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Preparation and Upconversion Emission Modification of Crystalline Colloidal Arrays and Rare Earth Fluoride Microcrystal Composites

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In this paper, highly ordered crystalline colloidal arrays containing rare earth fluoride microcrystals were fabricated. The upconversion emission property of rare earth fluoride microcrystals in crystalline colloidal arrays was studied and modified. A significant suppression and enhancement of the upconversion emission from the rare earth fluorides can be observed in the regions of the photonic band gap and its band edge, respectively. The suppression or enhancement factor was shown to be related to the ordered degree of the crystalline colloidal arrays and is critical in the preparation of upconversion displays and low-threshold lasers.

Photonic crystal materials are three-dimensional periodic dielectric materials that have recently attracted much research interest¹⁻⁶. The photonic band gap generated in photonic crystals is attributed to the periodic variation of the refractive index, which does not allow the propagation of light with a certain wavelength^{1,2}. This manipulation of the flow of electromagnetic waves can have a significant impact on the future of science and technology³⁻⁶. One important aspect to be controlled is the spontaneous emission. A low threshold laser with a photonic crystal structure can be fabricated due to the suppression of spontaneous emission, and highly efficient light emitting diodes (LEDs) can be designed via the inhibition of spontaneous emission by photonic band gap effects⁷⁻⁹.

To date, there have been numerous studies on the modification of spontaneous emission using photonic crystals. In previous studies, luminescence centers were planted in photonic crystals prepared by either top-down lithography or bottom-up self-assembly¹⁰⁻¹⁵. Top-down lithography is generally an expensive method for fabricating of photonic crystals, and the number of periodic layers in photonic crystals prepared by this method is limited, which greatly constrains the potential for spontaneous emission modification in such photonic crystals. Self-assembly has a disadvantage in the formation of defects including dislocations, grain boundaries, vacancies and stacking faults during the preparation process of photonic crystals. In addition, the self-assembly approach cannot easily prepare photonic crystals with a large area and thickness, which also precludes the effective modification of spontaneous emission.

Highly charged monodisperse colloidal microsphere suspensions with very low ionic strength can be used to prepare three dimensional ordered arrays because of electrostatic repulsion between adjacent microspheres. The ordered structure produced from such a suspension is called a crystalline colloidal array (CCA). Electromagnetic wave diffraction in CCAs, in accordance with the Bragg equation, results in the creation of a photonic band gap, which can enable a host of potential applications in color displays and sensors^{16–19}. The photonic crystals formed by CCAs are particularly attractive for investigations of spontaneous emission manipulation because the colloid volume is only limited by the volume of the container. The lattice parameter and ordered degree of CCAs are primarily influenced by weak electrostatic interactions within adjacent microspheres, which make tuning the photonic band gap positions relatively easy for applications and investigations^{20–22}. The modification of spontaneous emission from dyes in the CCAs has been extensively investigated. The ordered degree and stability of the CCAs could be affected by other factors such as ionic impurities and temperature, which could destroy the

balance of the gravitational and electrostatic repulsion interaction, thus resulting in disorder. Therefore, the active centers in CCAs investigated in previous works have generally been limited to florescent dyes^{23–25}.

Upconversion (UC) emissions from rare earth doped microcrystals have recently attracted considerable attention because of their application potential in solar cells, displays and bioimaging²⁶⁻²⁹. These applications require fundamental control of UC spontaneous emission. For instance, color tuning and purity, which are required for display and laser applications, could be achieved via the selective suppression of UC emission. Although CCAs effectively modulate the spontaneous emission of dyes $^{23-25}$, when introducing rare earth doped materials into CCAs, the CCAs tend to be disordered. Due to this difficulty, there has been no report thus far on the influence of CCAs on UC spontaneous emission from rare earth doped microcrystals. In this study, CCAs with rare earth doped microcrystals were prepared, and the UC emission property was successfully modified by band gap engineering. Because the modification of UC emission comes from the ordered structure of photonic crystals and the modification extent is related to the ordered degree, the effect of the ordering degree of CCAs on UC emission is also investigated in the present work.

Methods

Three types of mono disperse highly charged 135 nm polystyrene (PS) microspheres with volume fractions of 10 vol%, 8 vol% and 7 vol % were used to fabricate the CCAs. To remove ionic impurities in the PS microsphere suspensions, each suspension was exchanged for more than 1 month using anion (Amberlite 732) and cation (Amberlite 717) resins.

