Low-Dimensional CsPbBr$_3$@CoBr$_2$ Super-Nanowire Structure for Perovskite/PMMA Composite with Highly Blue Emissive Performance

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Abstract: In this study, low-dimensional CsPbBr$_3$@CoBr$_2$ super-nanowire (SNW) structures were synthesized via a one-pot heating strategy for highly blue emissions. By introducing CoBr$_2$ to CsPbBr$_3$ precursors, the shape of perovskite nanocrystals was changed from cuboids to a super-nanowire structure, as revealed through a transmission electron microscope. SNWs were formed from stacked segments of nano-plates (lateral dimension of 10–12 nm and thickness of ~2.5 nm) with lengths of several microns. The fabricated sample absorbs light at a wavelength of <450 nm, and it is emitted at a wavelength of 475 nm. It also has a radiant flux conversion efficiency of up to 85% when stimulated by a 430 nm LED light source. The average decay time of up to 80 µs indicates that they effectively prevent the recombination of electron–hole pair. The optical performance still remains over 65% when the ambient temperature is up to 120 °C compared with that under room temperature. The excellent color purity, optical quantum efficiency, long carrier lifetime, and thermal stability make CsPbBr$_3$@CoBr$_2$ SNWs highly promising for a range of photoluminescence applications, such as a high color rendering index lighting and transparent blue emissive screen.

Keywords: perovskite/PMMA composite; blue emission; transparent emissive screen; high color rendering index (CRI) lighting

1. Introduction

Inorganic perovskite materials (CsPbX$_3$; X = Cl, Br, I) have recently been chosen in the field of optoelectronics because their tunable bandgap energies correspond to the near-infrared and visible light regions, convenient for optoelectronic applications [1–3]. The green and red emissive nanocrystals (CsPbBr$_3$I$_{(1-x)}$, x = 0 to 1) could be synthesized for further applications, such as light-emitting devices and solar cells [4–10]. However, the blue emissive nanocrystals (CsPbBr$_3$Cl$_{(1-x)}$) still face great challenges because of their high reaction temperature; required PbCl$_2$ dissolving support agents, such as trioctylphosphine; and low working performance compared to red and green counterparts [11]. Another method to fabricate blue emissive perovskite nanocrystals is to reduce the particle size with the quantum confinement effect. The particle size could be reduced to 12, 8, and 4 nm corresponding to bandgap energies of 2.4, 2.5, and 2.7 eV, respectively [11]. However, the small crystals with high surface area have high surface trap state density that results in low stability and poor optical performance. High optical performance and long-time stability of low-dimensional (quasi-1D and 2D) perovskites were recently demonstrated by doping low-D perovskites into three-dimensional (3D) perovskite structures. The recent
report introduced 3,4,5-trifluoroaniline (TFA) hydrobromide (C₆H₃F₃NHzHBr, TFABr) precursors into CH₃NH₃PbBr₃ (MAPbBr₃) precursor solutions to form a quasi-2D perovskite (TFABr)MAₙ−₁PbₙBr₃n₊₁ film. The film stability was improved with no change in the XRD pattern in 2688 h in air [12]. A quasi-2D PEA₂(RbₓCs₁−ₓ)ₙ−₁PbₙBr₃n₊₁ perovskite for pure-blue PeLED applications in the whole blue spectral region (from 454 to 492 nm) were also presented, and the PLQY was roughly 82% [13]. Another study also reported an ultrahigh intrinsically water-stable all-inorganic quasi-2D CsPbBr₃ nanosheet via aqueous phase exfoliation method, with 87% PL intensity remaining after 168 h [14]. Thus, low dimensional crystals are one of the potential solutions in improving luminescent ability in the blue light region of CsPbX₃ material. Cobalts incorporated into CsPbBr₃ crystals were demonstrated to passivate the surface trap density, improve the crystal quality, and enhance the optical properties of the perovskite crystal [15–19]. To the best of the authors’ knowledge, no study on low-dimensional CoBr₂ incorporation CsPbBr₃ perovskite crystals have been reported thus far.

