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Robust $CsPbBr_3$ and Zn-Cd-S quantum dots co-doped nano-glass composites with broadly tunable emissions

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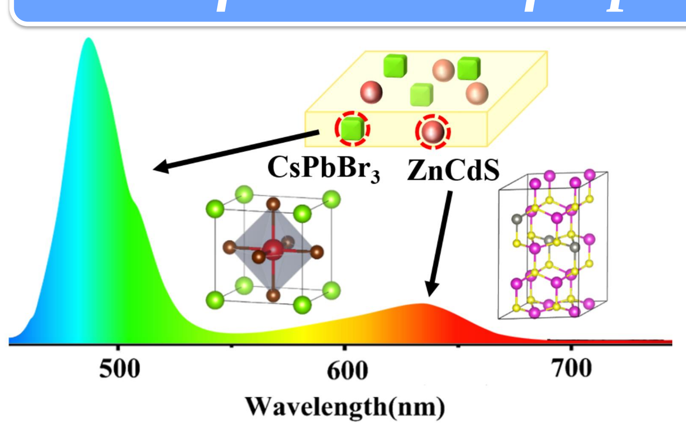
Introduction

Semiconductor quantum dots (QDs) possess the advantages of continuously adjustable emission colors and high photoluminescence quantum yields (PLQYs). They are widely used in lighting and displays, lasers, and fast scintillators for X-ray imaging. By encapsulation of QDs in mechanically robust and chemically inert inorganic glasses, the notorious thermal and environmental instability issue of QDs has been overcome. Recently, QDs-doped monolithic materials (e.g., glasses) with dual- or multi-band emissions under a single source excitation have attracted increasing attention. Such luminescent materials prove to be crucial for being applied as ratiometric fluorescent sensors. The fluorescence intensity ratio based sensors can eliminate fluctuations in emission intensity arising from unpredicted environmental, excitation or instrumental artifacts by means of self-calibration. This is particularly important in the field of radiation detection. However, most measurements rely on the change in the single-band emission intensity and thus need an extra calibration. A very promising alternative strategy has been recently developed for dual-band emissions from nano-glass composites (nano-GCs) embedded with biphasic QDs.

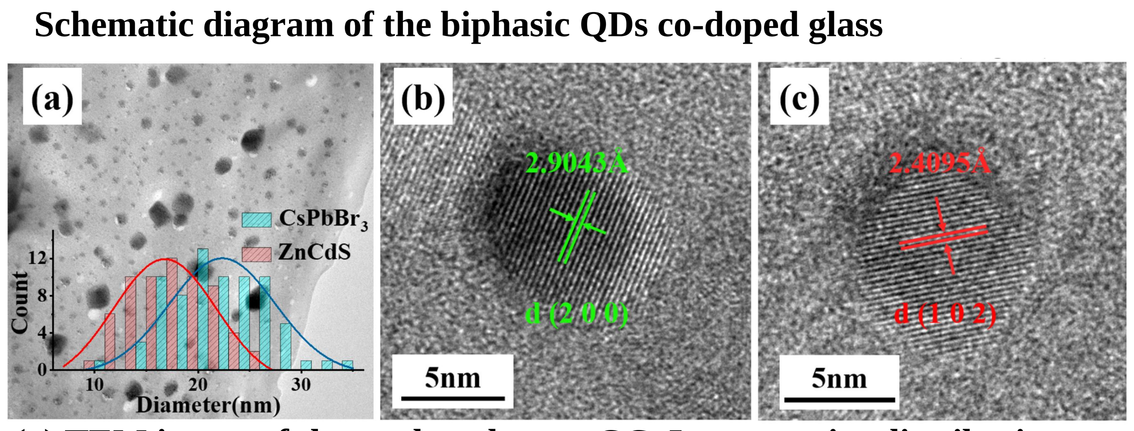
In this work, dual-band green and red emissions were realized in monolithic $CsPbBr_3$ and Zn-Cd-S QDs co-doped borosilicate glass. We demonstrated that the dual-band emissions could be adjusted either by varying the fraction of the biphasic QDs or the excitation wavelength. As a proof-of-concept, a self-calibrated X-ray dosimeter was constructed on the FIR of the dual-band emissions for the first time.

