Electronic Supporting Information

Glass Stabilized Ultra-Stable Dual-Emitting Mn-Doped Cesium Lead Halide Perovskite Quantum Dots Embedded Glasses for Cryogenic Temperature Sensing

Bin Zhuang^{a,c,+}, Yue Liu^{b,+}, Shuo Yuan^b, Hai Huang^{a,c}, Jiangkun Chen^{a,c}, Daqin Chen^{a,c,*}

^aCollege of Physics and Energy, Fujian Normal University, Fuzhou, 350117, China. E-mail: <u>dqchen@fjnu.edu.cn</u>

^bCollege of Materials & Environmental Engineering, Hangzhou Dianzi University, Hangzhou, 310018, China

^cFujian Provincial Collaborative Innovation Center for Optoelectronic Semiconductors and Efficient Devices, Xiamen, 361005, China

Experimental Section

Synthesis of Mn-doped PQDs@glass. The present nanocomposites were prepared by a traditional melt-quenching and subsequent heat-treatment. Herein, Mn-doped B-P-Zn-Cs-Pb based oxyhalide glass was designed with the compositions of P_2O_5 - B_2O_3 -ZnO- Cs_2CO_3 -PbX₂-KX-MnCl₂ (X=Cl or Cl/Br mixture). The raw materials were mixed well and ground into powders for a certain of time, and melted in a muffle furnace at 800°C for 20 min under ambient atmosphere to achieve precursor glass. Finally, Mn-doped PQDs@glass was obtained through in-situ glass crystallization via heat-treatment at 350 °C for 2 h. As a comparison, Mn-doped blank glass with composition of P_2O_5 - B_2O_3 -ZnO-KCl-MnCl₂ was prepared via a similar procedure. The nominal glass compositions for all the samples are tabulated in **Table S1**.

Structural Characterizations. XRD analysis was carried out to identify the phase structure of the as-prepared samples using a powder diffractometer (MiniFlex600 RIGAKU) with Cu K_{α} radiation (λ = 0.154 nm) operating at 40 kV. XPS data were acquired by using a VG Scientific ESCA Lab Mark II spectrometer equipped with two ultra-high vacuum 6 (UHV) chambers. All the binding energies were referenced to the C_{1s} peak of the surface adventitious carbon at 284.8 eV. FTIR spectra were measured via a Perkin-Elmer IR spectrometer using the KBr pellet technique. Raman spectra were determined by a LabRam HR Raman spectrometer operated with 633 nm as excitation source. EPR spectra were recorded by an E-580 Bruker Elexsys X-band EPR spectrometer. The microwave frequency was 9.8487 GHz, and the tests were conducted at 77 K. Microstructure observations of Mn-doped PQDs@glass were carried out on a JEOL JEM-2010 TEM operated at 200 kV accelerating voltage. STEM images were taken on a FEI aberration-corrected Titan Cubed S-Twin transmission electron microscope operated on a HAADF mode.

Spectroscopic Characterizations. Photoluminescence (PL), PL excitation (PLE) and Mn²⁺ decay curves for the Mn-doped PQDs@glass nanocomposites were recorded on an Edinburgh

Instruments (EI) FS5 spectra fluorometer equipped with continuous (150 W) and pulsed xenon lamps. Time-resolved PL traces for exciton emission of NCs were detected on a fluorescent lifetime spectrometer (Edinburgh Instruments, LifeSpec-II) based on a time correlated single photon counting technique under the excitation of 375 nm picosecond laser. The decay lifetimes are determined via the equation of $\tau = \int I(t)dt / I_0$, where I(t) is the time-related luminescence intensity and I_0 is the peak intensity. Temperature-dependent PL spectra were recorded on an Edinburgh Instruments FS5 spectrofluoremeter equipped with a Linkam THMS600 temperature controlling stage.

Table S1 Nominal glass compositions (mol%) for all the investigated nanocomposites. The

samples were prepared by melt-quenching and subsequent heat-treatment at 350 °C for 2 h.