In this study, low-dimensional CsPbBr₃@CoBr₂ super-nanowires (SNWs) were fabricated by a simple one-pot synthesis process with strong blue emission. Their structural and luminescent properties were studied by measuring PLE and PL spectra, PL efficiencies, X-ray diffraction (XRD), and transmission electron microscopy (TEM). Some prominent examples of applications of highly blue emissive CsPbBr₃@CoBr₂ SNWs, including high color rendering index (CRI) light source and transparent emissive screen, were also investigated.

2. Materials and Methods

Materials: All reagents were used without further purification. Lead chloride (PbBr₂, 99.999% metal basis), lead bromide (PbBr₂, 99.999% metal basis), cobalt (II) bromide (CoBr₂, 99.99% metal basis), cesium carbonate (Cs₂CO₃, 99.99% metal basis), oleylamine (OAm, 80–90%), oleic acid (OA, analytical grade), and toluene (>99%, analytical grade) were bought from Macklin Chemical.

Fabrication of CsPbBr₃@CoBr₂: CsPbBr₃ and CsPbBr₃@CoBr₂ SNW perovskite nanocrystals were fabricated via a one-pot strategy by directly heating perovskite precursors in toluene in air. First, Cs precursors were obtained by mixing 0.6 mmol of Cs₂CO₃ powder, 30 mL of octane, and 1.5 mL of OA together in a 100 mL stand-up flask and heating the mixture to 90 °C in a heating agitator until all the Cs₂CO₃ powder was dissolved. The CoBr₂/PbBr₂ with different mol feed ratios were mixed with 30 mL iso octane, 1.5 mL OA, and 3 mL OAm together in a 100 mL stand-up flask. The mixture was then heated to 90 °C in a heating agitator until all the powder was dissolved. The initial solution was centrifuged at 6000 rpm for 5 min to precipitate the large particles, and the supernatant was retained for subsequent use. The CsPbBr₃@CoBr₂ NC concentration in toluene was fixed at 10 mg/mL.

Transparent CsPbBr₃@CoBr₂/PMMA composite films were fabricated by mixing 5 mL of 10 mg/mL CsPbBr₃@CoBr₂ in toluene with 8.5 g of PMMA in 20 mL of toluene. The precursor solutions were processed onto PMMA substrates through blade coating at various thicknesses, followed by baking at 30 °C–75 °C for 1–8 h inside a glovebox.

Characterization: The crystalline structure of the powdered samples was analyzed by X-ray diffraction (XRD; Siemens, Bruker D5005, Germany) with Cu Ka radiation (λ = 0.154 nm) at a step of 0.02° (2θ) at room temperature. Transmission electron microscopy (TEM, JEOL-JEM 1010, Japan) was conducted to determine the morphology and distribution of the nano crystals. Excitation and fluorescence emissions were measured by a 450 W monochromatic light source Xe arc and spectrometer (NanoLog; Horiba Jobin Yvon, USA) at room temperature. The CsPbBr₃@CoBr₂/PMMA composite films, then were placed on the hot plate with a home-made temperature controller (from room temperature up to 120 °C) for the temperature dependent PL spectra measurement. The time-resolved photoluminescence (TRPL) were performed by a flash arc lamp (FL-1040, USA, flash time: 50 ms, delay increment and sample window time: 1μs, decay by delay mode). The CsPbBr₃@CoBr₂/PMMA composite samples were excited by a 430 nm diode
chip. The performance parameters of the LEDs were measured by an integrating sphere coupled to a GS-1290 spectroradiometer (RadOMA, UK).

3. Results and Discussion

The results of TEM and XRD pattern measurements are shown in Figure 1. For CsPbBr$_3$ samples, the nano-cuboid particles were well dispersed with a size of ~20 nm (Figure 1a,b). Figure 1c shows the TEM image of the CsPbBr$_3$@CoBr$_2$ sample with low CoBr$_2$/PbBr$_2$ mol feed ratio of 1/10. The morphology of the samples was moved from cuboids to unclear structure; it looks like a collection of nano-plates arranged in a disorderly manner. At the high CoBr$_2$/PbBr$_2$ mol feed ratio of 1/1, the shape of perovskite nanocrystals was changed from cuboids to SNW structure, as revealed in the TEM image shown in Figure 1d. The SNWs were formed from stacked segments of nano-plates with lengths of several microns. The TEM images of the sample with different magnifications are presented in Figure 1e,f. The results show nano-wires initiated from a lateral dimension of approximately 11 nm and a thickness of approximately 2.5 nm (see Figure 1g). In addition, when observed at the appropriate magnification, square shapes with an edge length of ~12–14 nm could be observed (white dash line, see Figure 1e). These results are similar to the CsPbBr$_3$ nanoparticles formed are wrapped by long-chain ligands, such as OLA and OA. However, with the appearance of CoBr$_2$, the CsPbBr$_3$ crystals formed in the form of nano-plates and bind together into low-dimensional CoBr$_2$@CsPbBr$_3$ SNWs.

