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# Dual-mode luminescence anti-counterfeiting and white light emission of NaGdF<sub>4</sub>:Ce,Eu,Tb/carbon dot hydrophilic nanocomposite ink

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NaGdF<sub>4</sub>:Ce,Eu,Tb nanocrystals were successfully prepared by a one-step hydrothermal method with Ce<sup>3+</sup> ions as sensitizers, Eu<sup>3+</sup> and Tb<sup>3+</sup> ions as activators, and polyethylenimine (PEI) as surfactants. Color-adjustable fluorescence emission was achieved by the energy transfer effect between rare earth ions. Blue fluorescent carbon quantum dots (CDs) with a double UV response under 254 nm and 365 nm excitation were synthesized by a one-step hydrothermal method. A hydrophilic NaGdF<sub>4</sub>:Ce,Eu,Tb/CD composite ink was prepared by an easy physical mixing method. Because of the electrostatic self-assembly effect, the color adjustable luminescence was achieved in a few seconds, and the white light emission with color coordinates of (0.32, 0.32) was obtained. A dual-mode luminescence anti-counterfeiting pattern was designed and achieved by excitation with ultraviolet light at 254 nm and 365 nm.

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## 1. Introduction

In recent years, with the rapid development of market economy, the ways and means of manufacturing and selling counterfeit goods have become more diverse and hidden. With the continuous expansion of anti-counterfeiting demand, the anti-counterfeiting technology faces new opportunities and challenges.<sup>1,2</sup>

Because of the excellent physical and chemical properties such as low phonon energy, high chemical stability and easy modification of surface structure, rare earth-doped fluoride has attracted much attention in the field of luminescent anti-counterfeiting materials.<sup>3–5</sup> Hu *et al.* prepared multicolor luminescent NaGdF<sub>4</sub> nanocrystals based on Ce/Yb/Ho triple doping with temperature responses.<sup>6</sup> The core nanocrystals can be directly used to manufacture anti-counterfeit inks without further processing, which provides a new idea for anti-counterfeiting technology. Li *et al.* designed and synthesized hyaluronic acid (HA)–lanthanide (Tb<sup>3+</sup>, Eu<sup>3+</sup>) composite anti-counterfeit luminescent materials with different luminescent colors and successfully constructed the luminescence pattern.<sup>7</sup> With the illumination of a handheld ultraviolet lamp, the encrypted information can be read quickly.

Carbon quantum dots (CDs) are a class of fluorescent materials with low toxicity, rich surface groups and excellent luminescence properties.<sup>8,9</sup> By combining rare earth ion-doped light-emitting materials with CDs, different light-emitting information can be displayed under different excitation light sources. It is a new type of light-emitting anti-counterfeiting material with a high anti-counterfeiting level. Wei *et al.* prepared NaYF<sub>4</sub>:Yb/Er@CD nanocomposites *via* electrostatic interaction.<sup>10</sup> In addition to the adjustable upconversion luminescence characteristics, the composite also shows blue emission under 365 nm radiation and excellent dual-mode luminescence performance. Li *et al.* proposed a new strategy for preparing NaYF<sub>4</sub>:Er,Yb (Tm) micron particle/CD composite anti-counterfeiting materials by a simple solvothermal method.<sup>11</sup> A colorless anti-counterfeiting ink was prepared using a mixture of rare earth upconversion luminescent materials/CDs and polyacrylic acid (PAA) aqueous solutions. Various dual-mode fluorescence patterns have been successfully obtained through screen printing, which has broad application prospects in the advanced optical anti-counterfeiting field. However, rare earth ion-doped micro nanocrystal/CD composite anti-counterfeiting materials mainly focus on upconversion luminescent systems, which have low fluorescence efficiency and need a 980 nm laser with high power for excitation source. The rare earth ion-doped nanocrystal/CD composite ink gets excited by a convenient ultraviolet light source to receive adjustable dual-mode luminescence, which needs further development.

White light-emitting materials have attracted widespread attention for potential applications in displays and lighting. The majority of reported white light-emitting materials have been

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multicomponent systems that are typically processed with organic solvents, accompanied by complex processing, hydrophobic nature, poor white-light quality and environmental pollution. Ghosh *et al.*<sup>12</sup> designed a single-component transparent white light-emitting nanocomposite composed of Ce, Tb and Sm-doped LaF<sub>3</sub> and N-doped C-dots with a dense silica (d-SiO<sub>2</sub>) shell coating over doped LaF<sub>3</sub> nanocrystals, which needs several elaborate preparation steps. Simple synthetic strategies with dual functions of anti-counterfeiting and white light emission of single-component hydrophilic nanocomposite inks need to be developed.

In this paper, using PEI as a surfactant, hydrophilic NaGdF<sub>4</sub> nanocrystals doped with rare earth Ce<sup>3+</sup>, Eu<sup>3+</sup>, and Tb<sup>3+</sup> ions with controllable luminescence from red to yellow were synthesized by a simple one-step hydrothermal method. As sensitizers, Ce<sup>3+</sup> ions enhance the visible light emission intensity. Using citric acid and urea as raw materials, CDs with dual-mode ultraviolet excitation were prepared by a one-step hydrothermal method. A hydrophilic nanocomposite ink with white light emission (CIE values of 0.32, 0.32) of NaGdF<sub>4</sub>:Ce<sup>3+</sup>,Eu<sup>3+</sup>,Tb<sup>3+</sup>/CDs was successfully constructed *via* electrostatic interaction between carboxylic groups with negative dots on CDs and positively charged amino groups on rare earth nanocrystals. Moreover, a dual-mode luminescence anti-counterfeiting pattern was successfully prepared. The preparation process and dual-mode luminescence design are shown in Scheme 1.

