Solvent-free Synthesis of Hybrid Copper Halides for High-performance White Emission and X-ray Imaging

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***Abstract*—Lead-free metal halides have received significant research interest due to their non-toxicity, cost-effectiveness, and remarkable stability coupled with superior optoelectronic characteristics. Nevertheless, conventional synthesis approaches for such materials predominantly rely on high-temperature solution processing in toxic solvents, characterized by prolonged reaction durations, which may hinder practical implementation. This work demonstrates a solvent-free strategy for room-temperature synthesis of hybrid copper halides ((TOA)$CuBr_2$, TOA: tetrabutylammonium) exhibiting bright green luminescence and exceptional stability. Because of these advantages, (TOA)$CuBr_2$ powders are successfully implemented as emitters and scintillators in white light-emitting diodes (WLEDs) and X-ray imaging systems. The WLEDs achieve a high color rendering index of 93 and a correlated color temperature of 5150 K. Furthermore, flexible scintillator films fabricated from these powders demonstrate high-performance X-ray detection performance, facilitating three-dimensional imaging via a space-reconfiguration method.**

Keywords—Solvent-free synthesis, copper halides, white emission, X-ray imaging

I. INTRODUCTION

The rapid advancement of sustainable and interconnected societal development underscores the critical urgency to prioritize healthy living environments, safety assurance, and efficient display. Notably, white emission and X-ray scintillation imaging have emerged as pivotal technologies, with white light-emitting diodes (WLEDs) being extensively deployed for display and X-ray scintillation imaging serving essential roles in medical diagnostics and security screening applications. Current research reveals that the performance of both WLEDs and X-ray scintillation systems exhibits fundamental dependence on the optoelectronic characteristics and operational stability of materials. However, conventional implementations face inherent limitations: WLEDs (e.g., GaN-based semiconductors and rare-earth phosphors) suffer from prohibitive fabrication costs and chemical instability, while commercial scintillators (e.g., CsI:Tl, $Lu_{1.8}Y_{0.2}SiO_5$:Ce, and $CdWO_4$) present challenges including toxicity and restricted radiation hardness.

Herein, a simple and green-chemistry mechanochemical strategy was proposed to synthesize hybrid copper halide ((TOA)$CuBr_2$, TOA: tetrabutylammonium) powders on a large scale at room temperature. As-prepared powders exhibited acceptable crystallinity and purity. The utilization of a simple and low-cost procedure, high reproduction, and avoidance of toxic solvents make this method ideal for commercialization of copper halides. Electronic structures and excited carrier distribution of (TOA)$CuBr_2$ were calculated and simulated, their emission is attributed to self-trapped excitons (STEs) in low-dimensional configuration. The efficient green emission of (TOA)$CuBr_2$ powders enable their promising potentials in WLEDs and X-ray scintillators. Remarkably, WLEDs involving (TOA)$CuBr_2$ powders, which were fabricated by depositing powders and red ceramics phosphors on optical chips, showed high color rendering index of 93 and a correlated color temperature of 5150 K, implying its potential feasibility for lighting and displaying. Furthermore, flexible X-ray films were achieved by mixing (TOA)$CuBr_2$ powders with polymethylmethacrylate (PMMA). Benefiting from a high light yield of fabricated scintillation films, they exhibited excellent imaging performance for complex and irregular objects. With the assistance of space reconfiguration, three-dimensional imaging results can be demonstrated.

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II. EXPERIMENTAL SECTION

A. Fisrt-principle calculation

The electronic band structures are studied by density-functional theory (DFT), as implemented in Vienna ab initio simulation package (VASP). Electronic properties were calculated at the theory level of Perdew-Burke-Ernzerhof - HSE06 hybrid functional, projector augmented-wave and norm-conserving pseudopotential were employed to calculate the electronic band structure and density of states, respectively.

B. Preparation of lead-free powders, as well as fabrication of WLEDs and X-ray scintillators

CuBr and (TOA)Br at a stoichiometric molar ratio of 1:1 were mixed in a mortar and grinded for 15 min at atmosphere. Afterward, prepared powders were washed with isopropanol for two times and then transferred in an oven to vacuum for 1 h to evaporate the residual isopropanol at room temperature. Fabrication of WLEDs and X-ray scintillation screens has been reported by our previous works.

III. Results and Discussion

With the assistance of crystal analysis, the crystal structure of $(TOA)CuBr_2$ is shown in Fig. 1a, indicating its zero-dimensional (0D) configuration with isolated $[CuBr_2]^-$ clusters and organic molecules. Moreover, the carrier distribution for LUMO and HOMO states is simulated and exhibited in Fig. 1b, suggestion most of excited electrons and holes locate near Br and Cu atoms. As a result, the $[CuBr_2]^-$ clusters are regarded as emissive centers.

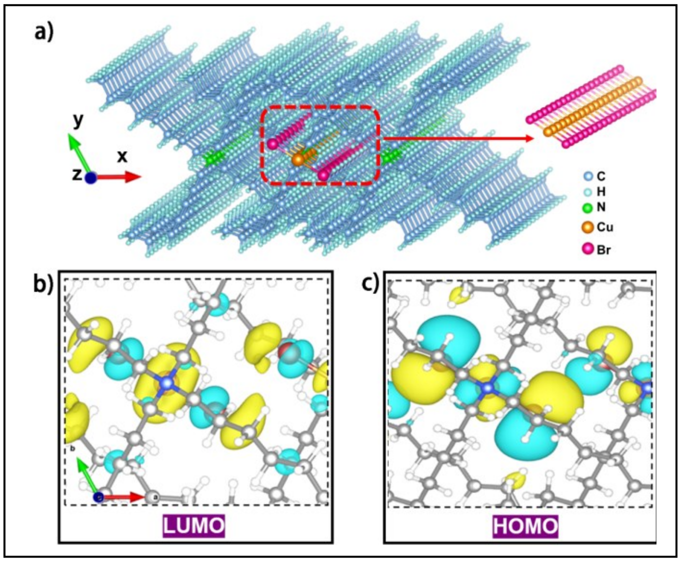

Fig. 1. a) Structure diagram of $(TOA)CuBr_2$. Electron wavefunctions of b) LUMO and c) HOMO of $(TOA)CuBr_2$.

