Dual upconversion nanophotoswitch for security encoding

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ABSTRACT Light-harvesting lanthanide ions (Ln^{3+}) doped NaYF_4 inks could provide polychromatic patterns for opposing counterfeiting commodity infestation because of their distinctive upconversion photoluminescence (UPL) properties. Herein, three kinds of core-triple-shell Ln^{3+} ions doped NaYF_4 upconversion nanocrystals (UCNCs) are synthesized through modified high-temperature coprecipitation, which demonstrate excellent UPL properties of independent emitting colors under 808 or 980 nm laser excitation. Additive mixing three kinds of 808 nm emitted red-green-blue (RGB) UCNCs colloid solution can precisely regulate the emissions of the suspension for achieving full-color display. The as-obtained RGB three-primary colors induced by 808 nm laser accomplish broader color gamut than traditional standard RGB (sRGB) model and printing cyan-magenta-yellow (CMY) model. In addition, various China zodiac patterns and complex multicolor images are printed by the as-formulated UCNCs inks through screen printing technology. The printed patterns present colorful and polychromatic sequential toning visualization patterns under 808 nm excitation, while present another succession of gradually changed versatile patterns under 980 nm excitation. As a proof of concept, transparent polyvinyl chloride (PVC) self-adhesive anti-counterfeiting label is attached to the bottle of wine package for practical application. The demonstration of multiple model patterns of Chinese zodiac and poetry images based on these core-triple-shell UCNCs can be selected as a conceivable substitute of traditional single model patterns, underlining the full-color anti-counterfeiting level.

Keywords: Upconversion, core-triple-shell UCNCs, wide color gamut, full-color model, anti-counterfeiting

INTRODUCTION

With the continuous development of high-technology and commodity market, the interpenetration of various anti-counterfeiting models is demanded to set up layers of obstacles and resistance for counterfeiters [1–4]. Encoding high-density and complicated data into an independent unit has been proved its significance to improve information security level [5–7]. The emission color of fluorescent materials are especially suitable for encoding information and optical multiplexing [8–11]. For instance, traditional semiconductor quantum dots (based on down-conversion (DC) mechanism, convert short wavelength to long wavelength) and fluorescent dyes could be readily printed as labels to form colorful code under certain wavelength irradiation [12–14]. However, those materials suffer from the disadvantages of high poisonousness, easy detection and relative unstability [15–17]. Alternatively, Ln^{3+} ions doped upconversion (UC) materials are particularly suitable for security application because of intrinsic upconversion photoluminescence (UPL) properties, including anti-Stokes fluorescence (converted long wavelength to short wavelength) [16,18], tunable multicolor emissions under near-infrared (NIR) light excitation [19,20], perfect biological compatibility and long fluorescent lifetime [21,22].

In the past few years, extensive studies have been devoted to investigating multi-color tuning of lanthanide doping materials, where the nanocrystals are synthesized through high-temperature coprecipitation method and solvothermal process [23–26]. The feature of UC materials is that the eventual emitting color could only be

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regulated under single model wavelength irradiation. However, the patterns based on single model fluorescence can be easily reproduced and are inadequate to conceal the authentic information. And in order to achieve optimal color displaying, continuous optimization of experimental parameters and dopant concentrations is required. One potential tactic used to simplify encoding process is to combine multiple model emissions with nanocrystals for replacing single model emissions [27–29]. Incorporating DC and UC mechanisms into a system for achieving multiple model fluorescence has been implemented [27,30,31]. For instance, in our previous work, carbon quantum dots (CDs) were combined with UC $\text{NaYF}_4:\text{Er},\text{Yb}$ (Tm) to realize dual-mode fluorescent patterns under 365 and 980 nm excitation, indicating outstanding anti-counterfeiting application [30]. Although they can serve for security, the drawbacks of presenting colors with relative narrow color gamut limit their further utilization. Various techniques coupled with Ln^{3+} UC materials have been developed for security application, including radio frequency identification (RFID) tags [32], inkjet printing [7] and laser holograms [33,34]. However, these techniques depend on high-cost production equipment, clean-room facilities and complex preparation procedure. Therefore, how to achieve true full-color and tunable fluorescence patterns through a simple technique becomes an urgent challenge in the anti-counterfeiting fields.