## 2. Experiment

### 2.1 Chemicals and materials

Polyethylenimine (PEI, branched, average MN = 10 000) was purchased from Sigma-Aldrich. Ln(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Ln = Gd, Ce, Tb, and Eu) was purchased from Macklin Biochemical Co., Ltd (Shanghai, China). Citric acid, ethylene glycol (EG, 99%) and

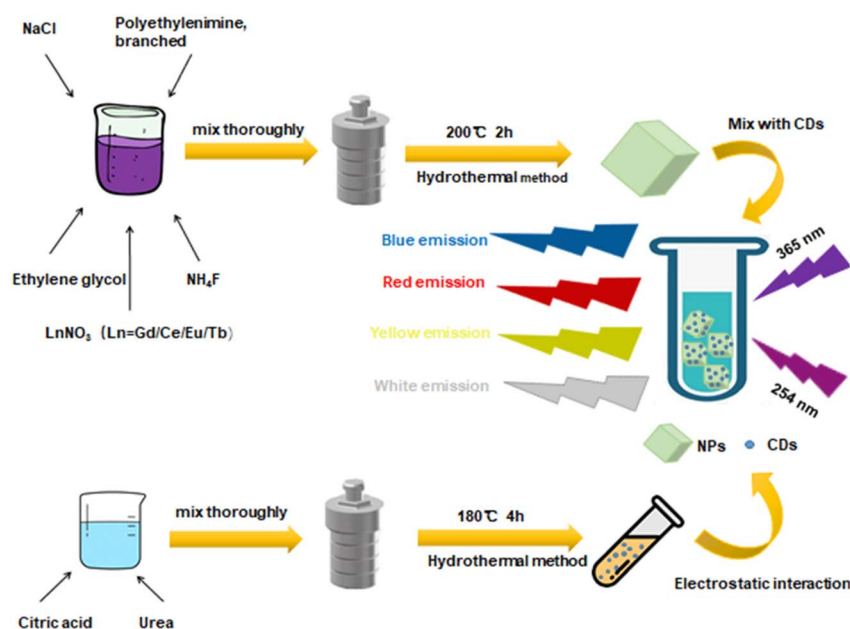
NH<sub>4</sub>F (96%) were purchased from Tianjin Yongda Chemical Reagent Company Limited (Tianjin, China). NaCl (99.5%) was purchased from Xilong Scientific. Urea (99%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd (Shanghai, China).

### 2.2 Preparation of Ln<sup>3+</sup>-doped NaGdF<sub>4</sub> nanocrystals

The synthesis of 1.2 mmol NaGdF<sub>4</sub>:20%Ce<sup>3+</sup>,1%Eu<sup>3+</sup>,2%Tb<sup>3+</sup> nanocrystals is taken as an example. A suitable proportion of rare earth nitrate with a total rare earth ion content of 1.2 mmol, 2.4 mmol NaCl, 6.24 mmol NH<sub>4</sub>F, and 0.4 g PEI were completely dissolved in 30 ml of ethylene glycol. The solution was transferred to a stainless steel Teflon-lined autoclave after dissolution and maintained at 200 °C for 2 hours. After the reaction, the system naturally cooled down to room temperature. The prepared sample was centrifuged, washed three times with ethanol and deionized water to remove other residual solvents, and dried in vacuum at 60 °C for 12 hours to obtain the sample.<sup>8,9</sup> Different concentrations of Ln<sup>3+</sup> (Ln = Ce; Ce, Eu; and Ce, Tb, Eu) ion codoped NaGdF<sub>4</sub> nanocrystals were prepared following similar steps. The prepared sample was ultrasonically dissolved in 10 ml deionized water for use as an ink for subsequent experiments.

### 2.3 Synthesis of CDs

First, 2.0 g citric acid and 4.0 g urea were dissolved in 20 ml deionized water, stirred for 10 minutes until they were completely dissolved, and the solution was transferred to a stainless steel Teflon-lined autoclave. The reaction took 4 hours at 180 °C. After the autoclave was cooled down to room temperature naturally, the reaction liquid was centrifuged at 10 000 rpm for 25 min to remove the precipitate. This centrifugation process was repeated three times. The supernatant was



Scheme 1 Schematic diagram of the preparation and dual-mode luminescence application.



then lyophilized and stored. Finally, 5 mg ml<sup>-1</sup> aqueous CD solution was prepared for subsequent experiments.<sup>10–12</sup>

#### 2.4 Synthesis of NaGdF<sub>4</sub>:Ce<sup>3+</sup>,Eu<sup>3+</sup>,Tb<sup>3+</sup>@CD nanocomposite inks

First,  $X \mu\text{l}$  ( $X = 100, 200, 300, 400, 500, \text{ and } 600$ ) CD aqueous solution was dripped into six identical 0.1 g ml<sup>-1</sup> NaGdF<sub>4</sub>:20% Ce<sup>3+</sup>,1%Eu<sup>3+</sup>,2%Tb<sup>3+</sup> nanocrystalline aqueous solutions, respectively. After continuous stirring, nanocomposite inks with different luminescent colors were obtained. In addition to the fluorescence spectrum, the amount of CDs in the nanocomposites tested was 400  $\mu\text{l}$ .

#### 2.5 Characterizations

Fourier transform infrared (FT-IR) spectra of the samples were recorded using an IRAffinity-1s Fourier transform infrared (FTIR) spectrometer (Shimadzu, Japan). The phase composition was recorded by powder X-ray diffraction (XRD) using a D-Max 2500 X-ray diffractometer (XRD, Rigaku, Co., Japan). A transmission electron microscope (TEM) (JEM-F200) was used to characterize the morphology and structure of samples at 120 kV. The zeta potential spectra of the samples were recorded using a zeta potential and particle size analyzer (pHpzc, 90Plus PALS, Brookhaven Instruments Co., USA). Photoluminescence spectra of the samples were recorded using a FLS920P Edinburgh Analytical Instrument. A ZF-2 ultraviolet analyzer was used as the excitation light source of anti-counterfeiting patterns at 365 nm and 254 nm. The anti-counterfeiting pictures were acquired using Huawei mobile phones.

### 3. Results and discussion

The crystal structure of NaGdF<sub>4</sub> nanocrystals doped with different Ce<sup>3+</sup> concentrations is shown in Fig. 1(a). The diffraction peak of the nanocrystals is consistent with that of the hexagonal phase (PDF#27-0699), when the nanocrystals are

undoped with Ce<sup>3+</sup> ions. With the increase in Ce<sup>3+</sup> ion doping concentration, nanocrystals transform from the hexagonal phase to the cubic phase. Even when the Ce<sup>3+</sup> ion doping amount increases to 40%, the crystalline phase of the nanocrystal still matches the standard cubic phase structure (PDF#27-0697), except that the position of the diffraction peak slightly shifts towards a larger lattice parameter direction. The radius of Ce<sup>3+</sup> ions (1.01 Å) is slightly larger than that of Gd<sup>3+</sup> ions (0.938 Å). The increase in lattice parameters proves that Ce<sup>3+</sup> ions replace Gd<sup>3+</sup> sites and form Na(Gd,Ce)F<sub>4</sub> solid solutions. According to a previous report,<sup>13</sup> the crystal structure of hexagonal phase NaGdF<sub>4</sub> has three crystal cation sites, namely, a unit point occupied by Gd<sup>3+</sup>(1a), a unit point randomly occupied by 1/2 Na<sup>+</sup> and 1/2 Gd<sup>3+</sup>(1f), and a double site (2h) partially occupied by Na<sup>+</sup>. In cubic NaGdF<sub>4</sub> crystals, Na<sup>+</sup> and Gd<sup>3+</sup> ions randomly occupy 4a (0,0,0) positions, and F<sup>-</sup> ions randomly occupy 8c (1/4,1/4,1/4) positions. Therefore, with the increase in Ce<sup>3+</sup> doping concentration, Ce<sup>3+</sup> ions in cubic phase NaGdF<sub>4</sub> were more likely to replace Gd<sup>3+</sup> ions than those in hexagonal phase NaGdF<sub>4</sub>, thereby forming a cubic phase Na(Gd,Ce)F<sub>4</sub> solid solution.<sup>14</sup>