NaYF₄ particles co-doped with Yb (20 mol%) and Er (2 mol%) were fabricated by using the hydrothermal approach. High purity RE₂O₃ (RE = Y, Yb and Er, 99.99%) and analytical reagent grade NaF, NH₄F and trisodium citrate were used as starting materials with no further purification. The RE₂O₃ was dissolved in a hot nitric acid (HNO₃) solution to prepare the corresponding rare earth nitrate (RE(NO₃)₃). The NaF and NH₄F were dissolved in hot water, the RE(NO₃)₃ was dissolved in a mixed solution of trisodium citrate and ethanol, and the dissolved NaF/NH₄F solution was then added into the RE(NO₃)₃ solution. After intense agitation for 1 h, the resulting mixed solution was poured into a stainless steel autoclave containing a Teflon liner, sealed and incubated at 200°C. After the natural cooling of the solution, NaYF₄: Yb³⁺, Er³⁺ microcrystals were precipitated from the solution and washed with deionized water more than ten times to eliminate ionic and nonionic impurities The washed

microcrystals were then added into the CCAs without the ion-exchange resins, and agitated for a few minutes to ensure homogeneous distribution in the suspension.

UC emission measurements of the CCAs including the NaYF₄:Yb³⁺, Er³⁺ microcrystals were performed under 980 nm excitation on an F-7000 spectrophotometer. Optical transmittance spectra of the CCAs before and after the addition of the NaYF₄:Yb³⁺, Er³⁺ particles were recorded by a spectrophotometer (HITACHIU-4100). An X-ray diffractometer (D8 ADVANCE) with Cu Ka radiation at a wavelength of 1.5406 Å was used to determine the crystal structure of the NaYF₄:Yb³⁺, Er³⁺ particles. The morphology of the NaYF₄:Yb³⁺, Er³⁺ microcrystals was observed by using a JEOL 2100 transmission electron microscope (TEM) operated at a 200 kV acceleration voltage. The microstructures of the CCAs were observed on a Leica DMI-5000 M optical microscope.

Results and Discussion

The XRD pattern of the Yb, Er co-doped NaYF₄ particles is shown in Fig. 1 (a). It shows that all of the XRD peaks can be indexed to the hexagonal structure of NaYF₄, (JCPDS: No. 00-16-0334), indicating that the pure phase Yb, Er co-doped NaYF₄ was successfully synthesized. The shapes of the NaYF₄:Yb³⁺, Er³⁺ sample were investigated by TEM image, as shown in figure 1(b). The TEM image shows that the sample is hexahedral in shape with a size of approximately 200 nm. Fig. 1(c) provides the compositional analysis of an individual particle measured by EDX. The peaks of the doped Er and Yb elements may be observed, demonstrating that the Er³⁺ and Yb³⁺ ions were effectively embedded into the NaYF₄ host lattice.

Once the anion and cation ion-exchange resins were added into the PS colloidal suspension, they settled rapidly. After approximately 30 min of gentle agitation (up and down reversal of the sample vials), the milky-white colloidal microsphere suspension gradually became iridescent, suggesting that the PS colloidal suspension self-organized into a three-dimensional ordered fcc structure attributed to the electrostatic repulsion between adjacent microspheres. The ordered CCAs are stable due to the electrostatic repulsive interactions between adjacent microspheres, although its energy is not at a minimum³⁰. The ordered property of the CCAs can be maintained for more than 10 years if their purity of can be ensured and if there is no evaporation of water³⁰. Three CCAs prepared using PS microsphere suspensions with volume fractions of 10 vol%, 8 vol% and 7 vol % were designated as CCA-I, CCA-II and CCA-III, respectively, and their optical transmission spectra are shown in Fig. 2. A distinct



Figure 1 | X-ray diffraction pattern (a), transmission electron microscope image (b) and EDX analyses (c) of NaYF₄:Yb³⁺/Er³⁺ microcrystals.





Figure 2 | Transmittance spectra of CCA-I (a), CCA-II (b) and CCA-III (c) before (black line) and after (red line) addition of NaYF₄:Yb³⁺, Er³⁺ microcrystals.

valley may be in all three spectra, which was attributed to the constructive interference of scattered light from the highly ordered (111) planes of fcc CCAs oriented parallel to the container surface. The valley wavelength from the CCAs was tuned from green to red after decreasing the PS microsphere density by increasing the volume of water in the CCAs, which increases the distance between microspheres, resulting in the red shift of the photonic band gap shown in Fig. 2. This process is reversible, and removing water by gentle heating will decrease the volume occupied by the CCAs. The tunable photonic band gap property of CCAs has many potential applications such as chemical, humidity and vapor sensors. The easy tuning of the photonic band gap is beneficial to the investigation of photo physical process modulation, such as suppression of spontaneous emission in the photonic band gap region and enhancement at its band edge. The distances between adjacent microspheres in CCA-I, CCA-II and CCA-III can be calculated using the following equations.

