Eco-friendly Mn-doped CsPbCl₃ Perovskite Nanocrystals Glass with Blue-red Emitting for Indoor Plant Lighting

Ya Chen

Wenzhou University

Linli Shen

Wenzhou University

Jianming Liu

Wenzhou University

Xiaojuan Liang

Wenzhou University

Weidong Xiang (✉ xiangweidong001@126.com)

Wenzhou University

Jianping Liu

Wenzhou University

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Abstract

Mn-doped CsPbCl₃ perovskite nanocrystals (PeNCs) glass was prepared by melt-quenching and in-situ crystallization. Under the protection of robust glass, PeNCs exhibit excellent moisture resistance and thermal stability. Due to the combination effect of thermal quenching and energy transfer of exciton-to-Mn²⁺, the emission intensity of Mn shows an abnormal temperature-dependence with the temperature increasing from 80 to 300 K, which can be explored further in the application of temperature sensor. Interestingly, by matching with ultraviolet chips, all-inorganic blue-red emitting conversion device consisting of PeNCs glasses were prepared for light-emitting diodes (LEDs), which can meet the light requirements of plant growth. The cultivation results indicated that growth of cabbages using PeNCs plant cultivation LEDs were greater than those cultivated using commercial w-LEDs. Therefore, Mn-doped CsPbCl₃ PeNCs can be used as a new-generation of solid fluorescent materials in the field of indoor plant cultivation LEDs.

1. Introduction

Recently, indoor plant cultivation has developed rapidly in the field of agriculture. Compared with traditional farming methods, it is not affected by seasons and natural disasters, and it can normally produce even under harsh conditions[1-5]. Besides, the yield of plants cultivated indoors has increased significantly because the light environment is more targeted. Therefore, plant lighting technology has become a crucial part in the construction of modern agriculture. Traditional plant lighting is mainly carried out by incandescent lamps, halogen lamps and high-pressure sodium lamps. Compared with traditional light resources, light-emitting diodes (LEDs) exhibit obvious advantages in the field of indoor plant lighting due to their small size, long life, low energy consumption, high photoelectric conversion efficiency and the adjustable spectrum (red/blue ratio or red/far red ratio). Meanwhile, plant lighting is becoming more and more mature with the rapid development of LED lighting technology. For instance, Zhou et al.[6] successfully synthesized a strong near-infrared red light emission phosphor Ca₁₄Al₁₀Zn₆O₃₅ co-doped with Ti⁴⁺, Mn⁴⁺ ions, which can greatly promote the cultivation of succulent plants and is expected to become one of the plant lighting devices. Xiang groups[7] reported a double perovskite-type La₂MgGeO₆ co-doped with Dy³⁺ and Mn⁴⁺, demonstrating its potential in plant lighting. Generally, plants were most sensitive to blue (400-500 nm), red (620-690 nm) and far-red (720-740 nm)[8]. However, the current research was mainly focused on the phosphors with red/far red emission[3,9,10], and there are few studies and reports on blue-red emission. A highly efficient and dual-color emitting light convertor was reported by Lei et al[11], in which CaAlSiN₃:Eu²⁺ and BaMgAl₁₀O₁₇:Eu²⁺ provide red and blue emission, respectively. The Dual-PiGP light converter can be used as a new-generation lighting devices in the field of indoor plant growth. According to the requirements of plants for light absorption, it is very meaningful to develop a material with high stability, strong luminous efficiency, and dual-color emission of red and blue.

