



Application Progress of Up conversion Luminescent Materials in Fluorescent Anti-counterfeiting Technology

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Author's contribution

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ABSTRACT

Rare-earth-doped up conversion luminescent materials possess advantages such as high luminescent efficiency, excellent spectral characteristics, ability to emit multiple colors, strong interference resistance, and accurate information response. These advantages make them suitable for various anti-counterfeiting needs, thus making them a key focus of research in the field of fluorescent anti-counterfeiting. This article provides a systematic review and summary of the luminescent principles, preparation conditions, substrate effects, applications in fluorescent anti-counterfeiting, and existing issues of upconversion luminescent materials. Finally, potential research and development directions for the future application of up conversion luminescent materials in the field of fluorescent anti-counterfeiting are proposed.

Keywords: *Up conversion luminescent materials; preparation methods; fluorescent anti-counterfeiting applications.*

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1. INTRODUCTION

In modern society, the issue of information security has become increasingly serious and has had a significant impact on various fields. In order to protect information security, anti-counterfeiting and encryption technologies have become common security measures. Among them, luminescent technology is widely applied in anti-counterfeiting and encryption design because of its high visibility, flexibility in design, and portability. Nowadays, people use various luminescent materials such as metal-organic frameworks, organic dye fluorescent powders, semiconductors, and carbon quantum dots to create luminescent anti-counterfeiting and encryption patterns, achieving good results. Rare-earth-doped upconversion luminescent materials, with characteristics such as long lifespan, low toxicity, high fluorescence quantum yield, and chemical stability, have attracted considerable attention. These materials have potential applications in areas such as bioimaging, food detection, and luminescent textiles, and have therefore received attention from research teams both domestically and internationally [1]. In summary, luminescent technology plays a crucial role in the anti-counterfeiting and encryption of information, and rare-earth-doped upconversion luminescent materials have broad development prospects in relevant applications due to their unique characteristics.

2. UPCONVERSION LUMINESCENT MATERIALS

2.1 Upconversion Luminescent Mechanism

The upconversion luminescence of rare-earth-doped materials is a type of anti-Stokes luminescence process, where shorter wavelength light is emitted through the excitation of longer wavelength light. Currently, the upconversion luminescence efficiency of rare-earth-doped luminescent materials is still relatively low, with a maximum efficiency of only 3%. To achieve upconversion luminescence, appropriate excitation power and excitation power density are required, with the excitation power density playing a more critical role. If the excitation power density is insufficient, upconversion luminescence cannot occur even with sufficient excitation power [2].

The upconversion luminescence process covers a wide range of wavelengths, spanning from visible light to near-ultraviolet. Although they are all forms of upconversion luminescence, the specific luminescent mechanisms vary due to various factors. Differences in rare-earth ions or different doping ratios can lead to variations in the luminescence process. While the $f-f$ transitions of rare-earth ions are generally unaffected by the matrix, the doping concentration of rare-earth ions in the material can also influence the upconversion luminescence process. In general, the upconversion luminescence process can be categorized into the following five situations:

a) Excited state absorption is the basic form of upconversion luminescence, where ions are excited to higher energy levels by absorbing photons and subsequently emit photons by radiative decay back to lower energy levels or the ground state.

b) Energy transfer refers to the situation where an ion in an excited state transfers its energy to another ion in the ground state, allowing the receiving ion to transition to an excited energy level. The excited-state ions can also undergo further energy transfer to higher excited energy levels.

c) Continuous energy upconversion involves the continuous transfer of energy between sensitizer and activator ions, enabling photon level transitions.

d) Cross relaxation refers to the situation where two ions simultaneously occupy adjacent excited energy levels, and one ion transfers its energy to the other, causing the receiving ion to transition to a higher energy level while the donating ion returns to a lower energy level or ground state. In simple terms, cross relaxation involves the mutual transfer of energy between two ions, leading to one ion being upgraded and the other being downgraded.

e) Photon avalanche, first observed in LaCl materials by Chivia et al. in 1979, refers to the upconversion luminescence phenomenon in which the P-doped rare-earth ions in LaCl materials are excited. The characteristic of photon avalanche is that it does not require absorption of the ground state light and is the result of the superposition of the processes of excited-state absorption and cross relaxation [3,4].

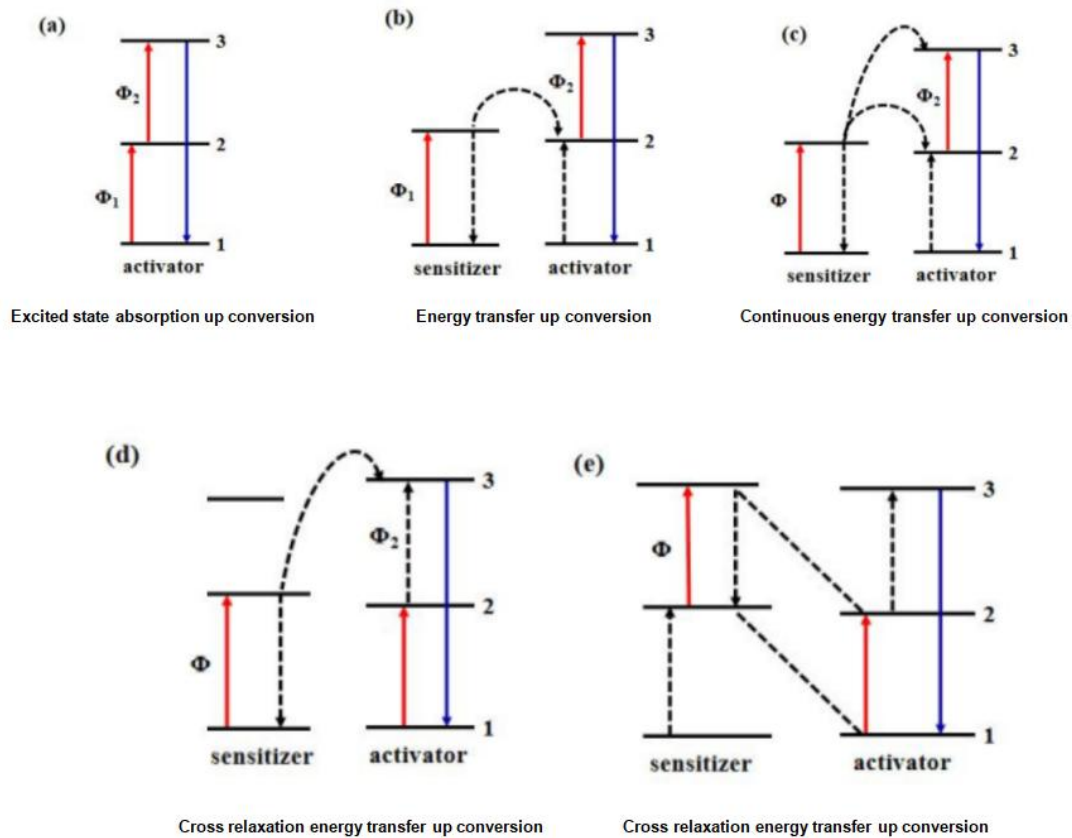


Fig. 1. Upconversion Luminescence Processes (a-e) [4]

2.2 Carrier Matrix of Upconversion Luminescent Materials

The choice of carrier matrix can influence the interaction between ions and the matrix, thus affecting the upconversion luminescence process. The matrix material plays a crucial role in upconversion luminescence, requiring both good optical properties and a certain level of chemical stability and mechanical strength. Common matrix materials include glass, ceramics, etc. which serve as platforms for upconversion luminescent materials. Currently, upconversion luminescent matrix materials can be classified into five major categories: fluorides, oxides, phosphates, silicates, and sulfides.

