Arch. Metall. Mater. **71** (2026), 2, 591-595

DOI: https://doi.org/10.24425/amm.2026.158848

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WHITE-LIGHT EMISSION FROM SINGLE-MATERIAL ZnSe-BASED QUANTUM DOTS SYNTHESIZED UNDER AQUEOUS CONDITIONS

Quantum dots (QDs) are promising luminescent materials due to their tunable bandgaps and high color purity. White-light emission was achieved using ZnSe-based QDs synthesized under low-temperature aqueous conditions. ZnSe/ZnS, Cu-doped ZnSe/ZnS, and Mn-doped ZnSe/ZnS QDs prepared in deionized water at 90°C exhibited blue, green, and orange emissions, respectively. A ZnS shell enhanced optical stability, and white light was realized by physically mixing single-family QDs with different dopant centers. Optimized mixing of peaks at ~370, ~514, and ~578 nm produced a broad spectrum (~350-580 nm), and a 1:5:6 mixture yielded chromaticity coordinates near the CIE D65 white point. This study demonstrates a simple, effective approach for white-light generation using aqueous-synthesized ZnSe-based QDs.

Keywords: Quantum dots; ZnSe; White light; Multi color; doping

1. Introduction

Conventional white light-emitting diodes (LEDs) typically generate white light by combining a blue light source with a yellow-emitting phosphor; however, this approach inherently suffers from limited color rendering capability and a low color rendering index (CRI) [1-2]. In contrast, quantum dot (QD)-based emission technologies enable precise bandgap tuning through control of particle size and composition, allowing for a wide color gamut and high color purity [3-6]. As a result, QDs have attracted significant attention as alternatives for the advanced display and lighting applications [7].

Nevertheless, most QD synthesis methods rely on high-temperature organic solvent systems, which introduce several drawbacks, including environmental toxicity, process complexity, and high manufacturing costs [8-9]. To address these limitations, low-temperature aqueous-phase synthesis routes have gained interest for their facile process, environmental friendliness, and low costs.

Previous studies have demonstrated the successful synthesis of ZnSe QDs under low-temperature aqueous conditions, yielding particles with sizes in the range of approximately 3-5 nm and exhibiting blue emission in the 370-380 nm region [10]. Furthermore, the incorporation of Cu and Mn dopants into ZnSe QDs has been shown to produce green and orange emission, respectively [3,11]. Based on these prior findings, the present study systematically investigates the feasibility of achieving white-light emission through a physical mixing strategy using doped ZnSe-based QDs. Multi-doping within a single quantum dot, however, often suffers from dopant-dopant interactions, reduced emission efficiency, and limited control over individual emission centers. Such challenges in doped QD systems have been widely discussed in the literature [12]. In this context, a physical mixing strategy using single-family QDs with different dopant centers provides an effective alternative for achieving multicolor and white-light emission.

Such a white-light emission strategy based on a single-core QD system not only offers potential for the development of high-CRI white LEDs but also presents promising opportunities for environmentally friendly lighting applications.

2. Experimental

2.1. Materials

All materials were of analytical grade. Zinc acetate ($Zn(CH_3COO)_2$, 99.99%), zinc nitrate hexahydrate

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($Zn(NO_3)_2 \cdot 6H_2O$, 98%), manganese(II) acetylacetonate ($Mn(acac)_2$), copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$), sodium hydroxide (NaOH), sodium borohydride ($NaBH_4$, 98%), selenium powder (Se, 99.99%), glutathione ($C_{10}H_{17}N_3O_6S$, 98%), thiourea (NH_2CSNH_2), and 3-mercaptopropionic acid ($C_3H_6O_2S$, 99%) were used as received. Reagents were purchased from DAEJUNG Chemicals and Sigma-Aldrich.

2.2. Synthesis

Cu- and Mn-doped ZnSe-based quantum dots were synthesized using an internal doping method. All synthesis procedures were carried out with deionized water as a solvent. To minimize oxidation and contamination, the entire synthesis process was conducted under a nitrogen (N_2) atmosphere inside a glove box.