All-inorganic cesium lead halide CsPbX_3 ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) perovskite nanocrystals (PeNCs) have attracted extensively attention for their unique and excellent photoelectric performance. Due to its advantages of high photoluminescence quantum yields (PLQYs), tunable emission wavelength, narrow band emission and wide color gamut, it shows an outstanding application prospect in the fields of white light-emitting diodes (w-LEDs), photodetector, reversible 3D laser printing, photocatalysis and plant lighting[12-18]. As a new type of semiconductor material, it still faces some challenges in commercial applications. The long-term stability of PeNCs is a crucial issue that must be considered in practical applications. In addition, the existence of heavy metal lead is another obstacle. Doping in PeNCs opens a new way in the research fields of reducing or replacing the heavy metal lead element[19-21]. Among these dopants, manganese ions (Mn^{2+}) is one of the most concerned transition metal ions. Due to the doping of Mn^{2+} ions, it opened a new spectral window of orange-red emitting[22]. This is due to the energy transfer from the semiconductor exciton to the Mn^{2+} ions, which causes the radiated luminescence of the Mn^{2+} ions between the $^4\text{T}_1$ and $^6\text{A}_1$ energy levels. Under ultraviolet light excitation, Mn-doped CsPbCl_3 (Mn:CPC) PeNCs glass shows double emission peaks, exciton emission from perovskite (also known as band edge Luminescence) and $^4\text{T}_1 \rightarrow ^6\text{A}_1$ transition luminescence of Mn^{2+} [23-25]. Moreover, doping Mn^{2+} ions can also make the peak of the excitation blue shift [21,25], and also improve the quantum efficiency of the matrix CsPbCl_3 (CPC).

Herein, we have successfully synthesized a series of Mn:CPC PeNCs with dual-color emitting in borosilicate sodium ($\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2-\text{Na}_2\text{O}$, ZBSN) glass by melt-quenching and heat-treatment method, which possess robust stability and can maintain fluorescence intensity almost unchanged even immersed in water for more than 45 days. We investigated the photoluminescence (PL) intensity of Mn:CPC PeNCs at the temperature range of 80-300 K, and an unusual temperature-dependent properties of Mn PL in Mn:CPC PeNCs is observed, which can be explored further in the application of temperature sensor. Interestingly, by matching with ultraviolet chips, all-inorganic blue-red dual-emitting conversion device consisting of Mn:CPC PeNCs glasses were prepared for light-emitting diodes (LEDs), which matches well with the light requirements for plant growth. Moreover, the assembled PeNCs LEDs were applied in indoor cultivation of cabbages, and the commercial w-LEDs were chosen as reference. The cultivation results indicated that growth of cabbages using PeNCs plant cultivation LEDs were greater than those cultivated using commercial w-LEDs. Therefore, Mn:CPC PeNCs glass can be an excellent candidate material for indoor plant cultivation LEDs.

2. Experimental Sections

2.1 Material

Boron oxide (B_2O_3 , 99.9 %), Silicon dioxide (SiO_2 , 99 %), Zinc oxide (ZnO , 99 %), Anhydrous sodium carbonate (Na_2CO_3 , 99.8 %), Cesium carbonate (Cs_2CO_3 , 99 %), Lead oxide (PbO , 99 %), Sodium chloride (NaCl , 99 %), and Manganese chloride tetrahydrate (MnCl_2 , 99 %) were purchased from Aladdin in Shanghai and without further purification.

2.2 Synthesis of Mn-doped CsPbCl₃ PeNCs glass

All the glass samples were synthesized by using traditional melt-quenching and heat treatment method. The raw materials (Table S1) need to be evenly mixed and ground into powders for about 30 minutes, and then were put into a corundum crucible and melted in a muffle furnace at 1220 °C for 15 minutes under ambient atmosphere. The molten glassy liquid was poured into a pre-heated steel template, and should be quickly moved to an annealing furnace once the liquid has solidified. In order to eliminate internal stress, prevent cracks, and improve the mechanical strength of glass, all the samples should be annealed at 400 °C for 3 hours.