2.2.1 Fluorides

Fluorides are commonly used carrier matrix materials for upconversion luminescence. They possess a characteristic of low phonon energy, which promotes upconversion luminescence and enhances the luminescence efficiency. This low phonon energy property makes fluoride materials

ideal for upconversion matrix, enabling effective energy transfer from low energy levels to high energy levels and producing visible light emission. The design and application of such materials play an important role in the fields of optics and optoelectronics, providing strong support for achieving efficient and stable upconversion luminescence [5]. The major drawback of fluoride matrix materials is their weak mechanical strength and chemical stability, which pose challenges during the preparation process and limit their application prospects.

2.2.2 Oxides

Compared to other materials, oxide materials have lower upconversion luminescence efficiency. However, they possess excellent mechanical strength and chemical stability, which make them perform well in various environments. Additionally, rare earth ions can be easily doped into oxide matrix materials, and the preparation process is relatively simple. Some common oxide matrix materials include Y_2O_3 , YVO_4 , $CaWO_4$, and $Nd_2(WO_4)_3$ [6]. By co-doping Tm^{3+} , Ho^{3+} , and

Yb^{3+} ions into CaWO_4 oxide matrix material, upconversion luminescent materials exhibiting white light emission can be prepared. Likewise, when Er^{3+} is doped into Y_2O_3 oxide material and excited by lasers at 816nm and 486nm, red and green fluorescence emission can be observed [6].

2.2.3 Fluorooxides

Fluorooxides are a hot research topic that combines the advantages of oxide and fluoride matrix materials for upconversion luminescence. They are capable of exhibiting upconversion luminescence phenomena. Initially, a fluorooxide glass ceramic material was discovered by French scientist Auzel. Subsequently, more fluorooxides capable of producing upconversion luminescence were reported. However, fluorooxides also have some disadvantages, such as low heat resistance, tendency to deform, and higher cost.

2.2.4 Halides

Researchers have started to explore other matrix materials to address the drawbacks of fluorides, oxides, and halides. Among them, rare earth-doped heavy metal halides are a widely studied new material. This material has lower vibrational energy levels, reducing the possibility of nonradiative relaxation and thus improving up conversion luminescence efficiency. However, the major drawback of halide materials is their instability and susceptibility to hydrolysis. Therefore, stricter requirements are imposed on the preparation and performance testing processes. In terms of stability and process ability, the order is oxide > fluoride > halide, while in terms of up conversion luminescence efficiency, the order is halide > fluoride > oxide. However, this order is exactly opposite to their stability and processability. Therefore, it is necessary to find matrix materials that exhibit both efficient luminescence and excellent chemical stability [6].

2.2.5 Sulfides

Sulfide matrix materials have lower phonon energy, which gives them unique physical properties within specific frequency ranges. However, the preparation process for sulfide materials is very stringent and requires operations in a completely sealed environment to ensure that the materials are not exposed to water molecules and oxygen. This is because

sulfide materials are highly sensitive to water molecules and oxygen, which may cause the materials to lose certain properties or undergo irreversible chemical reactions. Therefore, to ensure the quality and performance of sulfide matrix materials, researchers must conduct experiments under highly controlled conditions, often using closed reaction chambers or inert gas atmospheres to prevent impurities from entering. These strict operational requirements increase the complexity and difficulty of experiments, limiting large-scale production and application. Despite these challenges, scientists are continuously working on improving preparation techniques to address this issue and promote the application of sulfide matrix materials in various fields [6].

In addition to fluoride, oxide, and halide matrix materials, researchers have explored other types of materials. One example is rare earth amorphous phosphate glass materials. Rare earth phosphates are crystalline materials, but they can be transformed into amorphous states through specific treatments. In addition, crystalline materials are prone to cracking and deformation, with poor process ability, while rare earth amorphous phosphate glass materials can overcome these drawbacks. Through this approach, rare earth amorphous phosphate glass materials provide a new option to obtain efficient up conversion luminescence while overcoming the processing challenges associated with crystalline materials. This has made it a highly regarded matrix material. Further research can improve the performance of this material and expand its applications in optics, fluorescence detection, and other fields.

3. METHODS FOR PREPARATION OF UP CONVERSION LUMINESCENT MATERIALS

To synthesize materials with excellent upconversion luminescence performance, researchers have explored various preparation methods. Below are some commonly used methods.

High-temperature solid-state reaction is a mature synthesis method. It involves simple operations, where high-purity reactants are mixed together, heated at high temperature for reaction, and then undergo grinding treatment to obtain the final product. The advantages of this method are high luminescence intensity, convenience in operation, low equipment requirements, and

suitability for industrial production. However, it also has some drawbacks. Due to uneven temperature distribution, the particle size of samples tends to be large and unevenly distributed, making it difficult to control the morphology of the materials [7]. This method primarily involves mixing high-purity reactants according to specific stoichiometric ratios and conducting the reaction under appropriate high-temperature, atmospheric, and time conditions. Finally, up conversion luminescent materials are obtained through grinding treatment. For example, Lin et al. used this preparation method to mix Dy_2O_3 , SrCO_3 , Eu_2O_3 , Al_2O_3 , and a solvent in a specific stoichiometric ratio, sintered in a reducing atmosphere, and obtained yellow-green SrAl_2O_4 phosphor after grinding [8].

The sol-gel method is a common chemical synthesis method used to prepare nanoscale luminescent materials. This method typically uses oil-soluble alcohol salts or water-soluble salts as precursors. Through a reaction, a stable and transparent sol is formed, and organic substances are removed to ultimately prepare nano-sized particles [9]. The sol-gel method has several advantages. Firstly, the reaction temperature is relatively low, which helps in the preparation of materials with uniform distribution and smaller particle sizes. Additionally, this method can be used to synthesize various materials, such as $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$, $\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$, $\text{SrAl}_2\text{O}_4:\text{Eu}^{3+}, \text{Dy}^{3+}, \text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$, $\text{Y}_2\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}, \text{Tb}^{3+}, \text{SrAl}_2\text{O}_4:\text{Eu}^{3+}$, etc. However, the drawback of the sol-gel method is that the luminescence intensity of the obtained materials is not high. Currently, many teams have successfully synthesized various materials using the sol-gel method, such as $\text{Ca}_{0.8}\text{Zn}_{0.2}\text{TiO}_3:\text{Pr}^{3+}$, Na^+ nano-emitting particles (below 100nm) [10].

The precipitation method involves a chemical reaction between a precipitant and a specified metal salt solution, resulting in the formation of a precipitate. Then, through steps like separation, washing, drying, and finally heat treatment, the final product is obtained [11]. The precipitation method is particularly suitable for synthesizing luminescent materials, especially nanoscale luminescent materials. It has several advantages: Firstly, it has a simple process that is conducive to industrial production. Secondly, it can uniformly mix substances with different compositions. Lastly, the resulting samples have high purity and stable performance. However, samples prepared by the precipitation method may be affected by agglomeration, which affects

their morphology. Researchers, such as Chow et al., successfully used the co-precipitation method to prepare $\text{LaF}_3:\text{Ln}^{3+}(\text{Yb}^{3+}, \text{Er}^{3+}, \text{Tm}^{3+}, \text{Ho}^{3+})$ nanocrystals [12]. Compared to $\text{NaYF}_4: 20\% \text{Yb}^{3+}, 2\% \text{Er}^{3+}$ crystals, the yield of LaF_3 increased by 5-6 times. The particle size of the prepared LaF_3 up conversion nanomaterials is approximately 5 nanometers.

The hydrothermal method is a synthesis method that significantly reduces the reaction temperature (typically within the range of 100-200°C), but requires high-temperature and high-pressure reaction conditions to be provided. It allows for good control of the shape and size of the samples and can synthesize materials with high luminescence efficiency and good dispersibility without the need for subsequent heat treatment [13]. However, the hydrothermal method has higher requirements for the reaction environment, making it relatively more expensive compared to conventional methods. The hydrothermal method can be used to prepare up conversion materials doped with rare earth ions, especially fluoride materials. Zhao's research group synthesized ordered arrays of NaYF_4 nanocrystals using the hydrothermal method, and controlled their shape, crystal structure, and nanosize by adjusting reaction conditions such as reactant concentrations [14].