The crystal structure of CDs and NaGdF<sub>4</sub>:Ce<sup>3+</sup>,Eu<sup>3+</sup>,Tb<sup>3+</sup> nanocrystals before and after recombination with CDs is shown in Fig. 1(b). As can be seen from the figure, the XRD spectrum of CDs consists of a large broad peak with a center located near 25°, indicating that the synthesized CDs belong to an amorphous form. The crystal phases of NaGdF<sub>4</sub>:Ce<sup>3+</sup>,Eu<sup>3+</sup>,Tb<sup>3+</sup> nanocrystals before and after recombination with CDs are consistent with those of NaGdF<sub>4</sub> doped with the same Ce<sup>3+</sup> concentration in Fig. 1(a), indicating that the codoping ions do not affect the crystal structure. There are two possible reasons why no diffraction peaks of CDs are found in the composite sample: (1) CDs belong to an amorphous form and their addition amount is very small relative to the nanocrystals and (2) the strong crystallinity of nanocrystals cover the weak diffraction peaks of CDs.<sup>15,16</sup> The NaGdF<sub>4</sub>:Ce<sup>3+</sup>,Eu<sup>3+</sup>,Tb<sup>3+</sup> and NaGdF<sub>4</sub>:Ce<sup>3+</sup>,Eu<sup>3+</sup>,Tb<sup>3+</sup>@CD nanocomposites were prepared based on

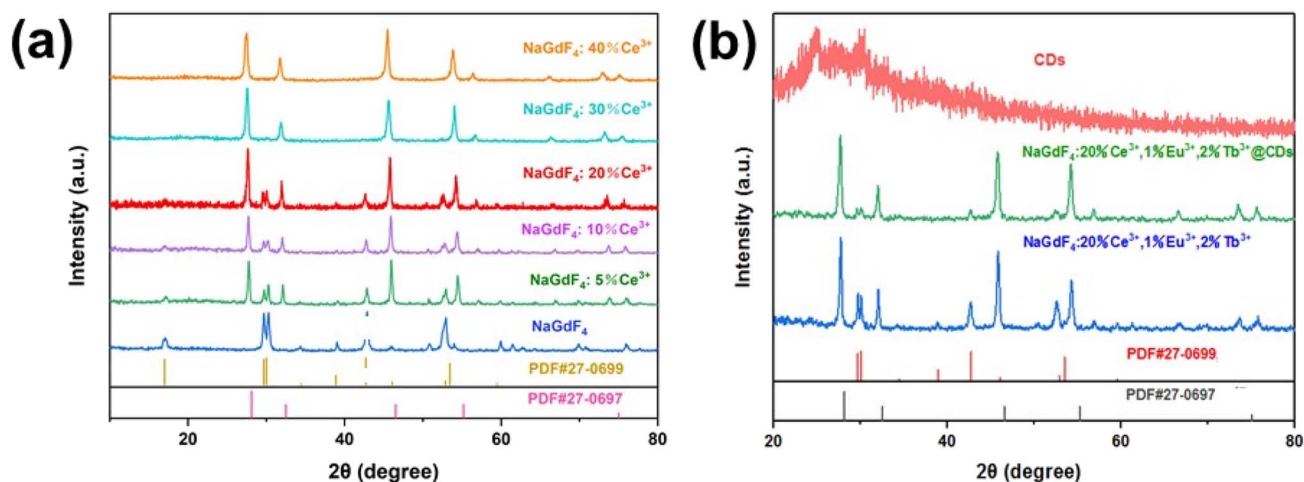


Fig. 1 (a) XRD patterns of NaGdF<sub>4</sub>:X%Ce<sup>3+</sup> ( $X = 5, 10, 20, 30, \text{ and } 40$ ). (b) XRD patterns of CDs, NaGdF<sub>4</sub>:20%Ce<sup>3+</sup>,1%Eu<sup>3+</sup>,2%Tb<sup>3+</sup> nanocrystals and NaGdF<sub>4</sub>:20%Ce<sup>3+</sup>,1%Eu<sup>3+</sup>,2%Tb<sup>3+</sup>@CD nanocomposites.

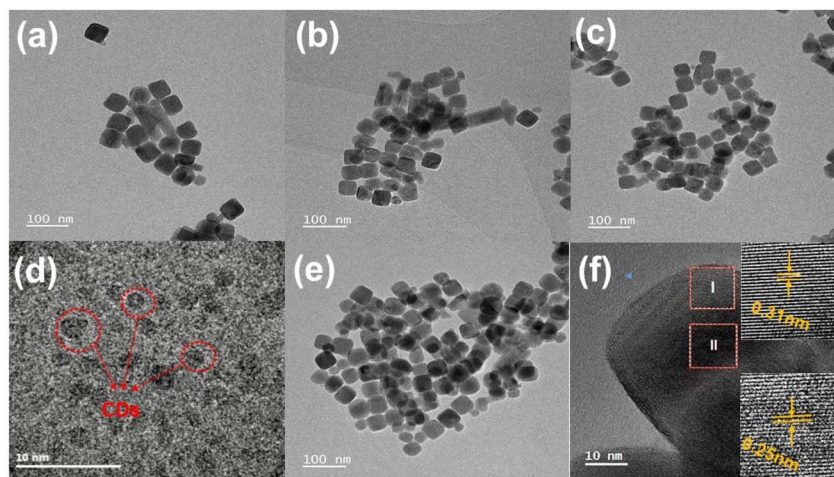


Fig. 2 (a–c) TEM images of NaGdF<sub>4</sub>:20%Ce; NaGdF<sub>4</sub>:20%Ce<sup>3+</sup>,1%Eu<sup>3+</sup>; NaGdF<sub>4</sub>:20%Ce<sup>3+</sup>,1%Eu<sup>3+</sup>, and 2%Tb<sup>3+</sup> nanocrystals. (d) TEM images of CDs. (e and f) TEM images of NaGdF<sub>4</sub>:20%Ce<sup>3+</sup>,1%Eu<sup>3+</sup>,2%Tb<sup>3+</sup>@CDs and the corresponding HRTEM images (the red circles show the CDs attached to the surface of NaGdF<sub>4</sub>:Ce,Eu,Tb nanocrystals).