	CsPb(Cl/Br) ₃ PQDs embedded glass
1	29.3P ₂ O ₅ -11.4B ₂ O ₃ -29.3ZnO-7.5Cs ₂ CO ₃ -7.5PbCl ₂ -15KCl
2	29.3P ₂ O ₅ -11.4B ₂ O ₃ -29.3ZnO-7.5Cs ₂ CO ₃ -7.25PbCl ₂ -0.25PbBr ₂ -14.5KCl-0.5KBr
3	29.3P ₂ O ₅ -11.4B ₂ O ₃ -29.3ZnO-7.5Cs ₂ CO ₃ -7PbCl ₂ -0.5PbBr ₂ -14KCl-1KBr
4	29.3P ₂ O ₅ -11.4B ₂ O ₃ -29.3ZnO-7.5Cs ₂ CO ₃ -6.75PbCl ₂ -0.75PbBr ₂ -13.5KCl-1.5KBr
5	29.3P ₂ O ₅ -11.4B ₂ O ₃ -29.3ZnO-7.5Cs ₂ CO ₃ -6.5PbCl ₂ -1PbBr ₂ -13KCl-2KBr
6	29.3P ₂ O ₅ -11.4B ₂ O ₃ -29.3ZnO-7.5Cs ₂ CO ₃ -5.5PbCl ₂ -2PbBr ₂ -11KCl-4KBr
	Mn-doped CsPbCl ₃ PQDs embedded glass
7	29.3P ₂ O ₅ -11.4B ₂ O ₃ -29.3ZnO-7.5Cs ₂ CO ₃ -7.5PbCl ₂ -15KCl-1MnCl ₂
8	29.3P ₂ O ₅ -11.4B ₂ O ₃ -29.3ZnO-7.5Cs ₂ CO ₃ -7.5PbCl ₂ -15KCl-2MnCl ₂
9	29.3P ₂ O ₅ -11.4B ₂ O ₃ -29.3ZnO-7.5Cs ₂ CO ₃ -7.5PbCl ₂ -15KCl-3MnCl ₂
10	29.3P ₂ O ₅ -11.4B ₂ O ₃ -29.3ZnO-7.5Cs ₂ CO ₃ -7.5PbCl ₂ -15KCl-4MnCl ₂
11	29.3P ₂ O ₅ -11.4B ₂ O ₃ -29.3ZnO-7.5Cs ₂ CO ₃ -7.5PbCl ₂ -15KCl-5MnCl ₂
	Mn-doped CsPb(Cl/Br) ₃ PQDs embedded glass
12	29.3P ₂ O ₅ -11.4B ₂ O ₃ -29.3ZnO-7.5Cs ₂ CO ₃ -7.25PbCl ₂ -0.25PbBr ₂ -14.5KCl-0.5KBr-3MnCl ₂
13	29.3P ₂ O ₅ -11.4B ₂ O ₃ -29.3ZnO-7.5Cs ₂ CO ₃ -7PbCl ₂ -0.5PbBr ₂ -14KCl-1KBr-3MnCl ₂
14	29.3P ₂ O ₅ -11.4B ₂ O ₃ -29.3ZnO-7.5Cs ₂ CO ₃ -6.75PbCl ₂ -0.75PbBr ₂ -13.5KCl-1.5KBr-3MnCl ₂
15	29.3P ₂ O ₅ -11.4B ₂ O ₃ -29.3ZnO-7.5Cs ₂ CO ₃ -6.5PbCl ₂ -1PbBr ₂ -13KCl-2KBr-3MnCl ₂
16	29.3P ₂ O ₅ -11.4B ₂ O ₃ -29.3ZnO-7.5Cs ₂ CO ₃ -5.5PbCl ₂ -2PbBr ₂ -11KCl-4KBr-3MnCl ₂
	Mn-doped blank glass
17	29.3P ₂ O ₅ -11.4B ₂ O ₃ -29.3ZnO-30KCl-3MnCl ₂



Figure S1 Enlarged XRD patterns of Mn-doped CsPb(Cl/Br)₃ PQDs@glass samples with various Cl/Br ratios (from bottom to top: 7.5:0, 7.25:0.25, 7:0.5, 6.75:0.75, 6.5:1, 5.5:2).