To address the above challenges, three types of core-multiple-shell UC nanocrystals (UCNCs) coupled with low-cost screen printing technique have been used as a promising strategy in our study. In the various layered UC nanostructures, diverse sensitizers and activators were confined in different layers for displaying multi-color. Intriguingly, the core-triple-shell UC nanoparticles display pure RGB color under 808 nm excitation and accomplish broad array of colors through straightforward additive mixing different volume ratio of RGB UCNCs colloidal solution. After inks formulation process, we employed the as-obtained UCNCs-poly(acrylic acid) (PAA) inks to screen-print designable and versatile patterns and complex large-area images, achieving the full-color model anti-counterfeiting for wine package.

EXPERIMENTAL SECTION

Materials and reagents

$\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (99.99% metals basis), $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9% metals basis), $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9% metals basis), $\text{TmCl}_3 \cdot 6\text{H}_2\text{O}$ (99.99% metals basis), $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (99.995% metals

basis), 1-octadecene ($\text{C}_{18}\text{H}_{36}$, ODE), oleic acid (OA, 85%) and poly(acrylic acid) 50% solution (PAA, $M_w = 3000$) were purchased from Aladdin Chemistry Co., Ltd. NaOH (AR), NH_4F (AR), methanol (CH_3OH , AR), cyclohexane (C_6H_{12}) and ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd.

Preparation of NaYF_4 core-triple-shell structured nanocrystals

The NaYF_4 core-triple-shell nanocrystals were fabricated by a modified high-temperature coprecipitation process. Typically, the step-by-step synthesis of $\text{NaYF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}@\text{NaYF}_4:\text{Nd}^{3+}@\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ nanocrystals (denoted as TNYE UCNCs, P1) was illustrated as follows:

Synthesis of $\text{NaYF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}$ core structured nanocrystals (denoted as T UCNCs). For the preparation of $\text{NaYF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}$ nanoparticles, 1 mmol of ReCl_3 precursor ($\text{Y}:\text{Yb}:\text{Tm} = 80\%:18\%:2\%$) was mixed into a 50 mL three-necked flask with adding 7.5 mL of OA and 15 mL of ODE. The suspension was heated to 160°C under argon atmosphere and kept at this temperature for 30 min while stirring. When it was cooled down to 35°C naturally, a mixture of NaOH (1 mol L^{-1} , 2.5 mL) and NH_4F methanol solution (0.4 mol L^{-1} , 10 mL) were immediately injected into the flask. And then the temperature of resultant mixture was increased to 50°C and maintained for 30 min to ensure the complete nucleation. Afterward, the reaction mixture was heated to 110°C for removing methanol and raised up to 300°C for 1.5 h immediately. Eventually, the resultant mixture was cooled down to 30°C gently under the protecting of slow argon flow. The precipitates were centrifuged and washed with ethanol, cyclohexane and water for several times successively and dispersed in cyclohexane for further utilization.

Synthesis of $\text{NaYF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}@\text{NaYF}_4:\text{Nd}^{3+}$ core-shell structured nanocrystals (denoted as TN UCNCs). The overcoating of $\text{NaYF}_4:\text{Nd}^{3+}$ shell layer was carried out with the similar process as above-mentioned preparation process of T UCNCs except that 2 mmol of ReCl_3 precursor ($\text{Y}:\text{Nd} = 80\%:20\%$) was introduced. And the T UCNCs cyclohexane colloidal solution (0.25 mol L^{-1} , 4 mL) was rapidly pipetted into three-necked flask which was stirred for 5 min before adding the mixture of NaOH and NH_4F methanol solution.

Synthesis of $\text{NaYF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}@\text{NaYF}_4:\text{Nd}^{3+}@\text{NaYF}_4$ core-double-shell structured nanocrystals (denoted as TNY UCNCs). The overcoating of the second NaYF_4 shell layer was carried out as similar as the above-mentioned preparation process of TN UCNCs but 1 mmol of

YCl_3 precursor was introduced. Then, 4 mL of 0.25 mol L^{-1} TN UCNCs cyclohexane colloidal solution was rapidly pipetted into three-necked flask which was stirred for 5 min before injecting the mixture of NaOH and NH_4F methanol solution.