$$l_c = 0.904 d\Phi^{-1/3} \tag{1}$$

$$l_m \!=\! 0.612 \lambda_p n^{-1} \tag{2}$$

where Φ and d are the volume fraction and the PS microsphere diameter, respectively, and λ_p and n denote the photonic band gap measured by the transmittance spectrum and refractive index of the CCA, respectively. d_m and l_c both refer to the distance between neighboring PS microspheres, as calculated by the two equations. In the present work, the refractive index of colloidal suspension (n) can take the value of water (1.333). The photonic band gaps of CCA-III, CCA-II and CCA-I were located at 658, 612 and 553 nm, respectively, as shown in the transmittance spectra. The d_c values of CCA-III, CCA-II and CCA-I are calculated to be 299, 282 and 257 nm, respectively and the d_m values are 298, 280 and 256 nm, respectively.

The transient instability of CCAs may be observed when it suffers from mechanical vibrations and contamination ionic impurities. When NaYF₄:Yb³⁺, Er³⁺ microcrystals are introduced into the CCA photonic crystals, the ordering of CCAs may be destroyed. Hence, the photonic band gap can be influenced by the presence of

Er³⁺ microcrystals were measured, as shown in Fig. 2. No significant shift of the peaks was observed for the transmittance spectra after the addition of the microcrystals, indicating that the microcrystals had little influence on the lattice constant of the CCAs. However, the valley of the transmission spectra became weaker and shallower, as a result of the ordered degree decrease of the CCAs after the introduction of the microcrystals. The ordered degree of CCAs is associated with its Bragg diffraction intensity. In general, a low Bragg peak intensity indicates a decrease in the ordered degree of CCAs caused by an increase of in the microsphere polydispersity³¹. In solid closepacked CCAs, Norris et al. found that the modulation depth of the interference fringe decreased when the distortion increased³². In our work, the presence of NaYF4:Yb3+, Er3+ ionic impurities resulted in an increase of the ionic strength, which screened the interactions between PS microspheres. As a result, the ordered arrangement of the PS colloidal particles was distorted, resulting in weaker and shallower valleys of the transmission spectra of CCA-I, CCA-II and CCA-III. As shown in Fig. 3, the ordered structure change of CCAs was also observed visually in their optical microscope images. The destruction of the three-dimensional ordered arrangement of PS colloidal particles was also revealed after the addition of NaYF₄:Yb³⁺, Er^{3+} to the CCAs, which was in agreement with the results of the transmission spectra in Fig. 2. To further observe the ordered microstructure of CCAs, the CCAs were polymerized in hydrogels, and polymerized crystalline colloidal arrays (PCCAs) were formed. 2,2diethoxyacetophenone and a solution of N,N'-methylenebisacrylamide and acrylamide in water were added to CCA-I with and without NaYF₄:Yb³⁺, Er³⁺ particles, each of which were then injected into a quartz cell. UV-light from a 50 W mercury lamp (CURE SPOTTM 50) was used to irradiate the CCA-I in the quartz cell for approximately 5 minutes to obtain PCCAs. Microstructures of the PCCAs before and after the addition of the NaYF₄:Yb³⁺, Er³⁺ particles was observed by the SEM, as shown in the supporting information (Fig. S 1). Highly ordered arrays were observed in the SEM image of CCA-I before the addition of NaYF4:Yb3+, Er3+ particles, but the ordering deteriorated upon the addition of NaYF₄:Yb³⁺, Er³⁺ particles.

NaYF₄: Yb³⁺, Er³⁺ microcrystals. The transmission spectra of CCA-I,

CCA-II and CCA-III after and before the addition of NaYF₄:Yb³⁺,





Figure 3 | Optical microscope images of CCA-I (a, b), CCA-II (c, d) and CCA-III (e, f) before (a, c, e) and after (b, d, f) addition of NaYF₄:Yb³⁺, Er³⁺ microcrystals.



Figure 4 | UC emission spectra of NaYF4:Yb³⁺, Er³⁺ microcrystals in CCA-I (a), CCA-II (b) and CCA-III (c) and reference sample.



Figure 5 | Propagation scheme of UC emission light from NaYF₄:Yb, Er particles in the CCAs. (a) UC emission light overlapping with photonic band gap of CCAs, (b) UC emission light overlapping with photonic band edge of CCAs, (c) UC emission light is far away from photonic band gap of CCAs.