Fig. 2a and b exhibit steady-state and transient photoluminescence (PL) spectra of as-prepared $(TOA)CuBr_2$ powders, respectively, which PL peak centered at 528 nm and PL lifetime is 53.2 μs. The luminescent features are attributed to formation of self-trapped excitons (STEs) in low-dimension structures of $(TOA)CuBr_2$ with significant structural distortion when it is excited.

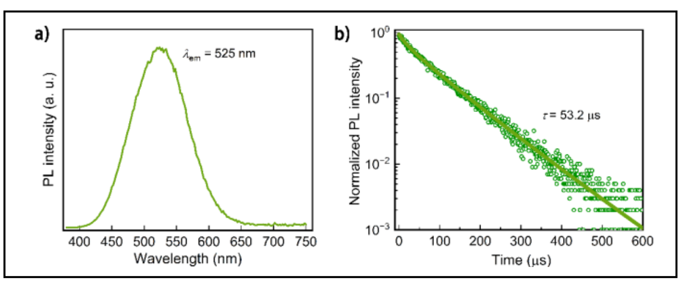

Fig. 2. a) Steady-state and b) transient PL spectra of $(TOA)CuBr_2$ powders at atmosphere.

Because of high-efficient and broadband green emission, well as and large-scale preparation of $(TOA)CuBr_2$ powders, they can be employed as emitters in WLEDs. The WLEDs were fabricated by coating mix of $(TOA)CuBr_2$ powders and red phosphors onto blue chips. Fig. 3a displays a series of electroluminescence (EL) spectra of fabricated WLEDs. As increase of driving voltages, EL intensity enhance gradually. Besides, the WLEDs demonstrate attractive performance, including a CIE color coordinate of (0.3418, 0.3612), a high CRI of 93, and a CCT of 5150 K (Fig. 3b). The WLEDs were operated continuously at 6.5 V for 720 h, exhibiting excellent operating stability, as shown in Fig. 3c and d.

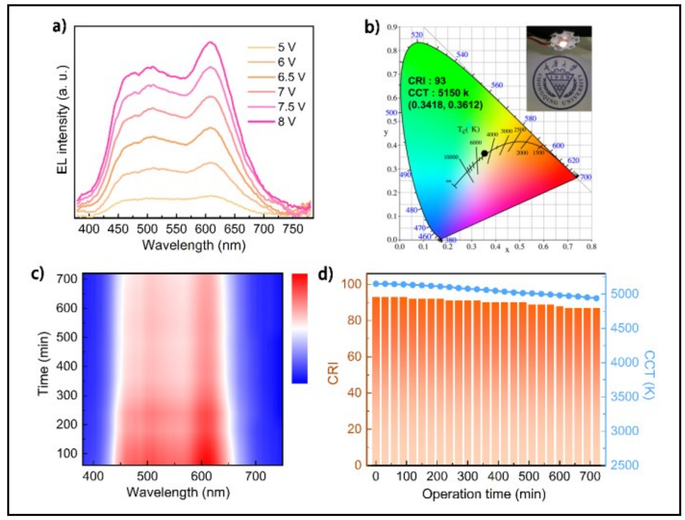

Fig. 3. a) Variety of WLEDs with increase of operating voltages. b) CIE chromaticity of the WLEDs. c) Pseudocolor image of EL and d) variety of CRI and CCT of WLEDs during the prolonged operation.

Moreover, flexible scintillation screens are fabricated and utilized in the X-ray imaging application. Due to the high emission efficiency of the $(TOA)CuBr_2$ powders, the clear X-ray imaging with 3D-reconfiguration of a spring pen is obtained and provided in Figure 4, confirming the prominent potential of the flexible screens in high-performance X-ray imaging.

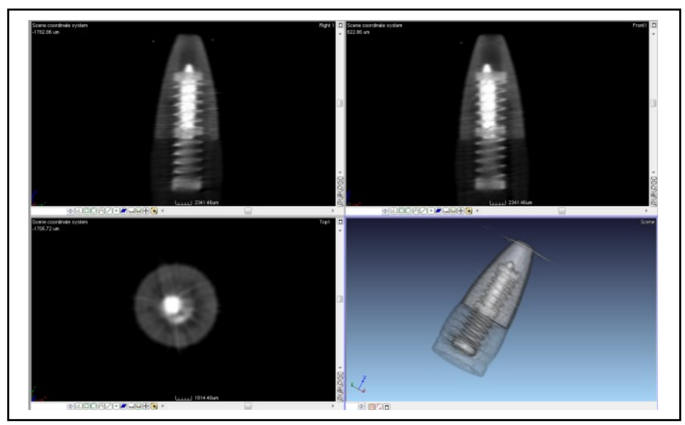

Fig. 4. 3D-reconfiguration of X-ray imaging for a spring pen with the $(TOA)CuBr_2$ screens.

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