows that the nanocrystals are highly monodispersed with mean size of ~ 11.2 nm (Figure 1a–b). The lattice fringes of high-resolution TEM (HRTEM) image for a nanocrystal show (100) facet ($d = 0.52$ nm) of $\beta\text{-NaGdF}_4$ (Figure 1c). The selected area electron diffraction (SAED, Figure 1d) and X-ray diffraction (XRD, Figure 1e) patterns confirm a pure hexagonal phase of the as-synthesized nanocrystals.

As shown in Figure 2a, under 975 nm excitation, $\beta\text{-NaGdF}_4\text{:Yb/Ce/Ho}$ nanocrystals exhibit temperature-dependent UCL enhancement at elevated temperature from 30 to 150 °C. The green and red emission intensities at 150 °C are ~ 1.7 - and 10.2- fold stronger than those at 30 °C, respectively (Figure 2b). The green band is almost unchanged, whereas the red band increases remarkably with increasing temperature. The intensity of green emission is nearly as strong as that of red one at room temperature. Because human eyes are more sensitive to green light, the whole emission color of nanocrystals is green upon excitation at 30 °C. At higher temperature, the enhanced red emission is absolutely dominant, leading to an interesting

Figure 1: (a) TEM image, (b) Particle size statistics, (c) HRTEM image, (d) SAED and (e) XRD patterns of $\beta\text{-NaGdF}_4\text{:20%Yb/30%Ce/2%Ho}$ nanocrystals.

color change from green to red. The color shifts are quantitatively evaluated by the following Eq. (1) [29]:

$$\Delta c = \sqrt{(\mu'_t - \mu'_o)^2 + (v'_t - v'_o)^2 + (\omega'_t - \omega'_o)^2} \quad (1)$$

where $\mu' = 4x/(3 - 2x + 12y)$, $v' = 9y/(3 - 2x + 12y)$, and $\omega' = 1 - \mu' - v'$. μ' and v' are the chromaticity coordinates in uniform color space, x and y are the chromaticity coordinates in CIE 1931 color space, and o and t are the chromaticity shift at 30 °C and a given temperature, respectively. The color coordinate at 30 and 150 °C are (0.42, 0.55) and (0.62, 0.38), correspondingly, and the calculated color shifts (Δc) is ~ 0.27 (Figure 2c). Thus, the β -NaGdF₄:Yb/Ce/Ho nanocrystals exhibit the temperature-responsive multicolor emission with large color shifts, which is also verified by the color changes of pattern printed with nanocrystal ink at elevated temperature (Figure 2d). It is worth noting that NaGdF₄:Ce/Yb/Ho nanocrystals are with a reversible temperature-induced enhancement (Figure S1).

To investigate the thermal-responsive color changes of the low concentration Ce³⁺ doped UCNCs, we first measure the temperature-dependent UCL of NaGdF₄:20%Yb/2%Ho NCs (Figure S2). The color coordinate (x, y) at 30 and 150 °C are (0.31, 0.68) and (0.27, 0.71), and the calculated value

Figure 2: (a) Temperature-dependent UCL spectra of β -NaGdF₄:30%Ce/20%Yb/2%Ho nanocrystals in air (power density: 1.6 W/cm²). (b) Integrated UCL intensities of red and green bands, noting that the intensities are normalized to that at 30 °C. (c) Temperature-dependent color coordinates of nanocrystals in CIE chromaticity diagram. (d) Temperature-induced color shifts of patterns printed with nanocrystal ink.

(Δc) is ~ 0.02 . This Δc (~ 0.02) is very small in comparison with the Δc (~ 0.27) of NaGdF₄:20%Yb/30%Ce/2%Ho UCNCs, so NaGdF₄:20%Yb/2%Ho UCNCs show inconspicuous color changes. From the spectrum variations of NaGdF₄:20%Yb/2%Ho UCNCs, not only the green emission increases to 4.3 times, but also the red emission increases to 2.3 times at elevated temperature. The enhanced red emission reduces the green saturation, resulting in the insignificant color changes. Besides, we also investigate the temperature-dependent UCL spectra of NaGdF₄:15%Ce/20Yb%/2%Ho NCs (Figure S3). The green and red emission intensities of the 15 mol% Ce³⁺ doped UCNCs increase by 2- and 6-fold, and the color shift value (Δc) is ~ 0.11 at temperature from 30 to 150 °C. Compared with the 30 mol% Ce³⁺ doped UCNCs, the green emission enhancement factor of NaGdF₄:15%Ce/Yb/Ho nanocrystals is much larger, but the red emission enhancement factor is smaller. This directly leads to a smaller color shift value. Thus, the relatively low concentration Ce³⁺ doping cannot effectively suppress the enhancement factor of green emission, and reduce the color shift value (Δc).