![Figure 1. TEM images of (a) CsPbBr$_3$, CsPbBr$_3$@CoBr$_2$ at low (c) and high (d–f) CoBr$_2$ to PbBr$_2$ mol feed ratio. (b,g) The size distribution of pristine CsPbBr$_3$ and CsPbBr$_3$@CoBr$_2$ calculated from Figure 1(a,g), respectively. Schematic representation of CsPbBr$_3$ cubic (left) and quasi-low dimension CoBr$_2$@CsPbBr$_3$ SNWs structure (right). (h,i) XRD pattern of CsPbBr$_3$ and CsPbBr$_3$@CoBr$_2$ at high CoBr$_2$ to PbBr$_2$ mol feed ratio.](image-url)

The schematic of the CsPbBr$_3$ cuboids (left) and low-dimensional CoBr$_2$@CsPbBr$_3$ SNWs (right) structures is illustrated in Figure 1h. As in previous work, Kubicki et al. provided evidence that Co$^{2+}$ could not be doped into the MAPbI$_3$ perovskite phase [21]. Thus, CoBr$_2$ molecules possibly participated in the formation process of CsPbBr$_3$ crystals, causing the formation of CoBr$_2$@CsPbBr$_3$ SNWs instead of Co$^{2+}$ ion doping into CsPbBr$_3$ crystals. The structure of CsPbBr$_3$ and CsPbBr$_3$@CoBr$_2$ nanocrystals was further explored via XRD measurement, as shown in Figure 1i. Two samples exhibited a pure cubic phase (PDF# 54-0752), confirming the integrity of the perovskite structure.
The PL and optical absorption of the as-prepared CsPbBr3@CoBr2 SNW samples were prepared to further understand the influence of CoBr2 on the optical properties of CsPbBr3. The results are shown in Figure 2. The emission peak of CsPbBr3@CoBr2 SNWs samples shifted from 515 nm to 495 and 475 nm, corresponding to 0, 1:10, and 1:1 CoBr2/PbBr2 mol feed ratio of precursors, respectively (Figure 2a). This finding is consistent with the above TEM results, in which the reduction in particle size resulted in blue-shifted emission. The blue-shifted emission initiated from the strong quantum confinement effect of the nano-plates (~2.5 nm), which is smaller than the Bohr diameter of CsPbBr3 crystals ~7 nm [12]. Figure 2b shows the optical absorption and PL of CsPbBr3@CoBr2 SNWs with a 1:1 CoBr2/PbBr2 mol feed ratio of precursors. The optical absorption curve revealed that CsPbBr3@CoBr2 SNWs had a large absorbance in the UV, and visible spectral region with band edges started at 450 nm. When observing the photos of the as-prepared samples, they were blue-violet in daylight. When exposed to a 380 nm light source, they emitted strongly in bright blue (inset of Figure 2b).

Figure 2. (a) PL curves of CsPbBr3@CoBr2 at different CoBr2/PbBr2 mol feed ratio; (b) optical absorption and PL curves of CsPbBr3@CoBr2 at high mol feed ratio (photos of CsPbBr3@CoBr2 samples with and without UV irradiation in inset of figure).