2.2.1. Synthesis of ZnSe/ZnS Quantum Dots

ZnSe/ZnS quantum dots (QDs) were synthesized by reacting separately prepared Zn and Se precursors. Zinc acetate was used as a Zn precursor and glutathione (GSH) was dissolved in deionized water (DIW), followed by pH adjustment to 11 using NaOH. The Se precursor was prepared by dissolving Se powder and $NaBH_4$ in DIW adjusted to pH 12, followed by dilution.

The prepared Se precursor was injected into the Zn precursor solution and heated at 90°C for 1 h to form ZnSe cores. Subsequently, zinc nitrate hexahydrate, thiourea, and 3-mercaptopropionic acid (MPA) were added, and the reaction was maintained at the same temperature for 1 h to grow the ZnS shell. After the reaction was finished, the solution was cooled at room temperature.

2.2.2. Synthesis of Cu:ZnSe/ZnS Quantum Dots

Cu-doped ZnSe/ZnS QDs were synthesized using an internal doping strategy, in which CuSe cores were first formed followed by stepwise injection of the Zn precursor. The Cu precursor was prepared by dissolving a Cu source and MPA in DIW, adjusting the pH with NaOH, and stirring the solution inside a glove box.

After the addition of the Se precursor, the mixture was held at 90°C for 30 min to form CuSe cores. The Zn precursor was then injected sequentially and reacted for 1 h to form Cu:ZnSe QDs. Finally, zinc nitrate hexahydrate, thiourea, and MPA were added, and the mixture was held at 90°C for 1 h to grow the ZnS shell.

2.2.3. Synthesis of Mn:ZnSe/ZnS Quantum Dots

Mn-doped ZnSe/ZnS QDs were synthesized using the same internal doping strategy. The Se precursor was injected into the Mn precursor solution to form MnSe cores at 90°C for 30 min. Subsequently, the Zn precursor was added stepwise to produce Mn:ZnSe QDs. The ZnS shell growth procedure was identical to that used for the Cu-doped ZnSe/ZnS QDs.

2.2.4. Preparation of Multicolor-Emitting Quantum Dots via Physical Mixing

To achieve tunable optical properties, the synthesized ZnSe/ZnS, Cu:ZnSe/ZnS, and Mn:ZnSe/ZnS QDs were physically mixed at various ratios. The mixed solutions were uniformly dispersed using ultrasonic treatment, and the resulting QD mixtures were used to investigate multicolor and white-light emission characteristics.

3. Results and discussion

ZnSe/ZnS, Cu:ZnSe/ZnS, and Mn:ZnSe/ZnS quantum dots (QDs) were synthesized based on previously reported aqueous-phase methods. All samples possess a core-shell structure, in which a ZnSe core was formed at 90°C followed by the growth of a ZnS shell. White-light-emitting QDs were prepared by physically mixing the three types of QDs at different ratios. Each QD was precisely weighed according to the target composition and uniformly dispersed by ultrasonication. To achieve white-light emission, a physical mixing strategy of quantum dots with different dopant centers was employed in this study, instead of a multi-dopant approach within a single particle. Such a physical mixing strategy has been previously reported to enable multicolor and white-light emission in mixed quantum dot systems [13].

In this study, QDs exhibiting red, green, and blue (RGB) emissions were individually synthesized to examine whether white-light emission could be realized solely through physical mixing. Fig. 1 shows the photoluminescence (PL) characteristics

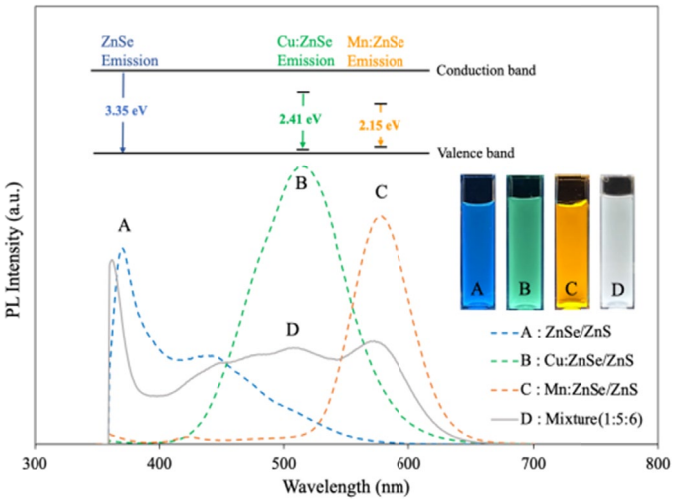

Fig. 1. PL spectra and emission images of ZnSe/ZnS,Cu:ZnSe/ZnS, Mn:ZnSe/ZnS, and a mixture of 1(ZnSe/ZnS):5(Cu:ZnSe/ZnS):6(Mn:ZnSe/ZnS)