2.3 Structural and Spectroscopic Characterizations.

Bruker D8 Advance with CuK α radiation was used to perform X-ray diffraction (XRD) analysis at 40 kV and 40 mA at a boundary of 10°-70° (2 θ) to identify the phase structure of the as-prepared samples. Microstructure observations of the specimens were conducted using a transmission electron microscope (TEM) (JEM-2100F, JEOL, Japan). Element distribution was analyzed using the energy-dispersive spectrometer (EDS) system attached to the TEM. X-ray photoelectron spectroscopy (XPS) was collected using an Axi Ultra DLD spectrometer with single-color Al K α radiation as the excitation source. Fluorescence spectra was recorded by Horiba Jobin Yvon Fluoromax-4P spectrophotometer. The UV-Vis absorption in the wavelength range of 400-700 nm was obtained by PerkinElmer Lambda 750 UV-Vis spectrometer at room temperature. The temperature-dependent PL measurements were performed using a vacuum liquid-nitrogen cryostat (Cryo-77, Ori[1]ental Koji), which is capable of giving a temperature change of 80-300 K.

3. Results And Discussion

3.1 Basic structural characterization of Mn-doped CsPbCl₃ PeNCs glass

The photos of CPC PeNCs glasses with different doping concentration of Mn ions under ordinary light and ultraviolet (UV) are shown in Figure.1(a). As the doping concentration continues to increase, the uniformity and brightness are effectively improved, however, this effect weakens while increasing the molar ratio of Mn ions. To determine that whether Mn ions were successfully doped in CPC PeNCs glass, we first analyzed the XRD pattern. Figure.1(b) shows the PeNCs glasses with different doping amounts of Mn²⁺. From the figure, we can see that the XRD diffraction peaks of pure CPC PeNCs glass can be well matched with the standard card of CsPbCl₃ (PDF # 18-0366). It can be easily observed that there are obvious characteristic peaks at approximately 22.433°, 32.006° and 39.437°, which correspond to the (101) crystal plane, (200) crystal plane and (211) crystal plane, respectively. The diffraction peaks of Mn-doped PeNCs are almost the same as the undoped PeNCs. The slight difference is that with the increase of Mn²⁺ doping concentration, the diffraction peaks at the (101) crystal planes have an obvious trend of large angle deviation (Figure.1(c)). This can be attributed to a part replacement of the larger radius Pb²⁺ (133p.m.) by the smaller radius Mn²⁺ (97 p.m.), which significantly reduces the lattice parameters and

causes the peak to move to a larger angle. That means Mn ions have been partially integrated into the PeNCs structure, rather than dispersed throughout the glass matrix[19]. The structural diagram of the replacement process is shown in Figure.1(d). By replacing Pb ions with Mn ions, the lattice parameters will be slightly reduced, and the recombination energy will be increased, thereby improving the stability [26,27]. In addition, we can observe that the intensity of the diffraction peak of the doped PeNCs glass is stronger than that of the undoped PeNCs glass, which indicates that the Mn^{2+} dopant can act as a nucleating agent to promote PeNCs crystallization[28].

As shown in Figure.2(a), TEM analysis showed that Mn:CPC PeNCs were uniformly embedded on the borosilicate glass substrate. HR-TEM observations revealed that the interplanar spacing of the doped CPC PeNCs (Figure.2(b)) were slightly reduced compared to the interplanar spacing of the undoped PeNCs, which were corresponding to the (101) planes of the cubic phase $CsPbCl_3$ (PDF#18-0366) standard card. Moreover, elemental mapping in scanning transmission electron microscope (STEM) mode was used to characterize the distribution of Mn:CPC PeNCs in the glass matrix. The EDX element diagram (Figure 2(d)-(g)) shows that the composition distribution of the four elements (Cs, Pb, Cl, and Mn) in Mn:CPC PeNCs is uniform, indicating that Mn is incorporated into CPC PeNCs. These results indicated that Mn:CPC PeNCs were successfully precipitated in the glass matrix and part of the smaller radius Mn ions could partially replace the Pb ions in the CPC host.