To clarify the origin of the multicolor emission, we measured the temperature-dependent UCL spectra of NCs in Ar, Ar/H₂O, and Ar/D₂O atmospheres, respectively (Figure S4). As shown in Figure 3a–c, the green emission intensity slightly increases by 0.2-fold in Ar/H₂O atmospheres, but decrease by $\sim 7\%$ in absence of H₂O atmospheres. In contrast, the red emission is significantly enhanced in Ar/H₂O and decreased in Ar or Ar/D₂O. In moisture atmospheres, the green emission is well suppressed, but the red emission is dramatically enhanced, leading to the fact that the whole luminescent color move towards the red domain. This is very beneficial to increase the color shift value (Δc). The UCL intensity in Ar decreases due to thermal quenching (Figure 3a). The temperature-dependent UCL decline reveals that the nanocrystals are still affected by thermal quenching, even though they exhibit temperature-dependent UCL enhancement in air. It is merely the fact that thermal induced UCL enhancement in air plays a dominant role, and the reduced UCL caused by thermal quenching is concealed. In Ar/H₂O atmosphere, however, the UCL intensity increases with increasing temperature (Figure 3b). The result suggests that H₂O molecules are the critical factor resulting in the temperature-dependent UCL enhancement. The temperature-dependent UCL decline in Ar/D₂O further confirms the H₂O quenching effect on the UCL, because the fact that the multiphonon relaxation of D₂O is less effective makes their quenching effect negligible [30].

In order to further elucidate the H₂O quenching effect, the downshifting emission decay curves of Yb³⁺²F_{5/2} at ~ 1050 nm

Figure 3: The UCL intensity of β -NaGdF₄:Yb/Ce/Ho nanocrystals in (a) Ar, (b) Ar/H₂O, and (c) Ar/D₂O. Noting that the UCL intensity is normalized to that at 30 °C (power density: 2.4 W/cm²). (d) Time-dependent downshifting luminescence of Yb³⁺ ²F_{5/2} energy level for the nanocrystals after 975 nm excitation at elevated temperature. Schematic representations of (e) upconversion process, and (f) energy transfer between active Ln³⁺ ions as well as between Yb³⁺ and H₂O.

were measured at elevated temperature in air. As shown in Figure 3d, the lifetimes increase from 28 to 67 μs with increasing temperature. The temperature dependence of Yb³⁺ lifetime in Yb/Ce/Ho triply-doped UCNCs is consistent with that in Yb/Ho double-doped ones [23]. The result indicates that H₂O molecules mainly quench the Yb³⁺ excited state energy. Furthermore, we also measured the temperature-dependent lifetimes of activators. In Yb/Ce/Ho triply doped system, the lifetimes of Ho³⁺ ⁵S₂/⁵F₄ (540 nm) and ⁵F₅ (645 nm) levels decrease with increasing temperature in air (Figure S5). This indicates that the UCL of Ho³⁺ ions are mainly affected by the thermal quenching. In other words, the effect of H₂O quenching on the Ho³⁺ ions is negligible due to a lower concentration. For NaGdF₄:Yb/Ce/Ho NCs with the size of ~11 nm, a large number of H₂O molecules in air can be adsorbed on their surface at room temperature due to a large surface-to-volume ratio. The Yb³⁺ excited state energies are directly quenched by an overtone energy transfer from an electric dipole of Yb³⁺ ion to an atomic dipole of H₂O molecule [31]. Only a small amount of Yb³⁺ excited state energy is transferred to the nearby Ho³⁺ ion, so the UCL is weak at room

temperature. When the temperature increases to 150 °C, H₂O molecules gradually desorb from nanocrystal surface, and the UCL is enhanced. Therefore, the temperature-induced UCL enhancement of NaGdF₄:Yb/Ce/Ho NCs results from the gradually-attenuated H₂O quenching effect.