Synthesis of $\text{NaYF}_4\text{:Yb}^{3+}, \text{Tm}^{3+} @ \text{NaYF}_4\text{:Nd}^{3+} @ \text{NaYF}_4 @ \text{NaYF}_4\text{:Yb}^{3+}, \text{Er}^{3+}$ core-triple-shell structured nanocrystals (denoted as TNYE UCNCs). The overcoating of the third shell layer, $\text{NaYF}_4\text{:Yb}^{3+}, \text{Er}^{3+}$, was carried out as similar as the above-mentioned preparation of TNY UCNCs except that 1 mmol of ReCl_3 precursor (Y:Yb:Er = 80%:18%:2%) was introduced before injecting the mixture of NaOH and NH_4F methanol solution. The TNY UCNCs cyclohexane colloidal solution (0.25 mol L^{-1} , 4 mL) was rapidly pipetted into the three-necked flask while stirring for 5 min. The resulting products were collected and washed with ethanol, cyclohexane and water for five times successively, and then dispersed in cyclohexane for further application.

Moreover, the synthesis process of $\text{NaYF}_4\text{:Yb}^{3+}, \text{Tm}^{3+} @ \text{NaYF}_4 @ \text{NaYF}_4\text{:Nd}^{3+} @ \text{NaYF}_4\text{:Yb}^{3+}, \text{Er}^{3+}$ nanocrystals (denoted as TYNE UCNCs, P2) and $\text{NaYF}_4\text{:Er}^{3+}, \text{Tm}^{3+} @ \text{NaYF}_4\text{:Nd}^{3+} @ \text{NaYF}_4 @ \text{NaYF}_4\text{:Yb}^{3+}, \text{Er}^{3+}$ nanocrystals (denoted as ETNYE UCNCs, P3) were similar with the preparation of TNYE UCNCs. While, the precursors of ReCl_3 were replaced as follows: P2, Y:Yb:Tm = 80%:18%:2%; P3, Y:Er:Tm = 88%:10%:2%. All the preparation parameters of samples are listed in Table S1 (Supplementary information).

Fabrication of anti-counterfeiting patterns by screen printing technology

Two screen plates with designable and versatile patterns were obtained for next utilization, which possess 300 mesh counts. The as-prepared UCNCs (90 mg) were mixed with PAA (3 mL) to formulate the UCNCs fluorescent inks, followed by screen printing versatile patterns on white cardboard.

Characterizations

Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) of samples were carried out using a JEM-2100 TEM with 200 kV accelerating voltage. Scanning electron microscopy (SEM) was recorded by a cold-field emission Hitachi S-4800 SEM. The room-temperature fluorescent spectra were characterized by using a Hitachi F-4600 spectrophotometer equipped with external 808 nm

(Changchun New Industries Optoelectronics Tech Co., Ltd) and 980 nm (Changchun Bright Optoelectronics Co., Ltd) fiber coupled laser system. The information and signatures of the patterns were recorded by using a Nikon D750 camera equipped with high throughput filters (400–700 nm) under adjustable excited source of 980 nm laser or 808 nm laser. The laser power density of 980 nm laser and 808 nm laser for the photoluminescence (PL) measurements were ca. 48 and 80 W cm^{-2} , respectively.

RESULTS AND DISCUSSION

For rational design of color-tunable UC nanoparticles, hexagonal-phase NaYF_4 is selected as the matrix material. And four types of Ln^{3+} (Yb^{3+} , Nd^{3+} , Tm^{3+} , Er^{3+}) are incorporated into specific layer with certain molar concentrations. The typical layer-by-layer epitaxial growth route is used to synthesize the TNYE UCNCs, which is schematic displayed in Fig. 1a. TEM and corresponding HRTEM images are illustrated in Fig. 1b–i, respectively. TEM images in Fig. 1b–f present the highly uniform and gradually increased core-multishell nanocrystals along with the synthesis procedures. Comparatively, the morphologies evolve from spheroidicity to short rod shape and the average lengths of UCNCs increase from ~34 to ~68 nm. The size distribution statistics are inseted in Fig. 1b–e. Meanwhile, corresponding HRTEM of the core-triple-shell UCNCs (Fig. 1f–i) present well-defined lattice fringes of 0.517 and 0.298 nm, indexing to the (100) and (110) plane of $\beta\text{-NaYF}_4$, respectively. They are verified by the results of fast Fourier transform (FFT, insets of Fig. 1g–i). Clearly, the lattice orientation has been changed after coating with the shell layer. Additionally, the SEM images and size distributions of other two kinds of TYNE UCNCs and ETNYE UCNCs are shown in Figs S1 and S2 (Supplementary information), respectively. The sequence evolution of the morphologies proves the successful construction of core-triple-shell UCNCs.