Figure S2 Absorption spectra for Mn²⁺-doped CsPb(Cl/Br)₃ PQDs@glass composites (from left to right: Br/Cl ratio gradually increases). Notably, the absorption bands of Mn²⁺ dopants are not detected owing to their weak spin-forbidden d-d absorption transition relative to strong semiconductor band-to-band absorption.



Figure S3 Comparison of absorption spectra for CsPb(Cl/Br)₃ PQDs@glass with and without Mn²⁺ doping. After Mn²⁺ doping, the absorption intensity of PQDs is greatly intensified.



Figure S4 (a) Low-magnification and (b) high-magnification TEM images of precursor glass, showing a typical amorphous structure of glass.



Figure S5 High-angle annular dark-field (HAADF) scanning TEM (STEM) micrograph of Mn-doped CsPb(Cl/Br)₃ PQDs@glass.

HAADF-STEM image can distinctly discern the obvious contrast for $CsPb(Cl/Br)_3$ PQDs (bright) and P-B-based glass matrix (dark) benefited from large difference of atomic number between Cs/Pb (Z=55/82) and P/B (Z=15/5).







Figure S7 Photographs of (a) CsPb(Cl/Br)₃ PQDs@glass samples with increase of Br content, (b) CsPbCl₃ PQDs@glass samples doped with increase of Mn²⁺ content and (c) Mn-doped CsPb(Cl/Br)₃ PQDs@glass samples with increase of Br content (from left to right) under the irradiation of day light (top) and UV lamp (down).

All the Mn²⁺-doped CsPbCl₃ PQDs@glass samples are transparent and the appearance color gets deep violet with increase of Mn²⁺ doping content, while the un-doped CsPb(Cl/Br)₃ PQDs@glass and Mn-doped CsPb(Cl/Br)₃ PQDs@glass samples turn to yellow with increase of Br content. Under the irradiation of 365 nm UV lamp, the un-doped samples exhibit blue luminescence assigned to exciton recombination of CsPb(Cl/Br)₃ PQDs, and the Mn-doped samples show typical Mn²⁺ orange luminescence benefited from exciton-to-Mn energy transfer.



Figure S8 (a) PL decay curves by monitoring exciton emission for a series of Mn^{2+} (x mol%, x=0, 1, 2, 3, 4 and 5) doped CsPbCl₃ PQDs@glass nanocomposites. (b) Decay lifetime of PQDs and exciton-to-Mn energy transfer efficiency (ETE) versus Mn^{2+} doping content.

Because of their non-single-exponential decay feature, the lifetime was determined by the expression of $\tau_{exp} = \int I(t)dt / I_p$, where I_p is the peak intensity in the decay curve, and I(t) the time-dependent PL intensity.

The energy transfer efficiency (ETE) can be calculated by the equation of

 $\eta_{\text{ETE}} = 1 - \frac{\tau_{PQDs-Mn}}{\tau_{PQDs}}$, where $\tau_{PQDs-Mn}$ and τ_{PQDs} are the lifetimes of exciton emission with

and without Mn²⁺ doping, respectively.



Figure S9 FTIR spectra for the blank glass, precursor glass and Mn-doped CsPbCl₃ PQDs@glass samples.

The band at ~550 cm⁻¹ is attributed to the vibration of loose BO₄ group and P-O bending mode of PO₄ group, the band at ~750 cm⁻¹ is ascribed to the symmetrical stretching of B-O-B linkages of boron-oxygen, and a broad band in the range of 800-1400 cm⁻¹ is assigned to the vibration of BO₃, BO₄ and PO₄ groups.



Figure S10 Raman spectra (λ_{ex} =532 nm) for the blank glass, precursor glass and Mn-doped CsPbCl₃ PQDs@glass samples.