Figure 3e shows the photophysical dynamics process of Ce/Yb/Ho triply-doped NCs. Under 975 nm excitation, the electrons at the Yb³⁺ ²F_{7/2} energy level are pumped to the ²F_{5/2} excited state via a ground state absorption. Afterward, the ⁵I₆ and ⁵S₂/⁵F₄ energy levels of Ho³⁺ ions are populated by an energy transfer (ET) from Yb³⁺ to Ho³⁺. Subsequently, two cross-relaxation (CR) processes involving between Ce³⁺ and Ho³⁺ increase the Ho³⁺ ⁵F₅ energy level's population, which consequently weakens the green emission but enhances the red emission. The energy transfer processes in the triply doped system are described by the derived rate equations as shown in Supporting Information (Section B: rate equations). The population densities of the related state of Yb³⁺ and Ho³⁺ are estimated according to the rate equations. Due to a large surface-to-volume ratio of small-sized nanocrystals, surface H₂O molecules in air quench

most of the excited state energies of Yb^{3+} , resulting in a large nonradiative transition rate (ω_{Yb1}) of Yb^{3+} . However, ω_{Yb1} decreases with increasing temperature, and this has been demonstrated by the increased lifetime of Yb^{3+} at elevated temperature (Figure 3d). From

$$n_3 \approx \left(\frac{\mu_3 C_1 n_{\text{Ce0}}}{\omega_1} + \frac{\mu_2 C_2 n_{\text{Ce0}}}{\omega_4 + C_2 n_{\text{Ce0}}} \right) \frac{n_0 \mu_1}{\omega_3 (\omega_2 + C_1 n_{\text{Ce0}})} \left(\frac{\rho \sigma n_{\text{Yb0}}}{\omega_{\text{Yb1}}} \right)^2 \quad (\text{Eq. (S11)}) \text{ and}$$

$$n_4 \approx \frac{n_0 \mu_1 \mu_2}{(\omega_4 + C_2 n_{\text{Ce0}}) (\omega_2 + C_1 n_{\text{Ce0}})} \left(\frac{\rho \sigma n_{\text{Yb0}}}{\omega_{\text{Yb1}}} \right)^2 \quad (\text{Eq. (S12)}), \text{ the } n_3 \text{ and } n_4$$

population densities of $\text{Ho}^{3+} {}^5\text{F}_5$ level (red emission) and ${}^5\text{F}_4$, ${}^5\text{S}_2$ level (green emission) increase with decreasing ω_{Yb1} at elevated temperature. The subsequently occurring cross relaxations further increase the n_3 population densities, but decrease the n_4 population densities. This suggests that the significantly enhanced red emission results from the gradually-attenuated surface H_2O quenching effect and the two cross relaxations. Although the green emission shows slightly increase or almost constant, energy transfer upconversion indeed occurs from Yb^{3+} to $\text{Ho}^{3+} {}^5\text{F}_4/{}^5\text{S}_2$ level, the population of which is deactivated due to a cross relaxation.

Combined with the previous discussion, the green emission intensity is almost unaffected by temperature, whereas the red emission is significantly enhanced, leading to the multicolor emission of UCNCs. Meanwhile, the red emission is dominant in the whole UCL, thus the temperature-responsive multicolor emissions also originate from the reduced surface H_2O quenching effect. The related energy transfer processes in $\text{NaGdF}_4:\text{Yb/Ce/Ho}$ NCs are illustrated in Figure 3f.

Power-dependent UCL of $\beta\text{-NaGdF}_4:\text{Yb/Ce/Ho}$ NCs are also investigated, shown in Figure S6. According to the power law of UCL ($I \propto P^n$), the red and green emission intensities should increase at the same rate with increasing the pump power due to their identical two-photon process. As expected, we observed the simultaneous increases of the red and green emissions in a low power density range ($< 2 \text{ W/cm}^2$). The emitting colors of UCNCs do not change, but the UCL intensities increase. In a high power density range from 2 to 4.8 W/cm^2 , however, the red emission intensity increases more quickly than the green one. The result indicates that the laser-heating effect results in the multicolor emission of NCs. The abundant phonons

originated from both the $\text{Ce}^{3+}/\text{Ho}^{3+}$ cross-relaxation processes and the Yb^{3+} nonradiative transitions generate a lot of heat, which is energetically favorable to the multicolor emission. Therefore, the power-dependent multicolor emissions are essentially induced by the heat.