NaGdF<sub>4</sub>:20%Ce<sup>3+</sup> nanocrystals due to their optimal luminescence intensity described later.

The transmission electron microscopic (TEM) image of the NaGdF<sub>4</sub>:20%Ce<sup>3+</sup>, NaGdF<sub>4</sub>:20%Ce<sup>3+</sup>,1%Eu<sup>3+</sup>, and NaGdF<sub>4</sub>:20%Ce<sup>3+</sup>,1%Eu<sup>3+</sup>,2%Tb<sup>3+</sup> nanocrystals are shown respectively in Fig. 2(a)–(c). It can be seen that the prepared nanocrystals exhibit mainly cubic shape with a particle size of about 26 nm. The TEM image of CDs is shown in Fig. 2(d). It can be seen that the prepared CDs are uniformly monodisperse spherical particles with a diameter of about 2.3 nm. The TEM images of NaGdF<sub>4</sub>:20%Ce<sup>3+</sup>,1%Eu<sup>3+</sup>, and 2%Tb<sup>3+</sup>@CDs displayed in Fig. 2(e) show that CDs adhere to the surface of NaGdF<sub>4</sub>, and there is no significant change in the morphology and size of the material after composite synthesis. Fig. 2(f) shows the HRTEM diagram of the nanocomposites, with lattice stripes spaced 0.31 nm and 0.25 nm corresponding to the (111) surface of cubic NaGdF<sub>4</sub> and the (020) surface of graphite carbon, respectively, further

illustrating the successful adsorption of CDs on the surface of NaGdF<sub>4</sub> nanocrystals.

The EDS elemental mapping of NaGdF<sub>4</sub>:20%Ce<sup>3+</sup>,1%Eu<sup>3+</sup>,2%Tb<sup>3+</sup>@CDs is shown in Fig. 3. The Na, Gd, F elements should belong to NaGdF<sub>4</sub>, while C and N elements might be from carbon quantum dots and PEI, which confirm the distribution of CDs and PEI on the surface of NaGdF<sub>4</sub> nanocrystals and also prove the successful doping of Ce<sup>3+</sup>, Eu<sup>3+</sup> and Tb<sup>3+</sup> ions.

The FT-IR spectra of the CDs, NaGdF<sub>4</sub>:Ce<sup>3+</sup>,Eu<sup>3+</sup>,Tb<sup>3+</sup> and NaGdF<sub>4</sub>:Ce<sup>3+</sup>,Eu<sup>3+</sup>,Tb<sup>3+</sup>@CDs composites are shown in Fig. 4(a). For CDs, the broad absorption band at 3050–3600 cm<sup>-1</sup> is due to the stretching vibration of –OH/N–H. The appearance of characteristic peaks at 2300–2410 cm<sup>-1</sup>, 1640 cm<sup>-1</sup>, and 1580 cm<sup>-1</sup> confirmed the presence of C≡N, C=O, and C=C, respectively. The absorption peak at 1350 cm<sup>-1</sup> is due to the vibration of carboxylic acid group (COO<sup>-</sup>). For NaGdF<sub>4</sub>:Ce<sup>3+</sup>,Eu<sup>3+</sup>,Tb<sup>3+</sup>, the absorption peaks at 2750–3000 cm<sup>-1</sup> are

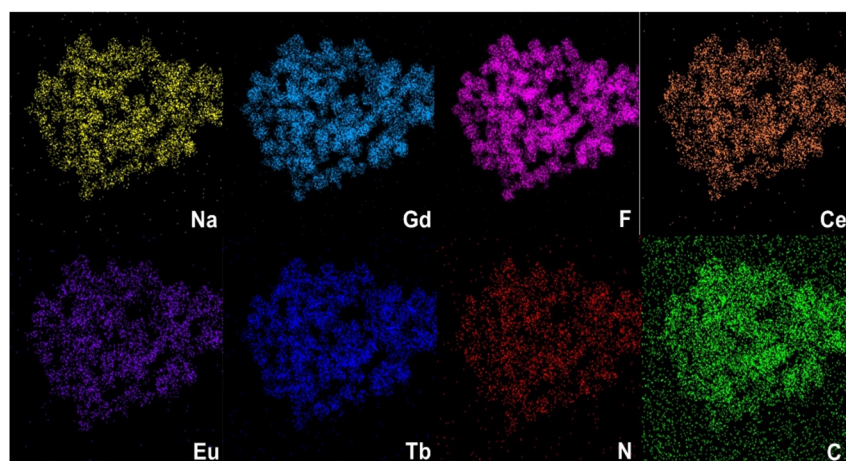


Fig. 3 EDS elemental mapping of NaGdF<sub>4</sub>:20%Ce<sup>3+</sup>,1%Eu<sup>3+</sup>,2%Tb<sup>3+</sup>@CDs.