The intense band at 1070 cm⁻¹ is associated with B-O and P-O bond stretching of both BO_4 and PO_4 tetrahedral units. A peak centered at 1230 cm⁻¹ is pertinent to symmetric stretching of BO_3 units with the incorporation of Zn-O into the structure. The band at 300 cm⁻¹ is assigned to vibrational modes of both BO_3 and BO_4 units. Weak Raman peaks at 675 cm⁻¹ and 735 cm⁻¹ could be ascribed to localized breathing motions of oxygen atoms in the boroxol ring.



Figure S11 XPS full spectra for (a) the Mn-doped precursor glass and (b) the corresponding PQDs@glass.

Figure S12 PL decay curves by monitoring Mn^{2+} d-d transition for the precursor glasses (PGs) and the corresponding PQDs@glass nanocomposites doped with different Mn^{2+} contents.

Figure S13 PL decay curve by monitoring Mn^{2+} luminescence for a blank glass without the addition of perovskite components (Mn-doped blank glass composition: $29.3P_2O_5$ -11.4B₂O₃-29.3ZnO-30KCl-3MnCl₂).

Figure S14 PL decay curves of Mn^{2+} : ${}^{4}T_{1}$ emitting state (monitoring wavelength: 600 nm) for the Mn-doped CsPb(Cl/Br)₃ colloidal PQDs with increase of Br/Cl ratio. The samples were prepared by a hot-injection method and the change Br/Cl ratio is achieved by anion exchange.

Figure S15 (a) HAADF-STEM image of Mn-doped CsPbCl₃ PQDs@glass, and the associated elemental mappings for (b) P, (c) B, (d) Cs, (e) Pb and (f) Mn. Bar in (a) represents 10 nm.

Mn²⁺ locations in nanocomposite

In the present work, CsPbX₃ PQDs were prepared via in-situ glass crystallization strategy, i.e., PQDs were precipitated from a specially design oxyhalide glass, which is totally different to synthesis of colloidal counterparts. Generally, glass crystallization strategy highly relies on elaborate design of glass network structure and appropriate control of nucleation/growth (or precipitation) of specific crystals from glass matrix.

For the present case, a critical point is to achieve the growth of PQDs and more importantly facilitate diffusion of Mn^{2+} dopants from glass into the precipitated crystalline lattice through heating glass above glass transition temperature. It is worthy of mention that the incorporation of Mn^{2+} dopants into PQD lattice in glass is quite difficult owing to the impeding role of glass network and the mismatching of ionic radius between Pb²⁺ (r=119 pm) and Mn^{2+} (r=83 pm). Fortunately, we found that Mn dopants in B-P-Zn-Cs-Pb oxyhalide glass with compositions of P₂O₃-B₂O₃-ZnO-Cs₂CO₃-PbX₂-KX-MnX₂ acted as nucleating agent to promote precipitation of PQDs from glass matrix, which was subsequently beneficial for the incorporation of Mn^{2+} ions into PQD lattice without requirement of long-distance ionic diffusion. Notably, only part of Mn^{2+} dopants, i.e., those acting as nucleating agent, can be incorporated into PQD lattice, others remain in glass. To confirm this, high-angle annular dark-field (HAADF) scanning TEM (STEM) observation is performed in the revised manuscript (**Figure S15**). STEM image distinctly discerns the contrast for CsPbCl₃ (bright) and aluminosilicate glass matrix (dark) due to large difference of atomic number between Cs/Pb (Z=55/82) and B/P (Z=5/15). Elemental mappings show the segregation Cs and Pb elements among B/P glass matrix. Importantly, the Mn signals are found to homogeneously distribute in the sample, verifying that Mn^{2+} dopants stay in both PQD lattice and glass matrix for the present nanocomposite.