The precursor thermal decomposition method is a method of heating and decomposing to prepare monodisperse nanoparticles at high temperatures (usually around 250°C). This method effectively controls the reaction rate, thereby improving the dispersion and crystallinity of the material particles. However, this method must be operated in a water-free, oxygen-free, and closed environment, resulting in higher energy consumption and expensive starting materials. This method was first proposed by Yan Chunhua's research group in 2006. By co-thermally decomposing $\text{Na}(\text{CF}_3\text{COO})$ and $\text{RE}(\text{CF}_3\text{COO})_3$, rare earth fluoride nanorods, polyhedra, nanoparticles, and nanosheets were synthesized in a single step [15]. In 2012, Liu Xiaogang's research group utilized this method to synthesize NaYF_4 upconversion nanomaterials by doping Gd ions, while simultaneously controlling and adjusting their crystal structure, nanosize, and optical properties [16].

The microwave method is a relatively new preparation method that utilizes microwave energy to induce reactions under certain

conditions for the synthesis of upconversion luminescent materials. By controlling the pressure, temperature, and time of the reaction, nanoparticles with high crystallinity, small particle size, high dispersibility, and high luminescence efficiency can be efficiently and environmentally friendly prepared. Compared to traditional methods, the microwave method offers advantages such as fast reaction rates, high efficiency, and shorter reaction times. Upconversion fluorescence materials prepared using microwave-assisted methods include $Y_2O_3: Eu^{3+}$, $CaWO_4$, $CaMoO_4$, $(Y,Cd)BO_3: Eu^{3+}$, $(Ce_{0.67}Tb_{0.33})MgAl_{11}O_{19}$, etc [17,18]. Yang et al. synthesized $(Ce_{0.67}Tb_{0.33})MgAl_{11}O_{19}$ using the microwave method, and the resulting product exhibited good crystallinity, small particle size, and uniform distribution. Zhang et al. reported the synthesis of rare earth-doped $NaLa(MoO_4)_2$ crystals using microwave-assisted hydrothermal method. The synthesis process is simple, involving the mixing of aqueous solutions of $La(NO_3)_3$ and $Na_2(MoO_4)_2$, followed by heating in a microwave reactor and subsequent washing and drying to obtain the final product [19].

4. CURRENT STATUS OF UPCONVERSION LUMINESCENT MATERIALS

The emission of upconversion luminescent materials doped with ions is mainly achieved through the cross-relaxation of energy between rare earth ions and the introduction of transition ions for quenching luminescence. The energy transfer between rare earth ions is achieved by doping with appropriate energy levels, which alters or enhances the process of energy transfer between different ions to achieve emission of a single color. This cross-relaxation can result in non-radiative transitions of electrons at intermediate energy levels, thereby achieving emission in a single wavelength band.

4.1 Changing Energy Transfer Mechanism

Rare earth ions possess diverse and complex energy level structures, allowing for energy transfer to the excited states of Er^{3+} and the observation of green and red emissions in nanocrystals. Researchers can further explore and control the energy interactions between rare earth ions to achieve singular green or red emission, thereby enhancing the quality and

efficiency of luminescence. For example, in nanocrystals doped with Sm^{3+} as an activator, Sm^{3+} undergoes energy transfer with specific energy levels of Er^{3+} by suppressing further electronic transfer to those levels, resulting in preferential emission of green light and quenching of red light emission [20] (Fig. 2a). Researchers also discovered that by doping Tm^{3+} into nanocrystals containing Er^{3+} , pure red emission can be successfully achieved. The electronic structure of Tm^{3+} enables efficient energy transfer from specific energy levels of Er^{3+} to specific lower levels of Tm^{3+} . Furthermore, the energy gap between Tm^{3+} 's specific levels and the ground state is large, almost prohibiting non-radiative multi-phonon relaxation processes. Therefore, the transferred energy can be effectively stored in Tm^{3+} 's level and promote the population of specific energy levels of Er^{3+} for red emission through Fig. 2b In 2014, Wei et al. proposed a research outcome that utilizes cross-relaxation (CR) between rare earth ions to regulate monochromatic emission. They conducted experiments using hexagonal-phase rare earth nanocrystals with $NaYbF_4$ as the host and Tm^{3+} as the luminescent center. It was found that as the concentration of Tm^{3+} increased, pure red emission was achieved, which was due to the strengthening of cross-relaxation between ions and the suppression of non-red emission. In $NaYbF_4:Tm^{3+}$ crystals, the energy transfer mechanism for upconversion luminescence is as follows: at low Tm^{3+} concentrations, the influence of ion interactions on the upconversion emission process is minimal, allowing efficient filling of the 1G_4 and 1D_2 energy levels Fig. 2c. However, with the increase of Tm^{3+} concentration, the upconversion luminescence process from non-red light to monochromatic red light can be realized. The reason is that when the content of Tm^{3+} is high, the luminescence at 475nm is suppressed due to the small energy mismatch, and at the same time, the two kinds of cross relaxation jointly improve the electron population to $^3F_{2,3}$ energy level, thus enhancing the red light emission at 698nm, as shown in Fig. 2d. Besides Tm^{3+} , Ho^{3+} and Ce^{3+} plasmas can also be used as energy capture centers to confine the excitation energy to the Er^{3+} level. This doping can simultaneously inhibit the luminescence quenching caused by cross relaxation and the energy migration to internal lattice defects, thus enhancing the red upconversion emission effect of Er^{3+} [21].