1. The formation of biphasic QDs co-doped nano-GCs

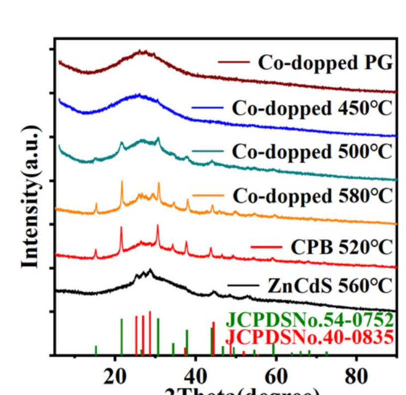


Schematic diagram of the biphasic QDs co-doped glass

- The formation of biphasic $CsPbBr_3$ and Zn-Cd-S QDs in the thermally-treated sample was confirmed.
- The average diameters of the $CsPbBr_3$ and Zn-Cd-S QDs were calculated to be ~ 20 nm and 15 nm, respectively.

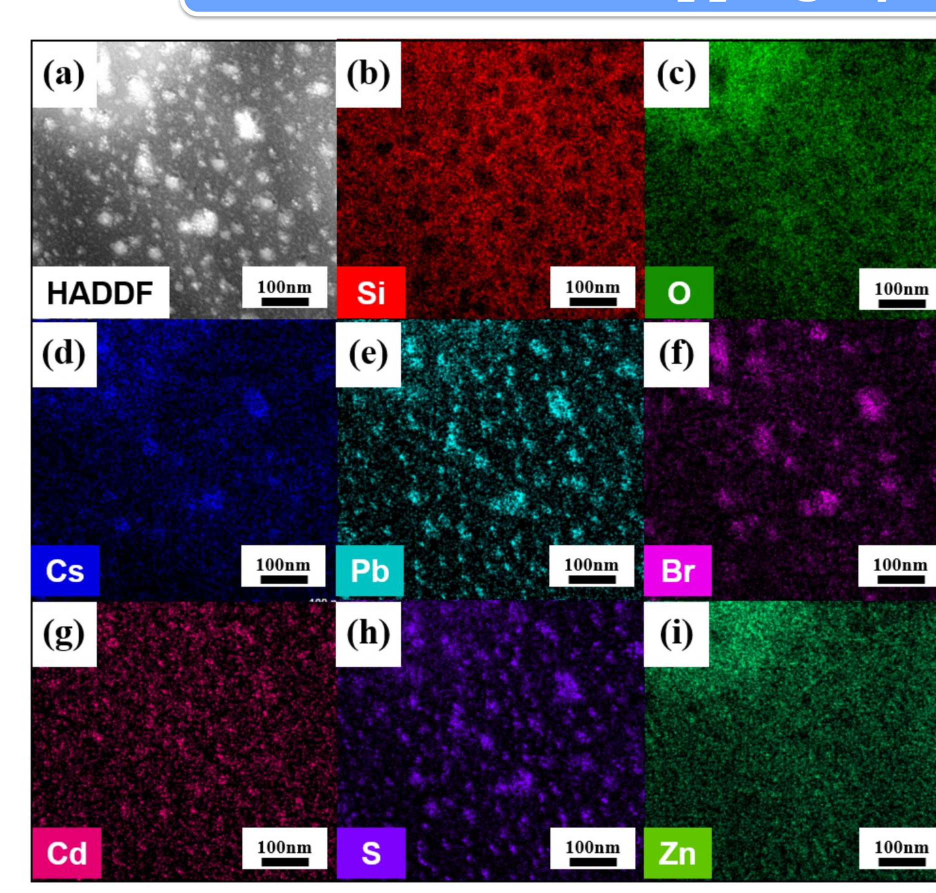


(a) TEM image of the co-doped nano-GC. Inset are size distribution histograms of QDs; HR-TEM images of (b) $CsPbBr_3$ and (c) Zn-Cd-S QDs.