A monodisperse PS colloidal suspension without exchanging was used as a reference sample to study the effect of the photonic bandgap on the UC emission property of NaYF4:Yb3+, Er3+ microcrystals in the CCA-I, CCA-II and CCA-III samples. Figure 4 shows the UC emission spectra under a 980 nm excitation. All of the samples exhibited sharp characteristic emissions at 525, 545 and 659 nm from Er³⁺. The 525, 545 and 659 nm UC emissions were attributed to the transitions of ${}^{2}\text{H}_{11/2} \rightarrow {}^{4}\text{I}_{15/2}, {}^{4}\text{S}_{3/2} \rightarrow {}^{4}\text{I}_{15/2} \text{ and } {}^{4}\text{F}_{9/2} \rightarrow {}^{4}\text{I}_{15/2},$ respectively. Note that the UC emission spectra of the CCA-II, CCA-III and reference sample are normalized 545 nm away from their photonic band gap. The UC emission band at 659 nm in CCA-I was far from its photonic band gap, so the normalizations of the UC emission spectra were performed at 659 nm for CCA-I and the reference sample. For CCA-I and CCA-III, it is clear that the UC emission is slightly suppressed in the photonic band gap region relative to the reference sample. As shown in Fig. 5 (a), the UC emission light overlapping with the photonic band gap suffered from Bragg reflection from (111) crystal planes in CCA-I and CCA-III causing less UC light to be collected at the direction of photonic band gap and resulting in the decrease of UC emission intensity observed in Fig. 4. The UC emission enhancement in the CCA-II can also be observed. The enhanced luminescence mechanism of active centers was previously reported in photonic crystals, and was considered to be a result of standing wave formation at the photonic band edges. The luminescence enhancement was observed at both the long and short wavelength edges of the photonic band gap. The luminescence enhancement was obtained at the long wavelength in high refractive index materials, whereas the luminescence enhancement at the short wavelength occurred in low refractive index materials³³. In our present work, the UC emission of NaYF₄:Yb³⁺, Er³⁺ microcrystals was enhanced at the long wavelength band edges of CCA-II, which suggests that the standing wave was formed in the high refractive index part of CCAs, leading to UC emission enhancement, as shown in Fig. 5 (b).

Interruptions in the periodic modulation of the refractive index caused by disorder decrease the diffraction efficiency of the CCAs. Thus, investigations have focused on improving the ordering degree. The resulting CCA-I, CCA-II and CCA-III solutions containing NaYF₄:Yb³⁺, Er³⁺ microcrystals were treated again by the exchange resins. The ionic strength of the CCAs containing NaYF₄:Yb³⁺, Er³⁺ microcrystals decreased further by the exchange process, which improved the ordered degree of the CCAs. Figure 6 shows the change in the optical microscope images of CCA-I containing $NaYF_4:Yb^{3+}$, Er³⁺ particles as the exchanging time increased. It can be clearly observed that the ordered degree of CCAs increases with the prolonging of the exchanging time. After 40 min of further resin exchange, the CCA-I containing NaYF₄:Yb³⁺, Er³⁺ particles reflected a bright iridescent green color, indicating that the completely ordered arrangement of colloidal particles returned. This was confirmed by the transmittance spectra. As shown in Fig. 6 (f), the valley in the transmittance spectra gradually became deeper as the exchange time increased. The changes in the transmittance spectra and optical microscope images for CCA-II and CCA-III upon the addition of NaYF₄:Yb³⁺, Er³⁺ microcrystals are similar to those for CCA-I, as shown in the supporting information (Fig. S 2–3).

Figure 7 shows the UC emission spectra of NaYF₄:Yb³⁺, Er³⁺ microcrystals in CCA-I, CCA-II and CCA-III with the increase the ordered degree of the CCAs. The high ordering of CCAs produces a significant photonic band gap effect and accordingly a greater enhancement or suppression of UC emission. For CCA-I and CCA-III containing NaYF₄:Yb³⁺, Er³⁺ microcrystals treated again by exchange resins, the suppression factor of the UC luminescence of NaYF₄:Yb³⁺, Er³⁺ particles in the region of the photonic band gap increased with the prolonging of the exchange time, which is caused by the increase of the ordered degree in the CCAs, as shown in both the optical micrograph and transmittance spectra. The suppression factor (SF) is defined as the ratio of UC emission intensity of a NaYF₄:Yb³⁺, Er³⁺ particle in the CCA to one in the reference sample. Figure 8 presents the SF as a function of resin exchange time. As the exchange time increased, the SF increased. SF values of 2.6 and 3.7 were achieved in CCA-I and CCA-III, respectively, when they became completely ordered. The red UC emission enhancement factor (EF) in CCA-II also increased with the increase in the ordered degree of CCA-II, and an EF of 2.1 was obtained in the completely ordered CCA-II sample, as shown in Fig. 8. It is well known that the modification of spontaneous emission is related to the ordered degree of photonic crystals^{24,33}. In the CCAs, the ordering was destroyed by the addition of NaYF₄:Yb³⁺, Er³⁺ particles, allowing UC emission light to escape through the defects, leading to the weak suppression effect shown in Fig. 5 (c). The small enhancement factor obtained in the CCA-II was because a standing wave cannot be formed in the defect regions.