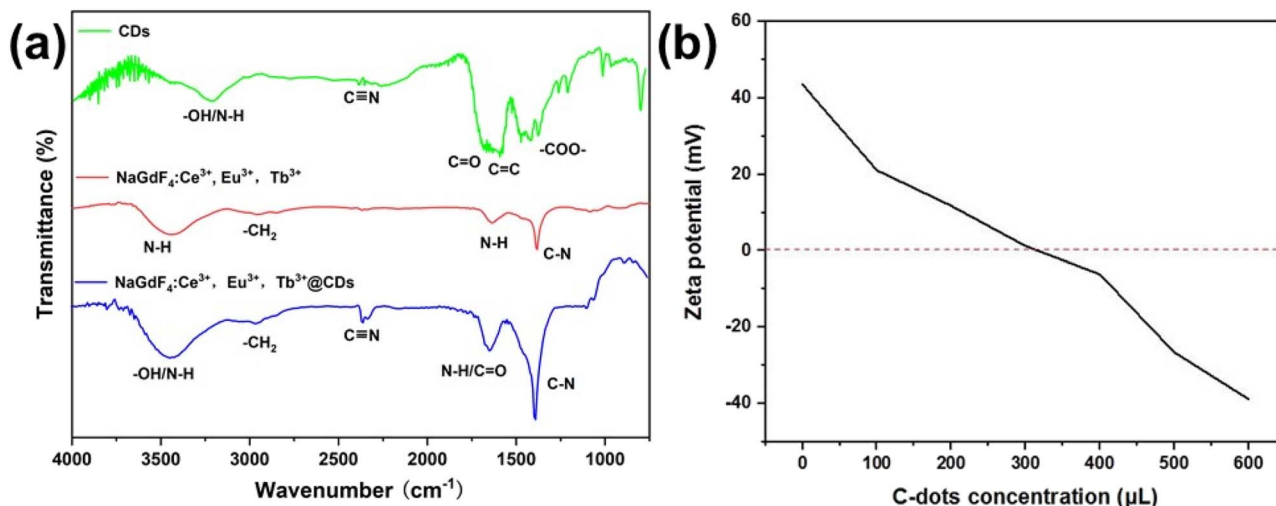


Fig. 4 (a) FT-IR spectra of CDs, NaGdF<sub>4</sub>:Ce<sup>3+</sup>, Eu<sup>3+</sup>, Tb<sup>3+</sup> and NaGdF<sub>4</sub>:Ce<sup>3+</sup>, Eu<sup>3+</sup>, Tb<sup>3+</sup>@CDs. (b) Change in the zeta potential of nanocomposites with the C-dot concentration.

attributed to the stretching vibration and bending vibration of CH<sub>2</sub>. The broad absorption band at 3150–3650 cm<sup>-1</sup> and the absorption peak at 1650 cm<sup>-1</sup>, which are the vibrations of N-H belonging to positively charged groups in PEI, also further illustrated the successful coating of PEI. The successful introduction of PEI not only provides the conditions for subsequent recombination with CDs, but also makes the nanocrystals well dispersed in water, providing the conditions for subsequent fabrication into inks.<sup>17</sup> In addition, it can be seen in NaGdF<sub>4</sub>:Ce<sup>3+</sup>, Eu<sup>3+</sup>, Tb<sup>3+</sup>@CDs that the absorption peaks of related groups at 3150–3650 cm<sup>-1</sup> and 2300–2410 cm<sup>-1</sup> as well as 1630 cm<sup>-1</sup> are all obviously enhanced, further indicating the successful recombination of CDs.<sup>18–20</sup>

The zeta potential changes of NaGdF<sub>4</sub>:Ce<sup>3+</sup>, Eu<sup>3+</sup>, Tb<sup>3+</sup> complexed with different amounts of CDs are shown in Fig. 4(b).

The potential of the nanocrystal before the composite was formed is about +43.56, which is caused by the -NH<sub>2</sub> groups on the surface of the nanocrystal. The zeta potential shifts from positive to negative with the increase in the amounts of CDs, which is related to the negatively charged groups (COO<sup>-</sup>) on the surface of CDs, indicating that CDs are successfully conjugated with NaGdF<sub>4</sub>:Ce<sup>3+</sup>, Eu<sup>3+</sup>, Tb<sup>3+</sup> due to strong electrostatic interactions.

The excitation and emission spectra of NaGdF<sub>4</sub>:Ce<sup>3+</sup> nanocrystals are shown in Fig. 5(a) and (b). The excitation spectrum of NaGdF<sub>4</sub>:Ce<sup>3+</sup> detected at 340 nm exhibits a strong broad absorption band at 240–310 nm, which is attributed to the 4f → 5d transition of Ce<sup>3+</sup> ions. Under excitation at 284 nm, the emission spectrum exhibits a strong absorption peak at 300–420 nm, which is caused by the electronic transition of Ce<sup>3+</sup> ions

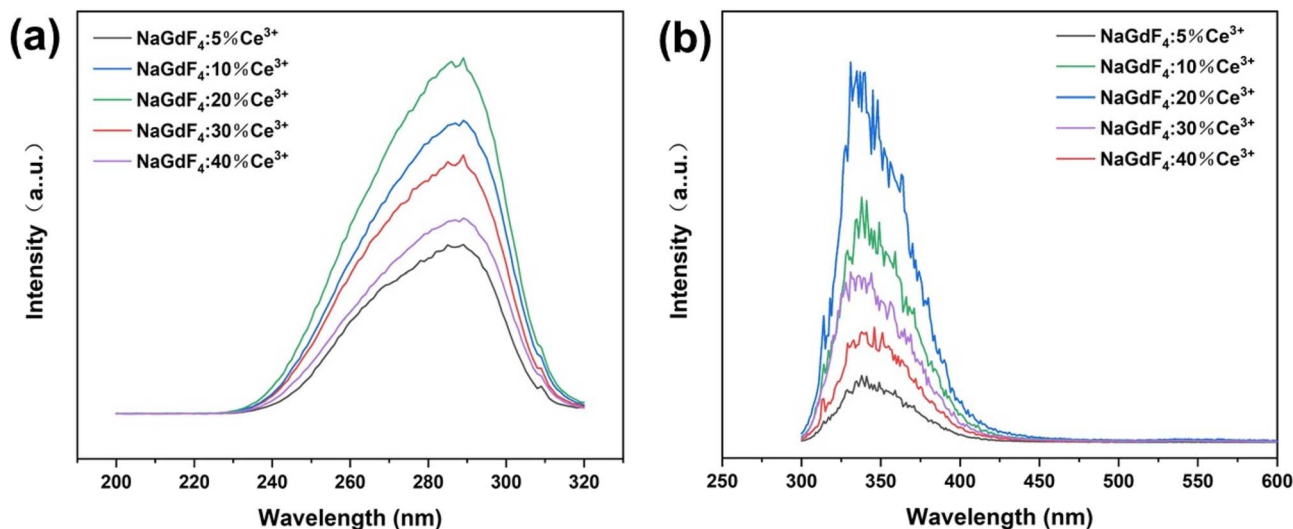


Fig. 5 (a) Excitation spectra of the NaGdF<sub>4</sub>:x%Ce<sup>3+</sup> (x = 5, 10, 20, 30 and 40) nanocrystals ( $\lambda_{em} = 340$  nm). (b) Emission spectra of the NaGdF<sub>4</sub>:x%Ce<sup>3+</sup> (x = 5, 10, 20, 30 and 40) nanocrystals ( $\lambda_{ex} = 284$  nm).



as  $^5d_1 \rightarrow ^4f_1$ . As the  $\text{Ce}^{3+}$  ion doping concentration increases, the emission intensity first increases and then decreases. When the  $\text{Ce}^{3+}$  ion doping concentration is 20%, the emission intensity reaches the maximum, and the concentration quenching effect occurs when doping continues.