of the individual and mixed QDs, where A, B, C, and D represent ZnSe/ZnS, Cu:ZnSe/ZnS, Mn:ZnSe/ZnS, and the mixture of the three QDs, respectively. ZnSe/ZnS, Cu:ZnSe/ZnS, and Mn:ZnSe/ZnS exhibited main emission peaks at approximately 370 nm (blue), 514 nm (green), and 578 nm (orange), respectively. These emissions originate from newly formed energy levels within the ZnSe bandgap (≈2.7 eV) induced by transition-metal dopants (Cu and Mn) [14-16].

To clearly understand the emission mechanisms, it is necessary to consider both the band structure of ZnSe quantum dots and the energy levels introduced by dopants, as illustrated in Fig. 2.

In ZnSe quantum dots, near-band-edge (NBE) emission arises from the recombination of photogenerated electron–hole pairs between the conduction band (CB) and valence band (VB), as reported in previous studies [17]. In this work, a blue emission centered at approximately 370 nm was observed, which can be attributed to strong quantum confinement effects.

As reported by Shao et al. [18], Mn^{2+}-doped ZnSe quantum dots exhibit localized energy levels within the bandgap originating from the 3d orbitals of Mn^{2+} ions. Upon photoexcitation, the energy of the electron-hole pairs generated in the ZnSe host is non-radiatively transferred to the excited state ($^4T_1$) of Mn^{2+}, followed by radiative relaxation to the ground state ($^6A_1$), resulting in characteristic orange emission around 578 nm. This emission can be understood as a host-to-dopant energy transfer mechanism [18].

Mabrouk et al. [19] reported that Cu-doped ZnSe quantum dots contain Cu-related acceptor levels within the bandgap, which are located near the top of the valence band. During photoexcitation, holes are trapped at these Cu levels, forming a transient Cu^{2+} acceptor state, while electrons in the conduction band undergo non-radiative relaxation and subsequently recombine with the trapped holes. This process leads to the reformation of the Cu^{+} state and results in green emission at approximately 514 nm [19].

Therefore, the blue emission originating from band-to-band recombination in ZnSe, the orange emission from Mn^{2+} via energy transfer, and the green emission from Cu via acceptor-level-mediated recombination arise from distinct emission pathways. The combination of these emission contributions plays a decisive role in achieving white-light emission through physical mixing. These results further indicate that such dopant-induced states enable long-wavelength emission, demonstrating that the emission wavelength can be effectively tuned by selecting appropriate dopant elements.

For white-light generation, a physical mixing strategy was adopted instead of multi-doping within a single core. The individual QDs exhibited different PL intensities, following the order Cu:ZnSe/ZnS > Mn:ZnSe/ZnS > ZnSe/ZnS. Taking these differences into account, the mixing ratios were optimized to achieve balanced white-light emission. As a result, the mixed QDs exhibited a continuous emission spectrum spanning approximately 350-580 nm, successfully producing white-light emission, as shown in Fig. 1.

Under UV excitation, each sample exhibited clearly distinguishable visible emission colors, confirming that multicolor emission can be achieved using a single ZnSe-based QD system. Fig. 3 presents the photoluminescence characteristics of QD samples prepared by mixing ZnSe/ZnS, Cu:ZnSe/ZnS, and Mn:ZnSe/ZnS at different ratios. As the proportion of Cu- and Mn-doped QDs increased, the emission intensity in the 520-580 nm region increased, whereas the blue emission near 380 nm gradually decreased (Fig. 3(a)). Accordingly, as the mixing ratio changed from 1:1:1 to 1:6:6, the emission color progressively shifted toward the white region, due to the change in the relative emission contributions of the mixed QDs (Fig. 3(b)).