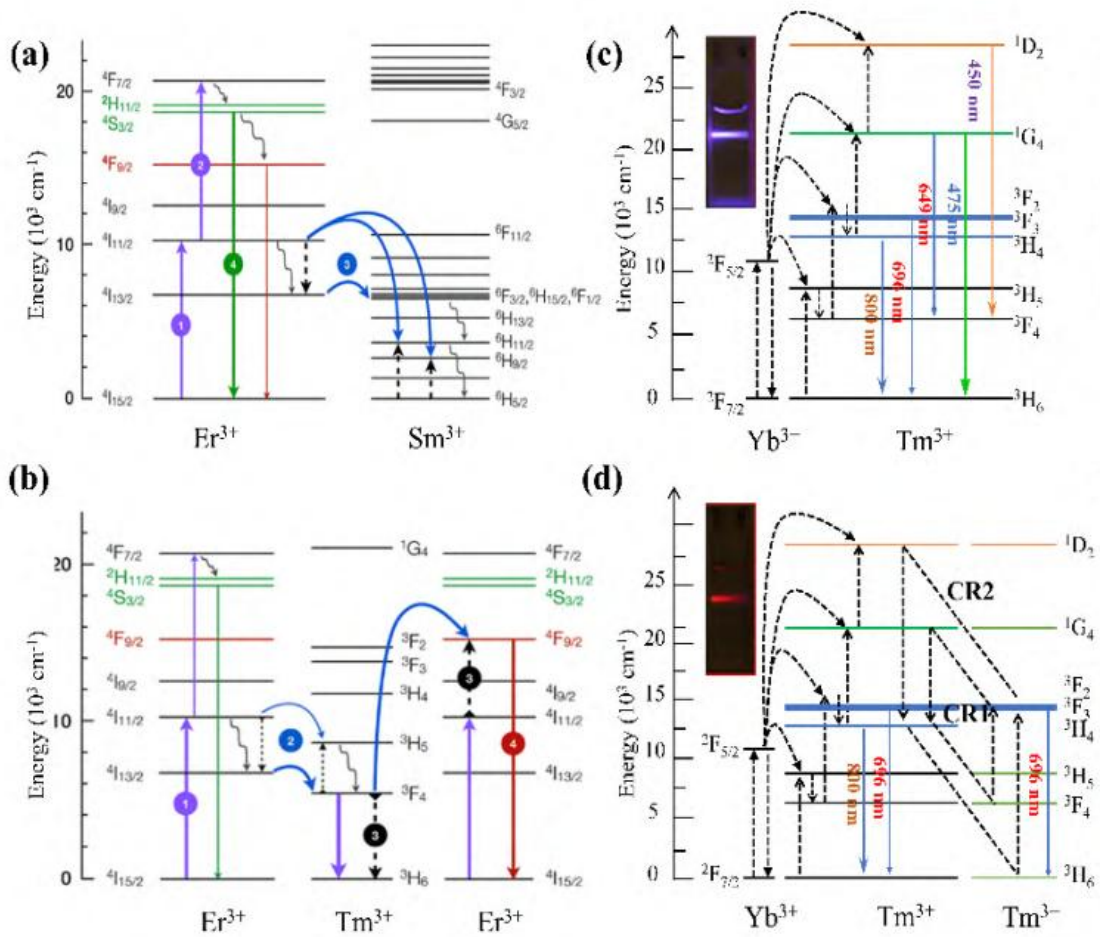


Fig. 2(a) illustrates the upconversion luminescence mechanism of Er³⁺/Sm³⁺.
 Fig. 2(b) illustrates the upconversion luminescence mechanism of Er³⁺/Tm³⁺.
 Fig. 2(c) illustrates the upconversion luminescence mechanism of NaYbF₄:Tm³⁺ at low dopant concentration.
 Fig. 2(d) illustrates the upconversion luminescence mechanism of NaYbF₄:Tm³⁺ at high dopant concentration [22]

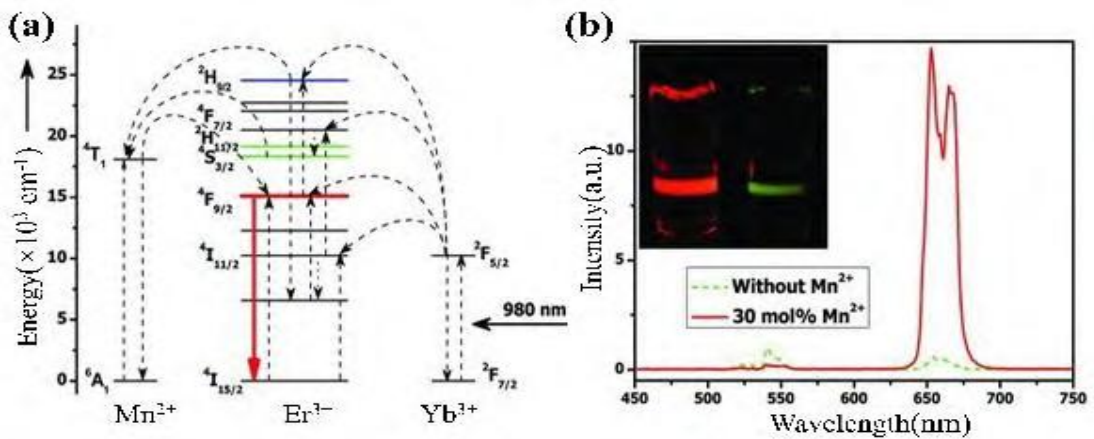


Fig. 3. (a) Mn²⁺ doped NaYF₄:Y/Er upconversion luminescence mechanism (b) upconversion emission spectrum comparison [22]

4.2 Introducing Transient Ion Quenching Luminescence

In addition to rare earth ions, transition metal elements are often used as co-dopants to modulate the upconversion luminescence process of rare earth ions. These transition elements have energy levels that match those of the luminescent ions and can serve as intermediate levels, facilitating electron transitions from the impurity levels to the desired emissive levels. In other words, transition elements act as bridging energy levels, enabling efficient upconversion luminescence of rare earth ions. In a study by [23], the doping of Mn^{2+} ions into $NaYF_4:Yb/Er$ was found to alter the electron transitions within the Er^{3+} energy levels, promoting red light emission and allowing for color tuning from green to red. This is because the 4T_1 level provided by Mn^{2+} acts as an intermediate transition level within the Yb/Er system. When the electrons of Yb/Er are at the ${}^2H_{9/1}$ and ${}^4S_{3/2}$ levels, they first undergo nonradiative energy transfer to the 4T_1 level of Mn^{2+} , followed by reverse energy transfer to the ${}^4F_{9/2}$ level of Er^{3+} , thereby transferring the energy originally intended for green light emission to the red light emission process, enhancing red light emission. By controlling the doping concentration of Mn^{2+} , the R/G ratio can be adjusted from 0.83 to 163.78, achieving color tuning from green to red, as shown in Fig. 3(a-b). Wang et al. [24] synthesized lanthanide-doped $KMnF_3$ nanocrystals using a novel oil-phase synthesis method, which exhibited single-band upconversion luminescence attributed to Er^{3+} , Ho^{3+} , or Tm^{3+} ions. The principle of this single-band upconversion luminescence is similar to the energy transfer process mentioned earlier between Mn^{2+} and Er^{3+} ions. Additionally, there are other materials containing Mn^{2+} in the host matrix, such as $NaMn_3F_{10}:Er^{3+}/Yb^{3+}$ [25,26], Tm^{3+}/Yb^{3+} [27,28], and $NaMnF_3:Er^{3+}/Yb^{3+}$ [29], which exhibit strong pure red upconversion emission in the presence of Mn^{2+} . In other words, these nanocrystals achieve single-color upconversion luminescence by utilizing Mn^{2+} as an intermediate energy transfer mediator, wherein the presence of Mn^{2+} induces intense red light emission. Liu et al. [28] successfully obtained UCNPs with a hollow cubic morphology by doping Mn^{2+} ions into $NaErF_4$. The unique structure of these UCNPs allows for high-concentration doping of Yb^{3+} and uniform distribution within the UCNPs. Under 980nm NIR

excitation, single red upconversion luminescence is observed. Additionally, besides Mn^{2+} , transition metal ions such as Fe^{3+} [30], Cr^{3+} [31], and Mo^{3+} [32] can also match the energy levels of Er^{3+} and participate in energy transfer processes. This energy transfer can enhance the color purity and intensity of the nanocrystal's luminescence. Therefore, by controlling the doping of different transition metal ions, we can further modulate the optical properties of UCNPs and achieve improved luminescence efficiency.

5. ANTI-COUNTERFEITING APPLICATIONS OF UPCONVERSION LUMINESCENT MATERIALS

5.1 Monomodal Anti-counterfeiting Application

In the past few years, researchers have prepared luminescent materials in a Y_2O_3 matrix by doping with elements such as Eu^{3+} , Tb^{3+} , and Ce^{3+} , which emit red, green, and blue light under ultraviolet illumination, achieving tricolor luminescence. These luminescent materials have been synthesized with polyvinyl chloride (PVC) ink and used in the production of anti-counterfeiting two-dimensional (2D) QR code patterns using simple printing techniques.

This has enabled the recognition of anti-counterfeiting QR codes. However, due to their monomodal nature, the anti-counterfeiting capability of these materials is relatively low, limiting their application scenarios [33]. Furthermore, other researchers have obtained $NaYGeO_4:Pr^{3+}$ and $Y_2GeO_5:Pr^{3+}$ samples through high-temperature solid-state methods. They have achieved tunable luminescent colors by adjusting the dopant concentration of Pr^{3+} and applied them in the field of anti-counterfeiting (Fig. (4)). However, the anti-counterfeiting level of these materials is relatively low, thereby not achieving better applications. In summary, current luminescent materials have some limitations in the field of anti-counterfeiting, such as monomodal luminescence and lower anti-counterfeiting capability. To develop better applications, further research and improvement of the characteristics of luminescent materials are needed to enhance their anti-counterfeiting level and expand their scope of application [34,35].