The intensity of the UC luminescence (I_{up}) is associated with the excitation power density (P), $I_{up} \propto P^n$, where n is the number of photons absorbed by the rare earth ions at the ground state, promoting them to the excitation state. Figure 9 (a) presents double logarithmic plots of the UC emission intensity (I_{up}) and the excitation power density (I_{up}) in the reference sample. The n values of 525, 545





Figure 6 | The change in optical microscope images and the transmittance spectra (f) of CCA-I containing NaYF₄:Yb³⁺, Er^{3+} microcrystals with an increasing in exchange time (a = 0 min, b = 10 min, c = 20 min, d = 30 min, e = 40 min).



Figure 7 | The change in UC emission spectra of $NaYF_4$: Yb^{3+} , Er^{3+} microcrystals in the CCA-I (a), CCA-II (b) and CCA-III (c) with an increase of exchange time.



Figure 8 | Suppression factor (SF) of CCA-I, CCA-III and enhancement factor (EF) of CCA-II as a function of exchange time.

and 650 nm UC emissions are 1.95, 2.02 and 1.75, respectively, indicating that the green and red UC emissions belong to the two-photon UC emission process. The corresponding UC emission mechanism is shown in Fig. 9 (b). The energy transfer (ET) process from Yb³⁺ to Er³⁺ and ground state absorption (GSA) stimulated the Er³⁺ ion at the ⁴I_{15/2} ground state to ⁴I_{11/2} excitation state. The population of the ⁴F_{7/2} excited state was achieved though excited state absorption (ESA) and/or ET. Both the ²H_{11/2} and ⁴S_{3/2} states were populated by nonradiative relaxation from the upper ⁴F_{7/2} state. The electrons at ⁴S_{3/2}and ²H_{11/2} transitioned radiatively to ground state ⁴I_{15/2}, resulting in the 546 and 525 nm emissions, respectively. The excited state electrons at ⁴I_{13/2} level, and the electrons at the ⁴I_{13/2} level then jump to the upper



Figure 9 | Dependence of the upconversion fluorescence intensity on the pump power for the NaYF₄:Yb³⁺, Er^{3+} (a) and schematic energy level diagrams of the upconversion emission mechanism for the NaYF₄:Yb³⁺, Er^{3+} (b).

 ${}^{4}F_{9/2}$ level by excitation from the ET and/or ESA processes. The pair of electrons located at the ${}^{4}S_{3/2}$ level can further relax and populate the ${}^{4}F_{9/2}$ level, leading to the 659 nm red UC emission attributed to the transition from the ${}^{4}F_{9/2}$ to ${}^{4}I_{15/2}$ state.

Conclusion

The upconversion emission property of Yb^{3+}/Er^{3+} co-doped NaYF₄ microcrystals was first investigated in a highly ordered crystalline colloidal array, and the modification of the upconversion emission of rare earth fluoride microcrystals was observed. At the regions of the photonic band gap and its band edge, the significant suppression and enhancement of upconversion emission from rare-earth fluoride were obtained in the crystalline colloidal arrays, respectively. By studying the influence of the ordered degree of crystalline colloidal arrays on the upconversion emission modification, we found that the obvious enhancement or suppression of UC emission could be obtained in the CCAs with high ordering. The suppression and enhancement of upconversion emission from rare earth fluoride microcrystals may be important for the development of low-threshold upconversion lasers and displays.

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Author contributions

Z.W.Y. and J.Y.L. developed the research plan as well as the experimental strategy and wrote the manuscript. S.F.L., B.S. and J.L. were active participants in sample collection and processing. Z.W.Y., J.B.Q., Z.G.S. and Y.Y. revised the paper. All authors discussed the results and commented on the manuscript. J.B.S. revised the paper and was an active participant in the polymerization of CCAs.

Additional information

Supplementary information accompanies this paper at http://www.nature.com/ scientificreports

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