In addition, when the proportion of Cu:ZnSe/ZnS QDs responsible for green emission was reduced, the overall emission color shifted from green toward white. At specific compositions, the emission spectra of the individual QDs were well balanced, resulting in visually near-white emission. Fig. 4 presents the photoluminescence images of QD mixtures prepared with various mixing ratios under UV illumination, demonstrating that physical mixing of two or three QD components enables not only white emission but also a variety of colors, including yellow,

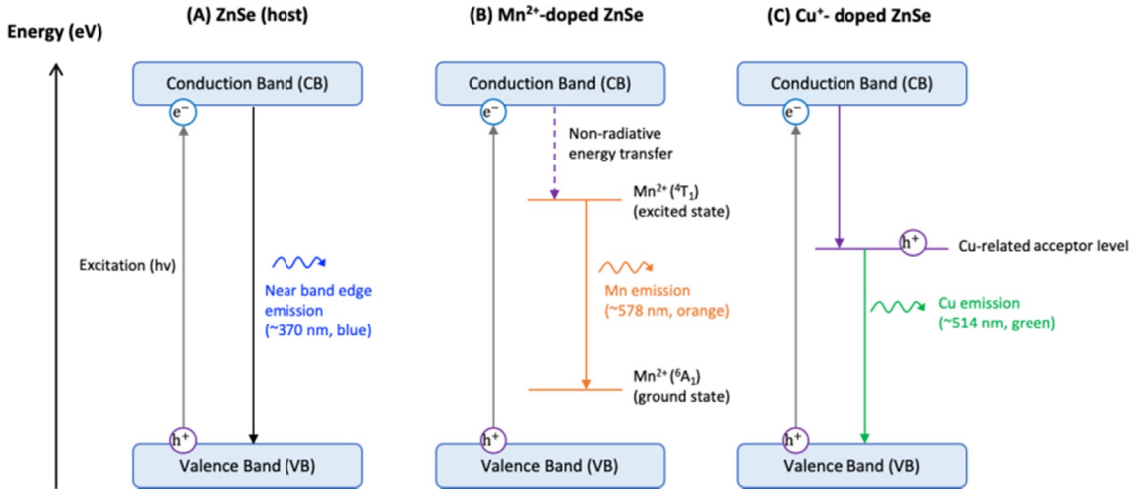

Fig. 2. Energy level diagrams and corresponding emission mechanisms of pristine ZnSe, Mn^{2+}-doped ZnSe, and Cu^{+}-doped ZnSe quantum dots

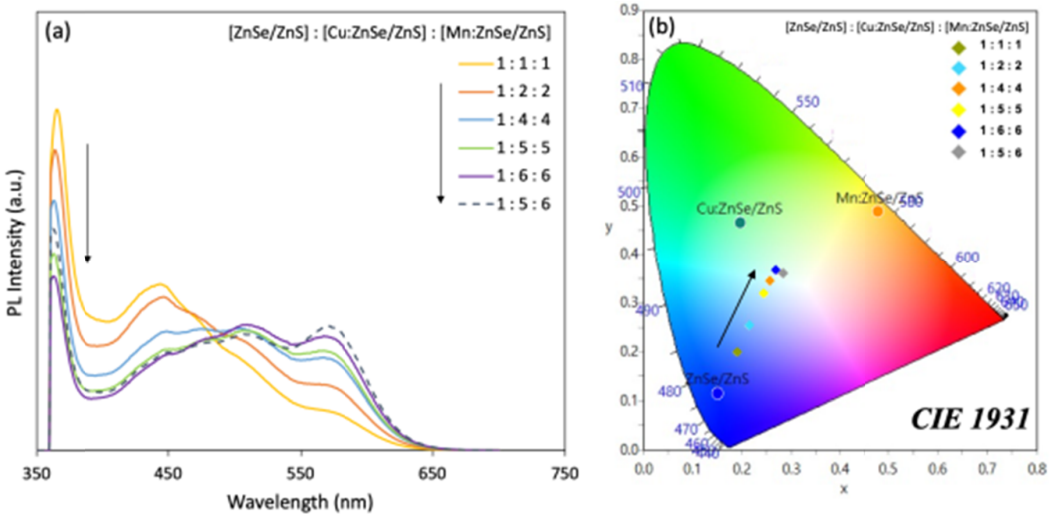

Fig. 3. (a) PL spectra of mixed QDs with different ratios of ZnSe/ZnS, Cu:ZnSe/ZnS, Mn:ZnSe/ZnS, (b) CIE chromaticity diagram showing the emission color coordinates of the mixtures