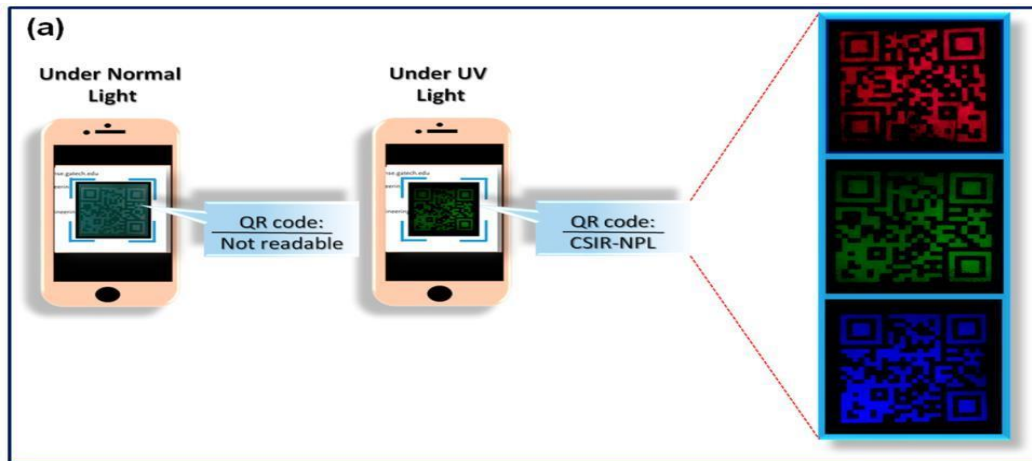


Fig. 4. Monomodal luminescent anti-counterfeiting QR code

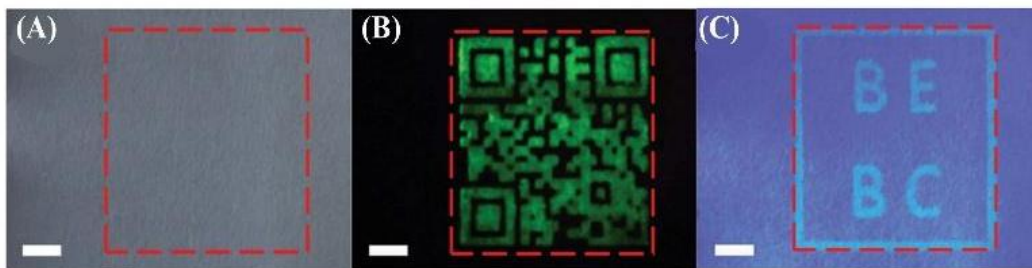


Fig. 5. Monomodal luminescent anti-counterfeiting pattern using $\beta\text{-NaYF}_4\text{:Yb}^{3+},\text{Er}^{3+}/\text{Tm}^{3+}$ fluorescent powder

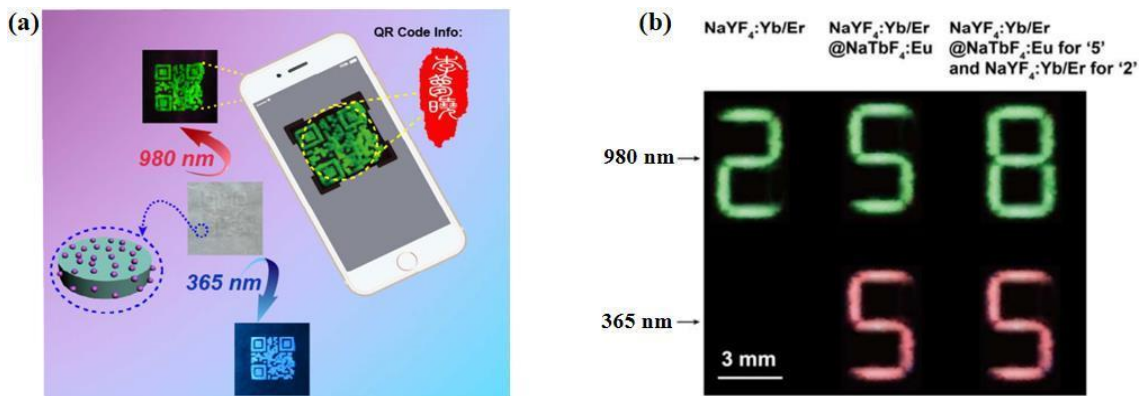


Fig. 6. Application effect of $\text{NaYF}_4\text{:Yb/Er}, \text{NaYF}_4\text{:Yb/ER@NATBF}_4\text{:Eu}$ material dual-mode luminescence anti-counterfeiting

The research group led by Xu [36] successfully synthesized $\beta\text{-NaYF}_4\text{:Yb}^{3+}, \text{Er}^{3+}/\text{Tm}^{3+}$ nanomaterials using a hydrothermal method. These materials emit green or blue light when excited by 980nm near-infrared light. By adjusting the ratio of anti-counterfeiting ink and fluorescent powder, and utilizing an inkjet printer, they successfully created anti-counterfeiting patterns with high resolution and high intensity luminescent effects (Fig. 5). This work provides a

new approach to achieve high brightness and colorful anti-counterfeiting patterns.

5.2 Advanced Application of Anti-counterfeiting with Bimodal Functionality

Li et al. made an anti-counterfeiting label by combining the two luminous modes of up and down conversion, as shown in Figure. The

pattern shows blue under a 365 nm laser and green under a 980 nm laser [37]. Han et al. [38]. successfully prepared $\text{NaYF}_4:\text{Yb}/\text{Er} @ \text{NaTbF}_4:\text{Eu}$ luminescent material. They used this material to achieve two luminescent modes and applied it in the anti-counterfeiting field. As shown in Figure three numbers "8" are used to design anti-counterfeiting patterns. $\text{NaYF}_4:\text{Yb}/\text{Er}$ material, it will emit green light under 980nm laser. Using this feature, they filled in the first number as a "2." For $\text{NaYF}_4:\text{Yb}/\text{Er} @ \text{NaTbF}_4:\text{Eu}$, it emits both green and red light under a 980nm laser. They took advantage of this by coloring in the second number as a "5." In the third numeric area, they filled the "5" with $\text{NaYF}_4:\text{Yb}/\text{Er} @ \text{NaTbF}_4:\text{Eu}$ sample and the remaining blank area with $\text{NaYF}_4:\text{Yb}/\text{Er}$ sample. In the end, when irradiated with 980nm laser, the anti-counterfeiting pattern will display a green "258", while under 365nm it will display a red "55". The unique combination of this material enables it to achieve two different luminescent

modes, thus enhancing its level of security in the anti-counterfeiting field. This will provide greater security and reliability to anti-counterfeiting labels.

Liu et al. [39] developed a method for preparing stable lanthanide-doped fluoride nanoparticles and mixed them with ink for dual-mode anti-counterfeiting applications. They demonstrated a transparent film that appeared patternless under natural sunlight, but when exposed to 980nm laser and 365nm ultraviolet light, the applied fingerprints and engraved characters became clearly visible (see Figure 6). The fingerprints were observed and analyzed using scanning electron microscopy to study their shape and patterns. This technology enables dual-mode anti-counterfeiting with high visibility and anti-counterfeiting capabilities (see Fig. 6). This study provides new ideas and approaches for dual-mode anti-counterfeiting applications.