Figure 3a shows the temperature-dependent PL performance of the SNW sample. The PL intensity decreased when the ambient temperature increased from 20 °C to 120 °C. As shown in the inset of Figure 3a, the integrated PL intensity still remained over 65% when the ambient temperature was up to 120 °C compared with that in room temperature. To study the thermal quenching, the activation energy (∆E) could be calculated according to the Arrhenius equation [22]:

\[
\ln \left( \frac{I_0}{I_T} \right) = \ln A - \frac{\Delta E}{kT}
\]  

(1)

where \(I_0\) and \(I_T\) represent the intensity of the phosphor at the room temperature and the testing temperature, respectively; \(A\) is a constant, and \(k\) is Boltzmann’s constant \((8.62 \times 10^{-5} \text{ eV} \times \text{K}^{-1})\). According to the Arrhenius equation, the plot of \(\ln [(I_0/I_T) - 1]\) versus \(1/kT\) yields a straight line, as displayed in Figure 3b. The activation energy of SNWs corresponding to the slope of the fitting line is 0.19 eV. This value is comparable to phosphor powders applied for LEDs such as \(\text{Y}_2\text{O}_3\):\text{Eu}^{3+}\) [22].

The time-resolved photoluminescence (TRPL) for CsPbBr3 NCs and CsPbBr3@CoBr2 SNWs were measured to further clarify the improvement in photoluminescence performance, as shown in Figure 3c. The two exponential decays are described in the following equation:

\[
I(t) = I_0 + A_1 \exp \left( -\frac{t}{t_1} \right) + A_2 \exp \left( -\frac{t}{t_2} \right)
\]  

(2)

where \(I_0\) is the luminescence intensity at time \(t\); \(I_0\) is the luminescence intensity at time \(t = 0\); \(t_1\) and \(t_2\) are short and long decay components, respectively; and \(A_1\) and \(A_2\) are their
pre-exponential factors, respectively. The average lifetimes (s) were evaluated using the following equation:

\[ t_{\text{avg}} = \frac{(A_1 t_1^2 + A_2 t_2^2)}{(A_1 + A_2 t_2)} \]  

Figure 3. (a) Temperature dependent PL spectra of CsPbBr\(_3@\)CoBr\(_2\) nanocrystals with a temperature ranging from 20 to 120 °C. Integrated PL intensity vs. temperature are shown in inset of figure. (b) the the plot of ln \([I(t)/I_0] - 1\) versus 1/kT calculated from Figure 3a. (c) PL delay curve of CsPbBr\(_3@\)CoBr\(_2\) SNWs in octane. (d) The electroluminescence (EL) spectrum of the 430 nm-LED chip and that of the perovskite-coated chip.

As shown in Figure 3c, it cannot see the decay curve of CsPbBr\(_3\) NCs sample due to its short decay time. For the CsPbBr\(_3@\)CoBr\(_2\) SNWs sample, the average lifetime was calculated at 80 µs, a thousand times higher than CsPbBr\(_3\) of 66 ns in previous work [21]. This finding revealed that the nanowire superstructure is highly effective in preventing electron–hole recombination. The very long in PL lifetime of the sample could be due to the reduction in the surface defect states within the bandgap.

The CsPbBr\(_3@\)CoBr\(_2\) SNWs crystals were coated on a 430 nm deep-blue LED chip to investigate their applicability. The electroluminescence (EL) spectra of the 430 nm-LED chip and that of the perovskite-coated LED are presented in Figure 3d. A bright-blue emission band peaking at 475 nm was observed in the EL spectrum of the phosphor-coated LED, aside from the contribution of the 430 nm deep-blue LED chips. The deep-blue to bright-blue radiant flux conversion efficiency (H%) could be calculated using the following equation:

\[ H(\%) = \frac{S}{(B_0 + B_1)} \]  

where S is the integrated radiant flux density of the secondary emission (\(\lambda = 460–500\) nm), \(B_0\) is the 400–460 nm radiant flux density of bare deep-blue LED, and \(B_1\) the radiant flux density of deep-blue light remaining after coating. Equation (4) shows that the value of deep-blue to bright-blue radiant flux conversion efficiency (H%) was approximately 85%. It is well known that for phosphor converted LED (pc-LED) application, the phosphor powder should be in micrometer size to absorb light better; moreover, the luminescent
center should be diluted to prevent the fluorescence suppression in high concentration [23]. It seems that the perovskite SNWs structure could be compatible with both of the above issues for pc-LED application.