The excitation spectra of  $\text{NaGdF}_4:20\%\text{Ce}^{3+},X\%\text{Eu}^{3+}$  ( $X = 0.5, 1, 2,$  and  $3$ ) under 618 nm light monitoring are shown in Fig. 6(a). A wide peak at 220–260 nm is caused by the  $4f \rightarrow 5d$  transition of  $\text{Ce}^{3+}$ , while the weak peak at 316 nm is caused by  $^7F_0 \rightarrow ^5D_4$  transition of  $\text{Eu}^{3+}$ . The excitation peak of  $\text{Ce}^{3+}$  ions can be found under the excitation of  $\text{Eu}^{3+}$  ion emission light, which confirms the energy transfer between  $\text{Ce}^{3+}$  and  $\text{Eu}^{3+}$ .<sup>9,21</sup> In addition, the sharp absorption peak near 275 nm is caused by the  $^8S_{7/2} \rightarrow ^6I_{11/2}$  transition of  $\text{Gd}^{3+}$ , which also indicates the energy transfer of  $\text{Gd}^{3+} \rightarrow \text{Eu}^{3+}$ .<sup>22</sup> The emission spectra of nanocrystals excited at 254 nm are shown in Fig. 6(b). Illustrated are the luminescence effects of  $\text{NaGdF}_4:20\%\text{Ce}^{3+},1\%\text{Eu}^{3+}$  nanocrystal aqueous solutions. The characteristic emission peaks of  $\text{Ce}^{3+}$  ions ( $^5D_0 \rightarrow ^7F_0$  at 588 nm,  $^5D_0 \rightarrow ^7F_1$  at 594 nm,  $^5D_0 \rightarrow ^7F_2$  at 610 and 618 nm,  $^5D_0 \rightarrow ^7F_3$  at 649 nm, and  $^5D_0 \rightarrow ^7F_4$  at 696 nm) are easily found in the emission spectra. With the

increase in  $\text{Eu}^{3+}$  doping concentration, the luminescence intensity also increases first and then decreases. When the  $\text{Eu}^{3+}$  doping concentration is 1%, the luminescence intensity is the highest. Continuously increasing  $\text{Eu}^{3+}$  concentration resulted in concentration quenching and decreased luminescence intensity.

Fig. 6(c) shows the excitation spectra of  $\text{NaGdF}_4:20\%\text{Ce}^{3+},1\%\text{Eu}^{3+},Y\%\text{Tb}^{3+}$  nanocrystals ( $Y = 0.5, 1, 1.5,$  and  $2$ ). We can see from the excitation spectra that a 220–320 nm wide peak appears under 544 nm monitoring. This is caused by the  $f-f$  transition of  $\text{Tb}^{3+}$  and the  $\text{Ce}^{3+}$   $4f-5d$  transition. It is proved that there is an energy conversion between  $\text{Ce}^{3+}$  and  $\text{Tb}^{3+}$  ions.<sup>4,23</sup> Fig. 6(d) shows the emission spectra of nanocrystals excited at 254 nm. Illustrated are the luminescence photos of  $\text{NaGdF}_4:20\%\text{Ce}^{3+},1\%\text{Eu}^{3+},2\%\text{Tb}^{3+}$  nanocrystal aqueous solutions. The characteristic emission peaks of  $\text{Ce}^{3+}$  ions at 300–400 nm,  $\text{Eu}^{3+}$  ions at 594, 618, and 696 nm and  $\text{Tb}^{3+}$  ions at 489 nm and 544 nm ( $^5D_3 \rightarrow ^7F_4$  and  $^5D_4 \rightarrow ^7F_5$  transition) can be seen in the emission spectrum.<sup>24–26</sup> It can be seen that with the increase in  $\text{Tb}^{3+}$  ion concentration, the characteristic emission intensity of  $\text{Tb}^{3+}$  increases while the intensity of the