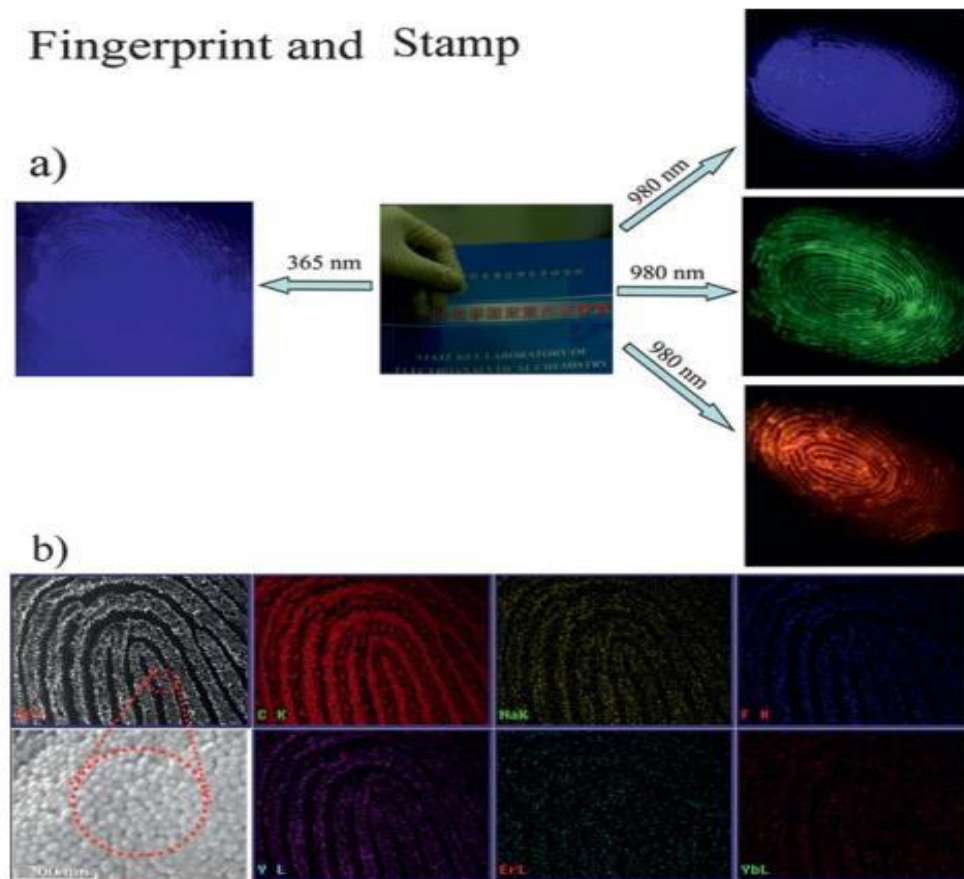


Fig. 7. Novel fingerprint anti-counterfeiting technology using lanthanide-doped fluoride nanoparticles

In 2022, a research team led by Wei et al. [40] designed and synthesized a novel dual-mode luminescent nanocomposite material named $\text{NaYF}_4:\text{Yb,Er}@\text{CDs}$. They prepared two anti-counterfeiting patterns, denoted as "Sc" and "Au", using $\text{NaYF}_4:\text{Yb,Er}@\text{CDs}$ and $\text{NaYF}_4:\text{Yb,Er}$, as shown in Fig. (7). These anti-counterfeiting patterns exhibited various colors under irradiation of 365nm ultraviolet light, 980nm near-infrared light, as well as 365nm and 980nm mixed light. This indicates the multi-modal luminescent properties of $\text{NaYF}_4:\text{Yb,Er}@\text{CDs}$. Furthermore, by using a 550nm filter, additional colors can be read, enhancing the level of anti-counterfeiting. The utilization of dual-mode excitation to obtain composite materials with different color characteristics is of great significance for advanced anti-counterfeiting. Although $\text{NaYF}_4:\text{Yb,Er}@\text{CDs}$ possesses favorable optical properties, its preparation conditions are stringent, reaction steps are complex, and it is costly with certain toxicity. Therefore, these drawbacks limit the widespread application of fluorescent carbon dots in the field of anti-counterfeiting.

In 2020, Wang et al. [41]. successfully prepared a multi-modal anti-counterfeiting material, $\text{CaTiO}_3:\text{Pr}^{3+},\text{Er}^{3+}$, with both up conversion and down conversion functions. This material exhibits color persistence. Moreover, under the irradiation of 980nm near-infrared light, this material also generates green up conversion luminescence. To utilize this phenomenon for anti-counterfeiting applications, the researchers blended this material with PDMS and used screen printing

technology to create 2D bar code anti-counterfeiting patterns, as shown in Fig. (8). This material not only enhances the difficulty of counterfeiting but also demonstrates high-level anti-counterfeiting effects. Subsequently, many scientists have further introduced other functionalities such as mechanoluminescence and thermoluminescence based on this foundation, bringing more possibilities for the development of anti-counterfeiting technology.

Pei Peng xiang et al. [42]. utilized the unique multi-modal luminescent properties of $\text{La}_4\text{GeO}_8\text{Eu}^{2+/3+},\text{Er}^{3+}$ phosphor and applied it in the field of anti-counterfeiting, as shown in Fig. (9). Under portable ultraviolet lamp irradiation, it exhibits red (254 nm) and green (365 nm) emissions. When illuminated with 980 nm or 808 nm near-infrared lasers on a two-dimensional code, it displays green emission. By using a portable ultraviolet lamp and near-infrared laser to irradiate the two-dimensional code, the hidden information embedded in the code can be easily read through the We Chat scan function. This indicates that $\text{La}_4\text{GeO}_8\text{Eu}^{2+/3+},\text{Er}^{3+}$ material possesses excellent information encryption and anti-counterfeiting capabilities. The application technology of this anti-counterfeiting material is simple and convenient, requiring only commonly used equipment such as ultraviolet lamps and near-infrared lasers to quickly scan and interpret the information inside the two-dimensional code. Such multi-modal luminescent properties provide an efficient and reliable solution in the field of anti-counterfeiting, effectively preventing information forgery and tampering.

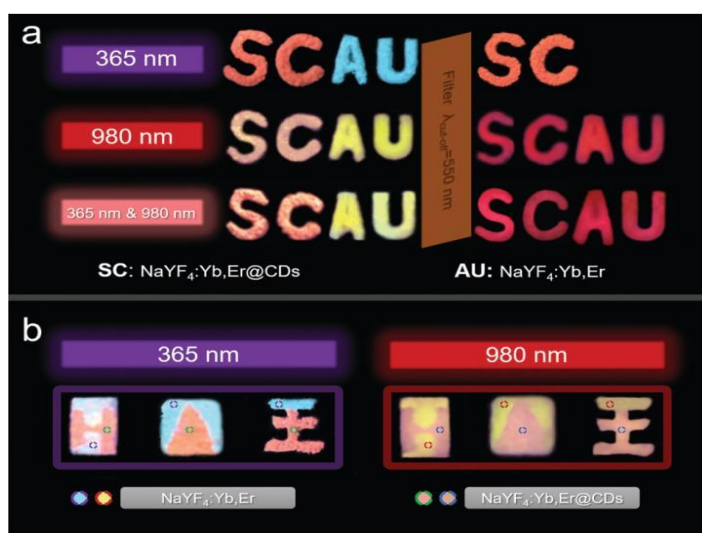


Fig. 8. (a,b) shows the luminescent anti-counterfeiting application patterns of $\text{NaYF}_4:\text{Yb,Er}@\text{CDs}$ nanocomposite material and $\text{NaYF}_4:\text{Yb,Er}$ phosphor

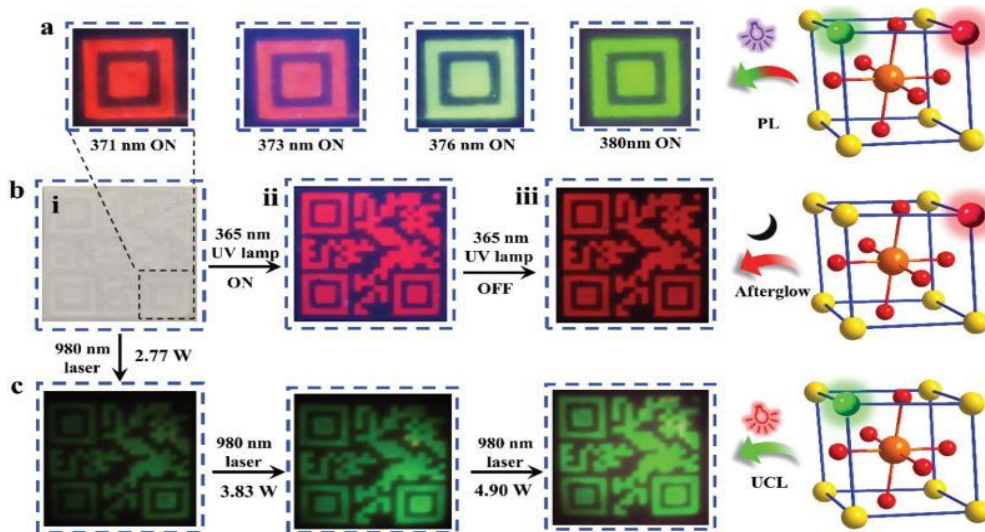


Fig. 9. (a,b,c): shows the multi-modal luminescent anti-counterfeiting pattern of $\text{CaTiO}_3:\text{Pr}^{3+},\text{Er}^{3+}$ phosphor