In order to further determine that Mn^{2+} has successfully replaced part of Pb^{2+} in PeNCs, we obtained XPS spectra of Mn:CPC PeNCs glass and compared it with undoped sample. Figure.2(h)-(k) shown the XPS spectra, of which the peaks corresponding to cesium, lead, chlorine and manganese elements, respectively. Cs, Pb, and Cl elements can be clearly observed in XPS of $CsPbCl_3$ products (Figure. 2(h)-(j)), and additional Mn signals can indeed be seen after doping (Figure. 2(k)). Interestingly, the Cs, Pb, and Cl signals slightly shifted to the direction of high binding energy after doping, which may be due to the change in the crystal field environment after Mn replaced Pb. The main peaks of Cs 3d, Pb 4f, Cl 2p and Mn 2p in Mn-doped PeNCs have similar binding energies as previously reported[29,30,31]. In summary, the structure and composition of the PeNCs were analyzed by XRD, TEM and XPS, and it was proved that part of Mn^{2+} was successfully doped in CPC lattice and maintains Mn^{2+} state[32].

3.2. Stability and temperature-dependent PL of Mn-doped $CsPbCl_3$ PeNCs glass

The absorption spectrum of Mn:CPC PeNCs shows smaller changes compared to pure CPC PeNCs, which indicates that the effect of doping Mn^{2+} has relatively weak influence on the electronic structure of PeNCs. The exciton PL emitting peak of pure CPC PeNCs and Mn-doped PeNCs are at 413 nm and 409 nm, respectively. In Mn:CPC PeNCs, another broad PL peak appears at 625 nm. This intensive emission peak can be attributed to ${}^4T_1 \rightarrow {}^6A_1$ transition of the Mn^{2+} ions, confirming that Pb^{2+} ions in the CPC PeNCs are replaced by Mn^{2+} ions. Under the excitation of 365nm radiation, the emission of Mn^{2+} can be ascribed to the direct absorption or energy transfer of Mn^{2+} ions by CPC exciton[25]. It can be seen from Figure 3(a) that absorption spectra of pure CPC and Mn: CPC PeNCs are almost the same, and there is

only one exciton absorption peak at 404 nm, indicating that Mn PL is related to the host exciton recombination. Therefore, the dual-emission PL spectra of Mn:CPC PeNCs can be assigned to the exciton-dopant energy transfer. Due to the doping of Mn^{2+} ions, dual-color emission with blue and red can be observed (Figure.3(b)). With the increase of Mn^{2+} dopants, the PL intensity of Mn^{2+} relative to exciton gradually increases, reaching the maximum at 2.012 mol%, and then decreases due to the concentration quenching. Moreover, at higher concentration of Mn^{2+} , the redshift of Mn^{2+} emission can be observed, which may be due to the formation of Mn^{2+} - Mn^{2+} pairs [33,34].

To further investigate the exciton-dopant energy transfer, the sample with a concentration of 2.021 mol% was selected to further investigate the PL spectra of temperature-dependence and shown in Figure.4(a). An unusual temperature-dependence of Mn PL intensity in Mn:CPC PeNCs is observed, with the temperature rising from 80 K to 300 K, the Mn PL intensity becomes stronger and then weaker. This can be explained by the competition between excitonic recombination and energy transfer to Mn^{2+} [35]. As shown in Figure.4(b), while the temperature increases from 140 K to 280 K, the thermal perturbations ($k_{\text{B}}T$) increases and carriers in the exciton state can be directly converted to another energy level, which is likely to be thermal excitation 4T_1 energy level of Mn^{2+} , and therefore enhance the PL intensity of Mn. It can be seen from Figure.3(c) that the intensity of the edge gradually decreases while the intensity of Mn^{2+} ions gradually increases. Based on the results obtained, the emission model of Mn-doped PeNCs is shown in Figure 4(d). The CPC host absorbs energy under the excitation of 365nm radiation, and emits 409nm radiation through the recombination of excitons between the ground and excited states of CPC. In addition to radiative recombination, there is a non-radiative relaxation process, which leads to energy loss through hole defects or electron defects. The substitution of Mn produces a new exciton recombination pathway, which has the property of exciton- Mn^{2+} energy transfer, making excitons change from one excited state to another, and has thermally activated electrons. Only excitons with sufficient thermal activation energy will undergo an intersystem crossing (ISC) process and eventually emit light at 625nm, showing a new exciton recombination pathway of Mn^{2+} ion d-d transition, namely 4T_1 - 6A_1 transition. Through Mn^{2+} doping, light induces the energy transfer of excitons from the CPC host to the doped Mn^{2+} ions, promotes the recombination of excitons through the radiation pathway, and enhances the PL intensity.