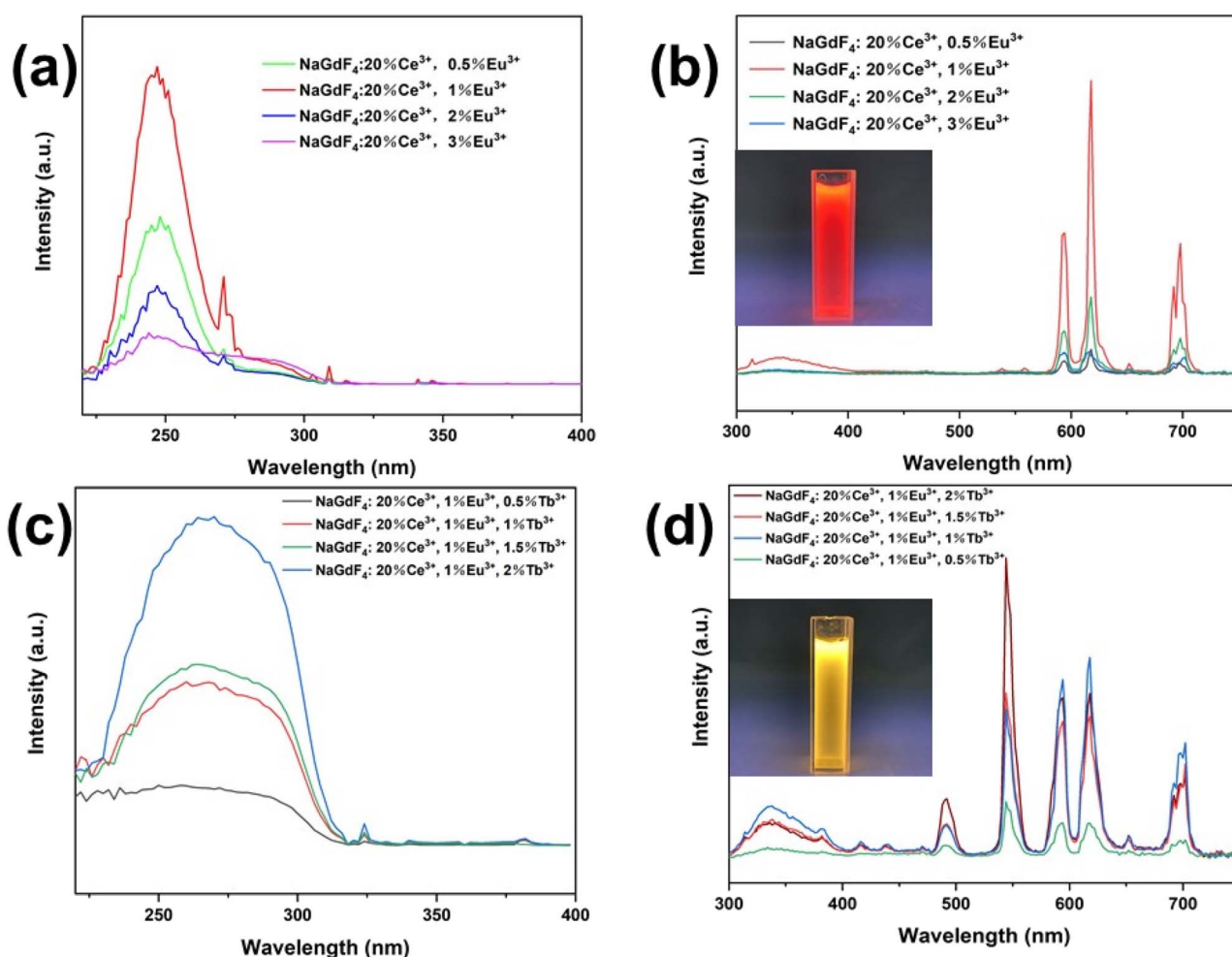


Fig. 6 (a) Excitation ( $\lambda_{em} = 618$  nm) and (b) emission spectra of  $20\%\text{Ce}^{3+}/x\%\text{Eu}^{3+}$  ( $x = 0.5, 1, 2,$  and  $3$ )-doped  $\text{NaGdF}_4$  samples ( $\lambda_{ex} = 254$  nm). (c) Excitation ( $\lambda_{em} = 554$  nm) and (d) emission spectra of  $20\%\text{Ce}^{3+}/1\%\text{Eu}^{3+}/Y\%\text{Tb}^{3+}$  ( $Y = 0.5, 1, 1.5,$  and  $2$ )-doped  $\text{NaGdF}_4$  samples ( $\lambda_{ex} = 254$  nm).



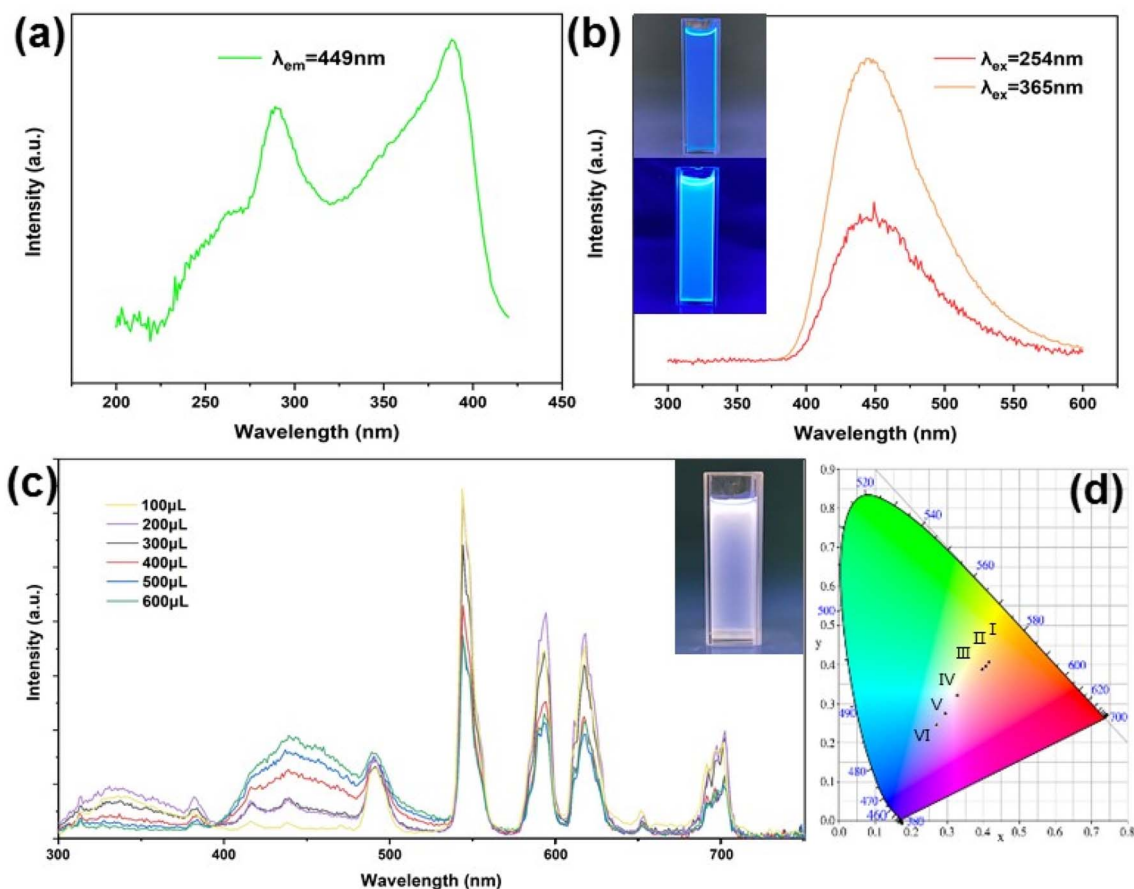


Fig. 7 (a) Excitation ( $\lambda_{em} = 449$  nm) and (b) emission spectra of CDs excited by 254 nm and 365 nm light. (c and d) Emission spectra of NaGdF<sub>4</sub>:20%Ce<sup>3+</sup>, 1%Eu<sup>3+</sup>, 2%Tb<sup>3+</sup> with different CD additions ( $\lambda_{ex} = 254$  nm) and CIE chromaticity value diagram of the inks.

characteristic emission of Eu<sup>3+</sup> ions is obviously enhanced, which indicates that there is energy transfer process of Ce<sup>3+</sup> → Tb<sup>3+</sup> → Eu<sup>3+</sup> ions.<sup>27,28</sup> NaGdF<sub>4</sub>:20%Ce<sup>3+</sup>, 1%Eu<sup>3+</sup>, 2%Tb<sup>3+</sup> nanocrystals with the highest luminescence intensity were selected for the follow-up processes.