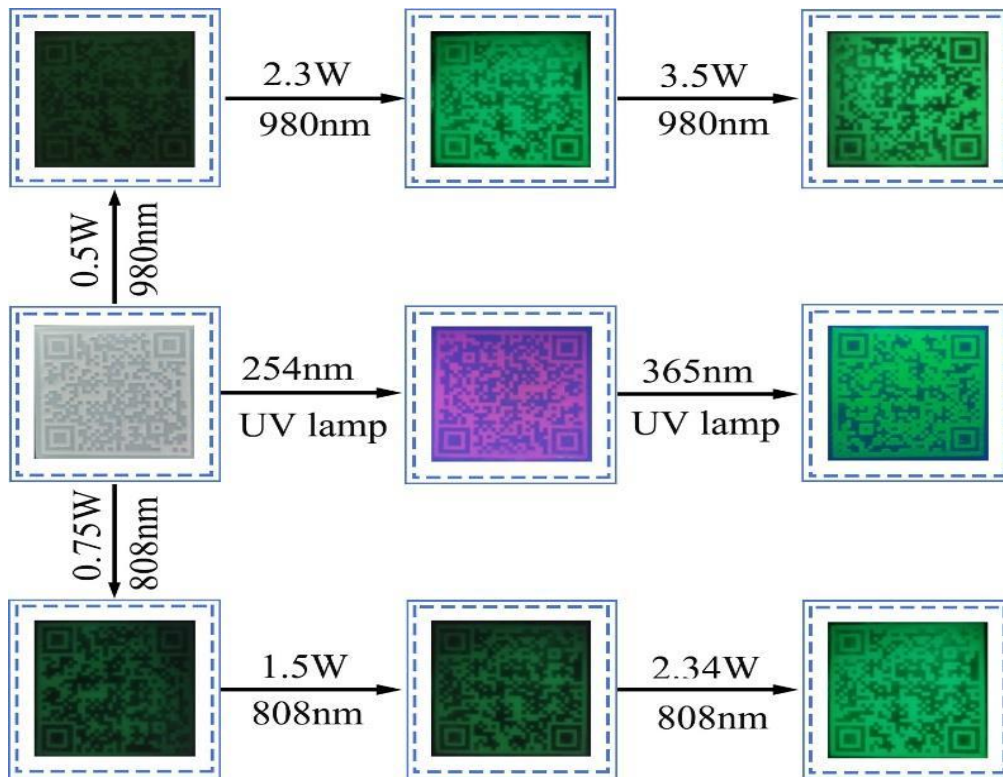


Fig. 10. Design of $\text{La}_4\text{GeO}_8\text{Eu}^{2+/3+},\text{Er}^{3+}$ multi-modal anti-counterfeiting QR code

6. CONCLUSION

Up conversion luminescent materials, as a new type of functional materials, have made significant progress in the application of fluorescence anti-counterfeiting technology. By rational design and optimization of the material's

chemical composition and crystal structure, researchers have successfully improved the luminescence efficiency and stability, achieving high brightness and long lifespan luminescence effects. Additionally, upconversion luminescent materials possess excellent spectral characteristics and multi-color luminescence

capability, making them widely applicable in the field of anti-counterfeiting for currencies, documents, and goods. However, up conversion luminescent materials still face some challenges in fluorescence anti-counterfeiting technology. Firstly, the synthesis methods and preparation processes need further optimization for large-scale production and high efficiency yield. Secondly, luminescence efficiency and stability still need enhancement to meet the requirements of long-term usage and practical applications. Furthermore, the cost of materials is also a factor to consider, as reducing costs would aid in promoting and popularizing this technology.

Looking ahead, the application of up conversion luminescent materials in fluorescence anti-counterfeiting technology has great development potential. Researchers can further optimize the synthesis methods and develop low-cost, large-scale production processes. Simultaneously, by controlling the structural modulation and ligand composition, the luminescence efficiency and stability can be further improved to meet the requirements of practical applications. Additionally, new material combinations and design ideas can be explored to achieve more diverse luminescent colors and multifunctional applications. Overall, although upconversion luminescent materials have made significant progress in fluorescence anti-counterfeiting technology, further research and development are still needed. With the continuous advancement of science and technology, it is believed that upconversion luminescent materials will gradually become an important technological means in the field of anti-counterfeiting, bringing more innovation and application possibilities to the commercial and security sectors.

COMPETING INTERESTS

Author has declared that no competing interests exist.

REFERENCES

1. Li S. Development trend of computer network security technology based on the big data era [J]. *Journal of Physics: Conference Series*, 2021;1744(4): 042223
2. Lu W L. Synthesis and spectral properties of rare Earth doped $Y_2(MoO_4)_3$ Blue and green up-conversion phosphors [D]. Dalian Maritime University; 2010.
3. Zhang R. Synthesis and anti-counterfeiting application of dual-color up-conversion $NaYF_4: Yb^{3+}/Ln^{3+}$ (Ln=Er, Tm) nanorods [D]. Harbin industrial university; 2021. DOI: 10.27061/, dc nki. Ghgdu. 2021.003607
4. Bai Ren auspicious. Based on rare earth conversion luminescence of anti-counterfeiting technology research [D]. Jilin architectural university; 2021. The DOI:10.27714/, dc nki. GJLJS. 2021.000070.
5. Zhang H X, Kam C H, Zhou Y, et al. Green upconversion luminescence in $Er^{3+}:BaTiO_3$ films [J]. *Applied Physics Letters*. 2000;77(5):609-611.
6. Liu J. Preparation and characterization of molybdate rare earth up-conversion luminescent materials by microwave assisted method [D]. Hainan University; 2015.
7. Ma Junjian, Jin Yinrong, He Yi, et al. Synthesis of $Sr_3Al_2O_6:Eu^{3+}$ red glass by solid state reaction [J]. *Journal of Xihua University: Natural Science Edition*. 2007;26(2):83-84.
8. Lin Yuan-Hua. Study on synthetic properties and excitation of Lin Yuan-hua Afterglow ceramics [D]. Beijing: Tsinghua University; 2001.
9. Yi GS, Chow GM. Synthesis of hexagonal-phase $NaYF_4:Yb,Er$ and $NaYF_4:Yb,Tm$ Nanocrystals with Efficient Up-Conversion Fluorescence [J]. *Advanced Functional Materials*. 2006;16(18):2324-2329
10. Lian Shixun, Zuo Chenggang, Yin Dulin, et al. Synthesis and red hair properties of nano $Ca_{0.8}Zn_{0.2}TiO_3:Pr^{3+},Na^{3+}$ phosphors [J]. *Chinese Journal of Rare Earth Sciences*. 2006;24(2):158-162.
11. Song YL. Preparation and biological application of hydrophilic rare earth up-conversion luminescent nanomaterials [D]. Donghua University; 2011.
12. Yi GS, Chow GM. Colloidal $LaF_3:Yb,Er;LaF_3:Yb,Ho$ and $LaF_3:Yb,Tm$ nanocrystals with multicolor upconversion fluorescence [J]. *Journal of Materials Chemistry*. 2005;15(41):4460-4464.
13. Sun X. Study on nano-luminescent materials doped with rare earth erbium (III) and europium (III) complexes [D]. Northeast Normal University; 2008.
14. Zhang F, Wan Y, Yu T, et al. Uniform nanostructured arrays of sodium rare-earth fluorides for highly efficient multicolor