In order to prove that PeNCs embedded in glass indeed enhance the stability, we studied the water stability and thermal stability of Mn:CPC PeNCs glass. After immersing in water for 45 days (shown as Figure 5(a)), the PL intensity of the sample remains almost unchanged, which can reach about 95.1 %, the emission spectra is shown in Figure 5(b). Moreover, the thermal stability of the glass also has been tested. The temperature-dependent intensity of Mn is measured at the range of 300 to 480 K, as the temperature increasing and the carriers in the exciton state decrease during thermal quenching, therefore, the PL intensity of Mn decreases. It can be seen that Mn:CPC PeNCs glass has excellent thermal stability. Overall, these stability tests indicated that the dense glass network structure provides effective protection for the network control system, thereby obtaining excellent stability.

3.3. Application of Mn-doped CsPbCl₃ PeNCs glass in plant lighting

As illustrated in Figure.6(a), we combined Mn: CPC PeNCs glass with ultraviolet chips to assemble an LEDs device (PeNCs plant cultivation LEDs) to meet the light requirement for promoting plant growth. Subsequently, the assembled LEDs device was used for indoor plant cultivation, as shown in Figure.6(b). The plant used for indoor cultivation was cabbage and the experimental period were 28 days. Firstly, we sown the seeds in a black plastic nutrient bowl, fully infiltrated with tap water to germinate and grow seedlings. When the seedlings had grown four or five true leaves, they were randomly divided into two groups of A and B (each group for 6) for the experiment and placed under the conditions of ambient temperature of 25 ± 5 °C, humidity of 65~75 % and nutrient solution pH: 6.5 ± 0.1 , Light conditions (group A: Commercial w-LEDs and group B: PeNCs plant cultivation LEDs). Figure 6(c) shows the Photographs of cabbages under different light irradiation. Compared with the commercial w-LEDs, PeNCs plant LEDs devices made of Mn:CPC PeNCs glass showed stronger red light in the range of 600-700 nm, which is more specific to the light source requirements for plant growth.

As shown in the Figure.6(d), the growth rate of cabbages under PeNCs plant cultivation LEDs is significantly faster than that under commercial w-LEDs and the average height of the cabbages is 1.4cm higher than those using commercial w-LEDs. Therefore, dual-color emitting PeNCs glass used for indoor plant cultivation, which obviously promotes plant growth. This is similar to previous reports[10,36-37]. We believe that the prepared dual-color emitting Mn:CPC PeNCs glass has potential application prospect in lighting systems for indoor plant cultivation.

4. Conclusion

In summary, a series of dual-color emitting Mn:CPC PeNCs were synthesized in borosilicate sodium glass by in-situ growth. Due to the effective protection of the glass matrix, the Mn:CPC PeNCs glasses showed excellent water resistance and thermal stability. Doping Mn²⁺ ions can prompt CsPbCl₃ crystallization, and part of Mn²⁺ ions can enter the CsPbCl₃ lattice to replace the Pb²⁺ ions and reduce its toxicity. With the temperature rising from 140 to 300 K, the Mn PL shows an unusual temperature-dependence, which can be explored further in the application of temperature sensor. In addition, The LEDs device assembled by Mn:CPC PeNCs glass and ultraviolet chips were used for indoor plant cultivation and significantly promoted plant growth, indicating that Mn-doped CsPbCl₃ PeNCs glass has a potential application in the fields of plant lighting.

Declarations

Conflict of interest

The authors declare no competing financial interest.

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Figures

Figure 1

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Figure 2

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