The excitation spectra of CDs monitored by 449 nm light are shown in Fig. 7(a). There are two strong absorption peaks at 250–400 nm, corresponding to the  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transitions of functional groups in CDs.<sup>29–31</sup> Emission spectra and photographs using common UV excitations at 254 and 365 nm are

shown in Fig. 7(b). The inset shows the emission photos excited under 254 and 365 nm from top to bottom. CDs have a strong emission peak at 449 nm, which is stronger at 365 nm than at 254 nm. The luminescence process is that the CDs first absorb the energy of ultraviolet light, and the electrons transit from the  $C\pi$  level to the  $C\pi^*$  level. Then, *via* the  $C\pi^*$ - $N\pi^*$  and  $N\pi^*$ - $O\pi^*$  processes, the electrons relax to the lowest level, and the energy transits to the  $C\pi$  level through blue light emission.<sup>32,33</sup>

The emission spectra of NaGdF<sub>4</sub>:20%Ce<sup>3+</sup>, 1%Eu<sup>3+</sup>, 2%Tb<sup>3+</sup>@CDs nanocomposite inks with different amounts of CDs

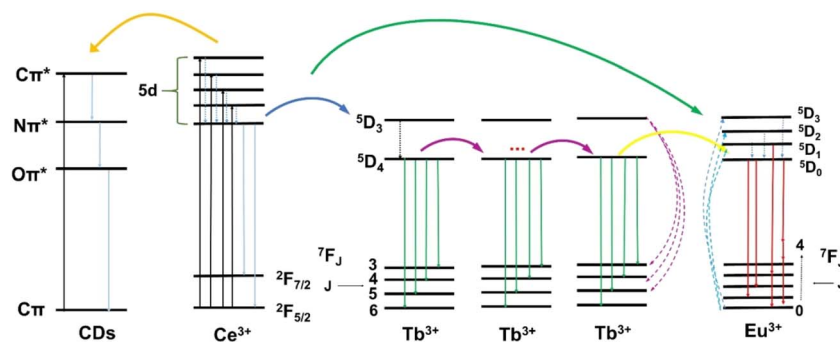


Fig. 8 Proposed energy transfer mechanism for Ce<sup>3+</sup>/Tb<sup>3+</sup>/Eu<sup>3+</sup> in the NaGdF<sub>4</sub> host.



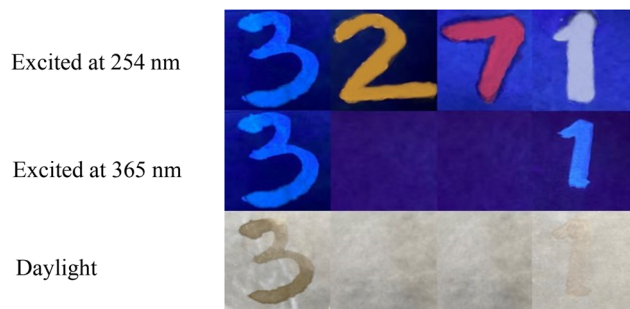


Fig. 9 Photographs of graphic security patterns made with CDs, NaGdF<sub>4</sub>:Ce, Eu, NaGdF<sub>4</sub>:Ce, Eu, Tb and NaGdF<sub>4</sub>:Ce, Eu, Tb@CDs (from left to right) inks under 254 nm and 365 nm irradiation for dual-mode anti-counterfeiting.

excited at 254 nm are shown in Fig. 7(c). It is obvious to find the characteristic emission peaks of Ce<sup>3+</sup> ions (300–400 nm), Eu<sup>3+</sup> ions (594 nm, 618 nm, 696 nm), Tb<sup>3+</sup> ions (489 nm, 544 nm) and CDs (400–500 nm). As the amount of CDs increases, the green light decreases, the red light first increases and then decreases, while the blue light increases significantly. This may be due to the energy transfer from CDs to rare earth ions.<sup>34–36</sup> When adding with different amounts of CDs (100–600 μl), the corresponding coordinate points are (0.41, 0.40), (0.40, 0.39), (0.39, 0.38), (0.32, 0.32), (0.29, 0.27), (0.27, 0.24) respectively, which is shown in Fig. 7(d). When the amount of CDs is 400 μl, white light emission is acquired, as shown in the inset in Fig. 7(c). The emission spectra of Ce<sup>3+</sup> overlap with the excitation peaks of CDs to some extent, and the emission intensity of Ce<sup>3+</sup> decreases with the increase in CDs, which confirms that there is fluorescence resonance energy transfer (FRET) process from Ce<sup>3+</sup> emission to the C-dots (N dopant state → π\*).<sup>37</sup> The energy transfer mechanism in this nanocomposite is shown in Fig. 8.

A simple anti-counterfeiting pattern was prepared as shown in Fig. 9. The numbers '3', '2', '7', and '1' were used by CDs, NaGdF<sub>4</sub>:Ce<sup>3+</sup>, Eu<sup>3+</sup>, Tb<sup>3+</sup>, NaGdF<sub>4</sub>:Ce<sup>3+</sup>, Eu<sup>3+</sup>, and NaGdF<sub>4</sub>:Ce<sup>3+</sup>, Eu<sup>3+</sup>, Tb<sup>3+</sup>@CDs (400 μl) ink respectively. Blue, yellow, red and white light can be obtained under 254 nm excitation, while only CD-containing inks emit blue light under excitation at 365 nm, resulting in an obvious dual-mode luminescence phenomenon.

## 4. Conclusions

In summary, we studied the change in the crystal phase of NaGdF<sub>4</sub> nanocrystals with the increase in Ce<sup>3+</sup> doping concentration, explaining the effect of Ce<sup>3+</sup> as a sensitizer on the luminescence intensity of NaGdF<sub>4</sub>:Eu, Tb nanocrystals and the energy transfer process between Ce<sup>3+</sup> and Eu<sup>3+</sup>, Tb<sup>3+</sup> ions. The negatively charged blue-emitting CDs were compounded with water-soluble nanocrystal surfaces of NaGdF<sub>4</sub>:Ce, Eu, Tb modified by PEI by a simple physical mixing method on the basis of electrostatic interactions. By changing the amount of CDs, fluorescent inks with adjustable emission colors were prepared and single-component water-soluble inks with white light emission were obtained. Using 254 nm and 365 nm dual-

wavelength excitation effects of CDs, a dual-mode anti-counterfeiting pattern was designed and obtained, which provides a new idea for the development of white light emission and new advanced fluorescence anti-counterfeiting technology.

## Conflicts of interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work reported in this manuscript.

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