- upconversion luminescence [J]. *Angewandte Chemie International Edition*. 2007;46(42):7976-7979
15. Mai HX, Zhang YW, Si R, et al. High-quality sodium rare-earth fluoride nanocrystals: controlled synthesis and optical properties[J]. *Journal of the American Chemical Society*. 2006; 128(19):6426-6436.
 16. Wang F, Deng R, Liu X. Preparation of core-shell NaGdF nanoparticles doped with luminescent lanthanide ions to be used as upconversion-based probes[J]. *Nature protocols*, 2014;9(7):1634-1644
 17. Liu F W, Hsu C H, Chen F S, et al. Microwave-assisted solvothermal preparation and photoluminescence properties of $Y_2O_3: Eu^{3+}$ phosphors[J]. *Ceramics International*. 2012;38(2):1577-1584
 18. Thongtem T, Kungwankunakorn S, Kuntalue B, et al. Luminescence and absorbance of highly crystalline $CaMoO_4, SrMoO_4, CaWO_4$ and $SrWO_4$ nanoparticles synthesized by coprecipitation method at room temperature [J]. *Journal of Alloys and Compounds*. 2010;506(1):475-481.
 19. Zhang J, Wang X, Zhang X, et al. Microwave synthesis of $NaLa(MoO_4)_2$ microcrystals and their near-infrared luminescent properties with lanthanide ion doping ($Er^{3+}, Nd^{3+}, Yb^{3+}$) [J]. *Inorganic Chemistry Communications*. 2011;14(11):1723-1727.
 20. Chan EM, Han G, Goldberg JD, Gargas DJ, Ostrowski AD, Schuck PJ, Cohen BE, Milliron DJ. Combinatorial Discovery of Lanthanide-Doped Nanocrystals with Spectrally Pure Upconverted Emission[J]. *Nano Lett*. 2012;12(7):3839-3845
 21. Wei W, Zhang Y, Chen R, Giggi JL, Ren NHuang L, Bhakoo KK, Sun HD, Tan TTY. Induced Pure Red Relaxation Upconversion in Activator- and Sensitizer-Rich Lanthanide Nanoparticles[J]. *Chem Mater*. 2014;26(18):5183-5186.
 22. Ji Haoli, Chen Dong, Dong Wenkun, et al. Research progress of rare earth doped monochromatic upconversion luminescent nanocrystals [J/OL]. *Chinese Journal of Rare Earths*:1-15[2023-10-23].
 23. Tian G, Gu ZJ, Zhou LJ, Yin WY, Liu XX, Yan L, Jin S, Ren WL, Xing GM, Li SJ, Zhao YL. Mn^{2+} Dopant-Controlled Synthesis of $NaYF_4: Yb/ Er$ Upconversion Nanoparticles for *in vivo* Imaging and Drug Delivery[J]. *Adv Mater*. 2012;24(9):1226-1231.
 24. Wang J, Wang F, Wang C, Liu Z, Liu X. Single band upconversion emission in lanthanide-doped $KMnF_3$ -Nanocrystals [J]. *Angew Chem Int Ed Engl*. 2011; 123(44):10553-10556.
 25. Bai ZH, Lin H, Imakita K, Montazami R, Fujii M, Hashemi N. Synthesis of Er^{3+}/Yb^{3+} codoped $NaMnF_3$ nanocubes with single-band red upconversion luminescence [J]. *RSC Adv*. 2014;4(106):61891-61897.
 26. Zhang Y, Lin JD, Vijayaragavan V, Bhakoo KK, Tan TTY. Tuning sub-10 nm single-phase $NaMnF_3$ nanocrystals as ultrasensitive hosts for pure intense fluorescence and excellent T1 magnetic resonance imaging[J]. *Chem Commun*. 2012;48(83):10322
 27. Bai ZH, Lin H, Johnson J, Gui SC, Imakita K, Montazami R, Fujii M, Hashemi N. The single-band red upconversion luminescence from morphology and size controllable Er^{3+}/Yb^{3+} doped MnF_2 nanostructures[J]. *J Mater Chem C*. 2014;2(9):1736.
 28. Liu YF, Guo CL, Pan GC, Zhao J, Zhang ZL, Gao HP, Zhang HF, Wei JS, Mao Y. Highly efficient upconversion single red emission of hollow cubic $NaErF_4$ nanoparticles by Mn/Yb heavy doping [J]. *Lumin*. 2020;228:117637.
 29. Ye S, Liang HD, Wang GS, Song J, Qu JL. Synthesis and spectroscopic study of $NaMn_3F_{10} Yb / (Er, Tm, Ho)$ Nanoparticles[J]. *Journal of synthetic crystals*. 2017;46(01):69-73.
 30. Tang J, Chen L, Li J, Wang Z, Zhang JH, Zhang LG, Luo YS, Wang XJ. Selectively enhanced red upconversion luminescence and phase/size manipulation via Fe^{3+} doping in $NaYF_4: Yb, Er$ nanocrystals [J]. *Nanoscale*. 2015;7(35):14752-14759.
 31. Wang CY, Cheng XH. Influence of Cr^{3+} ions doping on growth and up conversion luminescence properties of $NaYF_4: Yb^{3+}/Er^{3+}$ microcrystals[J]. *J Alloys Compd*. 2015;649:196-203.
 32. Yin DG, Wang CC, Ou YJ, Song KL, Liu B, Cao XZ, Zhang L, Han YL, Long X, Wu MH. Enhancing upconversion luminescence of $NaYF_4: Yb, Er$ nanocrystals by Mo^{3+} doping and their application in bioimaging [J]. *Dalton Trans*. 2014;43(31):12037-12043.
 33. Kumar P, Nagpal K, Gupta BK. Unclonable security codes designed from

- multicolor luminescent lanthanide-doped Y_2O_3 nanorods for anticounterfeiting [J]. ACS applied materials & interfaces. 2017;9(16):14301-8.
34. Xu H, Wang J, Hu W, et al. Luminescent colour modulation of a multicolour praseodymium-activated phosphor [J]. Ceramics International. 2019;45(7):9306-9.
35. Tian S, Wu H, Fu Y, et al. Color tuning dependence on cross-relaxation effect of Pr^{3+} -activated yttrium germanate phosphor [J]. Ceramics International. 2018;44(18):23293-6.
36. You M, Zhong J, Hong Y, Duan Z, Lin M, Xu F, Inkjet printing of upconversion nanoparticles for anti-counterfeit applications. [J]. Nano scale. 2015; 7(10):4423-4431.
37. Li M, Yao W, Liu J, et al. Facile synthesis and screen printing of dual-mode luminescent $NaYF_4: Er, Yb (Tm)$ /carbon dots for anti-counterfeiting applications [J]. Journal of Materials Chemistry C. 2017;5(26):6512-20.
38. Han Y, Gao C, Wang Y, et al. Spatially confined luminescence process in tip-modified heterogeneous-structured microrods for high-level anti-counterfeiting [J]. Physical Chemistry Chemical Physics. 2018;20(14):9516-22.
39. Liu Y, Aik, Lu L. Designing lanthanide-doped nanocrystals with both up- and down-conversion luminescence for anti-counterfeiting [J]. Nanoscale. 2011;3(11): 4804-4810.
40. Wei H, Zheng Y, Zhang X, Liang P, Xu X, Hu C, Zhang X, Lei B, Liu Y, Zhuang J. A rapid construction strategy of $NaYF_4: Yb, Er @ CD$ s nanocomposites for dual-mode anti-counterfeiting. Mater. Adv. 2022;3(11):4542-4547.
41. Wang Z, Pei P, Bai D, Zhao S, Ma, Liu W, Multicolor luminescence and triple-mode emission of simple $CaTiO_3: Pr^{3+}, Er^{3+}$ particles for advanced anti-counterfeiting. Inorg. Chem. Front. 2020;7(13):2506-2514.
42. Pei Peng Xiang. Preparation of rare earth doped multimodal luminescent material and anti-counterfeiting applications [D]. Lanzhou university; 2023. The DOI:10.27204 /, dcnki. Glzhu. 2022.003646.

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