In previous work, K$_2$SiF$_6$-doped Mn$^{4+}$ (KSFM) and CsPbBr$_3$/PMMA composite panel for a wide color gamut backlighting unit was studied. It showed a lower CRI due to its narrow-band emission than a blue LED/YAG:Ce [24,25]. In the present study, CsPbBr$_3$@CoBr$_2$ SNW crystals were used to improve the CRI of the white light-led sources. Figure 4 shows a comparison of a commercial blue LED/YAG:Ce and the blue LED/KSFM/YAG:Ce/CoBr$_2$@CsPbBr$_3$ SNWs at the same total radiant flux density, correlated color temperature, and its color coordinates. For blue LED/YAG:Ce, the CRI showed a poor value of 65 (Figure 4a). By adding a KSFM red phosphor, the blue LED/KSFM + YAG:Ce showed CRI of up to 87 (not shown here). Finally, the blue LED/KSFM/YAG:Ce/CoBr$_2$@CsPbBr$_3$ SNWs showed CRI as high as 94 (Figure 4b). The color coordinates of light sources turned from blue [(i); y = 0.01, x = 0.17] to white light [(ii); 0.33, 0.32], [(iii); 0.37, 0.315] of CIE 1931 diagram (Figure 4c).

![Figure 4. Electroluminescent spectrum and color coordinates of (a,b) Blue LED + YAG:Ce and (c) Blue LED + YAG:Ce + KSFM + CsPbBr$_3$@CoBr$_2$ composite nano crystals color coordinates.](image)

Another notable application is transparent emissive projection displays. In previous work, the authors used a short wavelength (405 nm) projector and green emission perovskite nanocrystals plate as the transparent emissive screen [26]. Herein, a transparent blue emissive screen was demonstrated on the basis of CsPbBr$_3$@CoBr$_2$ SNWs/PMMA composite film. Figure 5a shows the transmittance spectra of CsPbBr$_3$@CoBr$_2$ SNWs/PMMA composite film coated onto a PMMA plate substrate with various thicknesses by a doctor blade process (as shown in inset). The thickness of the coating layer increased from 10, 20, 30, and 40 micrometers with the corresponding number of coating times of 1, 3, 5, and 7, respectively. The results showed that the absorption edge at a wavelength from 475 nm corresponds to the bandgap width of CsPbBr$_3$@CoBr$_2$ SNWs at ~2.6 eV. The transmittance decreased slightly as the film thickness increased from 10 μm to 40 μm. In addition, the transmittance of the film remained above 90% for wavelengths longer than 475 nm. A live projection display with a MEMS laser projector and CsPbBr$_3$@CoBr$_2$ SNWs/PMMA composite film is demonstrated in Figure 5b. A short-wavelength (405 nm) projector was applied as the image source, and the CsPbBr$_3$@CoBr$_2$ SNWs/PMMA sheet (~30 μm corresponding to 5× of coating) was employed as the transparent emissive screen. Figure 5b
reveals that the highly transparent sheet displayed the blue image when irradiated with 405 nm light source. These results suggested the application of real-time information display on a transparent screen.

![Transmittance spectra of CsPbBr3@CoBr2 SNWs/PMMA composite sheet.](image)

**Figure 5.** (a) The transmittance spectra of CsPbBr3@CoBr2 SNWs/PMMA composite sheet with various thickness and its coating process shown in inset of figure. (b) A diagram of a live projection display with a MEMS laser projector and CsPbBr3@CoBr2 SNWs/PMMA transparent emissive screen.

### 4. Conclusions

By introducing CoBr2 in CsPbBr3 QD precursors through a one-pot heating method, the crystalline structure, PLQY, photoluminescence lifetime, and ambient stability of the sample could be significantly changed. With a highly CoBr2/PbBr2 mol feed ratio (1/1), the fabricated samples have a structure of nano-plates arranged sequentially together into low-dimensional super-nanowires with lengths of several microns. The as-synthesized sample absorbs light at a wavelength of <450 nm, and it is emitted at a wavelength of 475 nm. It also has an optical conversion efficiency of up to 85% when stimulated by 430 nm LED light source. It shows thermal durability when maintaining luminescence intensity above 65% at increased ambient temperature of 120 °C. The fabricated sample has an average decay time of up to 80 µs, revealing that this superstructure nanowire is highly effective in preventing electron–hole pair recombination. With excellent color purity, optical quantum efficiency, long carrier lifetime, and thermal stability, CsPbBr3@CoBr2 SNWs are highly promising for a range of PL applications, such as high CRI lighting and transparent blue emissive screen.

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