Inspired by this, we used 975 nm laser to irradiate the pattern printed with the $\text{NaGdF}_4:\text{Yb/Ce/Ho}$ ink at the power density of 4.8 W/cm^2 (Figure 4). Utilizing the intrinsic light-to-heat conversion ability of UCNCs [32], an obvious emission color change from green to red was observed by prolonging the irradiation time (20 s). The thermally-induced color changes of the nanocrystals are reversible and show good cyclic stability (Figure S7). Moreover, irradiation experiments show that the laser-heating effect at power density of 4.8 W/cm^2 is not enough to burn the printed paper (Figure 4). It should be pointed out that under a steady-state excitation at a relatively high power density ($> 4.8 \text{ W/cm}^2$), the responsive time of the color changes will be shorter and the color shift ($\Delta\lambda$) will be larger due to the high laser thermal effect. In addition, the sizes of nanocrystals play an important role in thermal-induced multicolor emission. The smaller the size is, the larger the color change is. This recognition method is convenient and efficient for anticounterfeiting authentication. The result indicates that $\beta\text{-NaGdF}_4:\text{Yb/Ce/Ho}$ nanocrystals are an excellent candidate for anticounterfeiting application.

In conclusion, we have synthesized monodisperse $\beta\text{-NaGdF}_4:\text{Yb/Ce/Ho}$ UCNCs ($\sim 11 \text{ nm}$) using a conventional coprecipitation method. Upon 975 nm excitation, these UCNCs exhibit temperature-responsive multicolor emissions at elevated temperature from 30 to 150°C . The emitting colors change from green to red, and the color shift ($\Delta\lambda$) reaches to 0.27. The temperature-responsive multicolor emission results from the gradually-attenuated H_2O quenching effect. Importantly, utilizing the intrinsic phonon heat of UCNCs, the multicolor emission can also be achieved by prolonging irradiation time at power density of 4.8 W/cm^2 . The recognition method is convenient and efficient for security authentication. These UCNCs with multicolor emission can be directly used to construct security patterns and offer a competitive alternative for anticounterfeiting applications.

Figure 4: The color changes of pattern printed with $\beta\text{-NaGdF}_4:\text{Yb/Ce/Ho}$ nanocrystal ink at various irradiation times and the printed paper before and after irradiation (power density: 4.8 W/cm^2 ; scale bar: 5 mm).

1 Experimental methods

1.1 Nanocrystal Synthesis

Hexagonal (β) phase $\text{NaGdF}_4\text{:Ce/Yb/Ho}$ and $\text{NaGdF}_4\text{:Yb/Ho}$ nanocrystals were synthesized using a coprecipitate method [33]. Detailed synthesis procedures of nanocrystals are provided in the Supporting Information.

1.2 Characterization

TEM and HRTEM images were taken with a Tecnai G2 microscope. XRD data was collected by a Shimadzu XD-3A X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). UCL spectra were collected by a portable spectrometer (Maya2000Pro, Ocean Optics Co.) using a continuous 975 nm diode laser as the excitation source. The temperature-dependent UCL spectra of solid-state nanocrystals were measured in air, Ar, Ar/H $_2$ O, and Ar/D $_2$ O atmospheres with the aid of a temperature-controlled heating cell. Temperature-dependent photoluminescence dynamics was investigated by a FLS980 fluorescence spectrometer (Edinburgh Instruments) upon excitation with a pulsed 975 nm laser. Luminescent images of the printed patterns under the 975 nm laser irradiation were taken by a digital camera of iPhone 7 (Apple Inc.).

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ASSOCIATED CONTENT

Supporting Information

Detailed synthesis procedures of all samples, ink preparation method, temperature-dependent UCL spectra in various atmospheres, power-dependent UCL spectra in air. The supporting Information is available free of charge on the ...

Supplementary data: Supplementary data to this article can be found online at <https://doi.org/10.1515/nanoph-2020-0136>.