XRD patterns of the QDs co-doped PGs and GCs

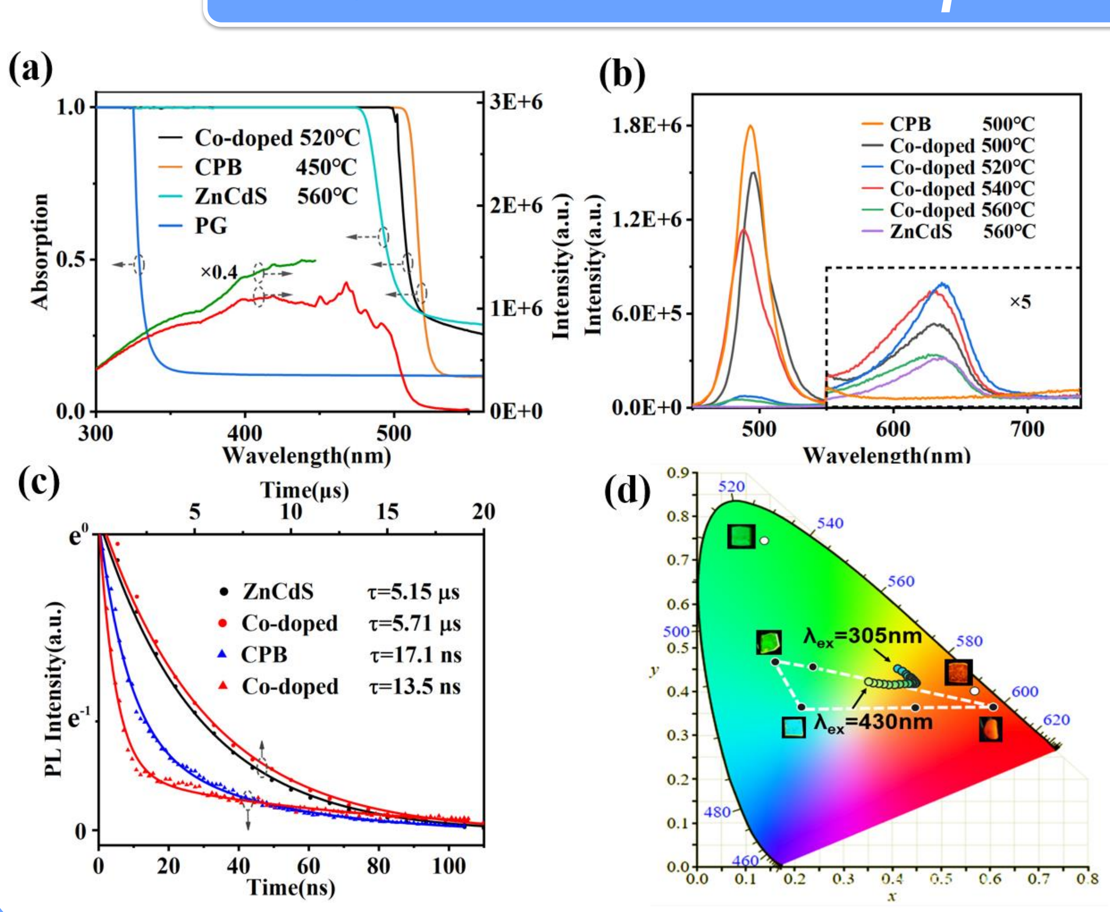
2. Elemental mapping of co-doped nano-GCs



(a) Dark field image of the biphasic QDs co-doped nano-GC; and the STEM-EDS mappings of the (b) Si; (c) O; (d) Cs; (e) Pb; (f) Br; (g) Cd; (h) S and (i)Zn elements.

- The QDs are uniformly distributed inside the glass matrix
- It is apparent that two types of QDs can be distinguished by their morphology and size: the larger cubic-like and the smaller round-shaped ones representing.
- Based on the TEM measurement, the crystallinities (volume fraction) of the biphasic QDs were obtained to be 4.92% and 1.29%, respectively, for the $CsPbBr_3$ and Zn-Cd-S QDs