The crystallographic phases of T UCNCs, TN UCNCs, TNY UCNCs, TNYE UCNCs are confirmed by XRD patterns, as shown in Fig. 2. The XRD pattern of T UCNCs demonstrates that all positions and relative intensity are consistent with the standard JCPDS card (28-1192) of $\beta\text{-NaYF}_4$. No external diffraction peaks appear with layer-by-layer epitaxial growing of different shells, because the doping of Ln^{3+} does not change the crystal structure of NaYF_4 mixture. Absence of any noticeable impurity phase indicates that the core-triple-shell UCNCs are successfully synthesized.

The optical properties of NaYF_4 nanoparticles can be

Figure 1 Typical schematic illustration of the synthesis procedure of TNYE UCNCs (a), TEM images (b–e, the insets are corresponding size distributions), corresponding HRTEM (f–i, the insets are corresponding FFT patterns) of T UCNCs, TN UCNCs, TNY UCNCs and TNYE UCNCs, respectively.

Figure 2 XRD patterns of T UCNCs (a), TN UCNCs (b), TNY UCNCs (c), TNYE UCNCs (d) and the standard JCPDS card of β - NaYF_4 (28-1192).

tailored by adjusting the Ln^{3+} dopants in both core and shell layers, which is an efficient method to incorporate different UC emissions into one single nanocrystal [35,36]. Therefore, the rationally designed NaYF_4 based core-triple-shell nanoparticles are expected to emit tun-

able color under irradiation of NIR lasers. Subsequently, the UPL properties of core-triple-shell nanoparticles are investigated, as shown in Fig. 3. Under 808 nm irradiation, the TNYE UCNCs present overwhelming blue color emission peak centered at 477 nm (Fig. 3a). Interestingly, there are also green emission peaks at 523 and 543 nm with lower intensity accompanying with the blue emission when excited under 980 nm laser (Fig. 3a). Eventually, the TNYE UCNCs in cyclohexane colloidal solution exhibit blue (B) and cyan color under irradiation of 808 and 980 nm lasers with filtering out of UV/IR interference signal, respectively (inset of Fig. 3a). Meanwhile, the UPL spectra of TNYE UCNCs are shown in Fig. 3b, which gave rise to two divergent green peaks at 523 and 543 nm under excitation at 808 nm laser, and a dominant blue peak under excitation at 980 nm laser. Thus, the photograph of corresponding colloidal solution appears pure green (G) and blue color (B) under 808 and 980 nm irradiation (inset of Fig. 3b). Additionally, Fig. 3c presents the fluorescence spectra of ETNYE UCNCs, which yield a sharp red peak (657 nm) under 808 nm laser irradiation, and two peaks (543 and 657 nm) under 980 nm laser irradiation. The ETNYE UCNCs in cyclo-

Figure 3 Tunable UC emission spectra of (a) TNYE UCNCs, (b) TYNE UCNCs and (c) ETNYE UCNCs. Top inset: corresponding schematic core-shell structures. Left inset: corresponding multi-color luminescence images of UCNCs in cyclohexane solution under the excitation of 808 and 980 nm lasers. Fluorescence photographs (d) of full-color tunable samples obtained by additive mixing certain amount of two kinds of as-prepared UCNCs cyclohexane solution. Color gamut of emissions under 808 nm (e) and 980 nm (f) marked on the CIE chromaticity diagram. The color spaces of sRGB and printing CMY are marked with white and blue triangles, respectively.