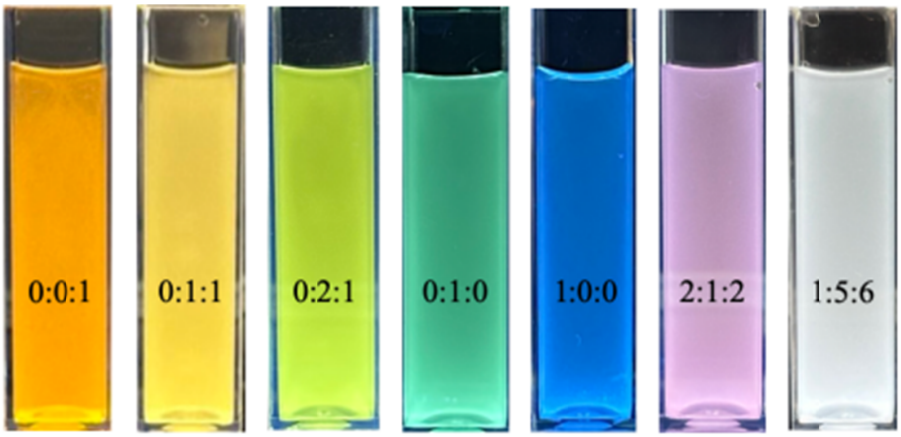

Fig. 4. Photoluminescence images of QDs synthesized with various ratios of (ZnSe/ZnS):(Cu:ZnSe/ZnS):(Mn:ZnSe/ZnS) under UV illumination

light green, and pale purple. In particular, the mixture with a ratio of 1:5:6 exhibited emission very close to standard white light.

Because each QD exhibited different photoluminescence intensities, determining the mixing ratios solely based on emission intensity led to excessive dominance of ZnSe-based blue emission. To address this issue, the present study adopted a strategy in which the proportion of ZnSe/ZnS was reduced while the relative ratios of Cu:ZnSe/ZnS and Mn:ZnSe/ZnS were adjusted, rather than relying on absolute emission intensities. As a result, emission progressively approaching white light was achieved while preserving the intrinsic ZnSe-based emission characteristics. Notably, since the emission intensity of Cu:ZnSe/ZnS is higher than that of Mn:ZnSe/ZnS, a slight reduction in the Cu fraction from the initial mixing ratio (1:6:6) yielded color coordinates closest to white. Furthermore, even in the presence of Mn doping, ZnSe excitonic emission was maintained [20], indicating that effective overall emission intensity can be achieved through physical mixing of single-family QDs, even with a reduced ZnSe fraction.

Finally, the chromaticity coordinates of the synthesized white-emitting QDs were quantitatively evaluated by calculating the Euclidean distance from the standard white point (D65) (Eq. (1)) [21].

$$d = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2} \tag{1}$$

Using the D65 coordinates (x = 0.3127, y = 0.3290) and the measured coordinates of the synthesized white-emitting QDs (x = 0.3033, y = 0.3674), the calculated distance was quite small, indicating that the white light generated in this study is in agreement with the commercially accepted CIE standard white point.

4. Conclusions

In conclusion, this study demonstrates that stable white-light emission can be effectively achieved by a simple physical mixing strategy using single-material-system ZnSe-based quantum dots. Without relying on complex multi-doping processes, precise control of the emission color was accomplished solely by adjusting the mixing ratios, thereby overcoming key limitations of conventional white-emitting QD systems. Ongoing work

focuses on improving the color purity of individual QDs and extending the orange-emitting QDs toward red-emitting QDs, which is expected to further enhance the color gamut. The ZnSe-based QD system proposed herein shows strong potential for a wide range of optoelectronic devices, such as QLED displays and high-color-rendering lighting devices.

Acknowledgments

This work was supported by the Sungshin Women's University Research Grant of 2025.

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