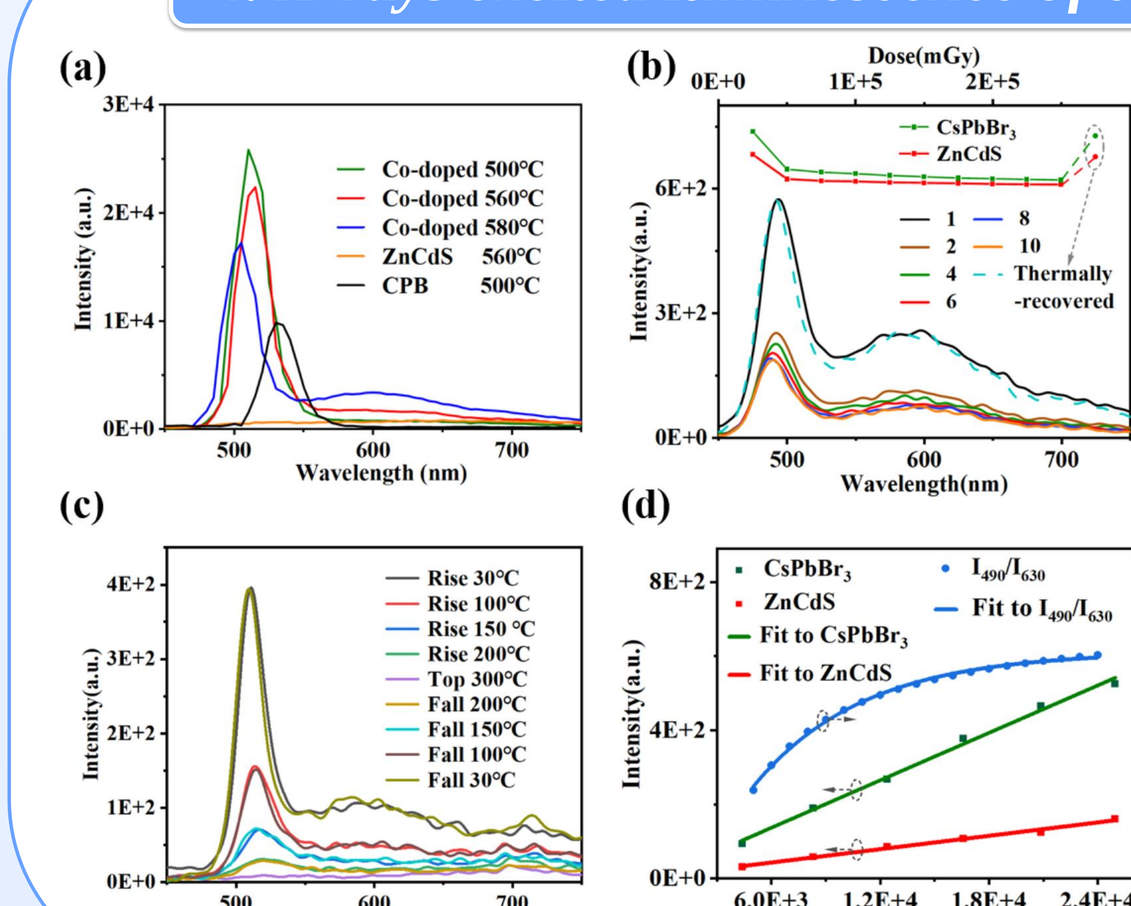
3. Photoluminescence of co-doped nano-GCs



(a) PL excitation (right Y-axis) and absorption spectra (left Y-axis); (b) Emission spectra under the 380 nm excitation; (c) PL decays; (d) Variation of CIE chromaticity of the nano-GCs obtained under different heating temperatures

- Two emission bands, a stronger green emission at ~ 500 nm($CsPbBr_3$) and a weak red emission at ~ 630 nm(Zn-Cd-S), are observed in co-doped nano-GCs.
- By changing the thermal heating scheme, the fluorescence intensity ratio (FIR) and thus the apparent color can be widely adjusted. The FIR can be also fine-tuned simply by varying the excitation wavelength.

4. X-rays excited luminescence of co-doped nano-GCs



(a) XEL spectra; (b) XEL spectra under repeated X-ray irradiation; (c) Variation of XEL spectra during a heating and cooling cycle; (d) Changes of the dual-band emissions curves excited by different power of X-ray tube without thermal reduction.

- The XEL intensity has barely changed in the following repeated irradiations (up to a total dose of 0.25 kGy).
- It is noted that the XEL can be restored to its original value after thermal annealing.
- Plotting the FIR (of the green to red emission) versus irradiation dose, the data can be well fitted by an exponential curve.

5. Conclusions

- The $CsPbBr_3$ and Zn-Cd-S QDs can be simultaneously grown in borosilicate glass as a result of the diffusion-limited crystallization of the glass.
- Owing to the different volume fraction or pump-energy harvesting ability of the biphasic QDs, the green to red emission ratio and thus the apparent color can be broadly adjusted.
- The tunable dual-band emissions can be also achieved under the X-rays excitation.
- Although the XEL weakening occurs possibly due to the X-rays induced photodegradation or defects, such adverse effect can be readily wiped off by post-thermal-annealing.
- A self-calibrated X-rays dosimeter with a good thermal stability is constructed on the FIR of the unique dual-band emissions.

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