hexane solution exhibit the pure red (R) and overlapped yellow color (Fig. 3c) under 808 and 980 nm irradiation, respectively. Additive mixing of ink is a straightforward approach to tune multi-color and extend the color gamut according to the overlay principle of RGB colors. Herein, we set the as-obtained RGB colors under 808 nm irradiation as the basic coordinates for tuning color display. To achieve this aim, certain amounts of two types of UCNCs in cyclohexane solution with similar fluorescence intensity under 808 nm excitation are mixed physically (denoted as P1, P2 and P3, respectively). The detail mixing parameters are listed in Table 1. By adjusting the volume ratio of P1 and P2, or P2 and P3, or P3 and P1 from 3/0 to 0/3, respectively, the gradient color emission

of UCNCs colloidal solution can be gradually generated (Fig. 3d). Furthermore, corresponding fluorescent spectra of UCNCs solution under different volume ratio are also explored and the detail coordinates are marked on the CIE chromaticity diagram (Table 1 and Figs S3–S5). Remarkably, they are accessible to broader color gamut (marked by the dark triangle, Fig. 3e) compared with sRGB (marked by the white triangle, Fig. 3e) and printing CMY (marked by blue dotted line of triangle, Fig. 3f) [37], providing essential condition for multi-color anti-counterfeiting model.

Theoretically, varied emission engineering is derived from doping Ln^{3+} ions that can absorb the different wavelength excitation light. Nd^{3+} and Yb^{3+} as ideal sensi-

Figure 5 Schematic design detail UC process of core-triple-shell TYNE UCNs and ETNYY UCNs nanostructure managing complicated energy transfer.

Figure 6 Power dependence of UC emissions for blue emission at 477 nm (a, d), green emission at 523 and 543 nm (b, e), and red emission at 657 nm (c, f) under 980 nm excitation.

blue emission at 477 nm is a UC energy transfer process involving three-photons. In response to 980 nm excitation, Tm^{3+} and Er^{3+} jointly act as dominating activators to absorb the transferred energy from Yb^{3+} ions, resulting in the excitation of blue and green emissions effectively. The green emissions located at 523 and 543 nm are achieved by populating the $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ energy levels of Er^{3+} ions [36,42,43]. The calculated number of sequential

photons (n) are 1.61 and 1.79, indicating the two-step involved UC process (Fig. 6b, e), respectively. In contrast, the emissions of TYNE UCNs centered at blue region (477 nm) under 980 nm excitation by incorporating less molar of $\text{Yb}^{3+}/\text{Er}^{3+}$ ions (1 mmol) in the outermost shell. Therefore, Tm^{3+} ions of the inner core become prominent ions to absorb energy transmitted by Yb^{3+} ions and excite blue emission more effectively. As illustrated, the green

Figure 7 (a) Demonstration of screen-printed procedure of versatile and full-color display on substrate of white cardboard. Kinds of screen-printed patterns based on the physical mixing of UCNCs under (b, d) 808 nm and (c, f) 980 nm irradiation, respectively. Scale bar is 1 cm.

color emissions can be attributed to Nd^{3+} sensitized procedure under 808 nm irradiation. The absorbed energy of Nd^{3+} is transferred to Er^{3+} through Yb^{3+} medium energy migration. Similarly, schematic emission engineering of ETNYY UCNCs is shown in Fig. 5. The state $^4\text{I}_{15/2}$ of Er^{3+} ions is required to absorb energy transferred from Nd^{3+} under 808 nm irradiation, and further jump to state of $^4\text{F}_{9/2}$ for red emission (657 nm) through a cross relaxation process between Tm^{3+} and Er^{3+} . Meanwhile, two emissions ($^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ at 543 nm and $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ at 523 nm) collaborate with red emission ($^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ at 657 nm, a two-photo process (Fig. 6c, f)) of Er^{3+} upon excitation at 980 nm. As aforementioned, all mechanisms are clearly ascribed to color-tunable of Tm^{3+} and Er^{3+} emission, along with the absorption of 808 nm photons by Nd^{3+} and sequential transfer to Yb^{3+} ions or direct absorption of 980 nm photons by Yb^{3+} ions.