As presented in the original manuscript, XPS and EPR spectra only get the information of Mn^{2+} in glass matrix, indicating that the content of Mn^{2+} ions in glass is far higher than in crystalline lattice. Fortunately, we can identify Mn^{2+} dopants in CsPb(Cl/Br)₃ crystalline lattice by time-resolved emission spectra. As evidence in (**Figure 2e**, **Figure S12**), Mn^{2+} radiative kinetics experience remarkable change following the precipitation of CsPb(Cl/Br)₃ PQDs in glass, i.e., Mn^{2+} lifetimes in PGs are ~10 ms, while those in nanocomposites are down to ~ 1 ms. As a comparison, Mn^{2+} decay lifetime in Mn-doped blank glass (without addition of perovskite elements) is found to be about 14 ms (**Figure S13**) and that in colloidal CsPbCl₃ PQDs is about 1 ms (**Figure S14**). Moreover, its lifetime value monotonously declines when the precipitated phase alters from CsPbCl₃ to CsPb(Cl/Br)₃ (**Figure 2f**), which is consistent with the case for Mn^{2+} in CsPb(Cl/Br)₃ colloidal PQDs (**Figure S14**). Therefore, it can be concluded that part of Mn^{2+} dopants indeed enter CsPb(Cl/Br)₃ lattice although a large amount of them are still residual in glass matrix.

Figure S16 Quantitative optical absorption spectra of (a) the Mn-doped blank glass and (b) the PQDs embedded glass for absolute absorption measurement (I_{abs}). The incident UV light is 365 nm and all the spectra were recorded by a spectrofluoremeter equipped with an integrating sphere. I_{abs} is determined by I_{ref} - I_{Mn} or I_{ref} - I_{PQD} , where I_{ref} , I_{Mn} and I_{PQD} are the integrated intensities for reference sample, Mn-doped blank glass and PQDs embedded glass, respectively.

Figure S17 The proposed exciton-to-dopant energy transfer processes in Mn-doped PQDs@glass nanocomposites.

Figure S18 (a) PL spectra of Mn-doped CsPbCl₃ PQDs@glass after directly immersing in water for different durations (0, 1, 5, 10, 20 and 30 days). (b) Integrated PL intensity and Mn-to-exciton intensity ratio versus storing duration in water, verifying that there is not obvious change for PL intensity and Mn-to-exciton intensity ratio with increase of durations up to 30 days. Time-resolved PL traces by monitoring (b) exciton recombination (λ_{em} =410 nm) and (c) Mn²⁺ d-d transition (λ_{em} =650 nm) for Mn-doped CsPbCl₃ PQDs@glass immersing in water for different durations (0, 1, 5, 10, 20 and 30 days).

Figure S19 Luminescence photographs of Mn-doped CsPbCl₃ colloidal PQDs after immersing in water for different durations (from left to right: 0, 1 h, 2 h and 24 h). The sample with Mn-to-Pb feeding ratio of 5:1 was prepared by a tradional hot-injection method.

Figure S20 Temperature-dependent PL integrated intensities for the Mn-doped CsPbCl₃ PQDs@glass nanocomposite via three heating/cooling cycles at 100, 150 and 200 °C, respectively.

Figure S21 Temperature-dependent exciton emission spectra for the Mn-doped CsPbCl₃ PQDs@glass sample.

Figure S22 Decay lifetime of Mn²⁺ in CsPbCl₃ PQDs@glass versus temperature.

Figure S23 Temperature-dependent (163~293K) PL spectra containing both exciton and Mn²⁺ emissions for the Mn²⁺ (3%) doped CsPbCl₃ PQDs@glass.

Figure S24 Temperature-dependent (83~293K) PL spectra containing both exciton and Mn²⁺ emissions for the Mn²⁺ (4%) doped CsPbCl₃ PQDs@glass.

Figure S25 Temperature-dependent (83~293K) PL spectra containing both exciton and Mn²⁺ emissions for the Mn²⁺ (5%) doped CsPbCl₃ PQDs@glass.

Figure S26 Relative sensitivity versus temperature for Mn-doped CsPbCl₃ PQDs@glass nanocomposites doped with different Mn^{2+} content (3%, 4% and 5%).

Figure S27 PL peak ratio between exciton emission and Mn²⁺ emission for the Mn-doped CsPbCl₃ PQDs@glass in cycles of heating (143 K) and cooling (80 K).