Taking advantage of laser-induced multiple fluorescence characteristics of core-triple-shell UCNCs, multi-stage coding and full color patterns can be implemented

and replace the single model of security mark. To achieve this concept, we dispersed the as-obtained UCNCs by additive mixing into PAA to formulate twelve types of UCNCs inks for further using. As a template-based printing technology, the screen printing provides us with a convenient, low-cost and efficient way for fabricating patterns. The detail screen-printing procedure of versatile and full-color patterns on substrate of white cardboard is depicted in Fig. 7. The as-obtained UCNCs inks are dripped onto the blank area primarily and subsequently continuously squeegee three times for printing designable patterns. And the entire screen plates are shown in Fig. S6a–c, where the printing patterns are magnified in Fig. S6d–e. As expected, under irradiation of 808 nm laser, a series of multi-color Chinese zodiac patterns are vividly presented on the substrate of white cardboards, such as green mouse, blue dragon and red monkey. Interestingly, another chain of colorful Chinese zodiac patterns are distinguished from previous patterns in response to 980 nm excitation, such as blue mouse, cyan dragon and

Figure 8 Screen-printed designable patterns on transparent PVC self-adhesive label for bottle of wine security application.

yellow monkey. Meaningfully, all emission colors of patterns are dependent on the mixing ratio of UCNCs, which is consistent with the UC fluorescence photography of colloidal solution (Fig. 3d). Additionally, full-color, large-area and high-resolution images are also generated by using the overprinting approach, just like the patterns of famous ancient poet “Li Bai” in Tang dynasty and poetry patterns of “Traveling is hard” (Fig. 7d, e). Furthermore, as a prototype of the concept for packaging-oriented anti-counterfeiting, the as-obtained core-triple-shell UCNCs inks are screen-printed to designable and versatile patterns on transparent PVC self-adhesive label (screen plate is shown in Fig. S6c, f). The fabricated labels are attached on the bottle of wine for protecting switch of authentic information, as shown in Fig. 8. All the screen-printed patterns and complex images are transparent under visible light, while displaying multicolor and diverse emissions under 980 and 808 nm irradiation, respectively. Undoubtedly, printing full-color labels based on fancy fluorescence properties of core-multi-shell UCNCs should be of great significance for developing high-level security and substituting traditional single model encoding.

CONCLUSIONS

Three types of core-triple-shell TNYE, TYNE and ETNYE UCNCs with distinguishing optical properties are fabricated through modified high-temperature coprecipitation process, achieving unusual multi-color emissions for potential security printing under NIR light irradiation. The TNYE UCNCs, TYNE and ETNYE UCNCs with uniform short rod shape structure exhibit pure blue, green and red emission colors under the excitation of

808 nm laser. And they also present cyan, blue and yellow emission colors when responding to 980 nm irradiation. Furthermore, the straightforward approach of additive mixing various volume ratio of RGB color models provides an efficient way to produce broader array of color gamut than sRGB and printing CMY. Note that blue emission is contributed to three-step luminescence of Tm^{3+} . Two-photos UC processes of Er^{3+} respond to green and red emissions. The unique UPL features of core-triple-shell UCNCs endow them with applications in full-color security designs, verified by a series of screen-printed multi-color patterns of Chinese zodiac and large-area complex images. And transparent PVC self-adhesive anti-counterfeiting label is fabricated for the wine package, envisioning that full-color and multiple encoding patterns based on core-triple-shell UCNCs can open the door to substitute current single model encoding for security application.

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Supplementary information Supporting data are available in the online version of the paper.

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用于安全编码的双模式上转换纳米光开关

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摘要 镧系离子掺杂的NaYF₄油墨由于其独特的上转换光致发光特性可以被应用到防伪领域. 本文首先通过高温共沉淀法合成了三种核-壳结构的镧系离子掺杂的NaYF₄上转换纳米材料, 它们在808和980 nm激光激发下均可以表现出差异性的上转换荧光性能. 其次, 通过物理混合808 nm激发的不同颜色的悬溶液红绿蓝, 可以调节混合液的发光颜色, 实现全彩色显示. 808 nm激发产生的颜色可以实现比sRGB和印刷CMY颜色空间模型更宽的色域. 最后, 我们使用传统丝网印刷技术印刷出中国十二生肖图案和其他大面积的复杂图像, 印刷图案在808 nm激发下可以呈现出一组多色连续的图案, 同时在980 nm激发下也可呈现出另一组逐渐改变的多色图案, 而且, 印刷在透明聚氯乙烯PVC标签的图案可以附在酒瓶包装上, 实现酒瓶包装的防伪. 基于NaYF₄的双模式荧光图案可以替代传统单模式荧光图案, 实现高水平的全色防伪及安全编码.